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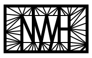

Influence of the Copper Smelter in Krompachy (Slovakia) on Atmospheric Deposition

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Abstract

The contribution deals with the evaluation of atmospheric deposition monitoring in 2009–2017 which was realised in the vicinity of the copper smeltery in Krompachy (Slovakia). The samples were collected from the seven sites, which are located from 1.2 to 10 km from the main pollution source. The atmospheric deposition fluxes of solid particles and elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) were determined separately for "water soluble" and "insoluble" fraction. The detailed analysis of deposition fluxes showed a significant effect of the copper smeltery. In addition to the expected high levels of deposition of copper (21–140), the above-average high deposition of lead (11–124), zinc (86–464) and cadmium (0.6–3.4 $\mu g.m^{-2}.day^{-1}$*) were measured in comparison with different areas. The highest values of deposition fluxes of these elements were detected at sites near the copper smeltery. The level of zinc deposition disagrees with its registered emissions.*

Keywords: atmospheric deposition, copper smeltery, emissions, metals

Introduction

At present the pollution of air by pollutants especially by the fine particles (PM – particulate matter) is regarded as the worst problem from the health and environmental point of view (WHO, 2013).

The anthropogenic sources of emissions of these particles are generally known – quantified and inventoried (NEIS, 2018). However, it is difficult to determine the share and the origin of the particles in real environment. The primary particles have origin in the mix of various local anthropogenic and natural sources and long-range transfer, the secondary particles from the photochemical reactions are also present (Querol et. al. 2007). The knowledge of their chemical composition and other characteristics is necessary for the identification of their sources, comprehension of their formation and the transport processes and also for the possibility to define the measures for control of their imissions (Putaud et. al., 2010). Metals are regarded as very good markers of the specific natural and anthropogenic pollution sources, to a large extent they are used in studies dealing with determination and division of sources of solid particles (Nicolás et.al., 2007). Solid particles from the atmosphere get to the Earth's surface by the process of atmospheric deposition (AD). The determination of AD metals and trace elements bound to solid particles, their reciprocal relations and seasonal variations are also suitable instrument as for identification of their origin and sources so as a certain indicator of the environment's quality (Mijic et.al., 2010, Zongze et.al., 2011, Kara et.al., 2014, Mehrazin et.al., 2017, Hančuľák et.al. 2011, 2014, 2016). The specific composition of emissions from the technologies of metallurgy has influence on constitution of atmospheric deposition, especially in the areas near this works. The copper smeltery in Krompachy is the only significant source of emissions in this area and so can be considered as a model area. The paper presents some results of the research of AD predominantly from viewpoint of deposition fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd and As) and solid particles in relation to emissions from the copper smeltery.

Characteristics of the area

The investigated area in the vicinity of copper smeltery in Krompachy (8,500 inhabitans) is situated in the Hornád river valley in the eastern part of Slovakia. The relatively narrow valley with general orientation east – west lies at 350–450 metres above sea-level, the surrounding mountains reaching 1100 meters.

The wind conditions are subject to the orography of the valley, which is relatively little wind, with frequent inverse conditions. In the area has been monitored a high 58% incidence of calms. The winds are dominated from the western and eastern directions, with a low average speed of 1 $m.s^{-1}$. (MŽP SR, 2009). In the copper smeltery, different types of waste containing copper-based on copper, brass, bronze and bimetal Fe-Cu, bimetal scrap have been pyrometallurgical processed. They are used also technology wastes, such as copper slag, dross, filter sludges, cakes and various other types of wastes containing copper above 5%. The final product is anode copper and copper wires. The secondary products of pyrometallurgy and intercepted releases are captured and processed hydrometallurgicaly to zinc sulphate heptahydrate. The main pyrometallurgy technologies are: blast furnace, which is the main source of emissions, converters and anode furnace. The emissions of particulate matter and metals that are registered by NEIS (National Emission Information System of Slovak Republic) are processed in Table 1.

Materials and methods

Total atmospheric deposition i.e. both wet and dry ones, were collected monthly (35 ± 5 days) from seven sites in the

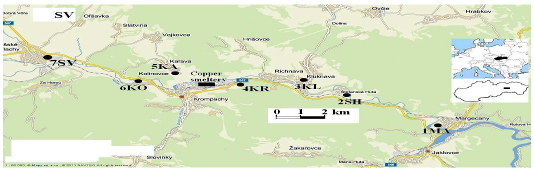

Fig. 1. Location of the sampling sites
Rys. 1. Miejsca pobierania próbek

Tab. 1. The emissions of particulate matter (PM) and metals from the Kovohuty, a.s. [t.year^{-1}]
Tab. 1. Emisja pyłu (PM) i metali z Kovohuty a.s. [t/rok]

Year/Element	2009	2010	2011	2012	2013	2014	2015	2016
PM	25.107	15.200	12.570	9.459	3.586	2.756	12.146	11.031
Cu	5.532	4.831	3.787	3.257	0.800	0.760	2.149	2.376
Zn	0.027	0.042	0.043	0.039	0.027	0.035	0.035	0.047
Cd	0.052	0.041	0.034	0.042	0.002	0.001	0.006	0.007
As	0.106	0.028	0.017	0.011	0.001	0.001	0.045	0.051

area of Krompachy. The sampling sites were at a distance from 1.2 to 10 km from the main source of pollution (chimney of the copper smeltery). The localization of sampling stations is illustrated in Fig. 1. The four sites were localised on a periphery of the villages away from small local emission sources and roads, at about 2.5 m above the ground: 1MA, 2SH, 4KR and 6KA. The stands of the sites 3KL, 7SV and 5KO were located on the roofs of buildings at 15 and 3 m above ground, respectively. The four open polyethylene cylinders (inside diameter – 12.5 cm) filled with 200 ml of pure deionized water fitted on a stand were used for sampling. In laboratory the contents of cylinders were filtered on a vacuum filtration through 0.40 μm membrane filters to separate the "water soluble" and "insoluble" fractions (PM). The soluble fraction was analyzed after each sampling. The insoluble fraction for analysis was prepared by cumulation of six monthly samples into the one semi-annual sample – summer and winter period (mid-April – mid-October) and by mineralization using a microwave digestion MWS-3 Berghof. The elements were analyzed by the atomic absorption spectroscopy using the device VARIAN AA240 FS with GTA 120 and VGA-77. Since October 2012, the device ICP MS Agilent 7700 has been used for analysis. In the article are processed results of 8 winter and 7 summer periods from October 2009 to April 2017.

Results and discussion

Table 1 presents the average daily fluxes ($\mu g.m^{-2}.day^{-1}$) of observed elements and solid particles – PM ("water insoluble" part of AD) from total bulk deposition and basic statistic parameters for all sampling sites and the whole monitored period (September 2009 – April 2017). The abundance of elements (average) was represented in order Fe ≈ Al > Zn v Cu > Pb > Mn > Cr > Cd ≈ As. The qualitative composition of atmospheric deposition significantly contributed to the ecological load of the individual sampling points that was caused by smeltery activities. Among various sampling sites high differences in the deposition were determined mainly for lead, copper, zinc, cadmium and arsenic. The highest values of these elements were measured in the sampling sites localized in vicinity of the copper smeltery, i.e. 4KR, and 6KO in the distance of 1.2 km and 2,4 km respectively. The lowest values of these elements were detected at the sampling site 1MA, that is furthest from the copper smeltery in the distance of 10 km. The average ratio between atmospheric deposition at the sites 4KR and 1MA (AD4KR/AD1MA) for the elements were in the range 3.8 to 10.9 (Pb = 10.9, Cu = 6.1, Cd = 6.0, Zn = 5.4 and As = 3.8). The relatively lower values of lead, copper and zinc were measured considering to the distance from the chimney (1.4 km) in the case of site 5KA. However, the site is outside the prevailing wind. In the area of Krompachy were not observed so high differences in the deposition of PM, iron, aluminum and manganese. In addition to the expected high levels of deposition of copper, the above-average high deposition of lead, zinc and cadmium were measured in the area. The level of zinc deposition several times exceeds deposition of copper, which is sharply in contrast with the data of registered emissions by NEIS mentioned in the Table 1. Emissions of copper are in individual years approx. 30 to 200 times higher than zinc emissions. This disproportion is probably due to the significantly higher actual emissions of this element as registered emissions.

In table 3 is shown the average percentage representation of the deposition of trace elements bound to the "water-insoluble" (PM) part of AD and the ratio between summer and winter atmospheric deposition of the monitored elements and PM. To the insoluble phase, the monitored elements in order of Al, Fe, Cr, Pb and As are bounded. The zinc, cadmium and a lesser extent of the copper were predominant bound on water soluble part of AD. The PM and elements: Al, Fe, As, Mn and Cr show a significantly higher presence in the summer period. The ratio between their deposition in summer and winter is 4.3, 2.5, 2.4, 2.3, 1.9 and 1.6, respectively. There are better conditions for aeolian erosion and resuspension of particles from soil horizon, road traffic, agricultural and construction activities. The increased presence of organic detritus in ambient air during the summer season also influences the amount of dust particles. In winter, the deposition fluxes of solid particles are partially deprived of these effects. In the case of elements which probably come predominantly from copper smeltery relatively balanced values were recorded for both seasons. The average ratio was 0.9, 1.0,

Tab. 2. The average daily fluxes of particles (PM – insoluble fraction) and analyzed elements from 7 summer and 8 winter monitored periods (October 2009 – April 2017), [µg.m^{-2}.day^{-1}]. (*Finished April 2015, ** Finished October 2013)

Tab. 2. Średni dzienny opad cząstek (PM – frakcja nierozpuszczalna) i analizowane pierwiastki z 7 letnich i 8 zimowych okresów monitorowanych (październik 2009 – kwiecień 2017), [µg.m^{-2}.dzień $^{-1}$]. (*Zakończone w kwietniu 2015 r., **Zakończone w październiku 2013 r.)

Site	**PM**	**Fe**	**Al**	**Mn**	**Zn**	**Pb**	**Cu**	**Cr**	**Cd**	**As**
1MA*	34170	689	916	27.8	85.9	11.4	23.1	3.0	0.56	0.55
2SH*	21959	687	557	19.6	158.9	24.0	28.7	3.6	0.91	0.86
3KL	22706	817	746	17.4	183.1	30.7	39.2	5.1	1.15	0.79
4KR	20888	783	619	25.1	464.4	124.6	139.9	3.6	3.37	2.06
5KA**	20544	378	476	15.2	132.3	12.3	40.3	3.5	1.39	2.25
6KO	28959	664	754	21.4	257.3	61.8	114.3	3.7	1.87	2.02
7SV*	44787	1295	1307	31.0	173.5	18.0	21.1	4.3	0.48	1.58
Average (n = 82)	27124	755	754	22.9	228.0	46.7	66.6	4.0	1.52	1.50
Min.	3080	106	76	3.5	26.2	1.1	7.4	0.7	0.08	0.01
Max.	111771	3062	3273	94.2	1389.6	293.3	380.7	33.7	10.46	13.86
Median	20947	674	683	19.0	147.8	25.3	38.0	3.0	0.82	0.90

Tab. 3. The average element abundances in insoluble fraction [%] and the ratio between summer and winter atmospheric deposition of the observed elements and PM

Tab. 3. Średnie zawartości pierwiastków we frakcji nierozpuszczalnej [%]
oraz stosunek atmosferycznego opadu obserwowanych pierwiastków i pyłów w lecie i zimie

Element	**PM**	**Fe**	**Al**	**Mn**	**Zn**	**Pb**	**Cu**	**Cr**	**Cd**	**As**
Element abundances [%]	-	96	97	58	23	58	42	71	24	65
Ratio between AD$_S$/AD$_W$	4.3	2.4	2.5	1.9	1.3	0.9	1.2	1.6	1.0	2.3

Tab. 4. The Pearson´s cross-correlation coefficients between fluxes of trace elements (n = 82)

Tab. 4. Korelacja krzyżowa Pearsona między strumieniami pierwiastków śladowych (n = 82)

	Fe	**Al**	**Mn**	**Zn**	**Pb**	**Cu**	**Cr**	**Cd**	**As**
PM	0.61	0.34	0.47	0.13	-0.05	-0.09	0.17	0.03	0.24
Fe	-	0.68	0.79	0.07	0.00	-0.10	0.32	-0.10	0.36
Al	0.68	-	0.67	-0.09	-0.12	-0.14	0.27	-0.23	0.29
Mn	0.79	0.67	-	0.04	0.04	0.00	0.32	-0.17	0.38
Zn	0.07	-0.09	0.04	-	0.54	0.52	0.09	0.79	0.35
Pb	0.00	-0.12	0.04	0.54	-	0.70	-0.01	0.53	0.31
Cu	-0.10	-0.14	0.00	0.52	0.70	-	0.03	0.62	0.28
Cr	0.32	0.27	0.32	0.09	-0.01	0.03	-	0.01	0.10
Cd	-0.10	-0.23	-0.17	0.79	0.53	0.62	0.01	-	0.10
As	0.36	0.29	0.38	0.35	0.31	0.28	0.10	0.10	-

Tab. 5. Comparison of annual deposition fluxes of the elements from different regions [mg.m^{-2}.yr^{-1}]

Tab. 5. Porównanie rocznej wielkości opadów w różnych regionach [mg.m^{-2}.rok^{-1}]

Location	**Fe**	**Mn**	**Zn**	**Pb**	**Cu**	**Cr**	**Cd**	**As**	**Ref.**
1MA	251	10.1	31.4	4.2	8.4	1.1	0.20	0.20	This study
2SH	251	7.2	58.0	8.8	10.5	1.3	0.33	0.31	
3KL	298	6.4	66.8	11.2	14.3	1.9	0.42	0.29	
4KR	286	9.2	169.5	45.5	51.1	1.3	1.23	0.75	
5KA	138	5.5	48.3	4.5	14.7	1.3	0.51	0.82	
6KO	242	7.8	93.9	22.6	41.7	1.4	0.68	0.74	
7SV	473	11.3	63.3	6.6	7.7	1.6	0.18	0.58	
Czech Republic	291	13.6	54.3	8.8	2.9	0.7	0.15	0.47	Prášková et al., 2008
England and Wales	-	-	22.1	5.4	5.7	0.8	0.19	0.31	Nicholson et al., 2008
Massachussetts Bay	140	3.4	7.8	1.8	2.5	2.7	0.27	-	Golomb et al., 1997
Delta Pearl River, China	555	9.0	104.0	12.7	18.6	6.4	0.07	-	Wong et al., 2008
Austria	-	-	35.2	3.7	10.5	1.3	0.24	-	Spiegel et al., 2008
Northern France	-	-	15.6	2.2	3.9	-	0.05	-	Azimi et al., 2005
Belgrade, Serbia	594	26.2	41.4	21.7	34.5	1.6	0.22	-	Mijić et al., 2011

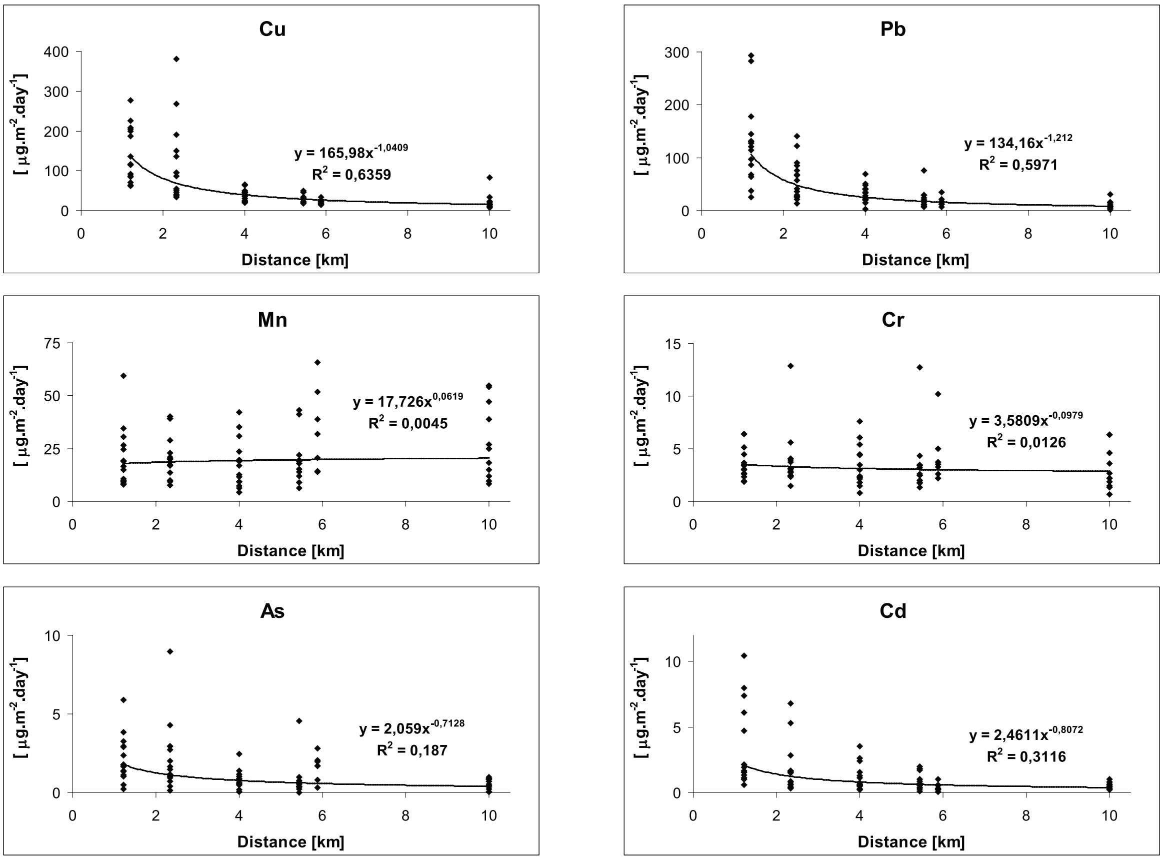

Fig. 2. The dependence between the deposition of the PM and observed elements and the distance from the copper smeltery
Rys. 2. Zależności pomiędzy opadem pyłów I badanych pierwiastków w różnych odległościach od huty miedzi.

1.2 and 1.3 for the deposition fluxes of Pb, Cd, Cu and Zn, respectively.

The relationship between the deposition of the PM and observed elements and the distance from the smelter was studied by regression analysis from all measured period. The results are presented in Fig. 2. The dependence was found in descending order for the copper, lead, zinc, cadmium and partially for arsenic. For the other elements, no relationship was found between the distance from the main emission source and the deposition of these elements.

The statistical dependence between individual atmospheric deposition of observed metals and PM was evaluated by Pearson´s correlation analysis. The coefficients are summarized in Table 4. The high positive values of the correlation coefficient were found for two relatively independent groups of elements. The values of the correlation coefficients in the range 0.52 to 0.79 were calculated between elements Zn, Cd, Pb and Cu. In the second group between elements Fe, Mn, Al, and partially PM and Cr, correlation coefficients in the range 0.34 to 0.79 were found. Chromium has a relatively low positive correlation with the elements Fe, Mn, Al and PM: 0.32, 0.27, 0.23 and 0.17, respectively. In the case of elements of first group (Zn, Cd, Pb and Cu), the chromium has coefficients close to zero. The source of chromium in addition to soil horizon is probably a remote transmission of particles. The arsenic has a specific position, when it has positive correlation coefficients with all elements and PM in the range from 0.1 to 0.36. Thus, particles from contaminated soil horizon due to historical mining and metallurgical activities can also be a source of arsenic in the area of Krompachy.

The deposition fluxes of the elements from this study are compared with results from other areas in Table 5. The deposition fluxes of Cd, Cu, Zn and Pb exceeded the corresponding data from these studies, especially at sites localized in the immediate vicinity of the copper smeltery (4KR, 6KO, 5KA).

Conclusion

Total atmospheric deposition i.e. the both wet and dry ones, was studied from seven sites in the area of copper smeltery in Krompachy from October 2009 to October 2017. The detailed analysis of deposition fluxes of selected elements and particles showed a significant effect of the copper smeltery on qualitative and quantitative characteristics of atmospheric deposition. In addition to the expected high levels of deposition of copper, the above-average high deposition of lead, zinc and cadmium were measured in comparison with different areas. The highest values of deposition fluxes of these elements were detected at sites near the copper smeltery. The level of zinc deposition disagrees with its registered emissions.

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Wpływ Huty Miedzi Krompachy (Słowacja) na poziom emisji do atmosfery

Artykuł dotyczy oceny poziomu emisji pyłów do atmosfery spowodowanej przez Hutę Miedzi Krompachy (Słowacja) w latach 2009–2017. Próbki opadu pobrano z siedmiu miejsc, które znajdują się w odległości od 1,2 do 10 km od głównego źródła zanieczyszczeń. Zbadano osadzanie się cząstek stałych i zawartości pierwiastków (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As). Zawartości pierwiastków określono oddzielnie dla frakcji rozpuszczalnej w wodzie i nierozpuszczalnej. Szczegółowa analiza źródeł opadów atmosferycznych wykazała znaczący wpływ huty miedzi. Oprócz oczekiwanego wysokiego poziomu zawartości miedzi (21–140), stwierdzono wysoką depozycję ołowiu (11–124), cynku (86–464) i kadmu (0,6–3,4 $\mu g.m^{-2}$ dzień$^{-1}$). Najwyższe zawartości pierwiastków w opadzie atmosferycznym wykryto w pobliżu huty miedzi. Stwierdzona zawartość cynku w opadzie nie odpowiada wielkości emisji.

Słowa kluczowe: opad atmosferyczny, huta miedzi, emisja, metale,

Securing Topsoil for Rehabilitation Using Fly Ash in Open-Cast Coal Mines: Effects of Fly Ash on Plant Growth

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Abstract

Rehabilitation is an important stage in mining operations for environmental conservation. However, the shortage of topsoil makes it difficult to achieve rehabilitation in open-cast coal mines. Securing topsoil by mixing soil with fly ash (FA), which is treated as an industrial waste, is expected to solve this issue in coal mines. While mixing soil with FA makes it possible to secure the topsoil and treat industrial waste simultaneously, the high alkalinity of FA and the dissolution of heavy metals from FA may inhibit plant growth. This study investigated the effects of FA in the topsoil on plant growth via vegetation tests with simulated topsoil mixed with FA using Acacia mangium, a species of flowering tree: the FA mixing ratios were set to 0%, 20%, 40%, 60%, and 100%. The growth of Acacia mangium was inhibited with increasing FA mixing ratio, especially from 60% to 80%. However, the growth rate of Acacia mangium in an FA mixing ratio of 100% was nearly comparable to that in a mixing ratio of 40%. Furthermore, there were no effects of the physical characteristics and pH conditions in the topsoil on the plant growth at any of the mixing ratios; meanwhile, the accumulated concentration of Al in the plant body increased significantly at an FA mixing ratio of 60%–80%. This suggests that the accumulation of Al, which inhibits plant growth, including root growth and its functions, in the plant body inhibited the growth of Acacia mangium. Therefore, the most important aspect in terms of rehabilitation concerning the use of FA for securing topsoil is not the mixing ratio of FA but the amount of Al in the FA and the accumulation of Al in the plant body.

Keywords: open-cast coal mine, fly ash, topsoil, rehabilitation, acacia mangium, aluminum (Al)

Introduction

Securing the topsoil is necessary for the rehabilitation of open-cast mines where disturbed mine soils inhibit plant growth (Eludoyin et al., 2017). Fly ash (FA), considered to be industrial waste, has been applied to topsoils to secure the amount of topsoil (Gorman et al., 2000; Truter et al., 2013). In addition, the application of FA to topsoils is expected to inhibit the effects of heavy metals on plant growth in soils by increasing the pH because FAs are highly alkaline (Basu et al., 2009; Shende et al., 1994). However, because several factors, such as high alkalinity and heavy metals in FA, may affect the growth of plants, the critical factors in the application of FA to topsoils should be determined in terms of their effects on plant growth (Pandey et al., 2010; Shende et al., 1994). Furthermore, the change in the physical characteristics of the topsoil after being mixed with FA plays an important role in the soil conditions for plant growth and, therefore, needs to be considered (Binal, 2016). Few studies have attempted to use FA to secure topsoil with a focus on the effects on plant growth taking into account multiple factors. This study discusses critical factors for the application of FA to securing topsoil in terms of the effects of FA on plant growth via a vegetation test with simulated topsoil with different FA mixing ratios from 0% to 100% in addition to some results that have already been reported (Hamanaka et al., 2017).

Materials and methods

Simulated soils with fly ash

The simulated soils were prepared by mixing decomposed granite produced by Gulin Kita-Kyu Co., Ltd. and Kyushu bentonite produced by Shinagawa Yogyo Co., Ltd. after screening based on soil texture, which was based on the post-mining land in a coal mine in Indonesia: the ratios of sand, silt, and clay were set to 51.1%, 25.2%, and 23.7%, respectively, which were within the range of the soil textures at the mine (sand: 22.0%–75.0%, silt: 8.0%–32.1%, and clay: 17.0%–48.0%) (Matsumoto et al., 2016; Matsumoto et al., 2018). The FA was sampled from a coal-fired power plant in Japan and was analyzed via X-ray fluorescence (XRF). Based on the chemical components of the XRF analysis, the FA was characterized according to ASTM C618-12a (ASTM C618-12a, 2012). The FA was homogeneously mixed with the simulated topsoil using the cone and quartering method at different mixing ratios (0% no FA, 20%, 40%, 60%, 80%, and 100%) and was labeled accordingly.

Material characteristics of the simulated soils with fly ash

To understand the physical characteristics of the simulated soils with FA, Atterberg limit tests were conducted based on the ASTM D4318-05 standard (ASTMD4318-05, 2005) in addition to particle-size distribution tests (ASTM D422-63, 2007), density tests (ASTM D854-14, 2014), and falling head permeability tests (ASTM D5084-10, 2010). Moreover, the

Tab. 1. Chemical composition of FA
Tab. 1. Skład chemiczny popiołów lotnych

Elements	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
(%)	67.4	1.08	18.7	4.16	0.03	1.10	2.87	0.67	1.23
Elements	P_2O_5	H_2O	SO_3	V	Cr	Cu	Zn	Pb	As
(%)	0.33	1.97	0.22	0.022	0.004	0.009	0.015	0.006	0.002

Tab. 2. Physical characteristics of the simulated topsoils with FA
Tab. 2. Właściwości fizyczne badanych składów wierzchnich warstw gleby z popiołem lotnym

FA (%)	Sand (%)	Silt (%)	Clay (%)	Soil Type	Paste pH	Density (g/cm^3)	Permeability ($\times10^{-5}$ cm/s)	Liquid Limit (%)	Plastic Limit (%)	Plasticity Index (%)
0	51.1	25.2	23.7	CL	5.54	2.41	29.4	28.1	17.4	10.8
20	40.3	37.4	22.3	CL	10.49	2.28	19.3	23.5	14.8	8.8
40	31.1	48.3	20.6	SiCL	11.08	2.23	9.2	-	14.1	-
60	23.0	60.4	16.5	SiCL	11.72	2.18	5.3	-	-	-
80	17.9	65.1	17.0	SiCL	11.55	2.13	3.8	-	-	-
100	9.0	75.3	15.7	SiCL	11.67	2.07	2.5	-	-	-

change in the pH was reported as paste pH after 12 h of the dissolution process at a 1:2 of mixing ratio of the samples and deionized water to characterize the chemical characteristics of the simulated soils with FA (AMIRA, 2002). The effects of the material characteristics were inferred based on the results because such soil conditions are known to affect the growth of plants (Keller and Dexter, 2012).

Vegetation test with *Acacia mangium*

A vegetation test with *Acacia mangium* was conducted using the simulated topsoil with FA to determine the critical factor for the application of FA to topsoil securing in terms of the effect of FA on plant growth. Due to its high adaptability, *Acacia mangium* was used for the vegetation test; the goal was to obtain a clear distinction in the plant growth for various mixing ratios. The seeds were obtained in Japan. *Acacia mangium*, which grows in tropical forests in Southeast Asian countries, is considered to be an Al-excluder plant and has a resistance to poor soil conditions (Osaki et al., 1997). *Acacia mangium* has been applied successfully worldwide to the reclamation of post-mine lands containing bauxite, copper, coal, and iron.

The prepared simulated soils at different FA mixing ratios (0% no FA, 20%, 40%, 60%, 80%, and 100%) were evenly mixed in each flower pot at a constant rate to provide uniform physical conditions in each pot to be used for the vegetation test. The vegetation test was performed in the phytotron glass room G-9 in the Biotron Application Center, Kyushu University, under the following conditions: 30°C room temperature and 70% relative humidity assuming the local climate at the mine site in Indonesia. The seedlings were transplanted at approximately 40–120 mm into the pots with different FA mixing ratios. Five plants were planted in pots for each FA mixing ratio, and their heights and diameters were measured every week. A total of 500 mL of water was supplied to the pots every 3–4 days. A liquid fertilizer, HYPONeX-R (N-P-K = 6-10-5), diluted to 1,000 mg/L with water was added to the pots once a week. The test was continued for 133 days until a clear distinction was observed (Hamanaka et al., 2017). The results were analyzed via the F test with the means compared via the Tukey test at a 5% level of probability (Dinardo et al., 1998). In addition, the pH and electric conductivity (EC) in the leachate from each pot were measured along with the measurement of the heights and diameters of the *Acacia mangium* plants.

At the end of the vegetation test, the accumulated concentrations of Al, As, B, Cd, Cr, Cu, Fe, and Zn in the *Acacia mangium* plants were determined by dissolving samples with acids. The plant samples were washed with deionized water using sonication (UT-106H, SHARP) at room temperature to remove soil particles. They were dried at 60°C for 72 h and pulverized using a mortar and pestle, including each part of the plants: leaves, stems, and roots. A total of 0.25 g of each part of the samples was digested by 5 mL of a mixture of 61% nitric acid (HNO_3) and 35% hydrochloric acid (HCl) at a ratio of 3:1 at 110°C in a DigiPREP Jr. (SCP Science, Quebec, Canada) until they were completely digested according to the description by Quadir et al. (2011). If the sample was not dissolved in the mixture, 1 mL of the mixture was added and the dissolution process was repeated. The volume of the solution was adjusted to 20 mL by adding deionized water, and the solutions were injected into an inductively coupled plasma-atomic emission spectrometer (ICP-AES, VISTA-MPX ICP-OES (Seiko Inst., Japan)) after filtration with a 0.45-μm membrane filter to measure the concentrations of Al, As, B, Cd, Cr, Cu, Fe, and Zn, which are thought to affect plant growth. The results were calculated in mg per dry unit weight (mg/g). In addition to the ratio of each part, the standard deviations of the accumulated ions in each part of the *Acacia mangium* plant were calculated.

Results and discussion

Table 1 shows the chemical composition of the FA, and Table 2 summarizes the material characteristics of the simulated soil with different mixing ratios of FA. The composition of SiO_2 has the highest value, followed by Al_2O_3 and Fe_2O_3. The CaO and MgO contents reflect the clay mineral content and the neutralization effects in the FA. Because the simulated soils with different FA mixing ratios can create alkaline soil conditions and provide dissolved metals, the effects of

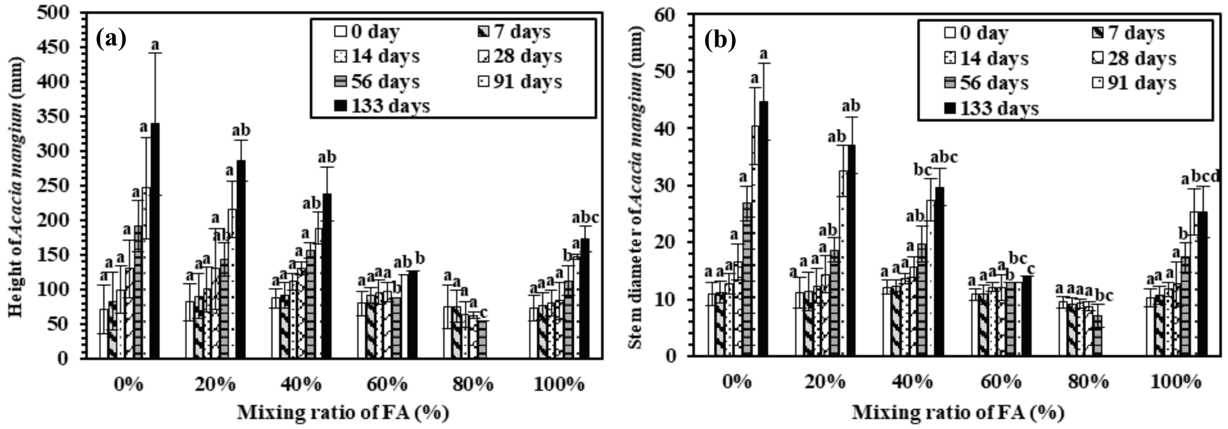

Fig. 1. Change in the (a) height and (b) stem diameter of Acacia mangium at different FA mixing ratios in the simulated topsoils. Means within the height and stem diameter of Acacia mangium with the same letter are not significantly different ($P < 5\%$) from each other according to the Tukey test

Rys. 1. Zmiana wysokości (a) i (b) średnicy Acacia mangium przy różnych dodatkach popiołów lotnych do badanych gleb. W teście Tukeya różnice dla tych samych wysokości i średnicy łodyg nie przekraczają $P < 5\%$.

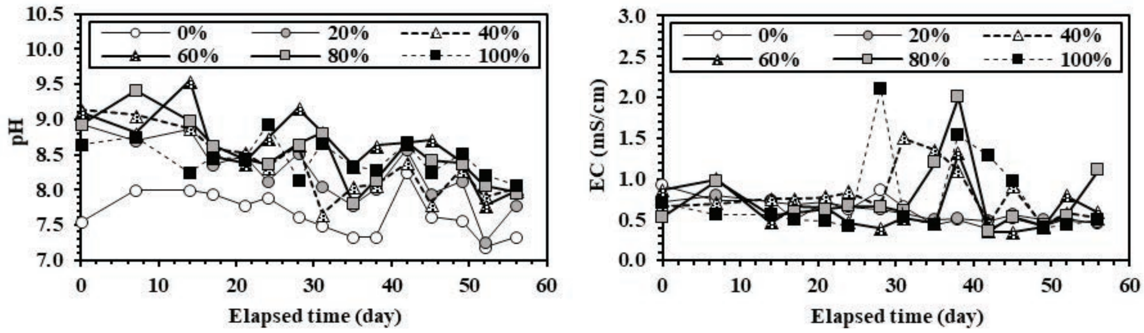

Fig. 2. Change in the pH and EC in the leachate during the vegetation test

Rys. 2. Zmiana pH i EC w odcieku podczas testu wegetacji

dissolved metals and the pH conditions on the plants needs to be investigated in this study. According to the classification by the chemical composition and the ASTM C618 standard, the FA in this study shows a similar chemical composition to class F, i.e., the $SiO_2 + Al_2O_3 + Fe_2O_3$ (%) was 90.3% (>70.0% which is assigned to class F). Considering that FAs that are classified as classes C and F have up to 5.0% SO_3, the level of SO_3 in the FA in this study had a relatively low value (Page et al., 1979). According to Table 2, the soil texture of the FA in this study primarily consisted of silt, decreasing the permeability with increasing FA mixing ratio in the simulated soil. The soil classification changed at 40% from CL to SiCL with a significant decrease in the permeability. Moreover, the liquid limits could not be measured at 40%, indicating that there was a significant change in the physical characteristics of the FA at a ratio of 40%. There was no remarkable change in the specific gravity of the simulated soil, which was 2.07–2.41 (g/cm³). The paste pH changed from 5.54 at an FA mixing ratio of 0% in the simulated soil to 11.67 at an FA mixing ratio of 100% due to the alkalinity of the CaO in the FA. The rapid change in the paste pH at an FA mixing ratio of 20% indicated that the alkaline condition might affect the growth of plants at this mixing ratio. Because physical effects of the soil on the plant growth have been observed due to the higher subsurface water retention resulting from the high permeability in addition to the pH effects, the effects of the physical properties of the soils at 40% and that of the pH effects at 20% need to be investigated during the vegetation test to determine if these are critical factors for the application of FA to topsoil in terms of their effects on plant growth (Korcak, 1996).

Figure 1 shows the change in the (a) height and (b) stem diameter of *Acacia mangium* at different FA mixing ratios in the simulated topsoils. The height and stem diameter decreased with increasing FA mixing ratio until 80%, and then they rose at 100%. After only 56 days at 80%, five plants withered during the vegetation test. These results suggest that the application of FA in the topsoil may inhibit the growth of *Acacia mangium*. Even though significant differences in the heights and stem diameters of *Acacia mangium* were not observed until 28 days for all mixing ratios according to the results of the F test, there were differences after 56 days for mixing ratios of 60% and 80%. This indicates that the mixture of FA affected the plant growth while the *Acacia mangium* plants were growing. Considering the significant change in the physical characteristics of the simulated topsoil with an FA mixing ratio of 40% and that of the paste pH at an FA mixing ratio of 20% in Table 2, the significant differences in the height and stem diameter of *Acacia mangium* after 56 days at FA mixing ratios of 60% and 80% suggest that the growth of *Acacia mangium* was not inhibited by the change in the physical properties and pH conditions in the simulated soil during the vegetation test. The change in the pH and EC in the leachate from 0 days to 56 days is plotted in Figure 2. The pH remained at approximately 8.0–9.0 at FA mixing

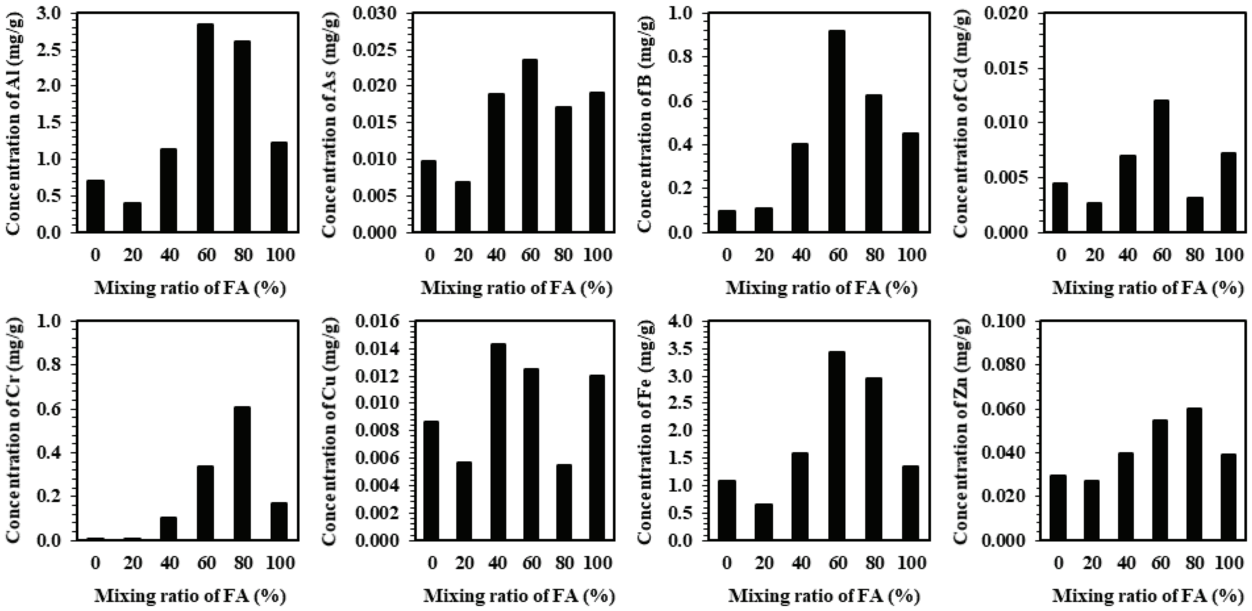

Fig. 3. Accumulated chemical concentrations in the body of *Acacia mangium*
Rys. 3. Skumulowane stężenia chemiczne w roślinie Acacia mangium

Tab. 3. Standard deviation of the accumulated ions in the body of *Acacia mangium*
Tab. 3. Odchylenie standardowe nagromadzonych jonów w Acacia mangium

FA (%)	Al	As	B	Cd	Cr	Cu	Fe	Zn
0	0.84	0.01	0.05	0.00	0.01	0.01	1.29	0.01
20	0.23	0.00	0.04	0.00	0.00	0.00	0.32	0.00
40	1.51	0.01	0.34	0.01	0.14	0.01	2.12	0.02
60, 80	-	-	-	-	-	-	-	-
100	1.84	0.02	0.46	0.01	0.41	0.02	1.32	0.03

ratios of 20–100% until 56 days, indicating that the growth of *Acacia mangium* was not affected by the alkaline conditions attributed to FA. The EC also remained at EC = 0.5–1.0 mS/cm at for all mixing ratios until 56 days, suggesting a continuous dissolution of ions from the simulated topsoil during the vegetation test.

Figure 3 summarizes the accumulated concentrations of Al, As, B, Cd, Cr, Cu, Fe, and Zn at the end of the vegetation test. High concentrations of Al and Fe were observed at FA mixing ratios of 60–80% compared to those at other FA mixing ratios: only Al and Fe showed more than 1.0 mg/g at FA mixing ratios of 60–80%. As Table 1 shows, the Al and Fe concentrations were attributed to the high content of Al and Fe in the FA. The lower concentrations of Al and Fe at an FA mixing ratio of 100% are thought to be due to the spatial distribution bias within the FA.

Tables 3 and 4 summarize the standard deviations of the accumulated ions in the body of *Acacia mangium* and the accumulated ions in each part of the body of *Acacia mangium*; the standard deviation could not be calculated at FA mixing ratios of 60% and 80% because they could not be separated into leaves, stems, and roots. The standard deviations of Al and Fe clearly increased with the FA mixing ratio and were greater than 1.0 at mixing ratios of 40% and 100%, showing an uneven distribution of Al and Fe in the plant body. In Table 4, approximately 90% of the Al and Fe accumulated in the roots (93–94% of the Al and 88–93% of the Fe at mixing ratios of 40% and 100%). The suction of water from the roots caused the accumulation of the metals on the roots. Al easily dissolves as $Al(OH)_4^-$ under alkaline conditions, inhibits nutrition absorption via nitrogen fixation on roots, and precipitates due to a detoxification mechanism of rhizotoxic mononuclear Al species, leading to a physical block to the transport of nutrients and other solutes into the apoplast necessary for root growth (Saifuddin et al., 2016; Stass et al., 2006). Even though As, Cd, Cr, and Cu accumulated on the roots at FA mixing ratios of 60–90%, the high concentration of Al (more than 2.0 mg/g at mixing ratios of 60–80%) indicates that the critical factor causing the inhibition of growth in *Acacia mangium* was the accumulation of Al derived from the FA in this study. In addition, the results show that the FA in this study can be applied to the simulated topsoil in ratios up to 40% in terms of plant growth; however, not only the FA mixing ratio but also the growth rate of plants and the accumulation of Al in the plants needs to be considered via continuous monitoring at mines. In addition, the effects of the application of FA to topsoil need to be investigated with other plant species without a resistance to poor soil conditions.

Conclusion

This study investigated the effects of FA on plant growth via vegetation tests with simulated topsoil mixed with FA using *Acacia mangium* plants; the FA mixing ratio was set to 0–100%. The growth of *Acacia mangium* was inhibited with

Tab. 4. Ratios of the accumulated ions in each part of the body of *Acacia mangium*
Tab. 4. Udział zakumulowanych jonów w poszczególnych częściach Acacia mangium

FA (%)	(%)	Al	As	B	Cd	Cr	Cu	Fe	Zn
0	Leaf	5	22	29	11	9	11	6	25
	Stem	4	9	13	10	10	10	3	18
	Root	91	69	58	79	81	79	91	56
20	Leaf	18	41	63	34	11	22	18	33
	Stem	8	31	19	35	14	22	8	36
	Root	74	28	18	31	74	56	74	31
40	Leaf	4	35	73	27	3	14	4	28
	Stem	3	8	5	7	4	6	3	13
	Root	93	57	22	66	93	81	93	59
60, 80	-	-	-	-	-	-	-	-	-
100	Leaf	5	73	69	38	4	17	11	39
	Stem	1	5	3	4	0	2	1	5
	Root	94	22	29	58	95	81	88	56

increasing FA mixing ratio, especially from 60% to 80%. Conversely, the growth rate of *Acacia mangium* at an FA mixing ratio of 100% was nearly comparable to that at an FA mixing ratio of 40%. Furthermore, there were no effects of the physical characteristics and pH conditions in the topsoil on the plant growth at all the mixing ratios; meanwhile, the accumulating concentration of Al in the plant body increased significantly at FA mixing ratios of 60–80%. This suggests that the accumulation of Al, which inhibits plant growth, including root growth and its functions, in the plant body inhibited the growth of *Acacia mangium*. Therefore, the most important aspect in terms of rehabilitation concerning the use of FA for securing topsoil is not the FA mixing ratio but the amount of Al in the FA and the accumulation of Al in the plant.

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Przygotowanie wierzchniej warstwy gleby do rekultywacji przy użyciu popiołu lotnego w kopalniach odkrywkowych: wpływ popiołów lotnych na wzrost roślin

Rekultywacja jest ważnym etapem w eksploatacji górniczej wzakresie ochrony środowiska. Brak wierzchniej warstwy gleby utrudnia osiągnięcie efektu rekultywacji w kopalniach odkrywkowych. Oczekuje się, że zabezpieczenie wierzchniej warstwy gleby przez zmieszanie gleby z popiołem lotnym (FA), który jest traktowany jako odpad przemysłowy, rozwiąże ten problem w odkrywkowych kopalniach węgla. Podczas mieszania gleby z FA możliwe jest jednoczesne zabezpieczenie wierzchniej warstwy gleby i utylizacja odpadów przemysłowych. Jednak wysoka alkaliczność FA i rozpuszczanie metali ciężkich z FA może hamować wzrost roślin. W artykule przedstawiono wpływ dodatku FA do wierzchniej warstwy gleby na wzrost roślin poprzez testy roślinności z symulowaną wierzchnią warstwą gleby zmieszaną z FA przy użyciu Acacia mangium i gatunków drzew kwitnących. Proporcje mieszanek FA zostały określone na 0%, 20%, 40%, 60% i 100%. Wzrost Acacia Mangium był hamowany wraz ze wzrostem zawartości FA, zwłaszcza od 60% do 80%. Jednak tempo wzrostu w mieszance FA w proporcji 40% było praktycznie takie jak bez dodatku FA. Ponadto nie zaobserwowano wpływu właściwości fizycznych i warunków pH w wierzchniej warstwie gleby na wzrost roślin w żadnej mieszance. Oznacza to, że skumulowane stężenie Al w roślinie znacznie wzrosło dla mieszanek z dodatkiem FA 60% -80%. Sugeruje to, że nagromadzenie Al, które hamuje wzrost roślin, w tym wzrost korzeni i jego funkcje, w organizmie rośliny hamuje wzrost Acacia Mangium. Dlatego najważniejszym aspektem rekultywacji z zastosowaniem FA do zabezpieczania wierzchniej warstwy gleby nie jest wielkość dodatku FA, lecz ilość Al w FA i akumulacja Al w roślinie.

Słowa kluczowe: kopalnia odkrywkowa, popiół lotny, wierzchnia warstwa gleby, rekultywacja, Acacia mangium akacja mangowa, aluminium (Al)

Possibilities of Siderite and Barite Concentrates Preparation from Tailings of Settling Pit Nearby Markušovce Village (Eastern Slovakia)

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Abstract

The contribution deals with recovery of useful minerals such as siderite and barite from tailings collected in settling pit nearby Markušovce village (East Slovakia). The material form the pit was subjected to gravity pre-concentration and magnetic separation under laboratory conditions with the aim to verify a possibility of siderite and barite concentrates preparation. A fraction of +0.2–1 mm forming a 40.56 wt% of total grain size scale of the material from the pit and containing 35.71% SiO_2, 22.55% Fe_2O_3, 7,12% Al_2O_3, 5.48% Ba, and 3.89% SO_4^{2-} was tested in upgrading process. Thus, 78.18% of SiO_2, and 60.41% of Al_2O_3 at loss 21.70% Fe_2O_3 and 2.09% of Ba were removed in gravity pre-concentration. The iron concentrate with the content of 44.33% Fe_2O_3 at Fe recovery of 77.29% in magnetic product was obtained. Barite pre-concentrate with the Ba content of 46.21% at Ba recovery of 91.95% in non-magnetic product was won.

Keywords: tailings, recovery, gravity pre-concentration, magnetic separation

Introduction

The contribution describes a laboratory test of useful minerals recovery from tailings of the Markušovce settling pit. These minerals was deposited in the pit as a result of low ore beneficiation efficiency in the past caused by e.g. incoordinated upgrading process, ore properties changes (mineral composition, intergrowth) at exploitation advance, actual unavailability of suitable dressing machines after such changes, error grains in the upgrading process, etc.

The settling pit lies between the Markušovce and Rudňany villages. Its construction and operation are connected with former and current mining activities on the Rudňany and Poráš-Zlatník polymetallic ore deposits. As to nomenclature the settling pit in older papers was named Rudňany after Rudňany deposit and the facility of Iron Ore Works. Newer publications usually use adjective Markušovce, because the settling pit is located in the cadastral districts of the Markušovce and Zavadka villages, and in the bottom part of the Markušovce valley (Jakabský et al., 2010). The area of the Markušovce settling pit occupies 35.1 hectares, the length attains 1,085 meters and the width ranges from 165 to 345 metres. The thickness of deposited materials varies in the dependence on initial ground levels and it may achieve maximally about 38 metres. The settling pit is bounded by the natural ground level of the valley and also by three earthen dams (Jakabský et al., 2010). Recently, the settling pit is in operation by the SABAR, Ltd. Markušovce. Altogether 9,800,000 tons of the tailings of so-called flotation sands at the density of 1.59 t.m–3 and a total volume of 6,200,000 m3 are deposited in the settling pit (Karoli et al., 2008).

It is needed to mention that history of the settling pit started with building-up of so-called “New Industrial Plant – NIP” for complex processing of polymetallic Fe–Cu–Sb–Hg and barite ores. The design capacity of NIP was of 1 Mt ore/year. The ore dressing plant and the sintering plant were put into operation in 1964, mercury plant in 1970. The ore dressing plant included comminution, high intensity magnetic separation and flotation. The feed of ore was upgraded as follows: magnetic separation (siderite concentrate, roughing 0.6T, scavenging 0.7T), non-magnetic product was subjected to flotation of sulphides, cell product from sulphide flotation to flotation of barite. The cell product from barite flotation was final refuse deposited in the settling pit. The fine-grained siderite concentrate was further processed in sintering plant for blast furnaces. So called “collective sulphide concentrate” was roasted in the mercury plant to obtain suitable feed for copper and antimony smelteries (modified after Fabry, 1992).

The dominant minerals of the ore veins were represented by siderite, barite, Hg-tetrahedrite (schwazite), chalcopyrite, pyrite, quartz, ankerite, dolomite, feldspars, cinnabar, etc. Thus, the gangue minerals, lost valuables and accompanying rocks of ore veins such as sericitic phyllite, chlorite phyllite, graphitic schist and fuchsite quartzite mainly occur in the settling pit (Jakabský et al., 1991).

In the first half of 90s of 20th century the “Program of metal-mines reduction” was proclaimed by Czechoslovak government mainly due to unfavourable metals price on the world market, low metal content in ores of Czechoslovak deposits, and ecological movements. In this time all mining

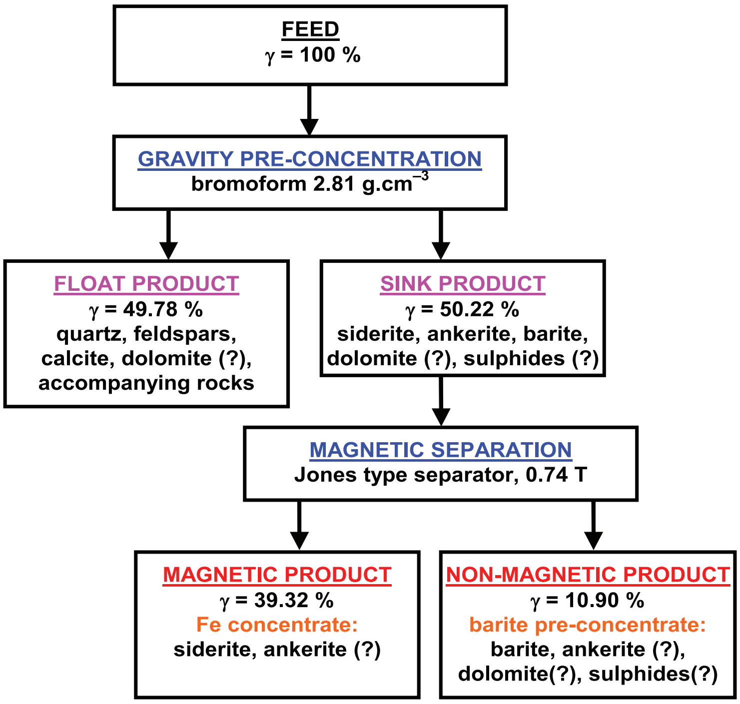

Fig. 1. Flow-sheet of performed upgrading
Rys. 1. Schemat przeprowadzonych badań laboratoryjnych

facilities were state-owned companies and realisation of the Program resulted in closing almost all metal-ore mines. As to Rudňany facility, mercury plant was closed in 1993, siderite exploitation was shut down in 1994.

Recently, residual proven and developed reserves of barite are mined and processed by the SABAR, Ltd. Markušovce. In 2014 annual mining output was of 21 kt at barite concentrate production of 15 kt (Shi, 2017). In 2016 the output of 23 kt is reported by Reichl et al. (2018). These published data correspond to personal information from the representatives of the company. For comparison Jakabský et al. (1991) reported production of 60 kt barite concentrate in 1990.

Considerations on tailings upgrading route

On the basis of above mentioned a question of the settling pit material upgrading way is still open. Generally, there are two basic contradictory concepts there. On the one hand there is intensive endeavour to attain maximal recovery of barite by direct feed of material to flotation (barite - froth product), followed by magnetic separation of cell product to obtain siderite concentrate. On the other hand there are considerations on pre-concentration of useful minerals to reduce necessary maximal capacity flotation line (and also magnetic separation capacity) with the aim to total upgrading cost minimization, but at an awareness of some barite losses in previous operations.

Thus, the various concepts can be considered after material excavation from the settling pit:

- flotation of sulphides (sulphides removal into froth, Cu-concentrate) → flotation of barite (cell product from sulphide flotation, barite recovery in froth) → magnetic separation of cell product from barite flotation to obtain siderite concentrate → non-magnetic product – sands for building industry,
- magnetic separation (Fe concentrate) → sulphide flotation of non-magnetic product (Cu-concentrate in froth product) → barite flotation of cell product from sulphide flotation (barite concentrate in froth) → cell product of barite flotation – sand for building industry (modified after Jakabský et al., 2010),
- gravity pre-concentration (quartz and waste rock removal in light product, sand for building industry) → magnetic separation of heavy product (Fe-concentrate) → barite flotation of non-magnetic product (barite concentrate in froth product or reverse flotation) → final flotation refuse – sulphides and residuum of other minerals.

Moreover, after above mentioned it must be taken into consideration, that sulphides are harmful admixture in all applicable/saleable products.

Materials and methods

The laboratory test of upgrading process was performed according to flow-sheet illustrated in Fig. 1. The grain size fraction of +0.2–1 mm was subjected to testing. This fraction has the highest mass yield and as to grain size it is suitable for the both heavy media separation and dry magnetic separation (also according to another flow-sheet, e.g. magnetic separation would be also the first step).

As to gravity pre-concentration the bromoform 97% stabilised with ethanol, with a density of 2.81 g.cm^{-3} (Alfa Aesar) was applied as a heavy media.

The Dry High Gradient Magnetic Separation (DHGMS) has been carried out using universal laboratory magnetic separator JONES in a cassette located between its poles. The cassette was lined by two grooved plates made of magnetically soft iron. The separation was performed at 0.74 T.

Tab. 1. Dependence of chemical composition on grain size – major elements [%]
Tab. 1. Zależność składu chemicznego od wielkości ziarna – główne pierwiastki [%]

grain size [mm]	γ [%]	κ	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba
+1.000	3.22	795	33.90	9.54	2.23	1.38	1.23	27.45	0.83	1.27	2.32	3.48	5.41
0.200–1.000	40.56	613	35.71	7.12	1.62	0.94	0.94	22.55	0.58	1.29	1.50	3.89	5.48
0.100–0.200	35.95	1671	27.96	7.52	1.86	1.29	1.24	26.05	0.80	1.40	1.67	4.55	7.18
0.071–0.100	3.50	4290	20.28	4.12	0.93	1.58	1.09	31.47	0.48	0.63	1.18	1.56	6.24
0.063–0.071	7.09	3448	20.95	4.46	1.20	1.59	1.02	31.68	0.49	0.78	1.17	1.77	5.66
0.040–0.630	5.36	4393	22.76	4.60	1.09	1.61	1.08	32.51	0.55	0.68	1.21	1.77	6.47
–0.040	4.33	3339	26.59	6.46	1.70	1.63	1.31	30.89	0.81	1.14	1.41	3.36	7.61
Feed	100.00	1649	30.19	6.88	1.65	1.21	1.09	25.82	0.66	1.23	1.53	3.74	6.27

Tab. 2. Dependence of chemical composition on grain size – minor elements [ppm]
Tab. 2. Zależność składu chemicznego od wielkości ziarna – pierwiastki towarzyszące [ppm]

grain size [mm]	γ [%]	κ	V_2O_5	Cr_2O_3	Zr	Ni	Co	Zn	Cd	Pb	Sr	Cu	Sb	As	Hg
+1.000	3.22	795	452	80	63	78	42	42	42	17	818	475	263	66	68
0.200–1.000	40.56	613	489	60	61	60	27	36	37	10	836	592	122	44	39
0.100–0.200	35.95	1671	563	410	45	70	43	34	48	16	1071	493	141	81	39
0.071–0.100	3.50	4290	151	100	66	70	33	49	43	23	780	602	181	138	51
0.063–0.071	7.09	3448	226	440	74	75	33	54	37	20	723	545	157	103	38
0.040–0.630	5.36	4393	253	280	95	82	36	49	43	21	858	655	214	208	68
–0.040	4.33	3339	370	300	141	93	58	59	58	28	1138	917	331	251	131
Feed	100.00	1649	466	240	62	68	36	39	43	15	927	567	152	83	46

Tab. 3. Distribution of chemical components into grain size classes - major elements [%]
Tab. 3. Rozkład zawartości składników chemicznych w klasach ziarnowych – główne pierwiastki [%]

grain size [mm]	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba
+1.000	3.61	4.46	4.35	3.66	3.62	3.42	4.01	3.32	4.87	2.98	2.77
0.200–1.000	47.98	41.95	39.89	31.40	34.92	35.43	35.34	42.53	39.68	42.15	35.43
0.100–0.200	33.30	39.27	40.60	38.19	40.83	36.27	43.20	40.91	39.16	43.68	41.15
0.071–0.100	2.35	2.09	1.97	4.55	3.49	4.26	2.52	1.79	2.69	1.45	3.48
0.063–0.071	4.92	4.59	5.16	9.28	6.62	8.70	5.22	4.49	5.41	3.34	6.39
0.040–0.630	4.04	3.58	3.54	7.10	5.30	6.74	4.43	2.96	4.23	2.53	5.52
–0.040	3.81	4.06	4.47	5.82	5.21	5.18	5.29	3.99	3.97	3.86	5.25
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 4. Distribution of chemical components into grain size classes - minor elements [%]
Tab. 4. Rozkład zawartości składników chemicznych w klasach ziarnowych – pierwiastki towarzyszące [%]

grain size [mm]	V_2O_5	Cr_2O_3	Zr	Ni	Co	Zn	Cd	Pb	Sr	Cu	Sb	As	Hg
+1.000	3.12	1.09	3.28	3.68	3.79	3.47	3.17	3.67	2.85	2.69	5.57	2.55	4.77
0.200–1.000	42.55	10.27	40.11	35.69	30.70	37.53	35.27	27.20	36.69	42.34	32.58	21.45	34.53
0.100–0.200	43.42	62.20	26.23	36.91	43.33	31.42	40.55	38.58	41.66	31.26	33.37	35.00	30.61
0.071–0.100	1.13	1.48	3.74	3.59	3.23	4.40	3.53	5.39	2.95	3.71	4.17	5.80	3.89
0.063–0.071	3.44	13.16	8.50	7.80	6.56	9.84	6.16	9.51	5.54	6.81	7.33	8.77	5.88
0.040–0.630	2.91	6.33	8.25	6.44	5.41	6.75	5.41	7.54	4.97	6.19	7.55	13.39	7.95
–0.040	3.43	5.48	9.89	5.90	6.99	6.60	5.90	8.10	5.33	7.00	9.44	13.03	12.36
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 5. Composition of float and sink products
Tab. 5. Skład produktów analizy densymetrycznej

product	γ [%]	κ	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
Float	49.78	78	56.07	8.64	0.88	0.31	0.55	9.83	0.42	0.57	1.90	0.22	0.23	53
Sink	50.22	1143	15.52	5.61	2.35	1.56	1.33	35.16	0.73	2.00	1.11	7.55	10.68	1613
Feed	100.00	613	35.71	7.12	1.62	0.94	0.94	22.55	0.58	1.29	1.50	3.89	5.48	836

Tab. 6. Recovery of chemical components into float and sink products
Tab. 6. Zawartości składników w produktach wzbogacania grawitacyjnego

product	γ [%]	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
F	49.78	78.17	60.42	27.07	16.46	29.07	21.70	36.32	22.03	62.92	2.83	2.09	3.15
S	50.22	21.83	39.58	72.93	83.54	70.93	78.30	63.68	77.97	37.08	97.17	97.91	96.85
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 7. Composition of magnetic and non/magnetic products
Tab. 7. Skład produktów magnetycznych i niemagnetycznych

product	γ [%]	κ	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
M	78.30	1449	17.13	6.36	2.63	1.990	1.61	44.33	0.45	0.58	1.22	0.60	0.83	134
N	21.70	39	9.69	2.92	1.33	0.001	0.31	2.08	1.74	7.14	0.71	32.59	46.21	6946
Sink	100.00	1143	15.52	5.61	2.35	1.560	1.33	35.16	0.73	2.00	1.11	7.57	10.68	1613

Tab. 8. Recovery of chemical components into magnetic and non/magnetic products
Tab. 8. Uzyski składników w produkcie magnetycznym i niemagnetycznym

product	γ [%]	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
M	78.30	86.44	88.71	87.70	99.99	94.93	98.72	48.26	22.66	86.11	6.22	6.08	6.51
N	21.70	13.56	11.29	12.30	0.01	5.07	1.28	51.74	77.34	13.89	93.78	93.92	93.49
Sink	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 9. Total balance: quality of separation products
Tab. 9. Bilans całkowity: jakość produktów wzbogacania

product	γ [%]	κ	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
Float	49.78	78	56.07	8.64	0.88	0.31	0.55	9.83	0.42	0.57	1.90	0.22	0.23	53
M	39.32	1449	17.13	6.36	2.63	1.99	1.61	44.33	0.45	0.58	1.22	0.60	0.83	134
N	10.90	39	9.69	2.92	1.33	0.001	0.31	2.08	1.74	7.14	0.71	32.59	46.21	6946
Feed	100.00	613	35.70	7.12	1.62	0.94	0.94	22.55	0.58	1.29	1.50	3.89	5.48	836

The products from gravity pre-concentration: Float and Sink were filtered and decanted by methanol and water to remove rest of bromoform, and dried. All separation products were weighed to determine a mass yields "γ", and assayed using XRF. The volume magnetic susceptibility was also measured to observe iron mineral distribution.

XRF spectrometer SPECTRO XEPOS model XEPO3 (Spectro Analytical Instruments, GmbH, Nemecko), at the element range of ^{11}Na – ^{92}U was used for assaying.

The volume magnetic susceptibility "κ" [10^{-6} SI units] was measured using the Kappabridge KLY-2, Geofyzika Brno at following conditions: the magnetic field intensity of 300 $A.m^{-1}$, the field homogeneity of 0.2 %, the operating frequency of 920 Hz, the range of $-1{,}999.10^{-6} \div +650{,}000.10^{-6}$ SI unit.

On the basis of mass yields and chemical analyses distribution / recovery of chemical component into grain size classes / separation product was calculated.

Results and discussion

The results of grain size analysis and quality of grain size classes are introduced in Tables 1–2.

The distribution of chemical components in grain size classes is reported in Tables 3–4.

The partial results of gravity pre-concentration and magnetic separation, respectively, are introduced in Tables 5–8. The quality of products and recoveries of observed chemical components within the frame of whole flow-sheet are described in Tables 9–10 (Feed = Float+Sink, Sink=M+N, Feed=Float+M+N).

The chemical analyses confirm known fact that main chemical components of the settling pit are SiO_2, Fe_2O_3, Al_2O_3, Ba and SO_4^{2-}. For the ore upgrading control the company usually observes contents of SiO_2, FeTOTAL, $BaSO_4$, and Cu. The occurrence of sulphides indicate above all the content of Cu, further Sb, Zn, Hg, and Pb. Strontium in the product of sieving and separation has similar distribution as barium. So, it indicates an occurrence of celestine ($SrSO_4$)

Tab. 10. Total balance: distribution / recovery of chemical components into separation products

Tab. 10. Bilans całkowity: rozkład składników użytecznych w produktach wzbogacania

product	γ [%]	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Sr
Float	49.78	78.18	60.41	27.09	16.47	29.11	21.70	36.32	21.99	62.93	2.83	2.09	3.16
M	39.32	18.87	35.12	63.95	83.52	67.30	77.29	30.74	17.68	31.92	6.04	5.96	6.30
N	10.90	2.96	4.47	8.96	0.01	3.59	1.01	32.95	60.33	5.15	91.13	91.95	90.54
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 11. Comparison of settling pit material composition [1 – after Jakabský et al., 2010; 2 – after Petrák et al., 2011 and Tóth et al., 2012]

Tab. 11. Porównanie składu materiału zdeponowanego w osadniku [1 – wg Jakabský et al., 2010; 2 – wg Petráku i in., 2011 i Tóth i in., 2012]

author	[%]											[ppm]			
	SiO_2	Al_2O_3	MgO	MnO	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	SO_4^{2-}	Ba	Cu	Sb	As	Hg
This work	30.19	6.88	1.65	1.21	1.09	25.82	0.66	1.23	1.53	3.74	6.27	567	152	83	46
1	38.12	n.a.	n.a.	n.a.	n.a.	22.02	n.a.	n.a.	n.a.	n.a.	4,77	460	n.a.	n.a.	n.a.
2	30.70	5.30	2.80	1.30	1.90	28.60	0.40	n.a.	1.40	5.09	6.34	624	115	48	118

Tab. 12. Comparison of Fe and Ba concentrates, and SiO_2-bearing product

Tab. 12. Porównanie koncentratów Fe i Ba oraz produktu zawierającego SiO_2

Fe–concentrate - Fe_2O_3				barite (pre-)concentrate - Ba				refuse / float – SiO_2			
Jakabský, 2010		This work		Jakabský, 2010		This work		Jakabský, 2010		This work	
β [%]	ε [%]	β [%]	ε [%]	β [%]	ε [%]	β [%]	ε [%]	β [%]	ε [%]	β [%]	ε [%]
39.90	83.48	44.33	77.29	53.74	75.18	46.21	91.95	64.22	79.26	56.07	78.18
α [%]	ε [%]	α [%]	ε [%]	α [%]	ε [%]	α [%]	ε [%]	α [%]	ε [%]	α [%]	ε [%]
21.22	100.00	22.55	100.00	4.78	100.00	5.48	100.00	39.63	100.00	35.70	100.00
γ [%]	44.40	γ [%]	39.32	γ [%]	6.69	γ [%]	10.90	γ [%]	48.91	γ [%]	49.10

as isomorphous admixture in barite in the frame of barite–celestine series.

A comparison of settling pit material composition is performed in Table 11, where differently reported chemical components after various authors were recalculated to the same analytes. Under consideration that samples come from various places of the settling pit, moreover, the analyses were also performed by various analytical methods, the differences are not significant.

Finally, comparison of separation products parameters is introduced in Table 12, where:

α [%] – a component content in the feed,
β [%] – a component content in given product,
ε [%] – a recovery of observed component into given product,
γ [%] – a mass yield of given product.

Jakabský et al. (2010) realized upgrading process as follows:
i) magnetic separation of siderite,
ii) barite flotation of non-magnetic product.

In this case the feed into separation had lower grade, i.e. lower content of useful components/minerals and higher content of silica. Under application this flow-sheet a higher recovery of iron was attained (by 6.19%), but the recovery of Ba was lower by 16.77%. On the other hand barite concentrate reported by Jakabský et al. (2010) has higher grade by 7.5 %, but it was won by flotation. Barite (pre-)concentrate prepared after flow-sheet in Fig. 1 represent "only" non-magnetic product after siderite separation.

Conclusion

The possibilities of tailings upgrading from the Markušovce settling pit using gravity and magnetic separation methods with the aim to prepare iron and barite (pre-)concentrates were studied.

An application of gravity pre-concentration enables to cut by half the feed for follow-up operation/s.

It means firstly an installation of smaller magnetic separators, i.e. half capacity in comparison with direct feeding of settling pit material into magnetic separation without gravity pre-concentration, and secondly also about 5-times lower capacity of flotation line. All these mentioned facts would be result in lower capital and running costs, respectively.

Moreover, laboratory test showed that losses of barite in light product of gravity pre-concentration and in magnetic product are low, i.e. 8.05 %. Thus, a flotation process would be applied for an enhancement of final product barite grade, naturally with some further losses of barite in a cell product of flotation.

Losses iron in light and/or non-magnetic products are disputable. It is well-known that accompanying rocks, mainly graphitic schist also contain iron, but bonded on (alumo-)silicates, which is unusable in iron metallurgy. So, the material balance calculated on the basis of total iron content as an analyte can distort the results of magnetic separation. The assaying of siderite iron would be more suitable for magnetic separation process control and adjustment.

Finally, a hydrocyclone would be applied in a gravity pre-concentration under full scale operation after laboratory and pilot plant verification.

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Możliwości pozyskania koncentratów syderytu i barytu ze stawów osadowych zlokalizowanych koło miejscowości Markušovce (Wschodnia Słowacja)

Artykuł dotyczy możliwości odzysku minerałów użytecznych takich jak syderyt i baryt z odpadów zdeponowanych osadniku w pobliżu miejscowości Markušovce (Słowacja Wschodnia). Materiał z odwiertu poddano wstępnemu wzbogacaniu grawitacyjnemu i separacji magnetycznej w warunkach laboratoryjnych w celu weryfikacji możliwości uzyskania koncentratów syderytu i barytu. Klasa ziarnowa 0,2-1 mm ma wychód 40,56% wagowo i zawartość 35,71% SiO_2*, 22,55%* Fe_2O_3*, 7,12%* Al_2O_3*, 5,48% Ba i 3,89%* SO_4^{2-} *była poddana wzbogacaniu. Uzyskano koncentrat o uzysku 78,18%* SiO_2 *i 60,41%* Al_2O_3 *. We wstępnym wzbogacaniu grawitacyjnym usunięto 21,70%* Fe_2O_3 *i 2,09% Ba w stężeniu grawitacyjnym. Otrzymano koncentrat żelaza o zawartości 44,33%* Fe_2O_3 *przy uzysku Fe 77,29% w produkcie magnetycznym. Uzyskano koncentrat wstępny (produkt niemagnetyczny) barytu o zawartości Ba 46,21% i uzysku 91,95%.*

Słowa kluczowe: odzysk, wstępna koncentracja grawitacyjna, separacja magnetyczna

Utilization of Blast Furnace Slag for Immobilization of Copper Ions from Solution

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Abstract

Disposal of wastes containing metal ions such as Cu(II) ions is serious problem nowadays. Various materials are utilized for the purpose of immobilization of Cu(II) ions. Attractive type of material is represented by slags – waste from the metallurgical industry. Raw and alkali-activated blast furnace slag were studied for the purpose of immobilization of Cu(II) ions from the aqueous solution and for disposal of Cu(II) containing wastes. Slags were saturated by Cu(II) ions. Amount of Cu(II) deposited on the raw slag was 6.35 ± 0.12 mg/g and amount deposited on the alkali-activated slag was 151.37 ± 0.95 mg/g. The saturated materials were thermally treated at 100, 500, and 1000°C. The thermal treatment leads to the slight structural changes in the case of raw slag and to the significant structural changes in the case of alkali-activated slag. Cu(II) ions probably incorporate to the matrix of materials. The materials based on alkali-activated slag exhibit higher stability to the leaching of Cu(II) ions compared to raw slag based materials when only 0.13% of the total immobilized amount of Cu(II) ions was released to the solutions during the leaching experiment in the case of alkali activated slag compared to 12% in the case of raw slag. The higher temperature of treatment leads to more stable material in the case of both initial slags. The studied materials are less stable under the acidic conditions in comparison with the neutral and alkaline conditions. Alkali-activated blast furnace slag could be promising material for the Cu(II) ions immobilization and for the safe disposal of Cu(II) containing wastes.

Keywords: slag, solidification, desorption, copper ions, thermal treatment

Introduction

Aluminosilicates of natural and artificial origin (clay minerals, slags) have been used in the field of waste processing and deposition for a long time. Attractive type of silicate material is represented by slag – waste needed to be safely deposited, but, on the other hand it finds its utilization in the building industry. Slag could be also used for the toxic waste immobilization (solidification) and thus to the hazardous waste disposal, e.g. the treatment of the contaminated waters (removal of inorganic and organic contaminants) (Shi et al., 2006; Repo et al., 2015). Number of studies (Dimitrova and Mehanjiev, 2000; Xue et al., 2009; Song et al. 2013) present slags as a cheap adsorbent of metals from the polluted waters. However, the slag adsorbents exhibit considerable heterogeneity and low stability of slag in the sorption processes (from disruption and change of structure up to matrix dissolution, leaching of some components causing the enormous pH enhancement of sorption medium, changes of chemical and mineralogical composition). Stabilization of slag for its application as adsorbent is necessary (Repo et al. 2015; Van Zomeren et al. 2011, Runti et al. 2016). The stabilization can be (in addition to other ways) performed by above mentioned alkali activation (Rovnaníková and Krmíčková, 2015; Pacheco-Torgal et al. 2015).

The aluminosilicate structure of slag creates with alkali activator (carbonates, hydroxides, sulphates) a solid matrix enabling to intercalate or encapsulate undesirable ions (Rovnaníková and Krmíčková, 2015). This way alkali activated slags are used to fixing and immobilization of contaminants in wastes (Jin and Al-Tabbaa, 2014; Zhang et al., 2017). In addition to the improvement of mechanical properties, the reduction of matrix dissolution represents a great advantage of the alkali activated slags (Kim et al. 2017). The formed hardened material (geopolymer) can be therefore suitable to the wastes processing (Shi et al. 2006; Wang et al. 2016; Liew et al. 2016). The utilization of the waste material – slag for the disposal of another local wastes represents a positive aspect from the point of view of the Ostrava Agglomeration.

Materials and methods

Blast furnace slag (BFS) was kindly provided by ArcelorMittal Ostrava a.s. (Ostrava, Czech Republic). Slag was milled in the laboratory mill (Testchem, Poland) and sieved through the sieve 0,5 mm. Alkali-activation was performed by the water glass (Kittfort Ltd., Prague, Czech Republic) solution which was treated by NaOH (Mach chemicals Ltd., Ostrava, Czech Republic) to obtain ratio SiO_2:Na_2O on the value 1:1. The portion of 250 g of slag was mixed with 250 mL of activation solution and the suspension was left for the 7 days with occasional mixing. The resulting gel was transferred to the plastic dishes and it was dried in the dryer at 60°C to the constant weight (7 days). The alkali-activated slag (AA BFS) was then milled and sieved to obtain particles below 0,5 mm. Both materials (raw and alkali-activated slag)

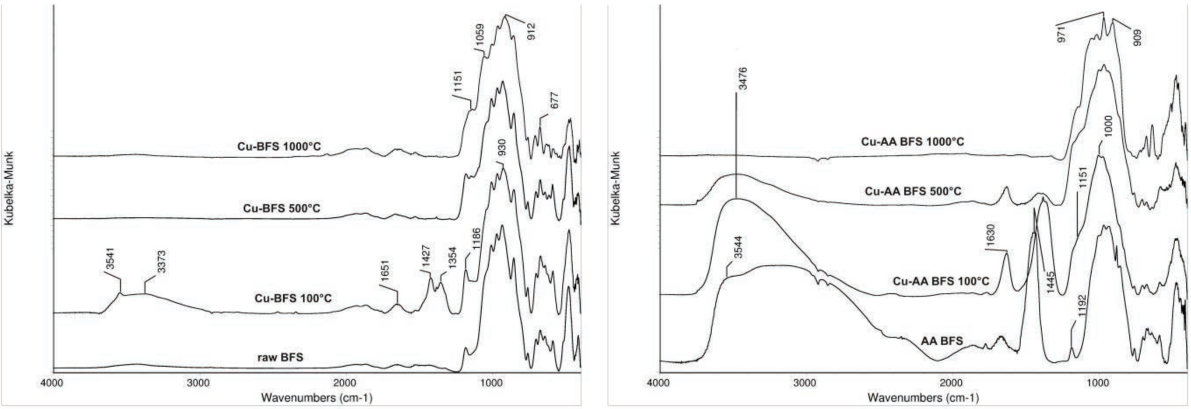

Fig. 1. Infrared spectra of the studied materials (BFS – blast furnace slag, AA BFS – alkali-activated blast furnace slag, prefix Cu – materials saturated by Cu)
Rys. 1. Widma w podczerwieni badanych materiałów (BFS – żużel wielkopiecowy, AA BFS – żużel wielkopiecowy aktywowany alkaliami, Cu – materiały nasycone jonami Cu

were saturated by Cu(II) ions when 100 g of slag was mixed with 2.5 L of Cu(II) solution of concentration 80 mmol/L (5084 mg/L) prepared from $Cu(NO_3)_2.3\ H_2O$ (Lachema, Brno, Czech Republic). Contact time 24 hours and ratio slag:solution 1:25 were selected according to the previous experiments (Bláhová et al., 2018). The suspensions were filtered after 24 hours and the solid materials were died in the air. After that the Cu(II) saturated materials were milled and divided to the 3 groups which were thermally treated at 100 (6 hours), 500 (2 hours) and 1000°C (2 hours) in the furnace (LAC Ltd, Rajhrad, Czech Republic). Samples were then milled and the structural changes were characterized by infrared spectroscopy at Nicolet 6700 (Thermo scientific, USA) spectrometer equipped with KBr beamsplitter and DTGS/KBr detector. Samples were measured by diffuse reflectance technique, 128 scans were accumulated, the resolution was set to 4 cm^{-1} and appodization Happ-Genzel was used. Experiments with leaching of Cu(II) ions were performed for all prepared samples of slag saturated by Cu(II) ions and thermally treated. Demineralized water with pH value adjusted to 3, 7 and 10 by HCl or NaOH (Mach chemicals Ltd., Ostrava, Czech Republic) and solution of $NaNO_3$ (Lachema Brno, Czech Republic) of concentration 0.05 mol/L were used as leaching solutions. Amount of materials weighted to the centrifugation tubes was 1 g. Then 50 mL of leaching solution was added to the tube and the suspensions were left for 24 hours with occasional shaking. The suspensions were centrifuged on the Jouan BR4i multifunction centrifuge (Thermo scientific, USA) on the 6000 rpm for 15 minutes after the 24 hours of contact time. The content of Cu(II) in all solutions after saturation of slags by Cu(II) ions and after leaching experiments were measured by the atomic absorption spectrometry (AAS, Varian AA240FS, Varian, USA) at the wavelength 324.8 nm with air-acetylene flame, with limit of quantification 0.034 mg/L.

Results and discussion

Raw and alkali-activated slag were saturated by Cu(II) ions. Initial solution as well as solutions after contact with slags were analysed by the atomic absorption spectrometry to determine immobilized amount of the Cu(II) ions. The immobilized amount of Cu(II) ions on the raw blast furnace slag (BFS) was 6.35 ± 0.12 mg/g and the amount of Cu(II) immobilized on the alkali-activated blast furnace slag (AA BFS) was 151.37 ± 0.95 mg/g. Thus it can be stated that alkali-activation leads to increase of the ability to immobilize Cu(II) ions from the aqueous solution.

The decrease of weight of the samples saturated by Cu(II) ions was observed after the thermal treatment. The decrease was insignificant (maximum 0.8% of initial weight) in the case of BFS. In the case of AA BFS the increase was higher (maximum 11.7% of initial weight before thermal treatment). Thus thermal treatment of AA BFS sample could lead to changes in the mineralogical composition probably with release of chemically bonded water (dehydroxylation process) which is present in the structure due to the alkali-activation process (Shi et al. 2006; Kim et al. 2017).

Infrared spectra of the starting materials (raw BFS and AA BFS) and materials after the saturation by Cu(II) ions and the thermal treatment are shown on the Fig. 1. It can be concluded according to comparison of the spectra of raw BFS and AA BFS that alkali activation leads to increase of the -OH groups content in the material (increase of the absorbance of bands around 3200 cm^{-1}) and it leads to increase of carbonates content (band around 1445 cm^{-1}) which can be caused by interaction with air during drying. The band of stretch vibrations of silicates (around 1000 cm^{-1}) exhibits less particular isolated bands and shoulders, which can be caused by increase of amorphous character after activation. The slight changes occur in the spectra of BFS saturated by Cu(II) and thermally treated. The material treated at 100°C contains the higher amount of the structural –OH groups (3541 cm^{-1}) as well as free water (3373 and 1651 cm^{-1}). Band 1427 cm^{-1} belongs to the carbonates probably formed during drying of material. Band 1354 cm^{-1} belongs probably to nitrates which are present in the material due to utilization of copper nitrate for the saturation of materials. Materials treated at higher temperatures (500 and 1000 cm^{-1}) do not contain water, structural –OH groups, carbonates, and nitrates. These temperatures are high enough to release of these components. The little changes can be observed in the area of Si-O, Si-O-Si, Si-O-Al and Si-O-H stretch vibrations (1200–850 cm^{-1}) for the materials treated at 500 and 1000°C, which can indicate incorporation of Cu to the mineral matrix of slag. The spectra of the AA BFS based materials exhibit larger changes in the compar-

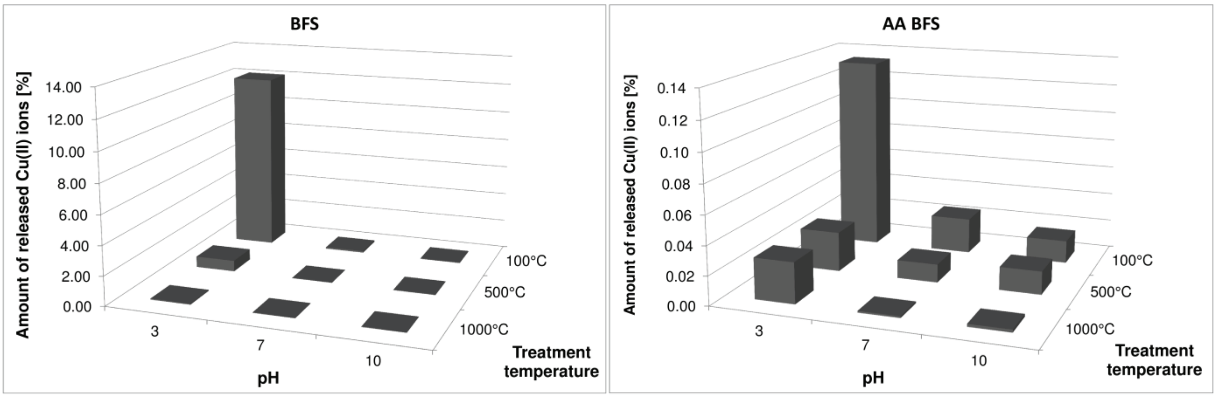

Fig. 2. Released amount of Cu(II) ions in the dependence on the pH value of the leaching solution. The released quantity is related to the content of immobilized Cu(II) ions in the individual materials

Rys. 2. Uwolniona ilość jonów Cu (II) w zależności od wartości pH roztworu ługującego.
Uwolniona ilość jest związana z zawartością unieruchomionych jonów Cu (II) w poszczególnych materiałach

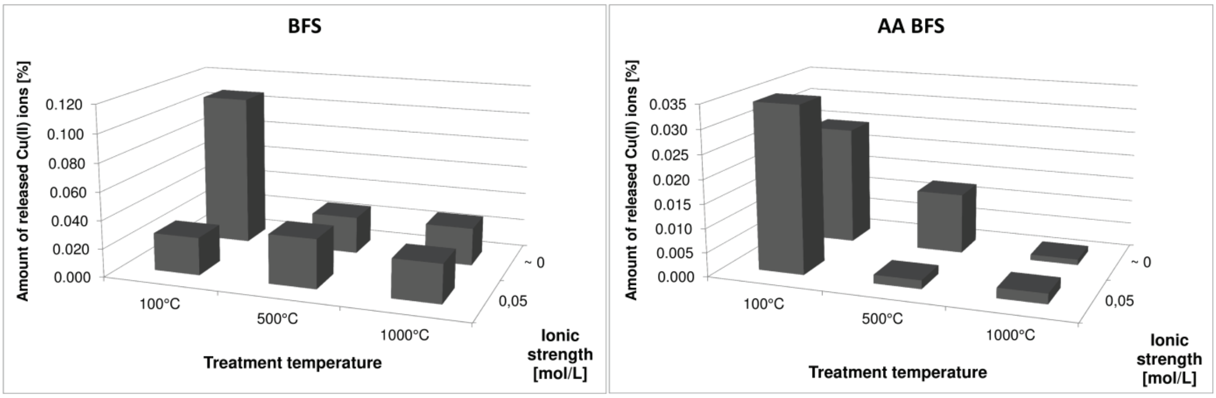

Fig. 3. Released amount of Cu(II) ions in the dependence on the ionic strength of the leaching solution. The released quantity is related to the content of immobilized Cu(II) ions in the individual materials

Rys. 3. Uwolniona ilość jonów Cu (II) w zależności od siły jonowej roztworu ługującego.
Uwolniona ilość jest związana z zawartością unieruchomionych jonów Cu (II) w poszczególnych materiałach

ison to the BFS based materials. The amount of free water (broad band around 3200 cm^{-1}) after treating of the Cu(II) saturated AA BFS material at 100°C decreases significantly compared to AA BFS and the shape of the band changes as well. These changes were probably caused by interaction of AA BFS with Cu(II) ions and by release some water during the thermal treatment. The decrease of the bands area in the O-H stretch vibration region is much higher than the decrease observed by the BFS based materials and it corresponds to the decrease of the materials weight after the thermal treatment mentioned above. The content of carbonates decreases and their mineral phase changes during the thermal treatment. It can be deduced from the decrease and shift of the band 1445 cm^{-1}. The broad band of Si-O, Si-O-Si, Si-O-Al and Si-O-H in the range 1200–850 cm^{-1} changes significantly during the thermal treatment, which can indicate the incorporation of Cu(II) to the mineral matrix of material as well as the increase of crystalline phases amount (Socrates, 2007).

The released amounts of the Cu(II) ions related to the total amount of copper present in the materials in the dependence on the pH value of the leaching solution are presented on the Fig. 2. It can be concluded that stability of the materials increase with the increasing temperature of thermal treatment and all materials are less stable in the acidic conditions. The absolute amount of Cu(II) ions released from the BFS material treated at 100°C was 0.771 ± 0.018 mg/g in the case of the leaching solution with pH 3, which is 12% of the total amount immobilized on the material. The released amounts at the pH values 7 and 10 were near the limit of quantification of the used AAS method. The BFS materials treated at 500°C and 1000°C were more stable, the released amounts for the leaching solution with pH 3 were 0.048 ± 0.019 mg/g (500°C) resp. 0.004 ± 0.003 mg/g (1000°C). The values obtained for the leaching solutions with the pH values 7 and 10 were under the limit of quantification of the used AAS method. The AA BFS based materials show higher stability of the Cu(II) binding in the comparison to the BFS based materials. Only 0.13% of the total immobilized amount of Cu(II) ions was released to the leaching solution with pH value 3 from the material treated at 100°C. This value corresponds to the absolute amount of the released Cu(II) 0.213 ± 0.134 mg/g of material. The amounts released from the above mentioned material by the solutions with the pH values 7 and 10 were around 0.05 mg/L. It can be stated that the materials based on the AA BFS and treated at 500°C and 1000°C are quite less stable than the materials based on BFS and treated at the same temperatures. The released amounts for the material AA BFS treated at 500°C and leached by the solutions with the higher pH values (3 and 10) were around 0.02 mg/g whereas the BFS treated at 500°C shows values below 0.002 mg/g, which is value for the limit of quantification of the used AAS method. The amount released from the AA BFS treated at 1000°C leached by the solution with pH 3 is higher in the comparison to the BFS treated at the same temperature. Both basic materials (BFS and AA BFS) are suitable for the immobilization of Cu(II) ions from the sight of stability to leaching, the AA BFS material has advantage in the higher immobilized amount of Cu(II) ions compared to BFS.

The stability of the prepared materials in the solutions with various ionic strengths was studied for description of foreign ions influence on the stability of materials, e.g. influence of ionic exchange processes (Fig. 3). The demineralized water was used as leaching solution with very low ionic strength near to 0 (~ 0 mol/L) and $NaNO_3$ solution of concentration 0.05 mol/L was used as leaching solution with ionic strength 0.05 mol/L. The material BFS saturated by Cu(II) ions and thermally treated at 100°C is more stable in the case of the higher ionic strength when the absolute released amount of Cu(II) was 0.007 ± 0,003 mg/g in the case of solution with ionic strength ~ 0 mol/L and under 0.002 mg/g (under the limit of quantification of the used AAS method) in the case of the solution with the ionic strength 0.05 mol/L.

The other materials (treated at 500°C and 1000°C) show no significant difference among the studied values of ionic strength and the released amount of Cu(II) was under the limit of quantification of the used AAS method. The material AA BFS treated at temperature 100°C exhibits a little bit higher stability in the case of the lower ionic strength, the absolute released amount of Cu(II) ions is 0.040 ± 0.022 mg/g (ionic strength ~ 0 mol/L) and 0.056 ± 0.010 mg/L (ionic strength 0.05 mol/L) . The AA BFS treated at 500°C exhibits an opposite trend but it is more stable than the material AA BFS treated at 100°C. In the case of material treated at 1000°C the released amount was very low and the difference between the ionic strengths was negligible.

Conclusion

The utilization of raw and alkali-activated blast furnace slag for the immobilization of Cu(II) ions was investigated. Alkali-activation was performed by solution of water glass and NaOH. Materials were saturated by Cu(II) ions. The immobilized amounts were 6.35 ± 0.12 mg/g in the case of raw slag and 151.37 ± 0.95 mg/g in the case of alkali-activated slag. The alkali-activated slag is more efficient in the immobilization of Cu(II) ions. The saturated materials were thermally treated at temperatures 100, 500, and 1000°C. The structural changes were studied by infrared spectroscopy. The thermal treating leads to the slight structural changes in the case of blast furnace slag but the changes of the material's structure were significant in the case of alkali-activated slag when dehydroxylation processes and decomposition of carbonates and nitrates probably take place. Changes in the silicate matrix structure were proved by infrared spectroscopy as well. The Cu(II) ions probably incorporate to the matrix of samples during the thermal treatment. Leaching of Cu(II) ions from the thermally treated materials by the solutions with various pH values (3, 7 and 10) and by the solutions with various ionic strengths (ionic strength set by the $NaNO_3$) was studied. The materials based on alkali-activated slag exhibit the higher stability to the leaching of the Cu(II) ions compared to raw slag based materials when only 0.13% of the total immobilized amount of the Cu(II) ions was released to the solutions during the leaching experiment in the case of alkali activated blast furnace slag compared to 12% in the case of raw blast furnace slag. The higher temperature of treatment leads to more stable material in the case of both types of slags. The studied materials are less stable at under the acidic conditions then under the neutral and alkaline conditions. Blast furnace slag, especially alkali-activated, can be promising material for the Cu(II) ions immobilization and for the safe disposal of the Cu(II) containing wastes.

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Wykorzystanie żużla wielkopiecowego do immobilizacji jonów miedzi z roztworów

Utylizacja odpadów zawierających jony metali, takich jak jony Cu (II), stanowi obecnie poważny problem. W celu immobilizacji jonów Cu (II) stosuje się różne materiały. Atrakcyjny rodzaj materiału reprezentują żużle – odpady z przemysłu metalurgicznego. Surowe i aktywowane alkalicznie żużle wielkopiecowe badano pod katem immobilizacji jonów Cu (II) z roztworu wodnego i możliwości składowania odpadów zawierających Cu (II). Żużle były nasycone jonami Cu (II). Ilość Cu (II) osadzonego na surowym żużlu wynosiła 6,35 ± 0,12 mg/g, a ilość osadzona na żużlu aktywowanym alkaliami wynosiła 151,37 ± 0,95 mg/g. Nasycone materiały poddano obróbce termicznej w 100, 500 i 1000°C. Obróbka termiczna prowadzi do niewielkich zmian strukturalnych w przypadku surowego żużla i znacznych zmian strukturalnych w przypadku żużla aktywowanego alkaliami. Jony Cu (II) prawdopodobnie wypełniają matrycę materiałów. Materiały na bazie żużla aktywowanego alkaliami wykazują wyższą stabilność wymywania jonów Cu (II) w porównaniu z żużlami surowymi. Uzyskano immobilizację wynoszącą 0,13% całkowitej unieruchomionej ilości jonów Cu (II)dla żużla aktywowanego i 12% w przypadku żużla surowego. Obróbka w wyższej temperaturze prowadzi do uzyskania bardziej stabilnego materiału w przypadku obu rodzajów żużla. Badane materiały są mniej stabilne w warunkach kwasowych niż w warunkach obojętnych i alkalicznych. Żużel wielkopiecowy aktywowany alkaliami może być obiecującym materiałem do immobilizacji Cu (II) i do bezpiecznego usuwania odpadów zawierających Cu (II).

Słowa kluczowe: żużle, stabilizacja, zestalanie, desorpcja, jony miedzi, obróbka termiczna

Recovery of Nutrients from Wastewater via Electrodialysis

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Abstract

The need to treat wastewater in a sustainable way to minimalize contamination and maximize the recovery of nutrients is widely recognized. The focus is mainly on the removal and recovery of nutrients because of eutrophication problems in receiving waters, limitations of mining resources and high costs affiliated with nutrient production. Removal of nutrients is also a growing problem for water authorities, as authorities often tighten standards of discharged waters to avoid unnecessary discharge of nutrients into water bodies.

The universally used technologies for nitrogen and phosphorus removal involve biological nitrification and denitrification and metal salt precipitation. However, applying these technologies nutrients are made unrecoverable for fertilizing. Electrodialysis (ED) is a membrane process capable of concentrating and separating ions from wastewater. Thanks to the applied current, the migration of ions occurs, and ions are concentrated in the concentrate solution. Laboratory scale ED showed the potential of nutrient recovery from wastewater sources.

In this study, nutrients were recovered in concentrate solution from wastewater sludge liquid discharge by using electrodialysis. Calcium and sodium values in concentrated solution increased 10 times, values of potassium and chloride 5 times. The amount of ammonia nitrogen raised from 60 mg/l to 1700 mg/l. The concentrate enriched by nutrients may be used in further processes, e.g. phosphorus and ammonia nitrogen can be precipitated into the form of struvite.

Keywords: electrodialysis, nutrient recovery, wastewater sludge, ammonia recovery

Introduction

The biologically treated secondary effluent from existing wastewater treatment plants still contain a certain amount of nutrients (such as NO3 - and $HPO_4{}^{2-}$) (Zuo, 2014) and salinity (such as Na^+, Ca^{2+}, K^+, Mg^{2+} and Cl^-). The insufficient treatment could lead to eutrophication (Wang, 2015) and influence the reuse of reclaimed water (Liang, 2013). Moreover, phosphorous is an important mineable resource (Wang, 2013), and recovering phosphorus (P) from wastewater streams for reuse can alleviate the problem of limited phosphate resource supply (O'Neal, 2013).

N and P contents in wastewater and surface water are increasing, while the reservation resources of them are being depleted, especially for phosphorus. N and P may thus be recovered from wastewater or surface water. After making a general survey of activated sludge process, interests in recovering nitrogen and phosphorus focus on the excess sludge developed based on some additional reforming operation and newly introduced technologies (Tong, 2009; Wang, 2013). Anaerobic digestion process can achieve the degradation of organic matters and the formation of biogas, and it has been widely used to treat the excess sludge. Sidestreams, or "return liquors", typically have a very high concentration of ammonia and phosphorus because they are released in the anaerobic digestion process: Ammonia is produced by the biological degradation of the nitrogenous matter, such as bacteria, proteins and urea; Phosphorus is produced by re-solution of the part incorporated into bacterial biomass in the enhanced biological phosphorus removal (EBPR) process (Münch, 2001). It is unwise to return the solution rich in ammonia and phosphorus back to the sewage treatment plant, because the containing nutrients will be aggregated in the newly produced excess sludge rather than through decontamination.

Recently, membrane filtration technologies, such as reserve osmosis (RO), nanofiltration (NF) and electrodialysis (ED), have drawn much attention to desalinize and recover useful materials in wastewater treatment (Werner, 2013). Pressure membrane processes, such as RO and NF, need a quite complex pretreatment to alleviate the membrane fouling (Jamaly, 2014; Byun, 2015), resulting in needless capital cost and energy consumption. Furthermore, RO is ion uncontrollable and highly relying on the size of molecules (Kwak, 2013). However, as an electrochemical membrane separation process, ED is capable of separating undesired ions from wastewaters more energy-efficient (Vaselbehagh, 2015) with an applied electric field as the driving force to get a higher water recovery (Kwak, 2013).

Materials and Methods

Feed water for this experiment consisted of wastewater sludge liquid discharge. The samples of wastewater were recovered three times over period of six weeks. Each sample was analyzed and run through electrodialysis (ED). The chemical analysis of the feed water used in this experiment is

Tab. 1. Physicochemical analysis of feedwater

Tab. 1. Analiza fizykochemiczna wody zasilającej instalację

Physicochemical characteristics	Sample A	Sample B	Sample C
pH [-]	6.56	7.83	7.99
Turbidity [FNU]	110.58	103.91	116.63
Conductivity [mS/cm]	2.03	5.67	5.80
COD [g/l]	438.59	316.87	331.18
Dissolved particles [mg/l]	1.11	0.95	1.12
Ammonia nitrogen [mg/l]	59.01	753.21	776.50
Phosphorus [mg/l]	55.42	52.81	50.68
Chloride [mg/l]	95.48	97.50	92.18

Tab. 2. AAS analysis of feedwater

Tab. 2. Analiza AAS wody zasilającej

Chemical elements	Sample A	Sample B	Sample C
Zn [mg/l]	0.027	0.036	0.012
Cu [mg/l]	0.071	0.031	<0.010
Ni [mg/l]	0.026	0.037	0.028
Fe [mg/l]	0.073	1.880	1.030
Mn [mg/l]	0.048	0.036	0.060
Ca [mg/l]	29.500	64.200	40.600
Mg [mg/l]	29.800	16.500	18.700
K [mg/l]	107.000	80.100	98.100
Na [mg/l]	171.000	95.300	105.000

shown in Table 1. The feed water was pre-treated by vacuum filtration.

Feed water was also analyzed by atomic absorption spectroscopy (AAS) to find out if the samples contained heavy metals. The AAS analysis is shown in Table 2.

A laboratory-scale electrodialysis module ED(R)-Z set-up was used in this study, and it was composed of electrode compartments, concentrated compartments, and diluted compartments. Compartments were separated by cation/anion exchange membranes, silicone gaskets and plastic partition nets. In addition, the specific parameters are summarized in Table 3. The membranes used in electrodialysis included cation exchange membranes and anion exchange membranes.

Result and Discussion

Concentrated solution from electrodialysis was obtained in total volume 0.5 l per sample and was analyzed, along with dilute (2 l per sample), in laboratory and by AAS. Samples of concentrated solutions were kept in a dark and cold place. Analysis was conducted the next day in the laboratory. Results of the concentrated solution analysis are shown in Table 4.

Samples were preserved with nitric acid and analyzed by AAS. Results of the concentrated solution analysis are shown in Table 5.

As it is clear from the presented results, the ED process was successful in concentrating elements, such as ammonia nitrogen, chloride, calcium, potassium and sodium. These elements, along with phosphorus, are essential plant macronutrients.

K can occur in unavailable, slowly available, or readily available forms in soils. Only a small amount of slowly available K is available for plant uptake during a single growing season. Readily available K is dissolved in the soil solution and readily taken up by plants. Potassium uptake is affected by soil moisture content, soil aeration and oxygen level, soil temperature, and competing ions.

Like K, Ca and Mg in soils originate from decomposition of bedrock and minerals that contain these elements. Compared to other minerals, Ca weathers relatively quickly and can become unavailable to plants via leaching in highly weathered (mature) soils.

Sodium is not an essential element for plants but can be used in small quantities, similar to micronutrients, to aid in metabolism and synthesis of chlorophyll. In some plants, it can be used as a partial replacement for potassium and aids in the opening and closing of stomates, which helps regulate internal water balance. Chloride is needed in small quantities and aids in plant metabolism, photosynthesis, osmosis (movement of water in and out of plant cells) and ionic balance within the cell.

Conclusion

The results demonstrate that a concentrated product could be achieved by concentrating nutrient ions from wastewater sludge liquid discharge to concentrate product stream via the ED process. The concentrated solution contains ions in a soluble form, therefore there is a need to continue this research and precipitate the said ions into forms that may be used as fertilizers.

Ammonia nitrogen and phosphorus could be precipitated into the form of magnesium ammonium phosphate, which is known to be an ideal alternative fertilizer since it is a non-odorous, non-sludgy crystal which releases nutrients slowly.

Tab. 3. Parameters of the electrodialysis module ED(R)-Z

Tab. 3. Parametry modułu do elektrodializy ED (R)-Z

Item	Parameters	Item	Parameters
Number of membrane pairs	10 pairs	Number of electrode cells	2
Number of dilute cells	10	Installed membrane area	2646 cm^2
Number of concentrate cells	10	Effective membrane area	1344 cm^2

Tab. 4. Physicochemical analysis of concentrated solution

Tab. 4. Analiza fizykochemiczna stężonego roztworu

Physicochemical characteristics	Sample A	Sample B	
pH [-]	8.06	7.99	
Turbidity [FNU]	46.32	43.13	
Conductivity [mS/cm]	16.99	17.68	
COD [mg/l]	410.00	381.18	
Dissolved particles [g/l]	5.79	3.27	
Ammonia nitrogen [mg/l]	1 739.36	2 795.40	
Phosphorus [mg/l]	73.54	71.72	
Chloride [mg/l]	489.62	480.39	

Tab. 5. AAS analysis of concentrated solution

Tab. 5. Analiza AAS stężonego roztworu

Chemical elements	Sample A	Sample B	
Zn [mg/l]	0.025	0.029	
Cu [mg/l]	0.032	0.019	
Ni [mg/l]	0.047	0.033	
Fe [mg/l]	0.064	0.300	
Mn [mg/l]	<0.010	<0.0100	
Ca [mg/l]	290.000	608.450	
Mg [mg/l]	68.100	19.700	
K [mg/l]	439.000	375.000	
Na [mg/l]	1660.000	693.000	

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Odzyskiwanie składników odżywczych ze ścieków przez elektrodializę

Powszechnie uznaje się potrzebę oczyszczania ścieków w zrównoważony sposób w celu zminimalizowania zanieczyszczenia i maksymalizacji odzysku składników odżywczych. W artykule skupiono się na usuwaniu i odzyskiwaniu składników odżywczych ze względu na problemy z eutrofizacją w wodach, ograniczenia zasobów górniczych i wysokie powiązania z produkcją składników nawozowych. Usunięcie składników nawozowych jest również coraz większym problemem dla gospodarki wodnej z uwagi na coraz bardziej rygorystyczne wymagania prawne i zaostrzające się standardy. Powszechnie stosowane technologie usuwania azotu i fosforu to biologiczna nitryfikacja i denitryfikacja i strącanie soli. Jednakże tak uzyskane składniki stają się niezdatne dla nawożenia. Elektrodializa (ED) jest procesem membranowym służącym do koncentracji i wydzielania jonów ze ścieków. Dzięki zastosowanemu prądowi następuje migracja jonów i są one skoncentrowane w roztworze. Badania w skali laboratoryjnej wykazały potencjał odzysku składników odżywczych ze ścieków za pomocą elektrodializy.

W przeprowadzonych badaniach wykazano efektywność odzysku składników odżywczych w procesie elektrodializy. Zawartości wapnia i sodu w stężonym roztworze wzrosły 10 razy, zawartości potasu i chlorku 5 razy. Ilość azotu amoniakalnego wzrosła z 60 mg/l do 1700 mg/l. Koncentrat wzbogacony w składniki odżywcze można stosować w dalszych procesach, np. azotan fosforu i amoniaku można wytrącić do postaci struwitu.

Słowa kluczowe: elektrodializa, odzyskiwanie składników odżywczych, osad ściekowy, odzysk amoniaku

Evaluation of Grindability Behaviors of Four Different Solid Fuels Blending by Using the Hardgrove Mill

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Abstract

Grindability measurements are widely used in mineral and coal processing industry to determine resistance of materials to comminution. Grindability measurement as testing methods can be divided into two general categories; the Bond and the Hardgrove grindabilities. Grinding characteristics of the mineral or coal blending have been studied by several researchers over many years and a wide range grinding variables has been investigated. In this study, because of the simplicity and the potential usage of the method for the determination of the grindability of coals and their blending in a comparative scale, a Hardgrove mill were used to investigated the grinding behavior of four different solid fuels and their blending. Grindability of four different solid fuels such as; petroleum coke, coke coal, lignite and bituminous coal and their binary, ternary and quaternary blending were investigated by the Hardgrove grindability test. The test results indicated that determine the existence of a very good relation between the Bond and the Hardgrove grindability of the fuels, and relationship between experimental and calculated HGI values of the fuels blending were also shown as a very good. However, there is not obtain a good relation between proximate analysis results of the solid fuels and HGI values of fuels blending.

Keywords: coal; coke; petroleum coke; fuels; hardgrove grindability; bond grindability; fuel blending

Introduction

In grinding process of materials, the yearly megawatt hour's amount to several hundred millions in terms of the energy expended. Many expressions of grindability have been proposed over the years, but of these two of them have come into prominence because they have become the recognized basis for design of certain types of mill. One of them is the Hardgrove grindability index, associated mainly with vertical spindle mills and the other is the Bond's grindability index, associated with tumbling mills (McIntryre and Plitt, 1980; Prasher, 1987).

The Bond grindability method is included in category one and widely used to determine grindability of minerals in mineral processing industry. However, this method is both excessively time consuming and susceptible to procedural errors because of the intensity of the experimental steps. The Hardgrove Method for coal can be given as an example to be second type of test. The main advantage of Hardgrove method is its simplicity to perform. However, Hardgrove method does not give any information about energy consumption of the mill. The Hardgrove grindability for lignite or other heterogeneous materials can be applied only as a qualitative grindability characteristic, for example, to categorise them as difficult, easy or mediocre grindable (Prasher, 1987; Csöke et al., 2003).

Coal grindability usually measured by Hardgrove Grindability Index (HGI) is of great interest since it is used as a predictive tool to determine the performance capacity of industrial pulverisers in cement factories and power station boilers. Although the HGI testing device is not costly, it is tedious to determine the grindability index experimentally. Therefore there exists an interest to predict HGI values from proximate analysis. However, the test does suffer from some limitations. For example, the measurement can be insensitive to the heterogeneous properties of coal that arise from different mineral contents, maceral constituents, moisture contents and levels of maturity etc. It is difficult to predict the HGI based on some basic coal quality, such as proximate analysis. As such, it often gives misleading results to understand and explain properties emerging from other analyses and testing. Therefore, it is necessary to predict the grinding behaviour of the individual components in blends to make the right product with the desired size distribution and composition (Cho and Luckie, 1995; Vutharluru et al., 2003; Chalgani et al., 2008; Malav et al., 2008).

Coal, one of the solid fuels, is a heterogeneous substance which is consisted of combustible (organic matter) and non-combustible (moisture and mineral matter) materials. The grindability of coal is an important practical and economic property to coal handling and utilisation aspects, particularly for pulverised coal fired utilities. In general, coal grindability characteristics reflect the coal hardness, tenacity, and fracture which are influenced by coal rank, petrography, and the distribution and the types of minerals. Therefore, the prediction of grindability index on the basis of the proximate analysis may not give accurate result if the age, rank and petrographic composition of coals are not similar (Vutharluru et al., 2003; Chalgani et al., 2008; Ozbayoglu, et al., 2008).

Some researchers have investigated the prediction of HGI based on proximate analysis, petrography, and vitrinite maximum reflectance of solid fuels with using linear, nonlinear multivariable regression and generalized regression neural

Tab. 1. Proximate analysis values of coal samples used experiments (base original)

Tab. 1. Analiza techniczna próbek węgla wykorzystywanych w eksperymentach

Sample Name	Moisture (%)	Ash (%)	Fixed Carbon (%)	Volatile Matter (%)	Net Calorific Value (kcal/kg)
Coke	7.96 1	1.32 7	9.97 0	.75	5528
Petroleum Coke	5.66 0	.60	83.14	10.66	7993
Lignite 2	5.07 2	2.70 2	7.69 2	4.97	3376
Bituminous Coal	14.14	11.70	52.50	21.66	5628

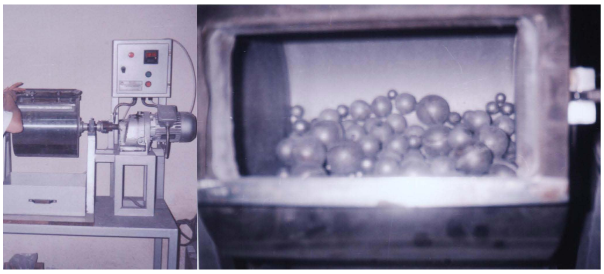

Fig. 1. The Bond ball mill

Rys. 1. Młyn kulowy Bonda

network. The result of these researches, there are several formulas available for predicting the Hardgrove grindability of coal, most of them are linear and do not simultaneously take into consideration most of the relevant factors (Li et al., 2005; Ozbayoglu et al., 2008).

Blending is another parameter which influences the grindability of a given coal. There have been some investigations in the past on the HGI of coal blends in relation to the additivity of the HGI, and although some coals show additivity, this is not usually the case. There is no general method of predicting the HGI of a coal blend, which must be determined experimentally on a case to case basis (Vutharlu et al., 2003).

The subject of this study was about the effects on the grindability value of proximate analysis values (Moisture, Ash, Volatile Matter, Fixed Carbon and Net Calorific Value) on solid fuels, and the effects on the grindability of binary, triple and quaternary blending of four different solid fuels. For this purpose, the solid fuels that called lignite, bituminous coal, coke and petroleum coke, used in the Votorantim Cement Factory in Corum (Turkey), were tested. In these tests, the Hardgrove mill has been used to determine the grindability index. In this research, simple linear regression techniques for the estimation of Hardgrove grindability index (HGI) values of solid fuels are studied.

Material and methods

Material

Four different fuel samples, called the lignite, the bituminous coal, the coke and the petroleum coke, taken from fed storage area belongs to Votorantim cement factory in Corum (Turkey), were used as the experimental materials. The proximate analyses of solid fuel samples used in experiments were presented in Table 1.

Method

In this study, firstly, the Bond grindability and the Hardgrove grindability tests were applied on the individual samples. Later, only the Hardgrove grindability tests were performed for blending operations.

The Test of Standard Ball Mill Bond Grindability

The standard Bond grindability test is a closed-cycle dry grinding in a standard ball mill (30.5x30.5 cm) and screening process, which is carried out until steady state condition is obtained. The standard Bond mill used in the experiments was shown in Figure 1. This test was described as follow (Bond and Maxson, 1943; Deniz and Ozdag, 2003; Deniz, 2004; Deniz et al., 2013):

The material is packed to 700 cc volume using a vibrating table. This is the volumetric weight of the material to be used for grinding tests. For the first grinding cycle, the mill is started with an arbitrarily chosen number of mill revolutions. At the end of each grinding cycle, the entire product is discharged from the mill and is screened on a test sieve (Pi). Standard choice for Pi is 106 micron. The oversize fraction is returned to the mill for the second run together with fresh feed to make up the original weight corresponding to 700 cc. The weight of product per unit of mill revolution, called the ore grindability of the cycle, is then calculated and is used to estimate the number of revolutions required for the second run to be equivalent to a circulating load of 250%. The process is continued until a constant value of the grindability is achieved, which is the equilibrium condition. This equilibrium condition may be reached in 6 to 12 grinding cycles. After reaching equilibrium, the grindabilities for the last three cycles are averaged. The average value is taken as the standard Bond grindability value (G_{bg}).

$$G_{bg} = \frac{P}{n} \qquad (1)$$

where, G_{bg} is the Bond grindability index of sample (g/rev); P is the net amount of ground products, (g), and *n* is revolution number of the Bond ball mill,

The Bond work index values (Wi) are calculated from Eq. (2).

Tab. 2. Status of binary, triple and quaternary blending of four different solid fuels using in the experiments

Tab. 2. Parametry mieszanek dwu, trzy i czteroskładnikowych paliw stałych wykorzystywanych w eksperymentach

Blending	Coke (A)	Petroleum Coke (B)	Lignite (C)	Bituminous Coal (D)
1. Blending	A/4	B/4	C/4	D/4
2. Blending	---	B/3	C/3	D/3
3. Blending	A/3	B/3	C/3	---
4. Blending	A/3	---	C/3	D/3
5. Blending	A/3	B/3	---	D/4
6. Blending	---	---	C/2	D/2
7. Blending	A/2	B/2	---	---
8. Blending		B/2	C/2	---
9. Blending	A/2	---	C/2	---
10. Blending	A/2	---	---	D/2
11. Blending	---	B/2	---	D/2

$$W_i = 1.1 * \frac{4\ .5}{P_i^{0.23} * G_{bg}^{0.82} * \left[\left(10/\sqrt{P_{80}}\right) - \left(10/\sqrt{F_{80}}\right)\right]} \tag{2}$$

where, W_i is the standard Bond work index, (kWh/t); P_i is test sieve size (106 µm); G_{bg} is the Bond standard ball mill grindability, (g/rev); P_{80} and F_{80} are the 80% of cumulative undersize curve of feed and product (µm), respectively.

Hargrove Grindability Index (HGI) Test Method

The Hardgrove grindability index (HGI) of coal is an important technological parameter in understanding the behavior of the grinding of coal. The design of the vertical spindle mill is mainly depended on the HGI. Although the device for testing of HGI is not costly, the measuring procedure to get a HGI value is toilsome and time consuming. In addition, it is not a routine testing item in coal fired power and cement plants which used vertical spindle mills (Peisheng et al., 2005).

In the United States, the HGI method is described in ASTM D409 "Standard Test Method for Grindability of Coal by the Hardgrove-Machine Method" (ASTM, 1951). This method consists of grinding a sieved sample in a grinder with defined dimensions and grinding energy, measuring the sieve size of the remaining product, and comparing the result with standard coal samples to produce the relative grindability index. A high HGI value of a coal indicates that the coal is easy to grind. The most often reported limitations of the HGI test include that the parameter is non-linear (e.g. HGI values changing from 40 to 50 can cause much more difference in grindability or mill capacity than from 90 to 100), not-additive as in cases of blend coals, and affected significantly by moisture content and thus pretreatment of coal samples. Some modifications of the standard test results in more confusion, e.g. the same coal may have different HGI test results.

The ASTM (1951) Hardgrove procedure was carried out, i.e. the test feed is 50 g sample of coal, which has been prepared in a specific manner and which has a limited particle size range, 1.18 x 0.6 mm, is placed in a stationary grinding bowl in which eight steel balls can run in a circular path. A loaded ring is placed on top of the set of balls with a gravity load of 29 kg. The machine is run (for 3 minute) for 60 revolutions of the mill at speed of 20 rev/min. The top is removed and the ground coal removed. This coal is sized and the quantity less than 75 microns recorded. This is converted to a HGI value using a calibration graph.

In this study, a mill with 5E-HA-60x50 model of the CKİC trademark, a made in Chinese, was used as the Hardgrove mill as shown in Figure 2a. The calibration graph created for the mill was also given in Figure 2b. Hardgrove Grindability Index tester (5E-HA-60x50 model) by using in experiments is distinguished from classical Hardgrove grindability testers in terms of advantage properties such as high automation, compact structure and intelligence control.

Experiments

Firstly, standard Bond grindability tests were obtained for four solid fuel samples, and Bond work indexes were calculated. Result of tests, the Bond grindability values of solid fuel samples (coke, petroleum coke, lignite and bituminous coal) were appeared 0.303 g/rev, 0.815 g/rev, 0.964 g/rev and 0.958 g/rev, and the Bond work index values of fuel samples were calculated 43.32 kWh/t, 24.13 kWh/t, 16.92 kWh/t and 17.71 kWh/t, respectively. Secondly, the Hardgrove grindability tests were obtained for four solid fuel samples, and Hardgrove grindability index values of fuel samples were calculated 26.15, 54.18, 63.56 and 69.56, respectively. Then, a good calibration has been established between the Bond and the Hardgrove grindabilities at the beginning of the tests as shown in Figure 3a.

Variation of Experimental and Calculated Hardgrove Grindability Indexes of Solid Fuels Blending

The Hardgrove grindability index of solid fuel blending (binary, triple and quaternary) were investigated for prediction from the weighted average of the Hardgrove grindability indexes of the individual fuels in the blending by using 11 different blending samples from four different solid fuels. The states of the mixture samples of 11 different blending used in the experiments were given in Table 2.

The test results were analyzed using the method of least squares regression. For the blending of four different fuel samples; the experimental grinding characteristic results of binary, triple and quaternary blending were almost similar results to that calculated HGI values. The relationships be-

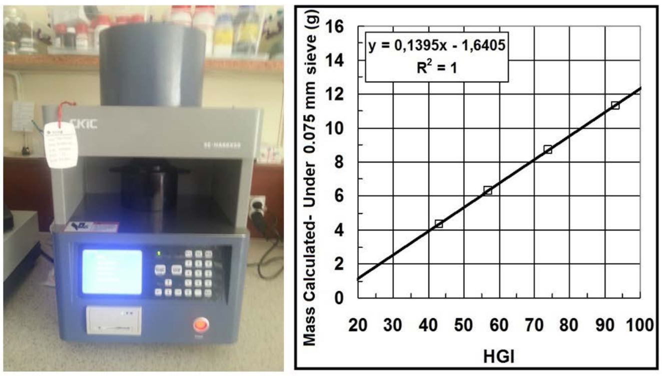

Fig. 2. Hardgrove mill (a) and Calibration graph (b) used in the experiments
Rys. 2. Młyn Hardgrove'a (a) i krzywa kalibracji (b) stosowane w eksperymentach

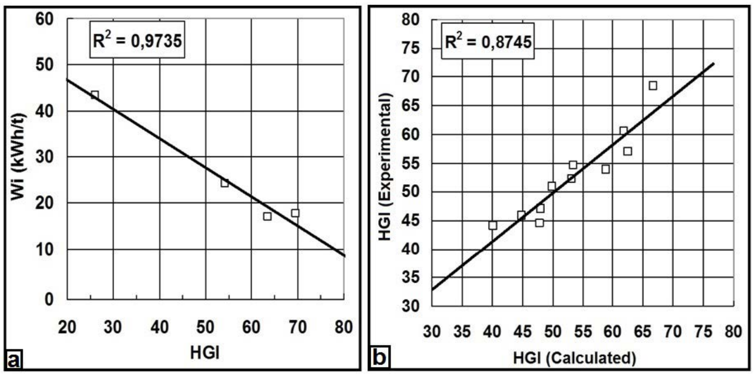

Fig. 3. (a) Relationship between Gbg and HGI value for four different solid fuels (b) Comparison of experimental and calculated HGI value for solid fuels
Rys. 3. (a) Związek między wartością Gbg i HGI dla czterech różnych paliw stałych (b) Porównanie doświadczalnej i obliczonej wartości HGI dla paliw stałych

tween calculated HGI values and experimental HGI values were presented with a good correlation (Figure 3b).

Hardgrove grindability index (HGI) of fuel blending showed similar as calculated HGI values of the weighted average values of the individual coals. In this study, a general conclusion could be drawn on the grindability behaviour of coal blends in contrast to Vutharlu et al. (2003). Similarity in grindability indexes have been observed from different blending of the same fuels.

The Hardgrove grindability index of binary, triple and quaternary fuel blends could be predicted from the weighted average of the Hardgrove grindability indexes of the individual fuels in the blending. The reason for this is unclear, but this was especially more meaning in the case of blending a lignite with a petroleum coke. However, this may have important implications in combustion performance as the feed to a pulverised-fuel cement factory using these types of blends could be quite different than specified. One potential method of avoiding this problem would be to blending the coals after grinding.

The Relationships of Between Proximate Analysis Values and Hardgrove Grindability Indexes of The Solid Fuels and Their Blending

The Hardgrove grindability indexes (HGI) were correlated with corresponding proximate analysis values (moisture, ash, volatile matter, fixed carbon and net calorific value). As shown in Figure 4, the HGI values of binary, triple and quaternary blending were no significant correlation result to that proximate analysis values (moisture, ash, fixed carbon and net calorific value) with blending contents of solid fuel samples except volatile matter content. The reason for the lack of good correlations is probably due to the fact that grinding is a complex phenomenon and depends on more than a fuel proximate analysis property. On the other hand, the relationship between HGI values and volatile matter content were presented with a good correlation. Volatile matter content has been found to be not only affected by quality of solid fuels content but also grindability of solid fuel.

Linear regression techniques by Windows Excel package were used for predicting the HGI values for the specified solid proximate analysis values. The relationships between HGI and proximate analysis values (moisture, ash, volatile matter, fixed carbon and net calorific value) for solid fuel samples are shown in Figure 4. It was found from statistical analysis that, the higher the fixed carbon and the net calorific value content in the solid fuels, the less the HGI will be. On the contrary, the higher the moisture, ash, volatile matter content in solid fuels, the higher the HGI will be. But the correlation between proximate analysis and HGI in solid fuels is nonlinear. The prediction equation of HGI reported in literature, which is based on proximate analysis of fuels and linear regression method, may not be correct for the solid fuels in this study.

Addition, the results show that there was no also acceptable correlation coefficient between the Hardgrove grindability index and the proximate analyses of the solid fuels. The insignificant results show that fuels' proximate analysis alone cannot be used to predict HGI. Examinations of the graphs in

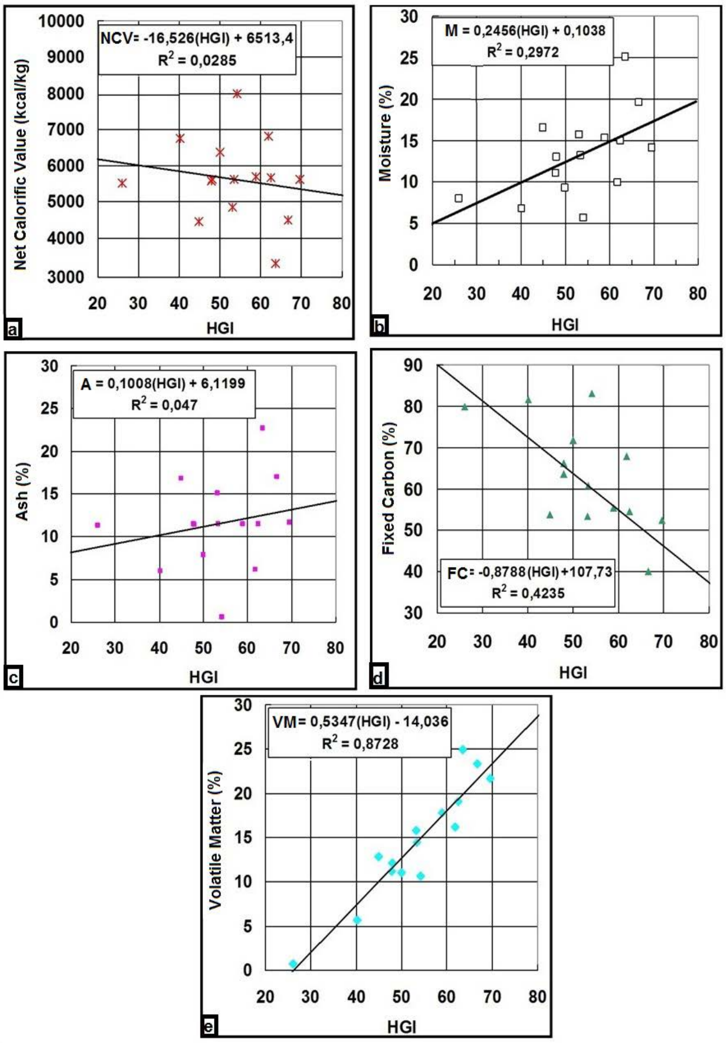

Fig. 4. Relationships between HGI and proximate analysis values (Net calorific value (a), moisture (b), ash (c), fixed carbon (d) and volatile matter (e))

Rys. 4. Zależności między HGI a przybliżonymi wynikami analizy technicznej analizy (wartość opałowa netto (a), wilgotność (b), popiół (c), stały węgiel (d) i substancje lotne (e))

Figure 4 demonstrated that moisture, ash, fixed carbon and net calorific value have no relationship to the Hardgrove grindability index. The best relationship was with volatile matter content of solid fuels and their blending. Volatile matter shows some promise as a predictor, but moisture, ash, fixed carbon and net calorific value were present in such low quantities, and their inclusion in the equation contributes little if anything to the overall regression. Solid fuels having high volatile matter content are found difficult to grind whereas coals which have medium and low volatile matter content are easy to grind. The different petrographic origin in solid fuel also exercises appreciable influence on the grindability. Consequently, there is not meaning that the better quality of solid fuels have, the easier grindability.

Variations in Hardgrove grindability indexes have been observed from different blending of the fuels are possibly due to varying origin as well as proximate analysis contents in the tested solid fuel samples. Hence, it is a poor correlation with HGI values and proximate analysis values. As similar pointed out by Ozbayoglu et al. (2008), it appears that there is no general method of predicting the grindability of a solid fuel blend from proximate analysis contents of the tested solid fuel samples, which must be determined experimentally.

Conclusions

In this study, the effect of blending, an important factor in the grinding of solid fuels was investigated. In the first stage, the calibration between the Bond grindability index (G_{bg}) and the Hargrove grindability index (HGI) for solid fuels was studied, and the relationship between them was presented with a good correlation. In the second stage, the calibration between the calculated and the experimental Hargrove grindability indexes for solid fuels blending was studied, and the relationship between them was also presented with a good correlation. In the third stage, the relationship between HGI and proximate analysis values in the solid fuels blending were not presented with a good correlation.

The tests made on the blending contents of four different solid fuel samples showed that they have similar grinding for experimental and calculated HGI values versus blending content whereas they have generally different grinding characteristics for proximate analysis values.

Hardgrove grindability tests on blending of solid fuels of varied volatile matter content showed an effect of volatile matter content on HGI. HGI values increases with increasing volatile matter content in the samples. Almost good correlation with volatile matter was found for all the samples tested; however, the range of variation of grindability with other proximate analysis content (moisture, ash, fixed carbon and net calorific value) varied among blending of the tested samples.

As a conclusion of this study, the determination of grindability of each solid fuel and each fuel blending versus proximate analysis values must be still done because they have different grindability characteristic in terms of their proximate analysis values.

Experimental results obtained from the present study would be further developed by the collection and analysis of different solid fuel samples from Votorantim Corum cement factory. This would prove to be valuable for fuel producers as well as solid fuel users in understanding the variations in HGI in terms of fuel compositions (origin and proximate analysis values) for a particular fuel.

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Ocena podatności na mielenie czterech różnych mieszanek paliw stałych za pomocą Młynka Hardgrove

Pomiary podatności na mielenie są stosowane w przemyśle przeróbki minerałów i węgla w celu określenia odporności materiałów na rozdrabnianie. Metody testowania można podzielić na dwie ogólne kategorie; oznaczenie podatności na mielenie wg Bonda i Hardgrove'a. Charakterystyka mielenia mieszanek mineralnych lub węglowych była badana przez wielu badaczy przez wiele lat i obejmowała szeroki zakres danych. W artykule przedstawiono wyniki oznaczenie podatności na mielenie według Hardgrove'a z uwagi na jej prostotę i potencjalne wykorzystanie jako metody porównawczej. Zbadano podatność na mielenie czterech różnych paliw stałych i ich mieszanek takich jak: koks naftowy, węgiel koksowy, węgiel brunatny i węgiel bitumiczny oraz ich mieszanki dwuskładnikowe, trójskładnikowe i czteroskładnikowe. Wyniki testów wskazywały, że istnieje związku między wynikami testu Bonda i Hardgrove'a (HGI). Przedstawiono porównanie wyników teoretycznych i laboratoryjnych. Stwierdzono również żebrak korelacji pomiędzy wynikami analizy technicznej paliw i oznaczeniem podatności na mielenie.

Słowa kluczowe: węgiel; koks; koks naftowy; paliwa; indeks Hardgrove'a, podatność mielenie, mieszanki paliwowe

Analysis of Distribution of Secondary Minerals and their Associations on The Surface of Diamonds and in Derrivative Products of Metasomatically Altered Kimberlites

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Abstract

The theoretical and experimental studies resulted in establishing regularities in the distribution of secondary minerals and their associations in metasomatically altered diamond-bearing kimberlites and products of their processing.

Based on integrated mineralogical research, it was found out that the composition of the altered kimberlites and the fine-dispersed clayey slurries formed during their processing constituted the basis of hydrophilic formations on the surface of diamond crystals not recovered by the methods of grease and froth separation. Particles of these minerals concentrate in fine-dispersed slurry products of kimberlite ore processing, interact with the crystal surface, reduce their hydrophobic properties and, accordingly, recovery in processes of grease and froth separations into concentrates.

Keywords: kimberlites, secondary minerals, associations, slurries, hydrophilic diamond, flotation

Introduction

One of the reasons for the decrease in recovery of diamonds from kimberlite is the hydrophilicity the surface of the crystals and pinning her slurry coatings [Chanturia et al, 2013, Dvoichenkova et al, 2014]. Hydrophilization the surface of the diamond is most pronounced in the processing of hypergene altered kimberlites (Chanturia 2016 et al., Zhang et al., 2012).

The upper horizons of kimberlite pipes have been thoroughly studied and the technology of diamond recovery at mineral separation plants has been perfected for them. In the transition to the development of deep horizons of diamond deposits, ore blocks of intensely altered kimberlite rocks of complex material composition were discovered (Westhyzen et al., 2013).

In altered ore blocks, kimberlites are transformed due to metasomatic processes into clay minerals and talc, which constitute up to 96% of the binder mass. In all rocks, clay minerals with smectite laminates were noted: Na-smectite, mixed lattice talc-smectite and chlorite-smectite. The main cause of changes in the mineral composition of kimberlites are hypergenic processes occurring in the field under the influence of hypergenic hydrogeological processes (Zinchuk, 1994, 2000, Podchasov et al., 2004).

The purpose of the given studies was to establish the regularities of distribution of secondary minerals and their associations in kimberlite ores, slurry products of their processing, mineral formations on the surface of diamonds for their subsequent systematization and classification.

Research objects and methods

Samples of altered kimberlites taken from different horizons of kimberlite pipes were studied as objects of research. Secondary minerals and their associations contained in the initial kimberlite samples, slurry fractions of their processing and mineral formations on the surface of diamonds were studied. An experimental analysis of the mineral composition of the studied objects was carried out using semi-quantitative X-ray and thermographic methods and the following equipment: X-ray diffractometers DRON-2.0 (Burevestnik), DMAX-2400 (Rigaku), ARL X`TRA-155 (Thermo scientific), DTG-60AH thermal analyzer (Shimadzu), X'tra-155 diffractometer. The chemical composition of mineral components is determined by the micro-X-ray spectral analysis using a JXA-8800R microanalyzer. The study of the diamond surface was carried out by comparing the reference infrared spectra of passing layered minerals with foreign material streaks on diamonds.

The experiments were performed in the laboratories of the Research Institute of Comprehensive Exploitation of Mineral Resources under the Russian Academy of Science and the Scientific Research and Geological Exploration Enterprise of PJSC ALROSA.

At the first stage of the research, the initial samples of refractory altered kimberlites selected from different horizons of kimberlite pipes of Western Yakutia, were studied. At the second stage of the research, experiments were carried out to study the distribution of secondary minerals, their associations

Tab. 1. Distribution of secondary minerals in the studied samples of altered kimberlites

Tab. 1. Rozkład minerałów wtórnych w badanych próbkach kimberlitów

Minerals	Mine						
	"Mir"	"Internatsionalnaya"	"Butobinskaya"	"Nurbinskaya"	"Ubileynaya"	"Aykhal"	"Udachnaya"
Serpentine	45	36	19	18	35	11	24
Mica	7	4	10	19	3	11	8
Chlorite	2	14	8	7	0	1	2
Talc	2	3	2	10	0	0,4	1,8
Calcite	34	5	31	17	41	20	49
Dolomite	0	14	17	20	3	47	11

in finely divided slurry products of processing rebellious kimberlite ores. At the third stage of the research, the surface of natural diamonds not recovered in the processes of grease and froth separations of altered kimberlites was studied.

Experimental work findings and their discussion

The performed studies in the samples of altered kimberlites helped diagnose secondary minerals and their associations. Regularities in the distribution of the diagnosed elements in the products of processing of kimberlite ores and on the surface of diamond crystals have been established [Chanturia et al, 2014].

Secondary minerals are the minerals formed in kimberlites at the postmagmatic stage during the hydrothermal transformation of rocks at temperatures below 600°C (Zinchuk, 1994, 2000; Podchasov et al., 2004)

At the first stage of the research, the mineral and phase composition analysis showed that in these samples these minerals make up the main volume of kimberlite rocks (90–95%), with the main ones being serpentine and carbonates. Associations of secondary minerals have been diagnosed: serpentine – carbonates, chlorite – serpentines, talc – serpentines, smectite – serpentines, talc-carbonates, smectite-carbonates.

Table 1 shows the average results of the performed study of the composition of kimberlite samples, and the distribution of the diagnosed secondary minerals in them.

The analysis of the Distribution of secondary minerals made it possible to conclude about the mineral composition and the degree of alteration of the kimberlite samples under study and classify them according to the following characteristics: secondary mineralization and the degree of alteration.

By the nature of secondary mineralization, the objects under study can be divided into four groups.

1. Serpentized and chloritized ones, represented by samples of altered kimberlites of “Mir” and “International” pipes.
2. Carbonatized with the dominance of calcite, represented by samples of altered kimberlites of “Yubileinaya” and “Udachnaya” pipes.
3. Carbonatized with the dominance of dolomite, represented by samples of altered kimberlites of “Aikhal” pipes.
4. Serpentized, chloritized and carbonatized with the same distribution of calcite and dolomite, represented by samples of altered kimberlites of “Nyurbinskaya” and “Botuobinskaya” pipes.

In accordance with the content of clay minerals and the distribution of associations of secondary minerals, the studied objects are classified into two main groups: altered and slightly altered. The first group includes samples of altered kimberlites of the “International”, “Botuobinskaya”, “Nyurbinskaya” and “Mir” pipes, in which secondary minerals and their associations are often diagnosed, and also in large quantities. The second group includes samples of altered kimberlites of the “Udachnaya”, “Aikhal”, “Yubileynaya” pipes, in which the secondary minerals and their associations are diagnosed less frequently and in smaller quantities.

At the second stage of the research, the distribution of secondary minerals, their associations in finely divided slurry products of processing of rebellious kimberlite ores were studied.

It has been established that the slurry sands contain fewer secondary minerals - serpentine, chlorite, talc, and calcite. However, the content of quartz increases in them, the amount of X-ray amorphous and amorphous phases represented by finely dispersed smectite and mixed layers also increases. The content of talc-smectite-serpentine associations, which have an enhanced ability to interact with the surface of diamond crystals, increases.

The studies of the distribution of secondary minerals in various granulometric classes of the fineness of shown in table 3, revealed that when the size of the slurry particles decreases, their content of smectite and X-ray amorphous phases increases. An intensive increase in the small classes of talc-serpentine and smectite-serpentine associations typical for altered kimberlites, has been established. At the same time, the fine classes of the slimes studied, the amount of talc-serpentine associations relative to the initial samples of kimberlites increases approximately twice and smectite-serpentine in 8 times.

At the third stage of the research, the surface of natural diamonds that are not recovered in the processes of grease and froth separations of altered kimberlites was studied.

Additional bands of mineral impurities on their surface in the region λ of 670 cm^{-1}, 1010 cm^{-1} and 3675 cm^{-1} were recorded in the IR spectra of the investigated diamonds. The presence of silicate minerals of talc group, similar to the composition of fine slurries of industrial pulps, was identified by the arrangement of lines in the IR spectra of the diamond surface.

The IR spectra of the diamonds studied disclosed additional streaks of mineral impurities on their surface in the region λ of 670 cm^{-1}, 1010 cm^{-1} and 3675 cm^{-1}. The presence of silicate minerals of the talc group similar to the composition

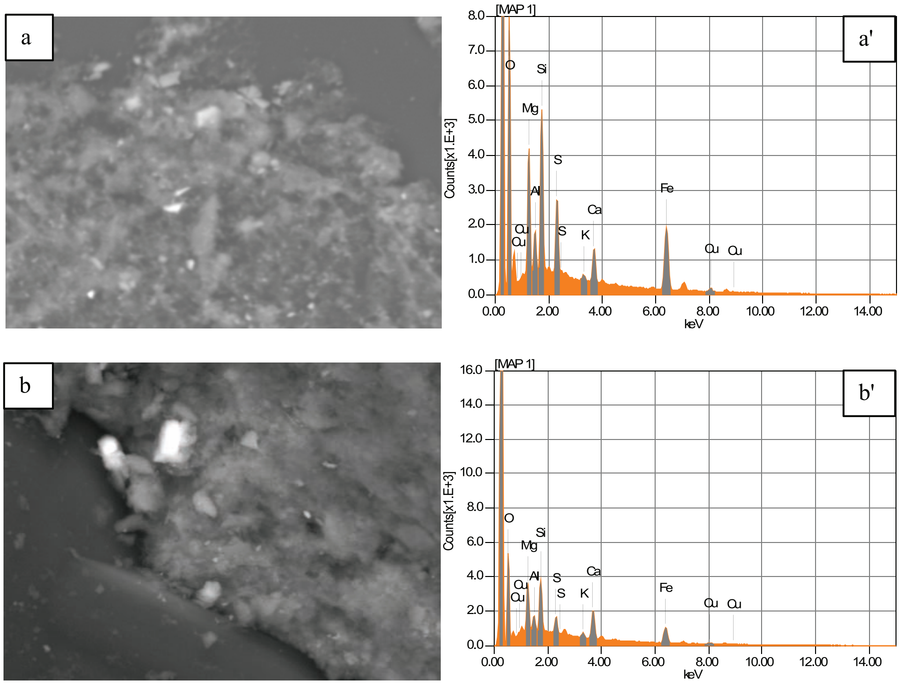
Tab. 2. Distribution of secondary minerals in slurry classes of pulp of altered kimberlites processing

Tab. 2. Rozkład minerałów wtórnych w klasach ziarnowych wzbogacanych kimberlitów

Minerals	Mine			
	the processed ore	Class -0.05 + 0.01 mm	Class -0.01 + 0.001 mm	Class -0.001 mm
Serpentine	18	12	11	15
Mica	17	3	3	1
Chlorite	8	7	7	7
Talc	9	2	1	1
Smectite	2	3	3	3
Calcite	17	7	5	3
Dolomite	19	17	8	3
Quartz	3	7	4	3
Fine minerals associations (x-ray amorphous)	1	37	53	72

Fig. 3. Talc is mixed-layer smectite formations on the surface of diamonds isolated from the kimberlites of the Mir (a) and Internatsionalnaya (b) pipes and results of their x-ray spectral analysis (a', b')

Rys. 3. Talk pod postacią warstw smektytu powierzchni diamentów wydzielonych z kimberlitów z Mir (a) i Internatsionalnaya (b) oraz wyniki spektralnej analizy rentgenowskiej (a', b')



of fine-dispersed slurries of industrial pulps was identified by the line locations in the infrared spectra of the diamond surface.

In addition, the identity of changes in the spectrograms of the diamonds surface in various deposits has been established (Figure 3).

The nature of the location of the Si-O and OH-lines on the spectrograms of the diamond surface in two kimberlite deposits enabled to establish the presence of the talc group silicates with an increased content of oxygen and aluminum.

The diagnosed hydrophilic mineral formations on the surface of the studied diamond crystals are identical in composition and distribution of secondary minerals and their associations to the initial samples and slurry classes of modified kimberlites. The obtained results give grounds to believe that fixing of slurry classes of hypergenic minerals on the surface of diamonds is an important reason for reducing their floatability.

Conclusions

Thus, based on the results of comprehensive mineralogical studies, it has been found that in accordance with the content of clay minerals and the distribution of associations of secondary minerals, the kimberlite ores can be classified into two main groups: altered and slightly altered.

The content of smectite, mixed-layer formations, quartz, talc and X-ray amorphous (finely dispersed) phases increases in slurry products of processed kimberlites with lower values of the quantity of main secondary minerals - carbonates, serpentine and chlorite. In the formed fine-dispersed slurry fractions, the number of paragenetic associations of secondary minerals of kimberlites decreases and the number of associations typical for altered kimberlites increases substantially. Hydrophilic mineral formations on the surface of the studied diamond crystals are identical in composition and distribution of secondary minerals and their associations to the original samples of altered kimberlites.

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Analiza rozkładu minerałów wtórnych i ich rozkładu na powierzchni diamentów i produktów pochodnych metasomatycznie zmienionych kimberlitów

Przeprowadzono analizę teoretyczną i badania eksperymentalne w celu ustalenia prawidłowości w rozkładzie minerałów wtórnych i ich związków w metasomatycznie zmienionych diamentach kimberlitowych i produktach ich przetwarzania. Na podstawie zintegrowanych badań mineralogicznych stwierdzono, że zmienione kimberlity i drobnoziarniste produkty ich metamorfozy stanowiły hydrofilowe formacje na powierzchni kryształów diamentu, które nie zostały odzyskane metodami flotacji pianowej. Cząstki tych minerałów koncentrują się w drobno zdyspergowanych produktach przerobu rudy kimberlitowej, oddziałują z powierzchnią kryształu, redukują ich właściwości hydrofobowe i odpowiednio przechodzą w procesach flotacji do koncentratów.

Słowa kluczowe: kimberlit, minerały wtórne, asocjacje, zawiesiny, diament hydrofilowy, flotacja

Sources of Magnetic Particles from Air Pollution in Mountainous Area

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Abstract

Measurement of magnetic susceptibility of topsoil represents a very useful tool for the detection of atmospherically deposited magnetic particles. The samples of forest soils from the Moravian-Silesian Beskydy Mountains (the Czech Republic) were used for identification of emissions sources of particles with magnetic ordering. Magnetic susceptibility was measured at bulk samples of grain size class under 2 mm. Microanalysis using electron microscope with an energy dispersive X-ray spectrometer was used for the determination of particles in the magnetic fraction. The samples of dust from the sintering plant of the Iron Works in the town of Třinec were analysed. The values of magnetic susceptibility of forest soils in the Třinec region are increased. In the relatively near vicinity of the industrial area, the average value for Javorový Mount was 7.90×10^{-6} *m*^{3}*/kg, for Ostrý Mount it was* 6.69×10^{-6} *m*^{3}*/kg. It was proved that they were higher than the average values from the Beskydy Mountains (*4.64×10^{-6} *m*^{3}*/kg). The concentrations of lead and magnetic susceptibility in soils showed significant correlation dependence (*$r_s = 0.85$*). The iron and steel industry represent the primary source of the pollution load in forest soils of the studied area. Statistically, significant dependences between the organic matter content and the lead and zinc concentrations as well as between the magnetic susceptibility values and the iron concentrations in forest soils were found. It was confirmed that the airborne particles are deposited on vegetation and accumulated in the organic horizon of forest soils.*

Keywords: magnetic susceptibility, microanalysis, soil pollution, atmospheric deposition, emissions from metallurgy

Introduction

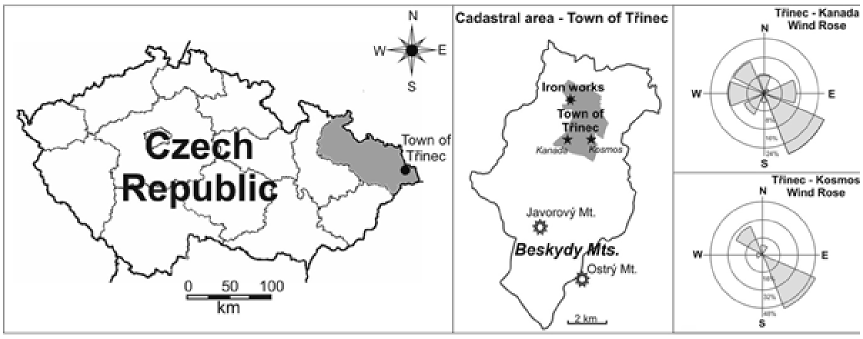
Magnetic properties of particulate matter (PM) are increasingly used for identification of contamination sources in various environmental materials (Cervi et al., 2014). Dust particles with a relatively large proportion of magnetic particles can be released into the environment by anthropogenic processes (combustion of coal and biomass, metallurgical processes, recycling of solid waste, transport). The concentrations of magnetic particles are increased in the uppermost layers of soils in industrial regions and in the vicinity of industrial sources (Lu et al., 2016). Technogenic magnetic particles (TMP) differ from magnetic particles originated by natural processes mostly by concentrations of risk elements. Particles formed during high-temperature combustion processes have characteristic spherical shape. Particles in emissions from transport and iron metallurgy form irregular non-spherical aggregates (Lu et al., 2016). Magnetic properties of soils are influenced by the mineralogical composition of soils and petrographic type of bedrock. The concentration of magnetic minerals (mostly magnetite) in soils can be expressed more simply as magnetic susceptibility (Magiera et al., 2006a). Magnetic properties of soils are manifestation of magnetite, maghemite and minerals of the spinel group: magnesioferrite (Matysek et al., 2008). The highest concentration of anthropogenic ferromagnetic particles is usually found in humus horizon of forest soils (Kapička et al., 2003). Lead has high concentrations in forest soils in the vicinity of the town of Třinec (37–841 mg/kg, median 211 mg/kg). It was found the statistically significant coefficient of correlation between magnetic susceptibility of forest soils and Pb concentration, $r = 0.68$ (Matysek et al., 2008). Concentrations of Pb reach values from 30 to 80 mg/kg in humus horizon of forest soils. Soils in relatively high altitudes above sea level contain concentrations of lead comparable with soils in the close neighbourhood of iron works. This trend is observable in the mountainous area south of the town of Třinec (Matysek et al., 2008). The town of Třinec (Figure 1) is located in the eastern part of the Moravian-Silesian Region (the Czech Republic). Metallurgical plant (Iron Works Třinec) situated in the town produces 2000 kilotons of iron and approximately 2600 kilotons of steel per year. It is reflected by the air quality in the region. The aim of this work is the determination of the origin of magnetic particles in forest soils of Třinec region and proving their relationship with high concentrations of Pb in soils.

Materials and methods

The study area is located in the vicinity of Třinec iron works: Mount Javorový (1044 metres a.s.l., distance of 7.5 km) and Mount Ostrý (1032 m a.s.l., distance of 10 km).

The sampling of soils and their processing was performed according to the Technical Standard ISO 19258. Thirty soil sampling sites were located at the slopes of Javorový Mt. and Ostrý Mt., samples were taken from the depth of 5 to 10 cm (after removing the detritus - uppermost horizon). The orientation of sampling was selected according to the prevailing directions of wind flowing in the region (NE, NW, SE), the height interval of sampling was 100 m of altitude. Sampling

Fig. 1. The Czech Republic, the Moravian-Silesian Region shaded. Study area in the vicinity of the town of Třinec. Prevailing directions of air flowing
Rys. 1. Republika Czeska, Region Morawsko-Śląski. Miejsce poboru próbek w pobliżu miasta Trzyniec. Dominujące kierunki przepływu powietrza.



Tab. 1. The mean values of mass magnetic susceptibility ($\times 10^{-6}$ m³/kg) with standard deviations obtained for altitudes from 500 to 1000 m a.s.l
Tab. 1. Średnie wartości podatności magnetycznej ($\times 10^{-6}$ m³/kg) dla wysokości od 500 do 1000 m nad poziomem morza.

Locality	500 m a.s.l.	600 m a.s.l.	700 m a.s.l.	800 m a.s.l.	900 m a.s.l.	1000 m a.s.l.	All samples
Javorový	2.48±1.26	9.96±0.90	10.62±6.41	10.46±2.77	5.98±5.29	-	7.90±4.72
Ostrý	-	5.14±2.44	5.96±1.88	4.17±1.73	7.19±4.40	10.97±3.11	6.69±3.45

sites of forest soils at both localities were located mostly in deciduous and mixed forests. Homogenized samples with the grain size of less than 2 mm were used for analyses. The determination of chemical composition of soils – concentrations of risk elements was performed by portable energy dispersive X-ray fluorescence spectrometer Innov-X DELTA Professional (InnovX Systems, U.S.A.). The mass magnetic susceptibility (χ) of the soil samples (fraction with grain size below 2 mm) was measured using the Bartington MS2 instrument and MS2B dual sensor at two frequencies: 0.465 kHz (low frequency) and 4.65 kHz (high frequency). Magnetic particles from soils were separated by hand magnet. The point chemical analysis of particles was performed by scanning electron microscope (SEM) FEI Quanta 650 FEG with energy dispersive analyzer EDAX. Mineralogical phase analysis of dust from Iron Works Třinec was performed by the method of X-ray diffraction (diffractometer Bruker Advance D8). The statistical analysis and the correlation analysis at the 0.5 level of significance were performed using the statistical software OriginPro 8.5.

Results and discussion

The study area (Javorový Mt. and Ostrý Mt.) is located in the area of flysch zone of West Carpathians. Flysch sediments are formed by characteristic intercalations of clay and sand rocks. In the region of Moravian-Silesian Beskydy Mts., volcanic rocks of teschenite association occur with minerals like magnetite and goethite. The mass magnetic susceptibility of flysch rocks (sandstones, siltstones, and shales) is relatively very low, approximately 7×10^{-8} m³/kg. These values vary widely and can be increased by the presence of siderite or glauconite in the rocks (Matysek et al., 2008). The research conducted by various authors in the regions under the influence of industrial emission indicates the anthropogenic character of the magnetic susceptibility, with the values higher than 60×10^{-8} m³/kg in the forest topsoil (Chlupáčová et al., 2010). The χ value of soils can vary depending on the region (lithology), emission sources (i.e., power industry, metallurgy) and distance from this emission sources (Łukasik et al., 2016). Accumulation of ferromagnetic mineral phases occurs mostly in the surface layer of forest soils in the O horizon (Strzyszcz and Magiera, 1998). The mean value of mass magnetic susceptibility for the area of Javorový Mt. is $7.90 \pm 4.72\times10^{-6}$ m³/kg and Ostrý Mt. $6.69 \pm 3.45\times10^{-6}$ m³/kg (Table 1). These values are higher than the average value determined in the Moravian-Silesian Beskydy Mts. – $4.64 \pm 4.41\times10^{-6}$ m³/kg (Matysek et al., 2008), and pronouncedly higher than the values of χ for selected mountain areas in Poland, e.g. Lasocki Ridge, eastern Karkonosze Mts. with the average value of $82.0 \pm 2.05\times10^{-8}$ m³/kg, and Jazwina (Sleza Massif) $120.2 \pm 96.38\times10^{-8}$ m³/kg (Magiera et al., 2006b). Table 1 presents the mean values of magnetic susceptibility and standard deviations determined in the altitude from 500 to 1000 m a.s.l. The highest values were found in the area of Javorový Mt. for altitude from 700 to 800 m a.s.l., for Ostrý Mt. in the altitude of 1000 m a.s.l. Figure 2 displays box-plot, which shows the increase of the values of magnetic susceptibility with the increasing altitude, what is in accordance with results published by Matysek et al. (2008) for the area of Moravian-Silesian Beskydy Mts.

High concentrations of lead in soils were found for the area of Javorový Mt. (311 ± 168 mg/kg) and Ostrý Mt. (316 ± 213 mg/kg). Sucharova et al. (2011) report significant variations between the minimal and maximal concentration (19 and 1863 mg/kg) for forest soils in the Czech Republic, with the median value of 78 mg/kg. The maximal concentration of Pb was described particularly from the eastern part of the republic. The high concentrations of Pb in forest soils in the Karkonosze National Park (soil layers 0–10 cm and 10–20 cm) in the ranges 19–248 and 4–196 mg/kg respectively were published by Szopka et al. (2013). From results listed in Table 2 it follows that concentrations of elements in organic horizon of forest soils in the area of Javorový Mt. and Ostrý Mt. are comparable with the exception of manganese. In the area of Ostrý Mt. and Javorový Mt., concentrations of Fe in forest soils are approximately 5× higher than the median value for forest soils in the Czech

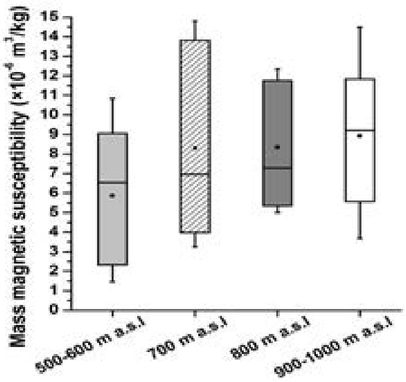


Fig. 2. Box plot – Mass magnetic susceptibility of soils in the altitude from 500 to 1000 m a.s.l

Rys. 2. Podatność magnetyczna gleb na wysokości od 500 do 1000 m npm

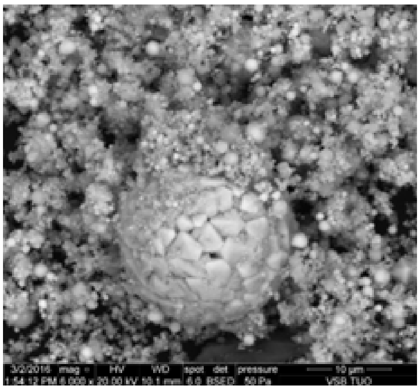


Fig. 3. Electron microphotograph of the spherical particle of magnetite in dust from the steel mill

Rys. 3. Mikrofotografia elektronowa sferycznej cząstki magnetytu w pyle z huty

Tab. 2. Concentrations of elements and content of organic matter in soil samples from the Beskydy Mts. and forest soil from the whole area of the Czech Republic [Explanations: S.D. – Standard deviation, OM – Organic matter, FS – Median of concentrations in organic horizon of forest soils]

Tab. 2. Stężenia pierwiastków i zawartości materii organicznej w próbkach gleby z Beskidów. i gleby leśne z całego obszaru Republiki Czeskiej [Wyjaśnienia: S.D. – Odchylenie standardowe, OM – Materia organiczna, FS – Mediana stężeń w organicznym horyzoncie gleb leśnych]

Locality	Fe	Mn	Zn	Pb	Cr	Cd	Cu	Zr	As	OM	Reference
	(mg/kg)									(wt.%)	
Beskydy Mts. mean	27588	464	178	226	81	-	19	91	30	-	*Matysek et al.,2008*
S.D.	*16351*	*495*	*92*	*101*	*32*	-	*16*	*42*	*12*		
Javorový Mt. mean	38363	660	303	311	71	1.6	58	161	52	67	*This study*
S.D.	*11050*	*344*	*106*	*168*	*17*	*0.44*	*27*	*53*	*22*	*14*	
Ostrý Mt. mean	36313	463	300	316	73	1.2	53	193	50	65	
S.D.	*9677*	*157*	*141*	*213*	*19*	*0.4*	*27*	*63*	*18*	*14*	
FS-Czech Republic	7200	392	63	78	22	0.56	23			81	*Sucharova et al.,2011*

Republic, for Pb 4×, for Cr 3×, and for Mn and Cu two times higher (Sucharova et al., 2011). Relationships between individual elements were studied using Spearman correlation coefficients with respect to identification of contamination sources. Statistically significant correlation coefficient was proved for Fe × Mn, Pb, Zn, As, Cu, Cr in forest soils in the areas of Ostrý Mt. and Javorový Mt. An enrichment factor (EF) was selected for expression of contamination degree of forest soils. It was calculated as a ratio: (concentration of risk element/concentration of Zr) in the sample of analysed soil/(concentration of element/concentration of Zr) in the lithogenic background. The geochemical background was determined as concentrations of elements in topsoil (Salminen, 2014). Zirconium was selected as a typical lithophile element. In the air deposits from the iron works in Třinec, it was present below the limit of detection of the analytical method. The highest value of enrichment factor was found for Pb, Zn, Cu, and As. The enrichment factor in forest soils was higher in the area of Javorový Mt. than in the area of Ostrý Mt. for all studied elements (Fig.4). The highest enrichment factor was determined for soils in both areas of summits of Ostrý Mt. and Javorový Mt. High levels of precipitation are strongly correlated with heavy metal deposition and seem to be the main source of heavy metal deposition at higher altitudes (Zechmeister, 1995). The highest concentrations of Pb in the summit areas are not in accordance with the results of Szopka et al. (2013), who reported concentrations of Pb to be significantly higher in the lowest altitudinal zone (500–750 m a.s.l.) compared to the highest zone (1250–1380 m a.s.l.), what can be explained by seeder-feeder effect and horizontal transport of pollutants.

Correlation analysis proved the statistically significant relationship between magnetic susceptibility and risk elements Cu, Fe, As, Pb, Zn together with organic soil component. At the same time, significant inverse proportionality was determined between magnetic susceptibility and lithogenic elements Si, Al, Ti, and Zr (Table 3). The statistically significant relationships were also found between concentrations of Pb, Zn and the content of the organic component in soils. The correlation coefficient for the content of organic matter in soils and Pb (Javorový Mt.) reached the value $r_s = 0.89^*$. Similarly, for the content of organic matter in soil and Zn, it was $r_s = 0.70^*$. The similar relationship for Pb was reported by Szopka et al (2013). Statistically significant correlation relationships were also found for the summit of Ostrý Mt. between the content of the organic component of soils and Pb ($r_s = 0.80^*$) as well as for Zn $r_s = 0.73^*$. The concentrations of Pb, Zn, and Fe in soils have relationships with the content of organic matter in soils. Metals are primarily caught by vegetation, which is the source of organic matter in humus horizon. The development of humus horizon is influenced by density and character of wood vegetation.

Chemical and mineralogical analyses of dust from the iron works in Třinec were performed in order to determine the origin of magnetic particles in soil samples. The results of mineralogical analysis of crystalline phase are presented in Table 4.

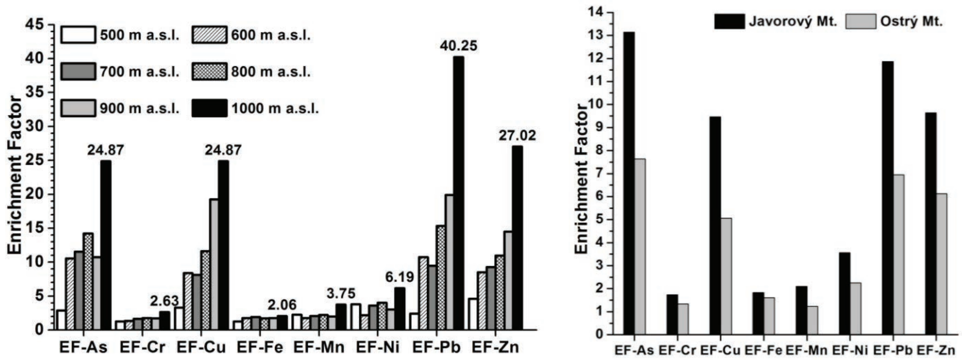


Fig. 4. Left: Relationship between the altitude above sea level and EF. Right: Median of enrichment factor EF for soils from Javorový Mt. and Ostrý Mt.
Rys. 4. Po lewej: Związek między wysokością nad poziomem morza a EF. Po prawej: Mediana współczynnika wzbogacenia EF dla gleb z Javorový Mt. i Ostrý Mt.

Tab. 3. The values of correlation coefficients for mass magnetic susceptibility and risk elements together with organic matter (n=30) for the Beskydy Mts. [Explanations: OM - Organic matter, *statistically significant relationships]
Tab. 3. Wartości współczynników korelacji dla masowej podatności magnetycznej i elementów ryzyka wraz z materią organiczną (n = 30) dla Beskidów. [Objaśnienia: OM – materia organiczna, *relacje istotne statystycznie]

Si	Al	Fe	K	S	Ti	Mn	Cu	Zn	As	Zr	Pb	OM
-0.79*	-0.59*	0.96*	-0.80*	0.81*	-0.73*	0.62*	0.91*	0.90*	0.93*	-0.73*	0.85*	0.71*

Tab. 4. The main mineral phases in dust from the iron works Třinec (wt.%) [Explanations of dust origin: AE – sintering plant, electrostatic separators. AB – sintering plant, bag filters. B – steel mill. C – secondary dust removal of oxygen-convertor steel mill. D – desulphurization of pig iron.]
Tab. 4. Główne fazy mineralne w pyłach z Huty Żelaza Třinec (% wag.) [Objaśnienia pochodzenia pyłu: AE – spiekalnia, separatory elektrostatyczne. AB – spiekalnia, filtry workowe. B – huta stali. C – wtórne usuwanie pyłu w stalowni konwertorowej. D – odsiarczanie surówki.]

Mineral	AE	AB	B	C	D
Sylvite - KCl	26.33	27.28			
Halite - NaCl	11.54	20.89			
Wuestite - FeO			3.34	0.45	
Magnetite - Fe_3O_4	19.66	1.87	31.1	49.26	42.19
Hematite - Fe_2O_3	23.07		2.11	29.81	18.85
Laurionite - PbCl(OH)	1.65				
Laurelite - $Pb_7F_{12}Cl_2$	0.98				
Penfieldite - $Pb_2Cl_3(OH)$	1.35				
Litharge - PbO		0.54			
Portlandite - $Ca(OH)_2$		32.11			
CaOHCl		5.34			
Calcite - $CaCO_3$		7.57			
Zincite - ZnO				3.77	
Cr-Mn-Fe spinel			53.1		
Gehlenite - $Ca_2Al(Si,Al)_2O_7$				4.88	4.64
Graphite - C			1.92	5.59	11.52
Magnetic susceptibility $\times 10^{-6}$ m^3/kg	7.78	1.45	18.18	1.81	9.47

Iron oxides (magnetite and hematite) form an essential part of dust AE, B, C, and D, where their average content is 55% of the crystalline phase. An example of spherical magnetite particle is in Figure 3. Chlorides (NaCl and KCl) are also important, and they can form up to 48% of the crystalline phase. In dust from the sintering plant, lead minerals were identified (laurelite, laurionite, and penfieldite), chlorides and hydroxichlorides of lead. In dust from oxygen-convertor steel mill, zincite (ZnO) was identified. Important mineral in dust from steel mill is Cr-Mn-Fe spinel. The average chemical composition of particles from dust determined by SEM+EDAX is presented in Table 5.

Dust AE contained particles with high Pb concentrations in the range from 4.1 to 39.1%. Dust B from steel mill has mostly Fe-Cr-Mn spinel as a major component in the crystalline phase. Dust C from oxygen-convertor steel mill contains relatively larger particles of size around 5 µm, with 1.96 to 3.42% of Zn. These particles are probably formed by hematite which contains 69.94% of iron and 30.06% of oxygen. Particles with relatively higher content of Zn (10–15%) are formed by magnetite. The high concentration of Zn in magnetite is possible due to the substitution of Fe2+and Zn2+ with very similar ion radii in magnetite ($Fe^{2+}Fe_2^{3+}O_4$), where Zn has ion radius of size 0.060 and Fe^{2+} 0.063 nm (Hansson et al., 2004). Iron oxide particles from dust D contain only minimal amounts of Zn admixture (0.93–3.36%), in less than 50% of analysed particles. From results of chemical composition of particles it follows that for particles from ore sintering plant (AE) there is typical element association of Fe × Pb, for particles from steel mill is typical association of Fe × Cr

Tab. 5. Chemical analyses of particles (average of 15 particles) by SEM +EDAX (wt.%)
Tab. 5. Analizy chemiczne cząstek (średnio 15 cząstek) metodą SEM + EDAX (% wag.)

	Fe	Mn	Cr	Zn	Pb	Cu	Si	O	Al	Mg	Ca	K	Na	Cl
AE	15.11		0.15		11.73	2.13	4.27	7.29	0.99	0.94	2.51	15.53	7.69	30.86
AB	0.51				6.60	1.38		11.97	0.67	2.54	31.57	8.47	4.39	25.26
B	37.56	12.79	5.74				4.03	29.12		5.52	6.54	0.48		
C	58.36	1.34		9.31			0.71	20.83	0.52	0.41	1.52	0.53		
D	50.57			2.25				21.06	2.78		6.05			

× Pb, and for particles from desulphurization of pig iron (D) as well as from oxygen-convertor steel mill it is association of Fe × Zn. Analysis of particles from dust and mineralogical analysis of dust confirmed that lead-bearing phases form separate minerals.

Conclusions

Mass magnetic susceptibility provides the whole series of statistically significant linear correlations with Fe, Zn, Pb, Cu, and As. Metals in forest soils are bound to iron oxide particles and the organic component of soils. Metals in forest soils in the areas of Javorový Mt. and Ostrý Mt. can be arranged according to the decreasing concentrations in the following way: Fe > Mn > Zn > Pb > Cr > Cu > As > Cd. Lead is neither part of the structure of magnetite nor minerals of the spinel group. It forms in dust from the iron works separate minerals. Together with magnetite, it forms mixed crystalline aggregates. Magnetic susceptibility has the statistically significant relationship with the content of the organic component in soils (r_s = 0.71*) which documents catching of these particles by vegetation and their subsequent deposition into humus horizon. From the value of correlation coefficient (r_s = 0.85) between magnetic susceptibility and concentration of Pb in soils, it follows that emissions from the sintering plant represent the main source of lead. The enrichment factor proved increased deposition load of forest soils (Pb, Zn) in the areas with the higher altitude above sea level. Lead had the highest enrichment factor.

Acknowledgement

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Źródła cząstek magnetycznych z zanieczyszczeń powietrza w obszarach górskich

Pomiar podatności magnetycznej wierzchniej warstwy gleby stanowi bardzo przydatne narzędzie do wykrywania osadzonych z atmosfery cząstek magnetycznych. Próbki gleb leśnych z Beskidu Morawsko-Śląskiego (Czechy) wykorzystano do identyfikacji źródeł emisji cząstek o właściwościach magnetycznych. Podatność magnetyczną mierzono w próbkach zbiorczych w klasie ziarnowej poniżej 2 mm. Mikroanaliza z użyciem mikroskopu elektronowego ze spektrometrem dyspersyjnym energii rentgenowskiej została użyta do oznaczenia frakcji magnetycznej cząstek. Przeanalizowano próbki pyłu ze spiekalni Huty Żelaza w Trzyńcu. Stwierdzono wzrost wartość podatności magnetycznej gleb leśnych w regionie Trzyńca. W stosunkowo bliskim sąsiedztwie obszaru przemysłowego Javorový Mount średnia wartość wynosiła 7,90 × 10^{-6} m^3/kg, w przypadku Ostrý Mount 6,69 × 10^{-6} m^3/kg. Wykazano, że były one wyższe niż średnie wartości dla Beskidów (4,64 × 10^{-6} m^3/kg). Zawartość ołowiu i podatność magnetyczna w glebach wykazały istotną korelację (r_s = 0,85). Hutnictwo żelaza i stali stanowi główne źródło ładunku zanieczyszczeń w glebach leśnych badanego obszaru. Stwierdzono statystycznie istotne zależności między zawartością materii organicznej a stężeniem ołowiu i cynku, a także między wartościami podatności magnetycznej a stężeniami żelaza w glebach leśnych. Potwierdzono, że zawieszone w powietrzu cząstki osadzają się na roślinności i gromadzą się w organicznym horyzoncie gleb leśnych.

Słowa kluczowe: podatność magnetyczna, mikroanaliza, zanieczyszczenie gleby, osadzanie atmosferyczne, emisje z hutnictwa

The Mechanism of Formation of Finely Dispersed Minerals on the Surface of Diamonds and the Application of Electrolysis Products of Water Systems for their Destruction

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Abstract

The composition of the surface of natural diamonds in interaction with kimberlite minerals and the aqueous phase in the deposit and enriched ore is studied. The sequence and conditions for the formation of minerals on the surface of crystals under conditions of processing of kimberlites have been determined. Confirmed the mechanism of hydrophilization of diamonds comprising crystallization of hydroxides and oxides of iron as a mandatory initial stage. A method of destruction or subsequent dissolution of minerals aggregates by the impact of electrolysis products of aqueous systems has been proposed, which allows to restore the hydrophobicity of diamonds. The use of electrochemically treated water in the froth separation cycle with high diamond recovery made it possible to increase their recovery in the factory's concentrate by 8.8%.

Keywords: kimberlite, diamond, mineral impurities crystallization, hydrophobic, hydrophilic, enrichment, electrochemically treatment

Introduction

The high content of altered minerals in kimberlite ores leads to the formation of hydrophilic films on the surface of the crystals, which reduce the degree of hydrophobicity of diamonds and increase their losses in the processes of greased and froth separation to 20–30% (Kurenkov, 1957, Chanturiya et al., 2005). This fact makes the of the identification of the objective of justification and selection of the method for restoring the hydrophobic properties of diamonds before the separation processes of their recovery presently topical.

Earlier studies have defined that a promising way to solve the problem of reducing the intensity of formation of mineral impurities on the surface of diamonds and increasing the enrichment of kimberlites is achieved through the use of physical and physicochemical methods of impacting on the solid and liquid phase of the pulp (Dvoichenkova, 2011; Chanturiya et al., 2016). An important task of the research that determines the achievement of the goal is to study and substantiate the mechanism of formation of minerals on the surface of diamond crystals. The theory of step crystallization was chosen as a working hypothesis for the mechanism of hydrophilization (Matusevich, 1968).

Research methods and objects

To study the mechanism and regularities of the process of buildup of surface formations on diamonds, diamond crystals from kimberlite ore derivatives are taken as the objects of research. Three types of natural diamond crystals recovered from kimberlite ore were used in the experiments:

- natural-hydrophobic crystals, which do not contain mineral formations on the surface;
- natural-hydrophobic crystals with an insignificant amount of mineral formations on the surface;
- natural-hydrophilic crystals, which surface is covered with dense mineral formations.

As a liquid phase, the mineralized circulating process water of the mineral separation plant and the products of its electrolysis in a bladderless vessel has been used.

Impurities on diamond surfaces are studied by using methods of optical microscopy, Auger and X-ray spectroscopy, infrared spectroscopy, UV-VIS spectroscopy and micro-X-ray spectroscopy. The chemical composition of mineral admixtures is determined by using a JXA-8800R microanalyzer.

The hydrophobicity of the diamond surface was determined by the measurements of the three-phase wetting angle. The flotation activity of diamonds was determined in laboratory conditions by the methods of froth separation at the facilities of the YAKUTNIPROALMAZ Institute. Industrial tests were carried out per the scheme of froth separation of diamond-containing raw materials at the beneficiation plant of the Mirny MPD. The experiments were performed in the laboratories of the Research Institute of Comprehensive Exploitation of Mineral Resources under the Russian Academy

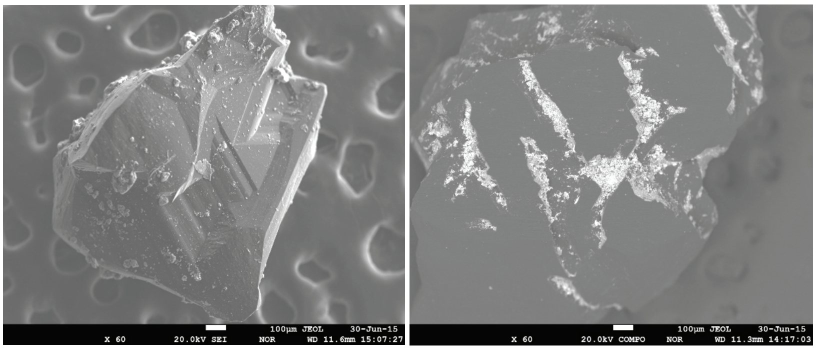

Fig. 1. The outer appearance of mineral impurities on the surface of diamonds
Rys. 1. Wygląd zewnętrzny zanieczyszczeń mineralnych na powierzchni diamentów

of Science, YAKUTNIPROALMAZ Institute and the Scientific Research and Geological Exploration Enterprise of ALROSA company.

At the first stage of the research, the composition of impurities on the surface of diamonds and the regularities of the processes of their formation were studied under the conditions of processing of refractory kimberlites. At the second stage of the experimental research, approbation of the application of electrolysis products of mineralized water was performed to remove mineral formations from the surface of diamonds under laboratory and industrial conditions. The results were mathematically processed and the corresponding graphical dependencies were built.

Experimental work findings and their discussion

An analysis of the mineral and phase composition of the surface of diamond crystals recovered from diamond-bearing kimberlite derived products made it possible to find on the diamonds the presence of mineral impurities in the form of finely dispersed clay minerals and a film-insular type of their attachment on crystals (Fig. 1).

According to the nature of the distribution in Fig. 2 x-ray maps of iron (a) and oxygen (b), respectively, it is possible to diagnose goethite or hematite, and the intensity of the distribution of calcium (b), sulfur (g) and oxygen (b) is diagnosed with gypsum ($CaSO_4 \times 2H_2O$).

Analysis of the composition and preferential location of surface mineral formations on the defects of diamond crystals gave grounds for the analysis of the processes of their hypergenic and technogenic hydrophilization to use the hypothesis of the formation and attachment of hypergenic secondary minerals and salt-like substances on diamond surfaces with a broken crystal structure most prone to epitaxial growth (Ryznar, 1944, Telkes, 1952). Analysis of the distribution of surface mineral formations on diamonds made it possible to adopt the crystallization process in the conditions of oversaturation as the most probable mechanism of their formation (Turnbull and Vonnegut, 1952).

In the case under consideration, the diamond surface serves as a matrix forming the phase of the crystallizing salt. The value of the variable of the crystallographic discrepancy is used as the criterion for the surface activity (substrate) (Volmer, 1939).

$$\delta = |a_{sf} - a_{cr}| / a_{cr}$$

where: a_{sf} – the parameter of the crystal lattice of the substrate;
a_{cr} – the parameter of the crystal lattice of the crystallizing substance.

The formation and growth of crystal nuclei occurs when the parameters of these crystal lattices differ by no more than 20% ($\delta = 0.2$) (Turnbull and Vonnegut, 1952). For example, the results of the micro-X-ray spectral analysis showed that serpentine and calcite are the main rock-forming minerals in kimberlite samples of the Mir pipe. Other primary and secondary aluminosilicate and carbonate minerals, as well as hydroxides and iron oxides, saltlike minerals are widespread (Table 1). Goethite is the mostly presented on the diamond surface among other minerals prone to crystallization.

According to the proposed mechanism for the formation of minerals on the surface of diamond crystals under the conditions considered, a primary change of the natural surface of a diamond can occur as a result of hypergenic processes and lead to the formation of films of metal hydroxides. For example, FeO (OH) (mineral of goethite), has the degree of lattice discrepancy with respect to a diamond is 0.15. Further, according to the crystallographic non-conformity of the goethite lattice with the diamond lattice (δ (c) is 0.15), this mineral can crystallize on the diamond crystal surface and be a substrate for the crystallization of other diagnosed minerals.

In accordance with the data on the crystallographic relationships of the lattices of the minerals considered given in the table and the hypothesis of the formation of mineral impurities, the minerals on the diamond surface are crystallized in the following sequence: diamond – goethite – hematite – phlogopite, halite, gypsum.

The electron image of mineral admixtures on the surface of the diamond recovered from the "Mir" mining kimberlites shown in Fig. 3 graphically is indicative of the joint attachment of hypergenic and saltlike minerals (phlogopite, gypsum and halite) on the film of iron minerals (goethite).

Using mathematical data processing, a proportional dependence of the decrease in the hydrophobicity of diamonds was obtained with an increase in the total impurity content on their surface (Figure 3).

At the second stage of the research, approbation of the application of electrolysis products of mineralized water was performed to remove hydrophylic mineral formations from the surface of diamonds. In previous studies we have shown

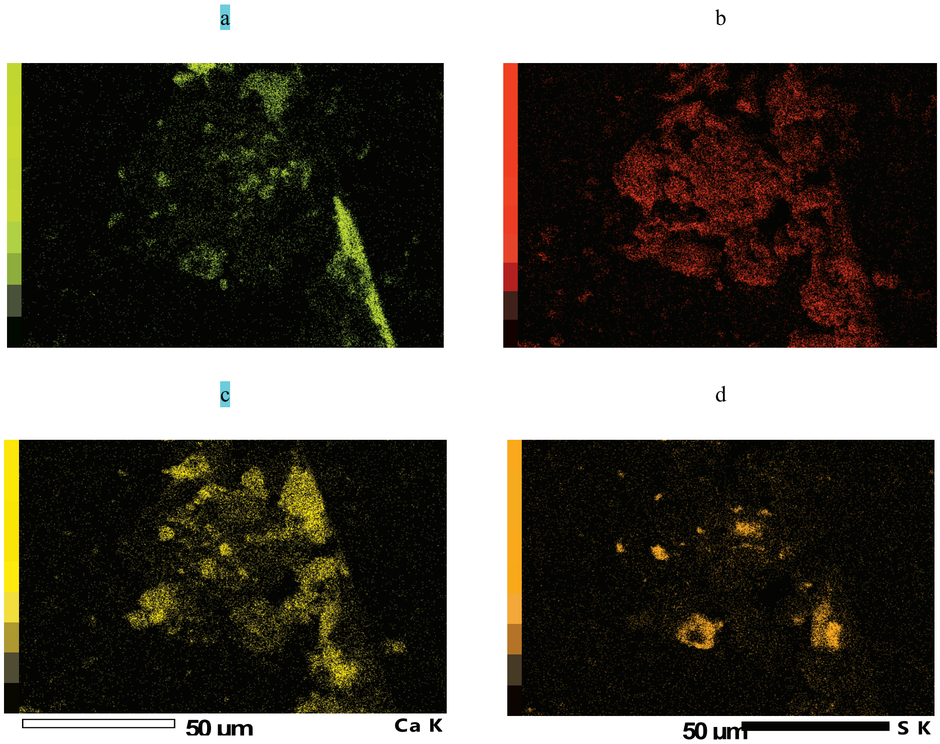

Fig. 2. X-ray maps of distribution of chemical elements: iron (a), oxygen (b); calcium (c); sulfur(d)
Rys. 2. Mapy rentgenowskie rozkładu pierwiastków chemicznych: żelazo (a), tlen (b); wapń (c); siarka (d)

Tab. 1. Mineral formations diagnosed on the surface of diamonds
Tab. 1. Formacje mineralne rozpoznane na powierzchni diamentów

Mineral, formula	Lattice parameter a, A^0			Crystallogr. discrepancy with the diamond			Crystallogr. discrepancy with the goethite			Crystallogr. discrepancy with the hematite		
	a	b	c	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)
Diamond, C	3.57	3.57	3.57	0	0	0	0.28	1.78	0,15	0.41	-	2.85
Гётит, FeO×OH	4.59	9.94	3.02	0.28	1.78	0.15	0	0	0	0.10	-	3.55
Hematite, Fe_2O_3	5.03	-	13.7	0.41	-	2.85	0.10	-	3.55	0	0	0
Phlogopite, $K_2(Mg, Fe)_6[Si_6Al_2O_{20}]$ (OH, F)$_4$	5.3	9.2	10.3	0.48	1.58	1.88	0.15	0.07	2.41	0.05	-	0.10
Halite, NaCl	5.64	-	-	0.58	-	-	0.23	-	-	0.12	-	-
Gypsum, $CaSO_4 \times 2H_2O$	5.68	15.2	6.29	0.58	3.25	0.76	0.24	0.53	1.08	0.13	-	0.54

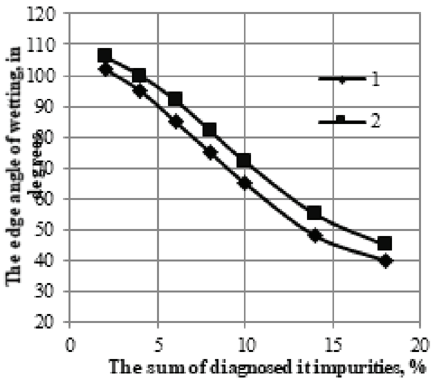

Fig. 3. Dependence of the edge angle of wetting of the diamond surface mine “Mir” (1)
and “Internationalnaya” (2) on the mass fraction of the sum of diagnosed it impurities Si, Ca, Mg, Fe

Rys. 3. Zależność kąta zwilżania dla minerałów z kopalni diamentu „Mir” (1)
i „Internationalnaya” (2) od zawartości zanieczyszczeń Si, Ca, Mg, Fe

Tab. 2. Change in the diamond surface composition and parameters after treatment with water electrolysis products

Tab. 2. Zmiana składu powierzchni diamentu i parametrów po obróbce produktami elektrolizy wodnej

Object of measurement	*the edge angle of wetting in degree*	The concentration on the surface,%					Relation of Σ Si, Fe, Mg of C concentration, %	Film area, %
		C (diamond)	Si	Fe	Mg	O		
hydrophilic diamonds before treatment	33.3	63.5	3.3	4.25	4.5	35.1	19	73
diamonds after treatment	99.8	80.1	1.4	0.7	2.3	15	5.4	19.9

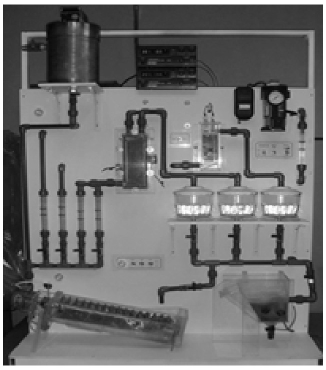

Fig. 4. Laboratory stand for research of the electrochemical conditioning of the water systems in the process of foam separation

Rys. 4. Stanowisko laboratoryjne do badań elektrochemicznego kondycjonowania roztworów wodnych w procesie flotacji pianowej

the possibility of using water electrolysis products for desorption of surface films from a diamond (Chanturiya et al, 2005).

Natural diamonds with a hydrophilic surface were used in the present experiments. Table 2 presents the average results taking into account previous studies.

It was experimentally determined that the crystal surface (group II) washed by the water electrolysis products is characterized by a low content of impurity elements (<5%) and an oxygen content of less than 15%. In this case, the area of the serpentine film armoring a clean surface is not more than 22%; and the amount of diamond carbon reaches 80%. On the initial hydrophilic crystals (group I) covered with mineral impurities, the values of analogous parameters characterizing the impurity film are 2–3 times higher.

Analysis of the absorption spectra of luminescent radiation by the surface of diamond crystals coated with mineral impurities (hydrophilic) and treated with products of electrolysis aqueous systems (hydrophobic) made it possible to determine that:

- the hydrophilic surface of diamonds is characterized by higher values of the absorption coefficient,
- a decrease in the values of the absorption coefficient after the treatment of crystals by electrolysis products of aqueous systems indicates the removal of mineral impurities from their surface.

The obtained results were used in experiments to enhance the efficiency of the process of froth separation of diamond-containing raw materials. To restore the floatability of diamonds, the technology of non-diffracting electrochemical conditioning of the circulating water of the foam separation cycle and the sticky separation cycle was used.

Laboratory tests were carried out on a special stand, which includes an electrolyzer, a foam separation unit and control devices (Fig. 4).

During the experiment, the parameters of electrochemical water treatment varied and optimal conditions were selected. Selected optimal parameters were tested in the course of the technological process at the concentrator plant at the Mirny MPD.

In electrochemical processing was achieved by changing the ionic composition of the water. Concentrations of calcium and magnesium ions decreased, pH decreased. Under these conditions, it was possible to increase the hydrophobicity of diamonds. Another positive effect was a significant increase in the concentration of dissolved gases contributing to the foam separation process.

The use of electrolysis products of aqueous systems in the laboratory experiment conditions made it possible to restore the hydrophobic properties of diamond crystals and increase their yield to the froth separation concentrate from 19.5% to 66.7%, and in the industrial approbation condition to increase the recovery of diamond in the factory's 8.8%.

Conclusions

The mechanism of the formation of mineral impurities on the surface of diamond crystals is represented by the process of crystallization under conditions of saturation of the aqueous phase by crystallizing elements (ions), when the surface of the diamond serves as a matrix forming the phase of the crystallizing salt. The value of the crystallographic disparity between the parameters of the crystal lattice of the substrate (diamond) and the crystallizing substance is used as a criterion for the activity of the surface (substrate).

The decrease of hydrophobicity of diamonds is proportional to the increase of the total content of impurities on their surfaces. The use of electrochemically treated water in the cycle of froth separation of kimberlite ores during the recovery of diamonds into a 98–99% concentrate increases their recovery in the factory averagely by 8.8%.

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Mechanizm tworzenia drobno rozproszonych minerałów na powierzchni diamentów i zastosowanie produktów elektrolizy systemów wodnych do ich zniszczenia

Zbadano skład powierzchni naturalnych diamentów w interakcji z minerałami kimberlitowymi i fazą wodną w złożu i wzbogaconej rudzie. Określono kolejność i warunki tworzenia minerałów na powierzchni kryształów w warunkach przetwarzania kimberlitów. Potwierdzono mechanizm hydrofilizacji diamentów obejmujący krystalizację wodorotlenków i tlenków żelaza jako stały etap początkowy. Zaproponowano sposób niszczenia lub późniejszego rozpuszczania agregatów minerałów przez wpływ produktów elektrolizy układów wodnych, co pozwala przywrócić hydrofobowość diamentów. Zastosowanie elektrochemicznie uzdatnionej wody w procesie separacji piany z wysokim odzyskiem diamentu umożliwiło zwiększenie odzysku w koncentracie o 8,8%.

Słowa kluczowe: kimberlit, diament, krystalizacja zanieczyszczeń mineralnych, hydrofobowe, hydrofilowe, wzbogacanie, obróbka elektrochemiczna

STUDIA PODYPLOMOOWE 2019/2020

Nazwa studiów podyplomowych:
PRZERÓBKA SUROWCÓW MINERALNYCH

Krótka charakterystyka studiów:
Studia są skierowane do absolwentów szkół wyższych (magisterskich lub zawodowych) wszystkich kierunków, w szczególności do pracowników zakładów wzbogacania surowców, pracowników biur projektowych i konstrukcyjnych, jednostek naukowo-badawczych oraz firm dostarczających rozwiązania technologie i urządzenia do wzbogacania surowców. Program studiów obejmuje opis operacji podstawowych stosowanych w przeróbce surowców i odpadów, układy technologiczne wzbogacania surowców (węgiel, rudy metali), ocenę i optymalizację procesów technologicznych. Studia obejmują wykłady, ćwiczenia laboratoryjne oraz ćwiczenia terenowe (zajęcia w zakładach wzbogacania węgla, rud miedzi i rud cynkowo-ołowiowych).

Program studiów:
1. Podstawy mineralogii i geologii inżynierskiej. Metody oceny jakościowej surowców
2. Gospodarka surowcami mineralnymi i odpadami
3. Rozdrabnianie i klasyfikacja
4. Fizyczne metody wzbogacania
5. Flotacja
6. Gospodarka wodno-mułowa, zagospodarowanie odpadów
7. Podstawy metalurgii (w tym hydrometalurgia)
8. Chemiczne i biologiczne metody wzbogacania
9. Automatyzacja, kontrola i modelowanie procesów przeróbczych, kontrola jakości i ocena procesów technologicznych
10. Technologie wzbogacania surowców, czyste technologie węglowe
11. Projektowanie i ekonomika procesów wzbogacania
12. Warsztaty terenowe – zajęcia w zakładach wzbogacania węgla, rud miedzi i rud cynkowo-ołowiowych
13. Seminarium dyplomowe oraz praca kontrolna

→ 68

Determination of The Optimal Dosage of Chemical Compounds in the Wastewater Treatment Process in Trang Bach Coal Mine: the Laboratory Scale

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Abstract

The pH index of Trang Bach coal mine wastewater ranges from 2,8 to 6, meanwhile, the content of Fe, Mn, and turbidity & suspended solids (TSS) are rather high and it is impossible to discharge the wastewater directly to the environment. In order to achieve the requirement of QCVN 40:2011/BTNMT standard – The national standard for industrial wastewater quality after treatment of Vietnam and other purposes, the wastewater need to be treated by several methods such as coagulation-flocculation or sedimentation. In this article, we intend to find the optimal dosages of chemical compounds for the TSS, pH, Fe and Mn treatment process for Trang Bach coal mine wastewater in the laboratory modular.

Keywords: Trang Bach coal mine, laboratory modular, optimal dosage

Introduction

The Trang Bach coal mine is located in Dong Trieu district, Quang Ninh province, 80km far from Hanoi, the capital city of Vietnam (Institute of Mining Science and Technology, 2011). The wastewater in Trang Bach coal mine, which has the large amounts and high concentrations of pollutants, is formed through the processes of depositing and moving water in the expanding underground coal mine activities under the complicated physical and chemical conditions (Institue of Mining Science and Technology, 2011). A large amount of FeS2 and some of the major mineral ores of manganese are contained in coal. Due to the coal exploitation, there is a significant amount of sulfuric acid, sulfuric acid (Fe(OH)3) that have been released into the wastewater. As a result, Trang Bach coal mine's wastewater is highly acidic and contains many suspended solids.

In the rainy season, due to a large amount of diluted rainwater, the acidity and content of pollutants in wastewater are reduced (Institute of Mining Science and Technology, 2014). Therefore, the content of pollutants in wastewater in the rainy season is lower than the dry season.The components of mining wastewater effluent directly to the quality of surface water resources, polluting the water sources, changing the habitat of aquatic fauna and flora. Therefore, coal mine wastewater must be treated before discharging into surface water or further treated with advanced technologies for other demands (R. K. Tiwary, 2001). Due to the above mentioned characteristics, the principle of treating coal mine wastewater is to use alkaline chemicals, neutralize acidic environment, create precipitation medium of Fe and Mn metals, then use PAC - Poly Aluminium Chloride to increase the possibility of suspended solids deposition (Le Anh Tuan, 2005). After the treatment processes, the wastewater quality will be compared with the level B of QCVN 40: 2011 / BTNMT standard - The national standard for industrial wastewater quality after treatment of Vietnam. Thus, the main objective of the research is to observe the optimal dosage in the treatment of pH, Fe, Mn and TSS of Trang Bang coal mine in laboratory scale.

The wastewater treatment in Trang Bach Coal Mine

The wastewater sample was collected from the mine at the furnace door (location of effluent pumped out of the pit) in end of January 2016. It was the dry season in Vietnam. The sample was analyzed in The Water Quality Laboratory, Hydrogeology Department, Faculty of Geosciences and Geoengineering, Hanoi University of Mining and Geology, Vietnam (Tab.1).

In comparison with the QCVN 40:2011/BTNMT, the content of Fe, Mn, TSS and the value of pH is higher than the standard, therefore, the wastewater quality is not good enough to be discharged directly to the surface water. The applied treatment method in this coal mine is quite simple, they use mainly the deposition method. The data of the quality of mine wastewater after treatment in 2014, 2015, provided by The Department of Environmental Technology, Institute of Mining Science and Technology also shows that the pH, Fe, Mn and TSS concentration sometimes was not fully treated (Tab. 2)

Methodology

The concept of the treatment of the mine wastewater which contains low pH value and high concentration of iron, manganese and TSS is coagulation and sediment. We will use calcium oxide to increase the pH, in parallel with it, the ion Fe^{2+} will be hydrolysed and accumulated and due to the oxidation, the ion Fe^{2+} will convert into the ion Fe^{3+}, theoretically, it will be appreciated as a result of the chemical reaction:

$$4Fe(HCO_3)_2 + O_2 + 2H_2O + 4Ca(OH)_2 \rightarrow$$

Tab. 1. The quality of wastewater sample in comparison with the B level of QCVN 40: 2011 / BTNMT standard

	pH	Fe (mg/l)	Mn (mg/l)	TSS (mg/l)
Result	3.31	5.9	24.4	148
B level - QCVN 40:2011/BTNMT standard	5.5 - 9	5	1	100

Tab. 2. The quality of wastewater of Trang Bach coal mine after treatment in 2014, 2015 (Source: Institute of Mining Science and Technology, Vinacomin, Vietnam)

No.	Value	2014			2015			QCVN 40:2011 /BTNMT
		5-2014	8-2014	11-2014	5-2015	9-2015	10-2015	B level
1	pH	6.8	4.8	5.2	3	5.6	5.9	5.5-9
2	TSS (x10 mg/l)	1.1	6	5.3	3.4	2.7	1.8	10
3	Fe (mg/l)	0.81	5.95	3.91	5.71	5.05	5.52	5
4	Mn (mg/l)	0.56	0.71	0.64	0.96	1.25	1.46	1

$4\ Fe(OH)_{3\downarrow} + 4Ca(HCO_3)_2$

Although the precipitated ion Fe^{3+} can be easily removed from the wastewater, iron ion still presents in the form of suspension. In fact, due to the lack of oxygen during the pumping process that brings the wastewater from the underground mine into the surface, the chemical reaction happened in another way (Tran Tu Hieu, 2003):

$Fe(HCO_3)_2 + Ca(OH)_2 \rightarrow FeCO_{3\downarrow} + CaCO_{3\downarrow} + 2H_2O$

On the other hand, calcium hydroxide also decreases the ion manganese concentration:

$Mn^{2+} + 2OH- = Mn(OH)_{2\downarrow}$

With the aim to separate the suspension and the mine wastewater, it is necessary to use the flocculant to increase the precipitation abilities of TSS, heavy metal's ions. The popular flocculant is PAC - Poly Aluminium Chloride ($Alm(OH)nCl3m-nxH_2O$, with $m \leq 10$, $2 \leq n \leq 5$) (V.K. Gupta et al., 2009).

In order to achieve the goals of this study, 2 experiments method were used. The chemical compounds are CaO 70% and PAC (with the concentration of $Al_2O_3 > 30\%$), provided by Hydrogeology Department, Faculty of Geosciences and Geoengineering, Hanoi University of Mining and Geology, Vietnam. All the experiments were done in the Water Quality Laboratory, High-Tech Analysis Center, Hanoi University of Mining and Geology. Firstly, the pH value of the wastewater will be increased by using calcium oxide, with the Jar-test stirring standard - 100 round per min in the first 3 minutes, 30 round per min in the next 10 minutes and wait for 30 minutes (A.P. Black et al., 1957). We started the experiments with 5 mg calcium oxide and then increased the calcium oxide content by 5 mg for the next test. The experiment had been repeated until the pH value reach to the B level of QCVN 40:2011/BTNMT standard. Secondly, the wastewater will be fully treated by PAC with the Jar-test stirring standard in the constant condition of pH value. The content of PAC for the first test is also 5 mg, and we also increased the content of PAC by 5 mg for the next test and the experiment had been repeated until the concentration of iron, manganese and TSS reached to the B level of QCVN 40:2011/BTNMT.

Results and discussion

Table 3 shows the results of the wastewater quality after being treated by CaO 70%. At the value of 280 mg CaO 70%, the pH value reached to the B level of QCVN 40:2011/BTNMT standard, in parallel with it, the concentration of Iron, Manganese and TSS also decreased as well. We continued increasing the content of CaO 70% till 320 mg and the pH value increased positively as well as the concentration of ion Iron, Manganese and TSS decreased.

After the first experiment, the optimal dosage of CaO 70% to increase the pH value to more than 5.5 is 280 mg/l, the concentration of ion Fe, Mn and TSS are 0,29; 8,50 and 23 mg/l respectively (Fig.1). Calcium oxide not only increased the pH value but also decreased the concentration of ion Iron because the ion F^{e2+} were also oxidized into ion Fe^{3+}, presented in the form of insoluble iron hydroxide and precipitated due to the neutralization of pH in the wastewater (Fig. 2). As a result, the concentration of Iron also reached to the B level of QCVN 40:2011/BTNMT but the concentration of ion Manganese and TSS were still higher than the B level of the standard, it is necessary to perform the second experiment with PAC.

With the pH value is 5,53 and the content of CaO 70% is 280 mg/l, we need 125 mg/l PAC to fully treat the concentration of ion Manganese and TSS. The sampling time is in the dry season, when the wastewater is diluted by the surface water in the rainy season, the concentration of ion Iron, Manganese, TSS will decrease and the pH value will increase and as a result, the content of CaO 70% and PAC that we need to treat the wastewater will be lower than 280 mg/l and 125 mg/l respectively (Fig. 3).

We were not able to perform the experiments with the wastewater samples in the rainy season due to the lack of fund and the lack of information. In order to apply this idea to build a wastewater treatment model in industrial scale, the further studies are still required. On the other hand, the coal

Tab. 3. The pH value and concentration of Iron, Manganese and TSS in wastewater samples after being treated by CaO 70%

CaO (mg)	pH	Fe (mg/l)	Mn (mg/l)	TSS (mg/l)
0	3.31	4.90	24.40	148
10	3.31	4,9	23.10	124
15	3.38	4.82	22.90	111
20	3.39	4.75	22.30	100
25	3.40	4.73	21.50	98
30	3.40	4.72	20.90	94
35	3.42	4.60	18.10	89
40	3.43	4.53	17.50	83
80	3.52	4.35	16.10	79
120	3.56	4.23	16.10	56
160	3.84	1.23	12.70	46
200	4.64	1.08	11.20	32
240	4.94	0.45	9.50	27
280	**5.53**	0.29	8.50	23
320	**5.85**	0.20	8.20	21
B level of QCVN 40:2011/BTNMT standard	5.50	5.00	1.00	100

Tab. 4. The concentration of contaminant in wastewater sample after being treat by PAC at the pH value by 5.53

PAC (mg)	0.00	40.00	80.00	120.00	125.00	130.00
Fe (mg/l)	0.20	0.16	0.12	0.11	0.11	0.11
Mn (mg/l)	8.20	5.34	3.27	1.15	1.00	0.93
TSS (mg/l)	21.00	17.00	13.00	4.00	0.00	0.00

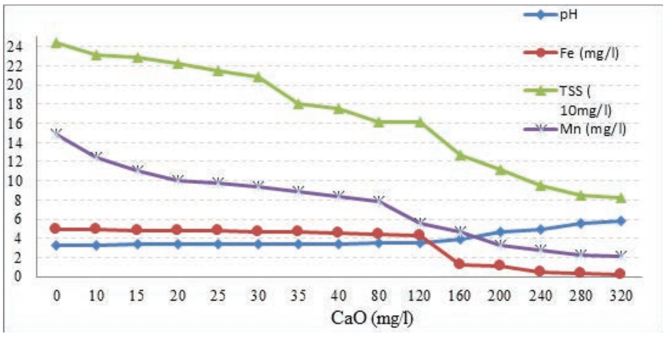

Fig. 1. The pH value and the concentration of ion Iron, Manganese and TSS after being treated by Calcium Oxide 70%

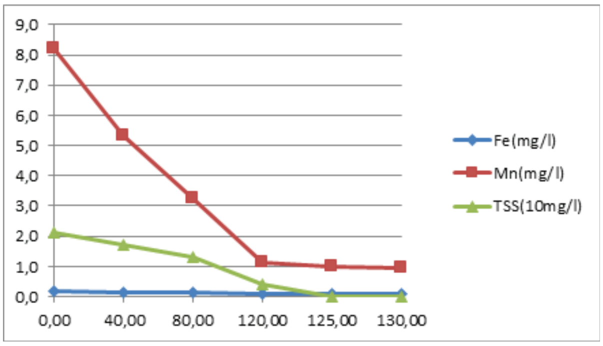

Fig. 3. The fluctuation of contaminants in the wastewater sample after being treated by PAC at the pH value by 5.53


a b c

Fig. 2. The precipitation process at the beginning (a), after 10 mintues (b) and after 30 minutes (c) of the wastewater sample after the first experiment with 280 mg/l Calcium Oxide 70% (Photo:Manh Ha Doan)

mines are located mostly in the North-West part of Vietnam, near several limestone mines so we have the potential to produce the chemical compounds for the industrial scale treatment locally.

Conclusion

The wastewater quality of Trang Bach coal mine is not good enough to be discharged immediately into the surface water. It contains the low value of pH, the high concentration of ion Iron, Manganese and TSS. In order to reach the B level of QCVN 40:2011/BTNMT – The national standard for wastewater quality after treatment of Vietnam, the wastewater need to be treated with 280 mg/l CaO 70 % and 125 mg/l PAC in laboratory scale.

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Improving the Efficacy and Efficiency of the Environmental Management System in the Romanian Powerplants on Coal – the Condition of the Environmental Performance

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Abstract

After a decade-long evolution, the use of coal for energy production is growing again. Carbon is still an important source of energy in Europe, covering about one-fourth of electricity production. There are plans to open around 50 new coal-fired power plants. But the continued use of coal has a price, we pay all, mainly with our health can be affected by excessive environmental pollution Today more and more emphasis on the concept of „green economy" that should be reflected in improving people's lives through effective management of environmental issues and reducing environmental risks Thus, through the present paper we aim to highlight those aspects that would allow the improvement of the environmental performance of coal-fired power plants in Romania by improving the efficiency and effectiveness of the Environmental Management System (EMS) as a component of the Integrated Management System along with the Quality, Health and Safety Management System . We start from the premise that the development and implementation of an effective and efficient environmental management system (EMS) becomes a priority for all companies in the field , especially since their activities based on coal burning , are considered among the most polluting.

Keywords: environmental management system, environmental performance, integrated management systems, sustainable development

Introduction

Every industrial activity has an effect on the environment. More and more companies, especially industrial ones, have become and become aware that they need to pay more attention to the management of their environmental impact. To that end, the development and implementation of an effective and efficient EMS system becomes a priority. Industrial producers have to meet the demands and challenges of the European Union. We mention here the initiative of the European Commission that launched a scheme (EMAS - eco-management and audit scheme) to which they can voluntarily join organizations, in accordance with European Regulation 1836/93, which was subsequently replaced by Council Regulation 761/2001, 1221/2009 last amendment being 1505/2017. So EMAS targets a set of environmental policy tools that allow companies to pursue both environmental objectives and competition objectives in a synergistic way .Implementation of a system environmental management can based on one of EMAS standards and / or ISO 14001 that allow organizations of any size or type to control the impact of their activities, products and services on the environment. The accession of industrial organizations to an environmental management and audit system such as EMAS is voluntary but once a what an enterprise decides to do join EMAS, then it have to fully comply with the provisions of the aforementioned regulation. Improving environmental performance is a goal set by EMAS. If the ISO 14001 : 2004 standard not established anything about the environmental performance, only an absolute dedication and involvement in the field of environmental protection, compliance with the law and the principle of continuous improvement , the new ISO 14001: 2015 standard (which replaces the old standard at the end of 2018) requires performance assessment and we recommend increasing focus on managing environmental performance improvements.

The environmental management system (EMS) has two areas of focus: environmental compliance and environmental sustainability.

The place of coal- fired power stations is in Romania's energy system

Coal remains a major energy pawn while being an important source of energy security even if the share of coal in the energy mix is to be diminished. Reality but emphasizes the importance of coal-based electricity. It turns out so that coal-fired power stations remain to play an important role in the production and delivery of energy and electricity in the National Energy System (NES), regardless of atmospheric conditions - frost, increased drought, when the wind does not blow to produce wind energy or the sun is not enough for normal photovoltaic power production. During 2017, thermo capacities produced 41% of the national electricity, accounting for 48.6% of the total installed power. By comparison, analyzing the weights of the components of the net production mix for 2017, we can see that the largest share (41%) is represented by the thermo component followed by the hydro component (25%) and the energy produced from renewable and nuclear sources have a weight of approximately 18% and 16%, respectively.

In Romania the production of electricity in the thermoelectric power plants is realized in:

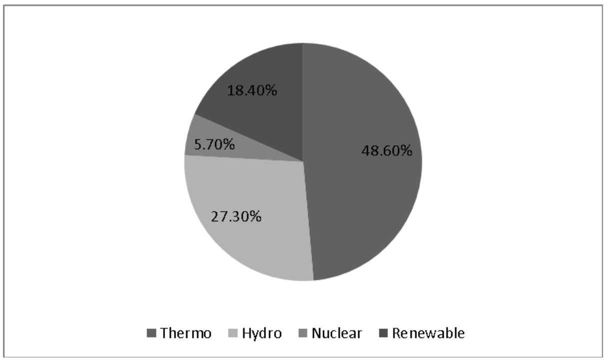

Fig. 1. Power installed on 9 months 2017 (24,738 MW, gross)
Rys. 1. Moc zainstalowana w ciągu 9 miesięcy 2017 r. (24 738 MW, brutto)

Tab. 1. The National Transition Plan for substantially reducing the amount of sulfur dioxide, nitrogen oxides and dusts emitted into the atmosphere (eg from 9 496 tonnes of sulfur dioxide in 2016 to 1980 tonnes in 2020)
Tab. 1. Krajowy plan zmniejszenia ilości dwutlenku siarki, tlenków azotu i pyłów emitowanych do atmosfery (np. z 9 496 ton dwutlenku siarki w 2016 r. do 1980 ton w 2020 r.)

	2016	2017	2018	2019	Sem 1.2020
SO_2	9.496	7.650	5.805	3.960	1.980
NO_2	26.096	23.605	21.115	18.624	9.312
Dusts	916	724	532	341	170

- 12 production capacities with an installed capacity of 6015 MW using coal as fuel; these plants belong to 7 companies.
- 13 production capacities with an installed capacity of 4445.6 MW, using hydrocarbons as fuel, these plants being owned by 8 companies.

The most important producers of coal-based energy are the Hunedoara Energy Complex and the Oltenia Power Complex. The Hunedoara Energetic Complex (CEH) owns the Lonea, Livezeni, Lupeni and Vulcan mines and Mintia thermal power plant (on Mures), with a 1,075 MW installed power, and the Paroseni electro-thermal power plant (Jiu), with an installed power of 150 MW. Their production covers 2% of national electricity production (data for year 2016). The Oltenia Energetic Complex operates 4 thermoelectric power plants: Işalnita (2 groups x 315 MW), Rovinari (4 groups x 330 MW), Turceni (6 groups x 330MW) and Craiova (2 groups x 150MW).

The problem that arises is related to the impact of the activities of these coal- fired power plants on the environment. It is not to be neglected that industrial organizations we refer face serious problems for alignment with European emission standards for reducing air pollution. It is important to emphasize that the reduction of pollutant emissions to the air at the legal level does not mean that coal-fired power plants no longer have an impact on health and the environment. Romania's coal-fired power plants are big polluters with dust, sulfur dioxide, nitrogen oxides, and carbon dioxide. In addition to coal-fired power plants harmul emissions, is the impact of coal extraction, in particular for lignite, which includes grazing large areas of forests, the destruction of some agricultural landfills and the production of large quantities of dust, as well as the pollution of groundwater. Compliance with emission standards can not be an object of negotiation, so it is necessary to treat these problems is with most seriousness, hence mandatory implementation of management systems such as the environment, quality and occupational health within these enterprises .

By approving the National Transition Plan by the European Commission by decision of 03.03.2016 (according to the provisions of Article 32 of Law 278/2013), a number of installations have been granted aderogation for different emissions until 30 June 2020 (Order No 1430/1063/2017 / 220/2018 on the approval of the Transitional National Transition Plan for Combustion Plants under the provisions of Chapter III of the Law No 278/2013 on industrial emissions).

But besides investment necessary measures that have to be taken to ensure compliance by all combustion installations of coal plants of the applicable emission limit values such as desulphurisation of the flue gases rehabilitation low NOx burners, rehabilitation electrostatic and the case Electrocentrale Deva in the Energy Complex Hunedoara, or installation and commissioning of a system to reduce noncatalitic selective nitrogen oxides from the flue gases (SNCR) in plants in the structure of the Oltenia Energy Complex, the focus should be on improving the efficiency and effectiveness of the Environmental Management System (EMS) implemented within these organizations.

Environmental performance – a criterion for the efficiency and effectiveness of the environmental management system

In recent years, the literature has been abundant in studies describing the elaboration, development, implementation and continuous improvement of the integrated systems of SIM quality management, environment, occupational health and safety management, social responsibility, etc., as well as their individual study. In the case of environmental management, the studies focused on the conditions of enterprises that decided to implement the environmental management system based on the ISI 14001 standard, its certification and, last but not least, its economic impact (Matuszak-Flejszman, 2009;

Marimon, et al., 2011; Narasimhan and Schoenherr, 2012; Bernal Conesa et al., 2016).

The relationship between the implementation of the environmental management system and the environmental performance has in turn prompted interest in recent years. Several international studies have shown that there is a positive relationship between ISO 14001 certification and improving environmental performance in countries such as Canada, France, Germany , Hungary, Japan, Norway, USA (Barla, 2007, Schultze, W. and Trommer. R, Arimura et al., 2012, 2016) or Malaysia (Goh, EA et at., 2006; Goh YN, 2011). However, other studies on the operation of industrial activities in Mexico (Blackman and Guerrero, 2012), Great Britain (Dahlstrom et al., 2003) or USA (King et al., 2005) do not bring any change in environmental performance or in pollution reducing behavior (Ziegler and Rennings, 2004) , while other studies offer inconclusive results. Furthermore, a research study by Hertin et.al, 2003, even in the field of electricity, concluded that environmental performance is not the main reason for the E MS implementation, which is why the poor relationship between EMS and performance becomes a plausible consequence, because there is no evidence to suggest that EMS implementation has a consistent and significant positive impact on environmental performance. But more recent studies, such as the (Arab, et al., 2017) highlighted the main success factors for the implementation of environmental management systems, with direct effect in improving environmental performance, including commitment and support of the manager, coordination and integration, education, effective participation and management of human resources, financial and non-financial resources and cost analysis -benefits, environmental objectives and policies and documentation control.

It is clear that starting from the literature on this topic, a set of specific indicators is set and monitored in practice. Crucially, however, is the selection of the most representative of them, so that the correlations between the groups of factors or the composite variables determine the efficiency and effectiveness of the EMS.

Results and discussion

With regard to the above-mentioned organizations, both representative industrial companies in the field of the coal-based electricity production have implemented and maintain an Integrated Management System in accordance with the requirements of the ISO 9001: 2008, ISO 14001: 2004, OHSAS 18001: 2007 through which it promotes a policy oriented towards the permanent satisfaction of the requirements of the clients and stakeholders towards the offered products and services, of reducing the negative impacts of its activities on the environment and of reducing the risks to the safety and health of the employees, visitors, subcontractors by conducting safe activities.

However, the immediate concern is to recertify the management systems according to the new standards (ISO 9001: 2015, ISO 14001: 2015, the old ones lose their validity at the end of 2018, and ISO 45001: 2018,replaces OHSAS 18001 health and safety standard).

The implementation of the EMS aims at demonstrating the organization's environmental performance, taking measures to control the impact of its activities / processes on the environment.

Identifying and analyzing best practice in the process of developing and implementing the EMS, based on the application of ISO 14001, it is necessary to analyze the factors that may determine the effectiveness and efficiency of EMS in thermal power plants using coal, the enhancement of the peculiarities of these firms in the energy field.

Improving environmental management and increasing the efficiency and effectiveness of EMS, based on ISO 14001, should take into account:

- A strengthening of the specific values of the organizational culture that to stimulate compliance with environmental requirements, respectively environmental legislation and regulations;
- Ensuring a strong and informed leadership in environmental management;
- Promoting integrated prevention strategies for environmentally competitive, economically and financially-friendly (profitability) ecological production where environmental pollution control systems (which are expensive) are replaced by focused measures to prevent pollution
- Obtaining information on the potential for enhancing environmental performance in order to apply organizational strategies to facilitate the assessment and valorisation of their potential to adopt and apply eco-friendly technologies and techniques, and to capitalize on the opportunities for eco-growth-efficacy.

Conclusion

An Environmental Management System or EMS can be a powerful tool to help businesses improve their environmental performance.

Many organizations implement an EMS that meets the requirements of ISO14001 certification, not necessarily to become a better environmental corporate citizen. However, they soon discover that implementing a robust EMS is beneficial and adds value to their business.

In the case of energy organizations studied, it is necessary that the investment measures necessary to maintain the safety of the national energy system to be correlated with the environmental compliance measures. We recommend developing a model of analysis that highlights the relationship between the efficiency and effectiveness of EMS and environmental management, motivational factors, market and regulatory and benefits in its implementation and development in power plant coal as electricity generation units from Romania, as well as the degree of integration of SME along with the leased systems (quality, health and occupational security, social responsibility). There are several reasons for integrating management, quality, occupational health and safety (OH & S) together with environmental management (Sanz-Calcedo, JG et al., 2015), such as: Reducing duplication of activities and therefore costs Balance conflicting objectives, eg between occupational health and the environment, Eliminate conflicting responsibilities and relationships , Harmonize and optimize practices, Create consistency, Improve communication, Facilitate training and development, Integrating management systems facilitates focus on the most important aspects of a company, Separate systems tend to put focus on every area instead of the common area.

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Poprawa skuteczności i efektywności systemu zarządzania środowiskowego w rumuńskich elektrowniach na węgiel – stan efektywności środowiskowej

Po trwającej lata ewolucji wykorzystanie węgla do produkcji energii ponownie rośnie. Węgiel jest nadal ważnym źródłem energii w Europie, pokrywając około jednej czwartej produkcji energii elektrycznej. Istnieją plany otwarcia około 50 nowych elektrowni węglowych. Ale energetyczne wykorzystanie węgla ma swoją cenę, płacimy głównie naszym zdrowiem wskutek nadmiernego zanieczyszczenia środowiska. Obecnie coraz większy nacisk kładzie się na koncepcję „zielonej gospodarki", która powinna znaleźć odzwierciedlenie w poprawie życia ludzi poprzez skuteczne zarządzanie środowiskowe i zmniejszanie zagrożeń środowiskowych. W artykule przedstawiono aspektów, które mogą pozwolić na poprawę efektywności środowiskowej elektrowni węglowych w Rumunii poprzez poprawę wydajności i skuteczności Systemu Zarządzania Środowiskowego (EMS) jako elementu Zintegrowanego Systemu Zarządzania wraz z Systemem Zarządzania Jakością i Bezpieczeństwem. Przyjęto założenie, że opracowanie i wdrożenie skutecznego i wydajnego systemu zarządzania środowiskiem (EMS) staje się priorytetem dla wszystkich firm w tej dziedzinie, zwłaszcza że ich działalność oparta na spalaniu węgla jest uważana za najbardziej zanieczyszczającą środowisko.

Słowa kluczowe: system zarządzania środowiskowego, efektywność środowiskowa, zintegrowane systemy zarządzania, zrównoważony rozwój

STUDIA PODYPLOMOWE 2019/2020

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Słuchacze nabędą wiedzę teoretyczną i praktyczną z zakresu wzbogacania surowców obejmującą identyfikację właściwości minerałów, procesów separacji, procesów pomocniczych, projektowania i optymalizacji technologii przeróbki. Ukończenie studiów podyplomowych zostanie potwierdzone świadectwem Akademii Górniczo-Hutniczej im. Stanisława Staszica w Krakowie zgodnie z wymogami Ministerstwa Nauki i Szkolnictwa Wyższego.

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Conductors in Cryogenic Environment Used in Power Engineering

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Abstract

The tendency to increase the carrying capacity of the electric load in the supply networks can be done in two directions, namely:

- *the construction of several transmission and distribution lines linking the energy source to the consumer (current trend), having the effect of damaging the environment, or*
- *limiting the construction of transport lines and, implicitly, the destruction of the environment by using technologies and materials capable of carrying a very large amount of electricity.*

Keywords: cryogenic environment, nitrogen, electric charge, cryogen cables, superconductivity

Overconductibility is a phenomenon that has, at least until now, been manifested only at cryogenic temperatures and which has been seen for the first time due the discovery of helium liquid. Overconductivity is given by the very rapid drop to zero of the electrical resistance below a specific temperature called superconducting transition temperature or critical temperature, Tc.

The electrical resistance of the conductors is directly proportional to the temperature through the relationship:

$$R = R_0\ (1+\alpha\Delta t) \qquad (1)$$

where:
R_0 is the conductor resistance at 20°C,
α is the coefficient of thermal expansion.

As the temperature rises, the electrical resistance is higher and so the electrical load carrying capacity of a conductor is reduced.

In order to increase the intensity of the electric current running through a conductor, two trends can be drawn, namely:

- increasing the section of conductors or constructing in parallel several electric lines,
- reducing the working temperature around the conductors.

Low temperatures around the conductors can be achieved with cryogenic fluids.

Liquid nitrogen is a cryogenic fluid that is in the form of isotopes and can be obtained by the fractionation of air.

The thermal conductivity of the nitrogen relative to the temperature is linear, that ranges from a conductivity of 0,94 W·m-1 x102 for the temperature T =100K, to 2,61 $W\cdot m^{-1}\ x10^2$ for the temperature T = 300K.

In the environment with very low temperatures, in the cryogenic field, the properties of the materials have an evolution that cannot be extrapolated to the environment with normal working temperatures.

The behavior of materials in a cryogenic environment is different; the study of main parameters may support the choice of materials to be used.

If the environment it takes a few hours to allow thermal equilibrium in cryogenic environment enough minutes.

Specific heat becomes an important dimension in the use of conductors in cryogenic environments.

Applying the quantum theory of thermal vibrations in solids and assuming that all the particles present in a crystal vibrate with the same frequency f0, the oscillator energy is:

$$E = n\cdot h\cdot f_0 \qquad (2)$$

where:
n is an integer
h is Planch's constant ($h = 6{,}63\cdot 10^{-34}$ Js)

Using Boltzman's law considering that all states are equally degenerate, the average energy of an oscillator can be written:

$$E_m = \frac{3\sum_{n=0}^{\infty} E_n \exp\left(-\mathrm{E}_{n/\mathrm{kT}}\right)}{\sum_{n=0}^{\infty} \exp\left(-E_{n/kT)}\right.} \qquad (3)$$

or

$$E_m = \frac{3hf_0}{e^{-\frac{hf}{kT}} - 1} \qquad (4)$$

The specific heat value will be:

$$C_v = \left(\frac{\partial U}{\partial T}\right) = 3\,R \left\{ \frac{(\frac{hf_0}{kT})^2 \exp(\frac{hf_o}{kT})}{\left[\left[\exp(\frac{hf_o}{kT}) - 1\right]\right]^2} \right\} = 3\ \mathrm{RE}\ (\theta_E\ /T) \quad (5) \qquad (5)$$

where θE = hf0/kT and is called Einstein's temperature for very low temperature values we will have:

$$C_v = 3\ \mathrm{RE}\ (\theta_E\ /T)^2 \exp\ (-\theta_E/T)) \qquad (6)$$

At low temperatures the quantification of the network reduces the specific heat in relation to the classical heat.

This is because the exponential variation of the specific heat, in this temperature range, is much faster than the T^3 variation observed at low temperatures.

Electrical conductivity

According to Ohm's law, when a current of electric intensity I pass through a conductor with the resistance R, there is a voltage U of value:

$$U = R\,I \tag{7}$$

Depending on the nature and properties of the material, the electrical resistance is given by:

$$R = \rho \cdot l/S \tag{8}$$

where:
ρ is the electrical resistivity of the material
l is the length
S is the section

With the passing of the electric current I, through a conductor, the Joule effect, its heating, generates electricity losses that can be determined with the relation:

$$P = R \cdot I^2 \tag{9}$$

The behavior of a metal's resistivity according to temperature in a cryogenic environment varies with the temperature cube.

The cryogenic medium which superconductivity occurs is given by the very rapid decrease to zero electrical resistance at a certain temperature of the superconducting transition.

An avalent resistivity determines an electrical system without "friction", electric circuits without Joule effect, ie without any dissipation of electrical energy.

For each superconductor there is a temperature range and a magnetic field below which the material is superconducting and over which it becomes normal.

The relationship between the critical field and the temperature is the parabolic one.

$$H_c = H_0 \left[1-(T/T_c)^2\right] \tag{10}$$

where:
H_0 represents the critical field for T = 0 K
T_c is the maximum temperature at which the material is in the superconducting state when H = 0.

Electric power currently transported by conventional underground cables is of the order of 1000 MVA. For such great powers, it is necessary to evacuate the heat generated by Joule effect, ie forced cooling with oil or water. To meet the growing consumption of energy has made other cable systems such as superconducting cables.

Although they have a very low electrical resistivity compared to other conductors, copper and aluminum only permit a current density of the order of 1÷2 $A \cdot mm^{-2}$ at 20°C (293.15 K), if we want to we avoid sensitive heating by Joule effect.

By cooling these conductors at the liquid nitrogen temperature (77 K), the electrical resistivity of copper decreases with an order of magnitude almost. This cooling is provided for non-superconducting or cryo-resistive cryocabs.

If we start from 4.2 K, the boiling temperature of the helium at atmospheric pressure, the superconducting alloys whose transition temperature is higher, are materials that have a zero resistivity to a direct current and a very weak resistance (10^{-6} times that of copper) for an alternating current of 50 Hz.

In practice, because of the limitations given by the critical current, in these superconducting cables we can have a current density of 200 $A \cdot m^{-2}$. So, there is a ratio of 1: 200 in the favor of superconducting cables.

This report justifies economically the use of these cables, despite the energy they that is needed to be cooled below their transition temperature. Cryocabs will also compulsory need to be underground, the environment being protected.

Increasing the allowable current density for a conductor of a certain section can also have the effect of reducing the overall dimensions of the power equipment.

For an electric circuit by a current of I = 1000 A is passed, the copper wire section, which may also be part of a secondary winding of a power transformer in normal environment, should be at least 500 mm^2, admitting a current density of Jrated = 2 $A \cdot mm^{-2}$.

In a cryogenic environment, the superconducting current density may be Jcryogenic = 200$A \cdot mm^{-2}$, which would mean that the winding of a transformer from a cryogenic environment could be executed with a 5 mm^2 section conductor, which would mean the reduction of the gauge of the equipment.

The favorable environmental impact is achieved by both reduced gauges and the reduced number of high-capacity underground electricity lines.

Conclusions

Using wires in cryogenic environment is beneficial:

- on the electric load carrying capacity,
- diminishing the dimensions of the power equipment,
- reducing the impact on the environment through the construction of cryogenic underground lines.

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Przewodniki w środowisku kriogenicznym stosowane w energetyce

Tendencja do zwiększania obciążenia elektrycznego w sieciach zasilających może być realizowana w dwóch kierunkach, a mianowicie: budowa kilku linii przesyłowych i dystrybucyjnych łączących źródło energii z konsumentem (obecny trend), powodujących uszkodzenie środowiska, lub ograniczenie budowy linii transportowych i w efekcie ograniczenia zniszczenia środowiska poprzez zastosowanie technologii i urządzeń zdolnych do przenoszenia bardzo dużej ilości energii elektrycznej.

Słowa kluczowe: środowisko kriogeniczne, azot, ładunek elektryczny, kriogeniczne kable, nadprzewodnictwo

AGH

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Characterisation of Purified Gypsum and Insoluble Impurities Obtained from Phosphogypsum Waste

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Abstract

In this study, the chemical and phase composition of two samples of phosphogypsum from the waste dumps of the Industry of Chemical Products "Elixir – Prahovo" (Serbia) were examined, as well as the possibility of recrystallization of gypsum from an aqueous suspension of phosphogypsum. The negative effect of higher temperatures on the solubility of calcium sulfate (13.08 mmol/dm^3 at 95°C vs. 15.43 mmol/dm^3 at 40°C) was utilized. In several repeated cycles, calcium sulfate component was progressively dissolved in water at room temperature and then precipitated at 100°C, using the same liquid phase throughout the experiment. Therefore, phosphogypsum was separated into recrystallized (purified) gypsum, insoluble residue and supernatant, and the mass balance for the experiment was calculated. Elemental, XRD and SEM-EDS analyses were performed on raw phosphogypsum, purified gypsum and insoluble residue. The whiteness of raw phosphogypsum and purified gypsum were determined and compared. The main objective of the study was to investigate the nature of insoluble impurities, in order to define and optimize the methods for their removal during a potential industrial processing of phosphogypsum.

Keywords: phosphogypsum, recrystallization, purified gypsum, insoluble impurities

Introduction

Phosphogypsum (PG) is a by-product of the production of phosphoric acid, during sulfuric acid digestion of phosphate rock. Currently, the annual PG production worldwide is about 160 million tons, of which 50 million tons are produced in China and 40 million tons in USA, according to the International Atomic Energy Agency (IAEA, 2013). It consists of hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$ or $CaSO_4 \cdot 0.5H_2O$) and impurities such as P_2O_5, fluorides, organic substances, and alkali metals (Hua et al., 2016; Walawalkar et al., 2016). A significant quantity of toxic and harmful elements (including U, Ra and Th) are transferred from phosphate rock into the phosphogypsum, thus limiting its commercial use (López et al., 2016).

Agriculture and road construction are areas where PG can be applied effectively and a large quantity of this material can be consumed; however, there is still a lack of information about the potential release of metals and radionuclides during the life time of certain applications (Cánovas et al., 2018). PG is also increasingly used by the cement industry and other building material manufactures (Hua et al., 2016).

The Industry of Chemical Products "Elixir – Prahovo" was founded in 1960, producing the superphosphates as a part of the Mining and Smelting Basin of Bor (Serbia). The production of phosphoric acid is achieved by dihydrate process, i.e. raw phosphates are dissolved by sulfuric acid, producing calcium sulfate dihydrate as a by-product. Phosphoric acid produced in "Elixir – Prahovo" is used for the production of NPK fertilizers in Prahovo and mineral fertilizers in Šabac, Serbia (http://www.elixirprahovo.rs/en/node/142).

Calcium sulfate and its hydrated species show the highest solubility between 30 and 50°C, with noticeable decrease both towards lower and towards higher temperatures. The negative effect of higher temperatures on the solubility of calcium sulfate is a general cause of the formation of gypsum scales in the industrial processes (Amjad, 1988). In this study, the difference in gypsum solubility at 25°C (15.19 mmol/dm3) and 100°C (11.97 mmol/dm^3; Cohen, 1989) was utilized as a driving mechanism for a recrystallization process. Using this laboratory method, it was possible to extract purified gypsum and also to isolate insoluble impurities from PG, which allowed their characterization. This could further help to select and optimize appropriate methods for their removal, during a potential industrial processing of PG.

Materials and methods

Raw phosphogypsum samples were obtained from the waste dumps of the Industry of Chemical Products "Elixir – Prahovo" (Serbia). The samples were dried at 50°C during a period of 48 h, homogenized and several probes of 10 g were taken. The first probe was used for ICP-OES, XRD and SEM-EDS characterization, the second one for whiteness measurement and the third for a recrystallization experiment. For that experiment, a 10g probe was mixed with 2 L of distilled water in a beaker. Using a magnetic stirrer, the mixture was stirred during 2h at 40°C and subsequently filtered through a filter-paper. Then the filtrate was heated in another beaker at 95°C, stirred using a magnetic stirrer during 1 h and allowed to settle for 7 h at the same temperature, allowing excess calcium sulfate to crystallize. Recrystallized gypsum was

Tab. 1. SEM-EDS elemental analysis of investigated samples [1 – Calculated by stoichiometry; 2 – Below detection limit; 3 – Quantitative results normalized to 100%]

Tab. 1. Analiza elementarna SEM-EDS badanych próbek [1 – Obliczone stechiometrycznie; 2 – Poniżej granicy wykrywalności; 3 – Wyniki ilościowe normalizowane do 100%]

Sample name	PG1	PG2	PG1R	PG2R	PG1P	PG2P
Sample description	Raw phosphogypsum, sample 1	Raw phosphogypsum, sample 2	Residue from sample 1	Residue from sample 2	Recrystallized gypsum from sample 1	Recrystallized gypsum from sample 2
Elements	wt. %					
O[1]	47.07	46.99	51.65	50.05	46.69	46.98
F	BDL[2]	BDL	0.56	1.68	BDL	BDL
Na	BDL	BDL	0.08	0.11	BDL	BDL
Mg	BDL	BDL	0.03	0.07	BDL	BDL
Al	0.26	0.25	0.77	1.33	0.30	0.12
Si	2.23	2.25	41.19	39.35	0.06	BDL
P	0.34	0.31	0.65	1.02	0.14	0.09
S	21.77	21.67	1.15	0.42	22.86	23.40
K	BDL	BDL	0.07	0.08	BDL	BDL
Ca	28.13	28.37	2.13	2.18	29.95	29.43
Ti	BDL	BDL	0.22	0.29	BDL	BDL
Fe	0.15	0.16	1.34	2.97	BDL	BDL
Sr	0.04	BDL	BDL	0.13	BDL	BDL
Ba	BDL	BDL	0.15	0.31	BDL	BDL
Total	100.00[3]	100.00	100.00	100.00	100.00	100.00

Tab. 2. ICP-OES elemental analysis of raw phosphogypsum and recrystallized gypsum

Tab. 2. Analiza elementarna ICP-OES surowego fosfogipsu i rekrystalizowanego gipsu

Elements	Units	Sample name	
		PG1	PG1P
Na	ppm	94.54	14.52
Mg	ppm	18.70	0.24
Al	ppm	260.05	12.55
Si	ppm	3529	74.63
P	ppm	2904.80	2426.13
S	wt. %	18.687	20.295
K	ppm	67.44	22.51
Ca	wt. %	25.049	27.508
Ti	ppm	121.44	36.96
Fe	ppm	605.15	24.24
Sr	ppm	412.99	374.42
Ba	ppm	94.81	6.45

filtered and washed with boiling distilled water. Supernatant liquid was mixed with the rest of PG from the first part of the experiment and this cycle was repeated several times, until the PG was reduced to an insoluble residue. In this manner, phosphogypsum was separated into recrystallized gypsum, insoluble residue and supernatant.

Scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS analysis) was performed using a JEOL JSM-IT300 scanning electron microscope, coupled to an Oxford Instruments XMax 50 mm^2 SDD energy-dispersive spectrometer, in high vacuum mode, at accelerating voltage of 20 kV and probe current of approximately 0.1 nA. SEM images were acquired on gold-coated samples, using magnification of 200×, while EDS elemental analyses were conducted on carbon-coated samples, using low magnification (50×) in order to avoid variations in chemical composition. SEM-EDS analysis was performed on raw phosphogypsum, recrystallized gypsum and insoluble residue.

The elemental composition of a raw phosphogypsum and a recrystallized gypsum was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Thermo Scientific iCAP 6500 Duo ICP-OES spectrometer

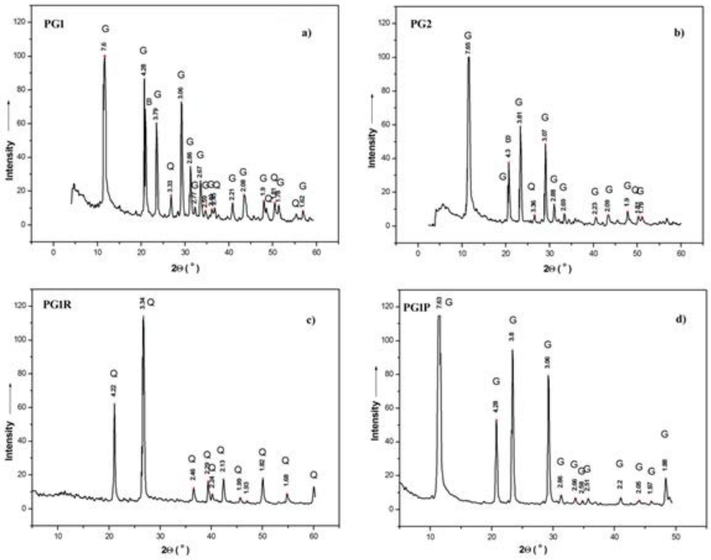

Fig. 1. XRD patterns of raw phosphogypsum (a, b), insoluble residue (c) and recrystallized gypsum (d). G – gypsum, B – brushite, Q – quartz
Rys. 1. Wzory XRD surowego fosfogipsu (a, b), nierozpuszczalnej pozostałości (c) i rekrystalizowanego gipsu (d). G – gips, B – kruchy, Q – kwarc

(Thermo Fisher Scientific, Cambridge, UK), equipped with a RACID86 Charge Injector Device (CID) detector. The detection limit for the elements analyzed was ~0.1 mg/L. The digestion was performed on an Advanced Microwave Digestion System (ETHOS 1, Milestone, Italy) using HPR-1000/10S high pressure segmented rotor.

X-ray diffraction (XRD) analysis was conducted using a Philips PW 1710 automated diffractometer. X-ray patterns were collected on powdered samples using CuKα radiation (λ = 1.54184 Å), with tube current of 30 mA and voltage of 40 kV. 2θ angles ranged from 4 to 60°, with a step of 1°/min.

The whiteness index values of a raw phosphogypsum and recrystallized gypsum were obtained from the diffuse reflectance spectra, using a Thorlabs CCS200 spectrometer with R45/45 geometry, in the region between 400 and 700 nm, according to the CIE (1932) method. The white standard was BaS and the light source was illuminant C. The whiteness was determined from the luminous reflectance, as described by Milošević and Logar (2017).

Results and discussion

Elemental EDS analysis, as well as a short description of the investigated samples, are given in Table 1. The samples of raw PG are dominated by Ca, S and O, as expected for calcium sulfate-based material. The major impurity is represented by Si, followed by small amounts of P, Al, Fe and Sr, which is typical for PG material from different deposits in the world (Jalali et al. 2106; Kandil et al. 2017; Zhou et al. 2016). Recrystallized samples present a purer form of calcium sulfate, with only small amounts of Al, Si and P. On the other hand, insoluble residue is a silicon-oxide based material relatively enriched in Fe, F, Al, P, Ti, Ba, Sr, Na, K and Mg, as well as essentially depleted in Ca and S.

A more precise elemental analysis was performed for PG1 and PG1P samples using ICP-OES

(Table 2). ICP-OES and SEM-EDS analyses are in general accordance, showing an enrichment of Ca and S and a drastic depletion of Si and Fe after the recrystallization.

The XRD patterns of the investigated samples are displayed in Figure 1. The most abundant minerals in PG1 and PG2 samples are gypsum, brushite and quartz (Figs. 1a, b; identified according to Михеев, 1957). These phases have rutinely been identified in PG by various researchers (e.g. Jalali et al., 2016; Roode and Strydom, 1990; Tian et al., 2016). The XRD pattern of PG1P is typical for pure gypsum (Fig. 1d). On the other hand, insoluble residue shows only the reflections of quartz (Fig. 1c). By means of XRD analysis, it was not possible to confirm the presence of other crystalline phases, which is in accordance with a low abundance of impurities, obtained by SEM-EDS and ICP-OES elemental analyses.

The mass balance of the recrystallization experiment for PG1 sample is given as follows: the yield of purified gypsum was 90.50%, leaving 4.29% of insoluble residue and 5.21% of original mass in the supernatant. These values are in accordance with elemental composition obtained by elemental analysis, i.e. with stoichiometrically calculated contents of calcium sulfate and insoluble oxides.

SEM image analysis revealed a significant increase in gypsum crystal size after the recrystallization (Fig. 2). Moreover, z/x axis ratio increased from 1–3 (PG1 sample) and 1–1.5 (PG2 sample) to >5 for recrystallized samples, producing long bladed crystals. A similar result was obtained by Sun et al. (2016), who synthesized calcium sulfate whisker from flue gas desulfurization gypsum using atmospheric acidification method. Insoluble residue is chiefly composed of coarse quartz particles: primary massive grains and secondary agglomerates, most probably resulting from an acid attack on primary silicates.

A value of the whiteness index (WI) changes from 52.5% for raw phosphogypsum PG1 to 80.5% for recrystallized gypsum PG1P (namely, the WI of 100% corresponds to a pure white color). A relatively low WI value of PG1 is caused by the significant content of iron (in the form of iron-oxide or iron-bearing minerals) that tends to produce brown to orange color. An increase of the value of WI after the recrystallization is in accordance with significantly lower content of iron in purified gypsum, as ICP-OES and SEM-EDS analyses confirmed.

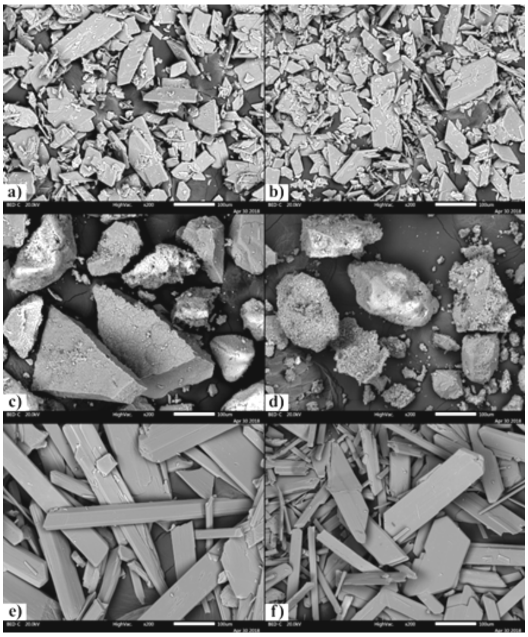

Fig. 2. SEM images of raw phosphogypsum (a, b), insoluble residue (c, d) and recrystallized gypsum (e, f). Magnification 200×, micron bar length 100 µm

Rys. 2. Obrazy SEM surowego fosfogipsu (a, b), nierozpuszczalnej pozostałości (c, d) i rekrystalizowango gipsu (e, f). Powiększenie 200 ×, długość skali 100 µm

Conclusion

The samples of raw phosphogypsum are dominated by Ca and S, in the form of calcium sulfate dihydrate, i.e. gypsum (CaSO4·2H2O). The major impurity is represented by Si in the form of quartz. Relatively low value of the whiteness index (52.5%) is caused by the significant content of iron, which produces light brown to light orange color.

The yield of recrystallized gypsum is slightly higher than 90 wt. %. It is composed of very pure calcium sulfate dihydrate, containing only small amounts of phosphorus. Gypsum crystal size significantly increased after the recrystallization process, forming long bladed crystals. The whiteness index reached a value of 80.5%, thus promoting a potential use of recrystallized gypsum in the civil engineering. Insoluble phosphogypsum residue is composed mainly of quartz and it is relatively enriched in impurities that originate from the raw phosphogypsum (e.g. Fe, F, Al and P).

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Charakterystyka oczyszczonego gipsu i nierozpuszczalnych zanieczyszczeń uzyskanych z odpadów fosfogipsu

W artykule przedstawiono skład chemiczny i fazowy dwóch próbek fosfogipsu ze składowisk odpadów Przemysłu Chemicznego „Elixir – Prahovo" (Serbia), a także możliwość rekrystalizacji gipsu z zawiesiny wodnej fosfogipsu. Wykorzystano negatywny wpływ wyższych temperatur na rozpuszczalność siarczanu wapnia (13,08 mmol/ dm3 w 95°C wobec 15,43 mmol/dm³ w 40°C). W kilku powtarzających się cyklach siarczanu wapnia stopniowo rozpuszczano w wodzie w temperaturze pokojowej, a następnie wytrącano w 100°C, stosując tę samą fazę ciekłą w całym doświadczeniu. W ten sposób fosfogips został rozdzielony na rekrystalizowany (oczyszczony) gips, nierozpuszczalną pozostałość i supernatant, kolejno obliczono bilans masy dla doświadczenia. Analizy elementarne, XRD i SEM-EDS przeprowadzono na surowym fosfogipsie, oczyszczonym gipsie i nierozpuszczalnej pozostałości. Określono i porównano biel surowego i oczyszczonego gipsu. Głównym celem pracy było zbadanie natury nierozpuszczalnych zanieczyszczeń w celu określenia i zoptymalizowania metod ich usuwania podczas przemysłowego przetwarzania fosfogipsu.

Słowa kluczowe: fosfogips, rekrystalizacja, oczyszczony gips, zanieczyszczenia nierozpuszczalne

Is Sludge Water Diluate Stream from Electrodialysis Suitable for Agricultural Purposes?

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Abstract

Sludge water, a product of drainage of primary and activated sludge from the municipal wastewater treatment process, is rich in nutrients, particularly nitrogen and phosphorus. Nitrogen and phosphorus are inorganic biogenic substances suitable for plant nutrition. Sludge water can be treated via electrodialysis. This process leads to two products, one is a diluate stream (solution less concentrated than the input, contains some nutrients) and the other is concentrate stream (solution in which nutrients are concentrated against the input). There is abundant research in nitrogen and phosphorus recovery from the concentrate stream, for example in the form of struvite used for fertilizing. However, little attention has been paid to the huge volumes of diluate stream. The diluate stream can be used in agriculture as water suitable for irrigation, where the bonus of this product is a partial fertilizing capacity. This way, wastewater can be used for irrigation and fertilizing having subjected the wastewater to agrochemical analyses. An important condition for the use of sludge water or diluate stream for irrigation is the absence of heavy metals and toxic substances. Still, if the water contains heavy metals, they can be removed with a relatively high success, for example by precipitation. Using wastewaster as water for agricultural purposes for irrigation is one of the new options to find new secondary sources of water. This theme is highly topical as it is important to reduce the consumption of quality water resources. These must primarily serve for drinking purposes, and therefore it is necessary to search for alternative water resources.

Keywords: sludge water, wastewater treatment, electrodialysis, irrigation water

Introduction

This paper deals with using of sludge water in the form of diluate stream from electrodialysis for agricultural purposes, especially for irrigation.

Sludge water is one by the wastewater treatment products and contains a huge amount of substances that have entered it after its use, for example, in man or in industry. In conjunction with agricultural use, it can contain substances beneficial as nutrients (nitrogen, phosphorus, calcium, magnesium or sodium), substances unsuitable for toxic substances, heavy metals and pathogenic organisms. Sludge water is not drained from the sewage treatment plant but is returned to the sewage treatment process or it can be further purified. One of today's discussed wastewater treatment processes is electrodialysis (Goodman, 2013). Electrodialysis is an electro-membrane process whose products are concentrate stream and diluate stream (MemBrain; Palatý, 2012; Nunes, 2006). Concentrate stream is a product in which substances are concentrated to several times. This product can be used for the gaining of concentrated substances, for example nitrogen and phosphorus can be precipitated to the form of a struvite which can be used as a fertilizer. Diluate stream is a product that is depleted by electrodialysis about excess concentrations of substances, but still can contain considerable concentrations of the substances removed. In agriculture, both the products of the concentrate stream as fertilizer as well as the diluate stream can be used, especially for its huge volume, for example water suitable for irrigation.

This use of waste products (in this case, the diluate stream) is being discussed today, as droughts are increasingly frequent and new sources are being sought (Akoto, 2015) but also because it may contain substances that are undesirable for plants or soil or do not comply the required limits for irrigation water. Surface water and groundwater are primarily determined for drinking purposes, so it is necessary to look for new alternative sources for other uses, for example for irrigation in agriculture.

Water suitable for use in agriculture for irrigation is important for the growth and production of plants. Irrigation water must comply legislative requirements, for example for the Czech Republic it is a document "ČSN 75 7143 Water quality. Water quality for irrigation". These waters must comply the maximum permissible values of physical (temperature), chemical (e.g. pH, dissolved substances at 105 °C or heavy metals), biological (e.g. pathogenic) and radioactive (e.g. radon and uranium) (Výživa rostlin, 2009; ČSN 75 7143).

Wastewater and sludge water used for irrigation are potential sources of heavy metals. The content of heavy metals in irrigation water may have impacts due to the accumulation in the environment (Barla, 2017), in agricultural land (Barla, 2017; Meng, 2016; Akoto, 2015), in groundwater (Balkhair, 2016), in cultivated crops (Barla, 2017; Ray, 2017; Balkhair, 2016; Akoto, 2015) and in food (Barla, 2017), may cause health risks (Meng, 2016; Balkhair, 2016), reduce microbial soil activity (Ray, 2017) and influence food safety (Meng, 2016).

Tab. 1. Measured selected indicators and values from the Czech legislation (ČSN 75 7143)
[* water suitable for irrigation, ** water conditionally suitable for irrigation, *** water unsuitable for irrigation]
Tab. 1. Mierzone wybrane wskaźniki i wartości z czeskiego ustawodawstwa (ČSN 75 7143)
[* woda odpowiednia do nawadniania, ** woda warunkowo odpowiednia do nawadniania, *** woda nieodpowiednia do nawadniania]

Selected indicators	Input	Diluate stream	Efficiency of removal (%)	ČSN 75 7143 category I*	ČSN 75 7143 category II**	ČSN 75 7143 category III***
t (°C)	20.3	20.6	-	35	40	>40
pH (-)	7.46	6.10	-	5 to 8.5	4.5 to 9	<4.5 to >9
DS105 (g.l^{-1})	1057.2	218.0	79.38	800	1200	>1200
Cd (mg.l^{-1})	<0.005	<0.005	-	0.01	0.02	>0.02
Co (mg.l^{-1})	<0.01	<0.01	-	0.5	1	>1
Cr_{total} (mg.l^{-1})	<0.01	<0.01	-	0.2	0.5	>0.5
Cu (mg.l^{-1})	0.04	0.02	50	0.5	2	>2
Mn (mg.l^{-1})	21.67	0.07	99.68	3	5	>5
Ni (mg.l^{-1})	0.03	0.03	0	0.1	0.2	>0.2
Pb (mg.l^{-1})	<0.01	<0.01	-	0.05	0.1	>0.1
Zn (mg.l^{-1})	0.03	0.03	0	1	2	>2
Fe (mg.l^{-1})	0.99	1.03	-4.04	10	100	>100

Tab. 2. Measured selected indicators suitable for agriculture for plant growth
Tab. 2. Mierzone wybrane wskaźniki odpowiednie dla rolnictwa dla wzrostu roślin

Selected indicators	Input	Diluate stream	Efficiency of removal (%)
$N\text{-}NH_4^+$ (mg.l^{-1})	70.62	69.36	1.78
$N\text{-}NO_2^-$ (mg.l^{-1})	0.77	0.44	40.26
$N\text{-}NO_3^-$ (mg.l^{-1})	0.88	0.32	63.64
P_{total} (mg.l^{-1})	52.97	7.80	85.27
Ca (mg.l^{-1})	44.77	0.10	99.78
Mg (mg.l^{-1})	21.67	0.07	99.68
Na (mg.l^{-1})	122.77	40.40	67.09

Beneficial indicators of proper concentration in irrigation water are, for example, nitrogen, phosphorus, calcium, magnesium, sodium, but also some heavy metals in trace amounts. In irrigation waters, concentrations of heavy metals, toxic substances and pathogenic organisms which have a phytotoxic effect on the growth and germination of cultivated plants are not suitable. For water use in agriculture, agrochemical analysis of water is required. For example, pH, nitrogen (ammonia, nitrite and nitrate), phosphorus, calcium and magnesium, organic contaminants (polychlorinated biphenyls) and microbiological indicators are monitored (Výživa rostlin, 2009).

This paper summarizes and compares the parameters as pH, temperature, dissolved substances and selected heavy metals (iron, manganese, lead, zinc, copper, chromium, cadmium, cobalt and nickel), but also nitrogen (ammonia, nitrite and nitrate), calcium, magnesium and sodium.

The sludge water, respectively the diluate stream contains nitrogen and phosphorus, which are important for plant growth. If it contains heavy metals and toxic substances can not be used in agriculture or have to be removed, heavy metals for example by precipitation at the appropriate pH.

Irrigation water is water that serves to irrigate the plants in order to grow them. It is a water that does not influence the state of health of people and animals, the amount of yields and crop quality, soil properties, the quality of surface water and groundwater and other environmental compartments. The quality of irrigation water depends on the soil and climatic conditions, the way of irrigation and the type of crops to be grown. Irrigation water is divided into three categories (ČSN 75 7143):

- category I – water suitable for irrigation; water for irrigation of all cultures without restrictions.
- category II – water conditionally suitable for irrigation; water that can be used provided that the degree and character of water pollution or local conditions are determined. It is necessary to register the amount and composition of irrigation water
- category III – water unsuitable for irrigation; this water that can be used for irrigation only after treatment to obtain the quality of the above-mentioned categories or to be used for irrigation according to the assumption of wastewater utilization.

The results of selected sludge water quality indicators are recorded and compared with normative values (ČSN 75 7143) when this water is suitable or unsuitable for use in agriculture as water for irrigation. Only physical and chemical indicators were determined for this research.

Another research that can be continue on the subject is, for example, testing the phytoxicity of the diluate stream on plants (Garden cress – Lepidium satuvum or Mustard white – Sinapis alba) or testing nutrients for soil and cultivated plants.

Materials and methods

For this paper, sludge water was used in the form of a diluate stream from electrodialysis. The electrodialysis was carried out on the waters collected at the sewage treatment plant. Samples were taken in three terms.

The quality of the sludge water (input) and the diluate stream itself has been evaluated by the laboratory analysis using selected physical and chemical parameters. Chemical parameters were pH, temperature, dissolved substances, ammoniacal nitrogen, nitrite nitrogen, nitrate nitrogen, total phosphorus, calcium, magnesium, sodium and selected heavy metals (cadmium, cobalt, total chromium, copper, manganese, nickel, lead, zinc and iron).

The sludge water was treated by electrodialysis to produce two products: concentrate stream and diluate stream, which is the aim of this research. Since three sampling was performed, the averages of these measured values were reported in the tables.

The diluate stream was subjected to laboratory analysis. Selected heavy metals, calcium, magnesium and sodium were analyzed by atomic absorption spectrophotometry (AAS), total phosphorus and nitrogen forms by traditional titration methods, pH and temperature by pH probe and dissolved substances drying at temperature 105°C.

The determination results were registered in the tables.

Results and discussion

This section summarizes the measured results of the input values and the dilution stream from electrodialysis of selected sludge water indicators.

Table 1 summarizes measured and legislative physical and chemical indicators. Depending on the measured values, the diluate stream can be used as water suitable for irrigation and this falls according to the standard in category I. Sludge water (input) before electrodialysis comply Category I requirements in pH, Cd, Co, Crtotal, Cu, Ni, Pb, Zn and Fe; Mn and dissolved substances (DS105) do not comply the conditions but can be removed from the diluate stream. The temperature indicator does not comply the limits because it is influenced by the temperature in the laboratory.

The removal efficiency for manganese was 99.68% for dissolved substances 79.38% and for copper 50%. Concentrations of cadmium, cobalt, total chromium and lead were very small and undetectable.

The nickel and zinc indicators have not been removed, yet they meet the limits for irrigation water. Conversely, the iron concentration increased during the electrodialysis process, maybe due to iron precipitation on the surface of the membranes.

Table 2 summarizes indicators that are suitable for plant growth in a reasonable amount, i.e. ammoniacal nitrogen, nitrite nitrogen, nitrate nitrogen, total phosphorus, calcium, magnesium and sodium. These are substances that are found in traditional fertilizers. By electrodialysis, the concentrations of all indicators were reduced in sludge water: calcium and magnesium with very high efficiency (99.68% and 99.78%), total phosphorus with an efficiency of 85.27%, sodium with an efficiency of 67.09%. Particular forms of nitrogen have also been removed, but it is very likely that the various forms are transformed among themselves.

Conclusion

This paper is related with possible using sludge water in the form of a diluate stream from electrodialysis based on selected physical and chemical indicators; biological and radioactive indicators were not explored in this research. On the base of the selected legislative regulation (ČSN 75 7143) and selected indicators, the diluate stream was evaluated as a product comping the chemical indicators for irrigation water. Nutrients (nitrogen forms, total phosphorus, calcium, magnesium and sodium) remain in the diluent stream and can therefore be considered water suitable for irrigation with fertilizer effect.

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Czy strumień rozrzedzonej cieczy znad elektrodializy nadaje się do celów rolniczych?

Woda ze szlamów, produkt drenażu osadu pierwotnego i aktywnego z procesu oczyszczania ścieków komunalnych, jest bogata w składniki odżywcze, w szczególności azot i fosfor. Azot i fosfor to nieorganiczne substancje biogenne nadające się do żywienia roślin. Woda szlamowa może być oczyszczana przez elektrodializę. Proces ten prowadzi do powstania dwóch produktów, jeden to strumień rozcieńczony (roztwór mniej skoncentrowany niż wsad, zawiera pewne składniki odżywcze), a drugi to strumień skoncentrowany (roztwór, w którym składniki odżywcze są skoncentrowane). Istnieje wiele badań nad odzyskiwaniem azotu i fosforu ze strumienia koncentratu, na przykład w postaci struwitu (fosforan magnezowo-amonowy) używanego do nawożenia. Jednak niewiele uwagi poświęcono ogromnym ilościom strumienia rozcieńczalnika. Strumień rozcieńczony może być wykorzystywany w rolnictwie jako woda do nawadniania, gdzie wartością dodaną tego produktu jest częściowa zdolność nawożenia. W ten sposób ścieki można wykorzystać do nawadniania i nawożenia, poddając ścieki analizom agrochemicznym. Ważnym warunkiem stosowania wody z szlamu lub strumienia rozcieńczonego do nawadniania jest brak metali ciężkich i substancji toksycznych. Jeśli woda zawiera metale ciężkie, można je usunąć ze stosunkowo dobrym powodzeniem, na przykład przez strącanie. Wykorzystanie wody odpadowej do celów rolniczych do nawadniania jest jedną z nowych opcji w poszukiwaniu nowych wtórnych źródeł wody. Temat ten jest bardzo aktualny, ponieważ ważne jest zmniejszenie zużycia wysokiej jakości zasobów wodnych. Woda czysta musi służyć do picia, dlatego konieczne jest poszukiwanie alternatywnych zasobów wody do celów rolnych.

Słowa kluczowe: woda nadosadowa, oczyszczanie ścieków, elektrodializa, woda do nawadniania

Comparison Access to Odor Problems in Selected European Countries

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Abstract

The effects of odor are not only annoying but can also cause serious health problems, resulting in an impact on the overall quality of the environment.

Most European jurisdictions classify odor as an atmospheric pollutant and regulate it at various levels of government. This paper summarizes the approach of selected European countries to this issue, comparison in terms of acceptable concentrations, comparison of instruments used in individual countries, requirements for the application of BAT technologies that ultimately lead to the reduction of odor emissions. Further are described, the basic features of odors, units, methods of analysis and dispersion´s modeling, application of odor removal technologies, with emphasis in relation to the Czech Republic.

Keywords: odors, odors jurisdiction, odors emission

Introduction

To understand odors issues, it is necessary first to clarify the concepts and influences that are related to the perception of odors. Odor can be characterized by concentration, intensity (perception), hedonic phenomenon (whether the odor is pleasant or unpleasant) and exposure time. The odor concentration is expressed by the amount of odorous substances in m3 and is the number of times the smear sample must be diluted with pure air to reach the smell threshold, that is, the odor value for the first time. If the odor concentration on the source is 100 ouE × m^{-3}, this means that if the air is diluted 100 times, odor will not be noticeable, will not be felt. One odor unit is the olfactory threshold, when we register a change in the nature of the air, but we do not have to know what types of odors it is. The average person registers up to 3 ouE × m^{-3}, with the value of 5 ouE × m^{-3} being able to describe the smell (for example, if it smells coffee, chocolate, or smell of decaying leaves).

Odor is a commonly complicated mixture of gaseous compounds and has a specific profile. The interaction between the odor and the concentrations of the individual components in the mixture alters the perceived strength of the mixture, and there are models that try to explain such phenomena as masking, countermeasures, neutralization, addition, synergism, etc. The lowest concentration levels at which chemicals cause irritant effects in humans to be below the level of the olfactory threshold, although the perception of odor prevents irritation in many industrial chemicals.

With regard to the construction and configuration of odor sources, it is possible to differentiate between sources with measurable airflow (active sources) and sources that emit odors but have no measurable external airflow (passive sources). The methodology for measuring odor concentration is very well defined in EN 13725 (in Czech Republic – ČSN EN 13725, 2003). This standard is recognized in odors detail throughout the world, or in Europe. This method is very repeatable and reproducible, and quite well standardizes the determination of odor concentration. This odor concentration determination provides directly comparable data on different types of odor and can be used as input for dispersion models, to determine the impact of odor from the point of view of annoyance and to assess the effectiveness of odor control measures.

Description

The following section describes the approach of state administrations of European states to the problem of odors as air pollutants. The selected countries represent: Germany, Austria, France, Spain, Italy, Ireland, Norway, Denmark, Netherlands, Belgium and Czech Republic.

In Germany, air quality is based on the provisions adopted by the European Union (EU) and subsequently implemented in German law. This ensures the consistency of EU and German legislation on air quality. In addition, the provisions on air quality control – the Act on prevention of environmental damage caused by air pollution, noise, vibrations and similar phenomena, on the basis of the Immunity Protection Act (BImSchG – Bundes Immissionsschutz Gesetz) and its administrative regulations, are in force at national level the implementing regulations governing mainly air quality control in Germany. All types of odors produced from any commercial device are considered to be annoying or unpleasant according to the BimSchG. Technical provisions on air quality control (TA-Luft, 2002, amendment 2017) are a tool for managing air pollution rates. The objective of TA-Luft is to protect the population and all environments from the harmful effects of air pollution and to provide preventive measures against the adverse effects of air pollution in order to achieve a high level of environmental protection. It includes, inter alia, a directive on preventive measures against environmen-

Tab. 1. Overview of individual criteria in selected countries

Tab. 1. Przegląd poszczególnych kryteriów w wybranych krajach

Competence	Odor criteria		Average time	Peak factor	Level of protection	
	c_t [odor units]	Percentile [%]				
Germany	1	98	1 s	4	irrelevant criterion	
		90			mixed and residential areas	
		85			agricultural, industrial and commercial areas	
Austria	1	97	1 – 5 s		spa areas	
	1 and 5 - 8	92 and 97			residential areas	
France	5	98	1 h	1	composting devices	
	5	98			constructions	exist devices
	5	99.5				new devices
Spain						
Catalonia	3	98	1 h	1	most unpleasant	
	5				moderately unpleasant	
	7				less unpleasant	
Italy						
Lombardy	1	98		2.3	new and exist devices	
	3					
	5					
Puglia	1, 2, 3, 4, …	98		2.3	new and exist devices	
		99.9				
		100				
	1	97	1 – 5 s			
	1 and 5 - 8	92 and 97				
Ireland	1.5	98	1 h	1	all options	
	3				new equipments for pig breeding	
	6				existing equipments for pig breeding	
Norway	1	99	1 h	1	residential areas + neighborhood	
	2				industrial areas + neighborhood	
Denmark	5 – 10	99	1 min.	7.8	industrial areas	
	5	99	1 h	1	livestock farming	residential areas
	7					countryside
	15					individual

Competence	Odor criteria	Average time	Average time	Peak factor	Level of protection
	c_t [odor units]	Percentile [%]			
Netherlands					
Dutch emission limits are custom-tailored according to individual industries (eg coffee roasting, asphalt mixing, slaughterhouses, etc.)					
North Brabant South Holland Flevoland Gelderland Overijssel Groningen Zealand	0.05 - 100	95 – 99.99	1 h	1	industrial new and exist devices, with value, including consideration hedonic phenomenon
Belgium					
Walloon	3	98	1 h	1	composting devices near habitation
	6				pig breeding
	10				poultry farming
Czech Republic					
	N/A				regional authority

tal damage caused by odors. (Jarass. 2015) However, TA-Luft does not set protection criteria or odor limits. This is covered by a specific national regulation called the Guideline on Odor and Ambient Air (GOAA, 2008).

GOAA deals with odors generated in industrial and animal establishments, but do not cover smells arising from household heating, road transport, manure spreading, vegetation and similar sources. The criteria outlined in this document are based on the determination of the recognizable odor and the overall odor concept. Odor in ambient air can only be detected if it can be determined by field measurements or determined in exposure estimates of dispersion models. (GOAA, 2008)

In Austria, the juristic system is divided between the thresholds that have a lawful basis and the target values that are only based on guidelines without a lawful basis. Only for spa treatment areas there is a limit value consisting of a percentile probability of 3% or a concentration threshold Ct = 1 ouE × m^{-3} (similarly to Germany). The Austrian Academy of Sciences (OAW, 1994) issued instruction with two limit values in 1994 (both of which must be considered as a more percentile criterion). However, it is proposed only subjectively.

The Air Quality Regulation in France is governed primarily by European Parliament directives, namely Directive 2008/50/EC on ambient air quality and cleaner air for Europe and Directive 2001/81/EC (NEC Directive) on national emission ceilings for certain air pollutants. French national legislation is based on Law No 96-1236 of 30 December 1996 on aviation and rational use of energy (LAURE), codified in the Environmental Code. Legislative and regulatory provisions on air quality are contained in paragraph II. Air and atmosphere II. books of the environmental code (Articles L220-1 to L228-3 and R221-1 to D228-1). (Brancher et al., 2017)

Spain has no specific federal-level tools for issuing emissions laws on odors. In general, odors are subjectively regulated by federal environmental laws. The Spanish regulation is still in the beginning and is based on municipal regulations or operating permits. (Brancher et al., 2017) Only in Catalonia, the local environment and housing department drafted a draft law on odor pollution in 2005. This proposal seeks to add new assessment tools used in other countries and conduct odor control campaigns in different facilities so that a future standard for Spanish territory. According to this proposal, odor emissions are measured for existing activities in accordance with UNEEN 13725: 2004. For new activities, emission estimates are achieved using emission factors.

Italy does not include specific criteria for environmental odors at national level. As regards odor pollution, the Italian Environmental Code does not set any limits by means of Legislative Decree 152: 2006. In the Italian legal system, Integrated Environmental Authorization is the implementation of the European IPPC. Italian regions have the autonomy to regulate air quality, with the exception of the following regions: Basilicata, Abruzzo, Emilia Romagna, Sicilia (Brancher et al., 2017), basically the maximum emission limits for composting and biogas stations. The Lombardy Region, one of the twenty administrative regions of Italy, published a special odor control with a maximum impact value based on the frequency of crossing this limits values.

In Ireland, the following air quality legislation is applied according to EPA Ireland (EPA, 2018): the Environmental Protection Act 1992 (as amended); Waste Management Act 1996 (as amended); Environmental Protection Act 2003 (as amended); Air Pollution Act 1987 (as amended) and Irish Directive SI No. 787 of 2005 – Sewage Treatment (Odor and Noise Prevention). Currently, there is no general legal regulation on odors concerning industrial equipment in Ireland. However, EPA Ireland (EPA, 2018) defined guidelines for intensive agricultural activities setting limits for pig breeding.

In Norway, odors are dealt with under the Law – Protection against Pollution (Law No 6 of 13th March 1981 Pollution and Waste Protection), where Chapter 3 provides for authorization for any activity that could cause pollution. The Directive TA-3019: 2013 was developed to assess the effects of odors. In general, the Guidelines set out a framework for: assessing the risk of odor, operation and activity and odor control plan. Odor risk assessment should describe the potential of odor at each stage of the process: map odor sources, determine odor emission levels, and promote dispersion modeling to simulate odors. Odor risk assessment in Norway is based on the KVALUR method, which is used in conjunction with norm NS 5814. The purpose of the method is to determine the risk of odor as an index and to indicate whether episodes of odor could be considered relevant to the affected receptor. (Brancher et al., 2017)

In Denmark, two different types of equipment are assessed to assess the impact of odors: one focuses on industrial emissions and the other on livestock. A detailed description of the procedures applied in Denmark with respect to air quality emissions can be found in the Guidelines for Air Emissions Control - Air Pollution Control of Equipment. The Danish unit of odor, Lugtenheder (LE), is almost equivalent to ouE × m^{-3} because it uses the same samples dilution. (DEPA, 2002)

The Netherlands access to odor problems has the longest history around Europe. In the Netherlands, environmental directives on air pollution are implemented in the Environmental Protection Act (Wet Milieubeheer) and the Environmental Protection Regulation (Activiteitenbesluit milieubeheer).

The Industrial Emissions Directive (IED 2010/75 / EU) regulating emissions from large industrial sources is also implemented in the Activity Decree. This Directive lays down rules for large combustion plants, waste incineration plants, VOC solvents and IPPC facilities. Emissions that are not covered by the generally binding rules of the Decree are subject to authorization. The general principle of Dutch odor policy is to minimize odor pollution and prevent new pollution. This principle, together with the use of BAT, is a main element of the odor policy in the Netherlands.

In the Netherlands since 2004, the odor thresholds are measured according to European Standard EN 13725: 2003 (EN13725, 2003). The European Standard was introduced in this country as NEN-EN 13725: 2003.

Local authorities in individual provinces can regulate the interpretation of national odor politics.

In this regard, for example, the provinces of North Brabant, South Holland, Flevoland, Gelderland, Overijssel, Groningen and Zealand have their own regulatory framework.

In Belgium, the Odor Emissions Regulation is set at the national level. Basically, the regulatory framework is set for impact criteria for the Flemish and Walloon regions. Objective determination of the odors concentration of the gaseous sample by means of dynamic olfactometry with human evaluators is performed using the national standard NBN EN 13725: 2003. (Brancher, 2017)

In the Czech Republic, basic environmental protection is implemented in Act No. 17/1992 Coll.,

On the Environment, which defines the formation of natural conditions for the existence of all organisms. (Tuháček and Jelínková, 2015) Odor protection is further specified in Act No. 201/2012 Coll., On air protection in § 2 letter b) where: "a pollutant is any substance that has a presence in the air or can have harmful effects on human health or the environment, or annoys the odor" (UZ1223, 2017) At present the executive power to evaluate odor emissions is left at the level of regional authorities for both new installations and the assessment of existing facilities.

The assessment of the odor load can take place on the basis of several procedures: physico-chemical and analytical procedures; Olfactometric method, which is well described in ČSN EN 13725 (EN implementation); statistical methods

- questionnaire surveys according to ČSN EN 16841-1, „odor feet“ measurement according to ČSN EN 16841-2, or an increasingly popular “electronic nose”.

Results and discussion, Conclusion

As can be seen from Table 1, most European countries have legislated thresholds for odors and their implementation (location, classification, etc.). Concerning the variance of the values, considerable differentiation (values of 1–100 ouE) is evident as well as the percentile evaluation approach (85–99.9%). The guidelines drawn up for impact assessments in individual European countries lead to suppressing causes at a tolerable level other than zero odor values. As the essence of the complexity of the odors itself is, the regulation itself is complicated. A positive factor is that judging at individual jurisdictions takes into account individual cases according to predefined criteria.

However, there are no limits in the Czech Republic, so the assessment at regional authority level remains, and only on the subjective approach of individual regions. What is the key to the long-term success of environmental odor control? An unambiguous response (not only for the Czech Republic) is the introduction of clear and objective smell rules based on an integrated strategy.

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Porównanie podejścia do problemów odorów w wybranych krajach europejskich

Skutki nieprzyjemnego zapachu są nie tylko irytujące, ale mogą również powodować poważne problemy zdrowotne, co wpływa na ogólną jakość środowiska.
Większość europejskich jurysdykcji klasyfikuje odory jako zanieczyszczenia atmosferyczne i reguluje je na różnych szczeblach władzy. W niniejszym artykule podsumowano podejście wybranych krajów europejskich do tego problemu, porównanie pod względem dopuszczalnych stężeń, porównanie instrumentów stosowanych w poszczególnych krajach, wymagania dotyczące stosowania technologii BAT, które ostatecznie prowadzą do zmniejszenia emisji zapachów. Dalej opisano podstawowe cechy zapachów, jednostki, metody analizy i sposobu rozpraszania, zastosowanie technologii usuwania zapachów, ze szczególnym uwzględnieniem Republiki Czeskiej.

Słowa kluczowe: zapachy, odory, prawodawstwo odorowe, emisja zapachów

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Bacterial Community of Neutral Mine Drainage of Elizabeth's Shaft (Slovinky, Slovakia)

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Abstract

Neutral mine drainage is the less frequent subject of the interest than acid mine drainage but it can have adverse environmental effects caused mainly by precipitation of dissolved Fe. The aim of the study was to characterize the composition of bacterial population in environment with high concentration of iron and sulfur compounds represented by neutral mine drainage water of Elizabeth's shaft, Slovinky (Slovakia). The pH value of drainage water decreased from 7.1 to 6.5 during the years 2008–2014. Direct microscopic observations, cultivation methods, and 454 pyrosequencing of the 16S rRNA gene amplicons were used to examine the bacterial population. Microscopic observations identified iron–oxidizing Proteobacteria of the genera Gallionella and Leptothrix which occurrence was not changed during the years 2008–2014. Using 454 pyrosequencing, there were identified members of 204 bacterial genera that belonged to 25 phyla. Proteobacteria (69.55%), followed by Chloroflexi (10.31%) and Actinobacteria (4.24%) dominated the bacterial community. Genera Azotobacter (24.52%) and Pseudomonas (14.15%), followed by iron–oxidizing Proteobacteria Dechloromonas (11%) and Methyloversatilis (8.53%) were most abundant within bacterial community. Typical sulfur bacteria were detected with lower frequency, e.g., Desulfobacteraceae (0.25%), Desulfovibrionaceae (0.16%), or Desulfobulbaceae (0.11%). Our data indicate that the composition of bacterial community of the Elizabeth's shaft drainage water reflects observed neutral pH, high level of iron and sulfur ions in this aquatic habitat.

Keywords: bacterial community, neutral mine drainage, high-throughput sequencing

Introduction

Mining activities and ore processing result in irreversible changes in landscape in the form of heaps and sewage sludge beds of waste material. These deposits are permanent source of toxic substances, especially heavy metals that contaminate all environmental compounds. Changes of water and soil quality affect also biodiversity of mining area (Angelovicova et al., 2012; Xu et al., 2016). The properties of drainage water depend on many factors, including mineralogical, geochemical properties, hydrogeological conditions, and the activity of lithoautotrophic microorganisms. Oxidative dissolution of sulfide minerals generates acidity and releases sulfate, iron, and associated metals to pore waters.

This phenomenon is known as acid mine drainage (AMD). However, neutral mine drainage (NMD) conditions may persist in an abundance of carbonate minerals (Lindsay et al., 2009; Lindsay et al. 2015).

Slovinky mining area (north part of Slovak Ore Mountains territory, Spišská Nová Ves district, Slovakia) is considered the largest source of cooper ores in Slovak region but it is also rich in iron ores (e.g. chalcopyrite, cuprite, siderite, pyrite). The most frequent secondary and tertiary minerals are iron oxides such as goethite or crystalline hydrous ferric oxide (Kucerova et al., 2014). Mining in Slovinky was stopped in 1999 but due to sludge bed vulnerability represent high-risk area threatening all environmental components. The mine dumps are near-neutral or slightly alkaline (pH 7.2–8.8) because the acidity generated by the decomposition of the sulfide ores is efficiently neutralized by the abundant carbonate minerals (Angelovicova et al., 2012; Kucerova et al., 2014). Elizabeth's shaft was built in 1900 and it works as mining drainage water system. Sulfide minerals exposed by mining and erosion are unstable in the presence of atmospheric oxygen and water; the resulting oxidation of sulfides can release sulfate and iron ions into the drainage water (Lindsay et al., 2015). Regular monitoring of physico-chemicals parameters of mine drainage water demonstrated that an average iron concentration did not exceed 0.5 mg/l for many years. In addition, a high concentration of SO_4, Mn, As, and Sb have been long-term monitored (Bajtoš et al., 2015). Based on these characteristics, we assumed a high incidence of iron and sulfur bacteria within bacterial community in drainage water.

The original aim of this study was to examine the occurrence of iron-sulfur bacteria in a neutral mine drainage of Elizabeth's shaft using direct microscopy and cultivation methods and to investigate their seasonal dynamics over several years. Since some changes in pH of drainage water have been recorded during the period of investigation, we decided to analyze the structure of bacterial community in NMD using a high-throughput sequencing technique in order to detect bacteria that could contribute to (or responsible for) these

Tab. 1. Physico-chemicals parameters and microscopic observation of abioseston and bioseston of mine drainage water from Elizabeth's shaft measured in the years 2008–2014 (Slovinky, Slovakia)

Tab. 1. Parametry fizyko-chemiczne i obserwacja mikroskopowa abiosestonu i biosestonu wody kopalnianej z szybu Elżbieta mierzona w latach 2008–2014 (Slovinky, Słowacja)

Years	2008 (n = 2)	2009 (n = 2)	2010 (n = 2)	2011 (n = 2)	2012 (n = 4)	2013 (n = 4)	2014 (n = 4)	P value
pH[a]	7.1 ± 0.3	7 ± 0.1	6.9 ± 0.1	6.9 ± 0.3	6.8 ± 0.3	6.7 ± 0.2	6.5 ± 0.2	> 0.05
EC [mS/m][a]	42 ± 1.4	50 ± 1.4	49 ± 4.2	54 ± 2.8	57.3 ± 2.3	61.5 ± 1.3	63.5 ± 1.3	< 0.001
TDS [mg/l][a]	172 ± 2.8	181 ± 1.4	185 ± 2.8	198 ± 4.2	201.5 ± 3.1	200.3 ± 1.7	220.3 ± 2.6	< 0.001
Gallionella spp. [b]	1 ± 0.0	2 ± 0.0	1 ± 0.0	1 ± 0.0	1.5 ± 0.7	1 ± 0.0	1 ± 0.0	> 0.05
Leptothrix spp. [b]	1 ± 0.0	2 ± 0.0	2 ± 0.0	2 ± 0.0	1 ± 0.0	1.5 ± 0.7	1 ± 0.0	> 0.05

[a] Values are expressed as arithmetic mean value ± standard deviation of measurements in a given year (n)

[b] Values are expressed as arithmetic mean value ± standard deviation of the percentage of coverage of 10 different microscopic fields measurements in a given year (n)

EC - electric conductivity, TDS – total dissolved solids, P value - result of Kruskal-Wallis test (one-way ANOVA) electric conductivity, TDS – total dissolved solids, P value - result of Kruskal-Wallis test (one-way ANOVA)

changes. The overall results of this study are published by Kisková et al. (2018) (in press).

Materials and methods

Mine drainage water samples were collected directly from the water flowing out from Elizabeth's shaft in Slovinky village, Slovakia (48°52′43″N 20°50′38″E). Fivehundred microliters of water was taken two times a year in the period from 2008 to 2011 (first week in March and October), and four times a year in the years 2012–2014 (first week in March, June, August, and October) into sterile bottles. The water was transported under cold, dark conditions to the laboratory. Physico-chemical parameters (pH and electric conductivity) were measured directly in the field with WTW Multi 340i instrument (WTW Gmbh, Weilheim, Germany) equipped with a pH electrode WTW Sen Tix 31-3 and standard WTW TetraCon 325 electrode for an electric conductivity (total dissolved solids, TDS) measurement.

Direct microscopic observations, cultivation, bacteria determination and high-throughput sequencing analysis of 16S rRNA gene were performed as described Kisková et al. (2018) (in press). The next generation 454 pyrosequencing was performed using Roche 454 GS-FLX Titanium instrument (LaRoche, USA) and reagents according to the manufacturer's guidelines. DNA sequencing data were processed using the Mothur bioinformatics software package (version 1.36.1) (Schloss et al., 2009).

Non-parametrical Kruskal–Wallis test (one-way ANOVA) was used to analyze the changes in physico-chemical parameters and occurrence of iron bacteria and/or other microorganisms detected by microscopic observation during the period of investigation.

Results and discussion

Drainage water flowing from Elizabeth's shaft is characterized by high concentration of iron, manganese, arsenic, and sulfate ions (Bajtoš et al., 2015). Concentration of copper and zinc did not overexpress limit values according of Regulation of the Government of the Slovak Republic. Continual increase of TDS concentration is probably due to the gradual release of metal(loid)s during sulfide mineral oxidation and bacterial metabolic activity. The Elizabeth's shaft drainage water could be defined as circumneutral, since acid generated via sulfide mineral oxidation (e.g. pyrite or chalcopyrite) is neutralized by the dissolution of carbonate minerals as siderite or malachite. On the other side, our results indicate a slight shift to the acidic pH during the examined period (Table 1). Slow reduction of pH of drainage water is supported by earlier studies demonstrating pH value of 8.24 in 1999 and 7.56 in 2000 (Bajtoš and Záhorová, 2007). Therefore, we performed an analysis of the bacterial community using a high-throughput sequencing technique to find out bacteria that could be involved in reducing pH of drainage water.

Despite expectations, direct microscopic observations and the high-throughput analysis have shown a low abundance of *Gallionella* spp. (percentage of coverage ranged from 1.0 to 2%) (Table 1). Even *Gallionella* spp. was not detected by 454 pyrosequencing. The low occurrence of these bacteria may be due to preference for more acidic conditions as well as other environmental factors (e.g. heavy metals). *Leptothrix* spp. are heterotrophic Fe/Mn-oxidizing inhabitant of aqueous environments (Kunoh et al., 2015).

Acidithiobacillus species was detected neither by cultivation methods nor by 454 pyrosequencing. These findings confirmed the preference of the genus *Acidithiobacillus* of acidic environment, despite the high sulfur and iron content in neutral mine drainage water.

Cultivation analysis on the selective medium confirmed the presence of *Ferribacterium* species in each sampling during the period of investigation. *Ferribacterium* is a genus of the family Rhodocyclaceae and up to now, only one species is known (*F. limneticum*). This bacterium belongs to Fe(III)-reducing bacteria and was first isolated from mining-impacted fresh lake sediments containing heavy metals (Cumming and McCann, 1978). Its presence in drainage water of Elizabeth's shaft was confirmed by cultivation as well as 454 pyrosequencing.

During the years 2008–2014, the salinity (TDS) of Elizabeth's shaft drainage water significantly increased from 172 to 220.25 mg/l (pH < 0.001) and pH value slightly degreased from 7.1 to 6.5 ($P > 0.05$) but these changes did not affect the incidence of observed bacteria (Table 1).

After trimming, denoising, quality, and length filtering and removing chimeras, a total of 7095 high-quality sequenc-

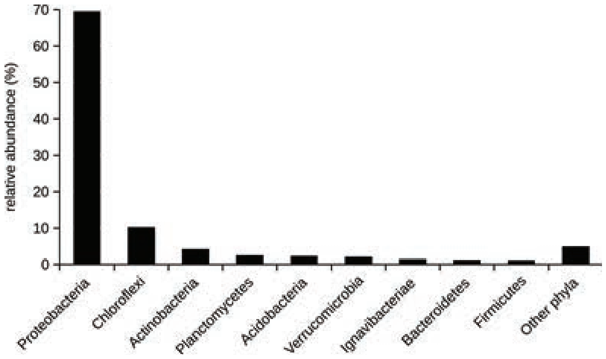

Fig. 1. Bacterial composition at the phylogenetic phylum level of mine drainage water of Elizabeth's shaft (Slovinky, Slovakia). The category "Other phyla" groups bacterial phyla whose relative abundance was below 1%

Rys. 1. Skład bakteryjny na poziomie budowy filogenetycznej wody drenażowej szybu Elizabeth (Slovinky, Słowacja). Kategoria „Inne rodzaje" obejmuje gromadę bakteryjną, której względna z zawartość była poniżej 1%

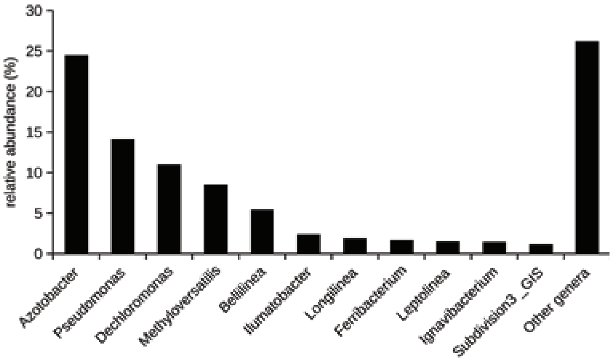

Fig. 2. Bacterial composition at the phylogenetic genus level of mine drainage water of Elizabeth's shaft (Slovinky, Slovakia). The category "Other genera" groups bacterial genera whose relative abundance was below 1%

Ryc. 2. Skład bakteryjny na poziomie rodzaju filogenetycznego wody drenażowej szybu Elizabeth (Slovinky, Słowacja). Kategoria „Inne rodzaje" grupuje rodzaje bakterii, których względna zawartość była poniżej 1%

es were obtained. Sequences were clustered into 813 OTUs, while 414 were non-singletons. One OTU was classified as Archaea, phylum Aigarchaeota (represented by two sequences). Other sequences were classified into 22 known bacterial phyla and three candidate phyla. The majority of sequences belonged to Proteobacteria (69.55%) followed by Chloroflexi (10.31%), Actinobacteria (4.24%), Planctomycetes (2.57%), Acidobacteria (2.35%), and Verrucomicrobia (2.14%). Other phyla were represented by less than 2% sequences (Figure 1).

Genus *Azotobacter* was most abundant genus (24.52%) followed by *Pseudomonas* (14.15%), *Dechloromonas* (11%), *Methyloversatilis* (8.53%), and *Bellilinea* (5.46%). Other genera were represented by less than 5% of sequences (Figure 2).

Proteobacteria such as *Dechloromonas* spp. (11%) and *Ferribacterium* spp. (1.73%) dominated within iron bacteria. Other most abundant iron bacteria were Chloroflexi such as *Bellilinea* spp. (5.46%), *Longilinea* spp. (1.93%), and *Leptolinea* spp. (1.54%).

Generally, Proteobacteria, Nitrospirae, Actinobacteria, and Firmicutes are most frequently detected phyla in AMD (Kadnikov et al., 2016; Travisany et al., 2012). Proteobacteria, Deinococcus/ Thermus, Gemmatimonadetes, Acidobacteria, and Actinobacteria were found with high frequency also in neutral mine drainage (Pereira et al., 2015)]. While lithotrophic genera such as *Acidithiobacillus*, *Acidiphilum*, *Ferrovum*, *Leptospirillum*, *Gallionella*, and *Sulfobacillus* dominate AMD environments (Kadnikov et al., 2016; Travisany et al., 2012), heterotrophic Proteobacteria such as *Pseudomonas* spp., *Bacillus* spp., and *Stenotrophomonas* spp. were found with high abundance in neutral copper mine drainage (da Costa et al., 2016) and other mining samples (Choudhary and Sar, 2011).

Pereira et al. (2014) assumed that the abundance of tolerant bacteria in areas of extreme environmental conditions increases, while that of more sensitive microorganism's decreases. Analysis of microbial composition of wastewater of Elizabeth's shaft showed a trend to increase the abundance of tolerant bacteria leading to a reduction of the total bacterial diversity. Proteobacteria represent almost 70% of the total diversity of bacterial community. These bacteria have been found to be predominant phylum in many mine environments indicating the high adaptability of members to extreme mining environments (Halter et al., 2001; Pereira et al., 2014).

Genus *Pseudomonas* are characterized by great deal of metabolic diversity and they are able to colonize a wide range of environments. A number of studies have been demonstrated its resistance to heavy metals and its capability to degrade a wide range of pollutants (Kumar et al., 2013; Naz et al., 2016).

Azotobacter spp. were found mainly in neutral soil and aquatic environments and they are capable of atmospheric nitrogen fixation due to iron requiring enzymatic system and can survive in contaminated environments by heavy metals.

Thus, isolates resistant to heavy metals could be employed in bioremediation processes (Abo-Amer et al., 2014).

Rhodocyclales, Rhizobiales, Rhodobacterales, and Rhodospirillales formed relatively large group within Proteobacteria. Many members of these taxa exhibit very versatile metabolic capabilities allowing them survive under various extreme environmental conditions (Frigaard and Dahl, 2009). They were found with high frequency in neutral mine drainage (Pereira et al., 2015), in slightly alkaline mine sediments (Halter et al., 2001) as well as in AMD (Kadnikov et al., 2016). In this study, the highest number of sequences was affiliated to the genus *Dechloromonas*. These bacteria are known as nitrate-dependent neutrophilic iron-oxidizers and perchlorate reducer (Chakraborty and Picardal, 2013). Bacteria belonging to this genus were found in soil high concentration of iron also in circumneutral or slightly acidic mine waters contaminated by many different heavy metals (Drewniak et al., 2016; Watanabe et al., 2013).

The phylum Chloroflexi with the predominant family Anaerolineaceae represents about 10% diversity of bacterial community in this study. Similarly, phylum showed a high abundance in alkaline river sediments contaminated with heavy metals (Reis et al., 2013) and in neutral copper mine drainage (Pereira et al., 2014), but was not detected in AMD (Kadnikov et al., 2016).

While sulfate-reducing bacteria have been commonly identified in tailings deposits and sulfide mine wastes (Lindsay et al., 2009; Schippers et al., 2010), representatives of this bacterial group (Desulfobacterales, Desulfovibrionales, Desulfuromonadales, and Syntrophobacterales) were detected with relative low frequency in this study. In addition, typical sulfur-oxidizing bacteria (e.g. *Acidiferrobacter* spp. *Thiofaba* spp., *Thiococcus* spp.) were found with low abundance.

Conclusion

In conclusion, relatively low abundance of typical iron and sulfur-bacteria in microbial community indicates that in addition to high concentration of iron and sulfur, other environmental factors significantly affect the composition of bacterial community and bacterial species with a great metabolic diversity dominate among bacteria. The pH of the drainage water is still nearly neutral, however we detected slightly shift to acidic. Sulfide mineral oxidation and possibly metabolic activity of iron/sulfur oxidizers could lead to the continual decrease of pH and to the deterioration of environmental impact of mine drainage of Elizabeth's shaft. Monitoring of the pH value continues and any changes in the bacterial community will be verified by further metagenomic analysis.

Acknowledgements

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Bakteryjna wspólnota neutralnej kopalni Drenaż szybu Elizabeth's (Slovinky, Słowacja)

Odciek kopalniany o odczynie obojętnym jest rzadszym przedmiotem zainteresowania niż odciek kopalniany kwaśny, ale może mieć niekorzystne skutki środowiskowe spowodowane głównie przez wytrącanie rozpuszczonego Fe. Celem artykułu jest scharakteryzowanie składu bakterii w środowisku o wysokim stężeniu związków żelaza i siarki reprezentowanych przez obojętne wody drenażowe kopalni szybu Elizabeth, Slovinky (Słowacja). Wartość pH wody drenażowej spadła z 7,1 do 6,5 w latach 2008–2014. Bezpośrednie obserwacje mikroskopowe, metody hodowli i pirosekwencjonowanie amplikonów genu 16S rRNA wykorzystano do zbadania populacji bakterii. Obserwacje mikroskopowe zidentyfikowały proteobakterie utleniające żelazo z rodzajów Gallionella i Leptothrix, których występowanie nie uległo zmianie w latach 2008–2014. Przy użyciu pirosekwencjonowania 454 zidentyfikowano 204 rodzajów bakterii należących do 25 typów. Proteobakterie (69,55%), a następnie Chloroflexi (10,31%) i aktynobakterie (4,24%) zdominowały społeczność bakteryjną. Rodzaje Azotobacter (24,52%) i Pseudomonas (14,15%), a następnie proetobakterie żelazo utleniające Dechloromonas (11%) i Methyloversatilis (8,53%) były najbardziej rozpowszechnione w społeczności bakteryjnej. Typowe bakterie siarkowe wykryto z mniejszą częstotliwością, np. Desulfobacteraceae (0,25%), Desulfovibrionaceae (0,16%) lub Desulfobulbaceae (0,11%). Uzyskane dane wskazują, że skład flory bakteryjnej wody drenażowej szybu Elżbieta odzwierciedla obserwowane neutralne pH, wysoki poziom zawartości jonów żelaza i siarki w środowisku wodnym.

Słowa kluczowe: flora bakteryjna, neutralny drenaż kopalniany, sekwencjonowanie

Flowability Of Moist Coal Combution Fly Ash

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Abstract

In the combustion of coal the mineral contents remain as ash. The fine size fraction of the ash leaves the combustion zone with the off-gas from which it is separated as fly ash. Depending on the physical and chemical properties these fly ashes can be utilized. An essential parameter for the design and operation of transport equipment and storage facilities for fine grained materials is their flowability. The moisture content of the material has considerable influence on the flowability because of the increasing influence of the liquid bridges between the particles and the resulting capillary forces. In this study the influence of the moisture content on the flow characteristics of a coal combustion fly ash was investigated. The fly ash sample was collected from the dust discharge of the electrostatic precipitator of a power plant using Polish hard coal as fuel. The mass median diameter of the fly ash was approximately 20 μm. Microscopic images show that most of the particles are spheres. The flow properties of the fly ash were measured using a ring shear tester. The moisture content of the sample was adapted by addition of water. The dry fly ash was characterized by very good flow properties, the flowability ffc was in the category 'easy flowing'. Significant decrease in flowability was found at increased moisture contents. Additionally, the bulk density of the fly ash was influenced by the moisture content. Thus, the flow-relevant parameters which have to be considered in design of transport and storage facilities of fine granular material worsened with increasing moisture content.

Keywords: fly ash, coal combustion, moisture content, flowability

Introduction

When coal is combusted most of the mineral content of the coal remains in the form of ash. The coarse fraction of the ash is discharged at the furnace bottom, while the fine fly ash fraction has to be separated from the combustion off-gas. An annual production of coal combustion fly ash worldwide of 500 million tones is estimated (Ahmaruzzaman, 2010). From an environmental point of view this huge amount of fly ash should be utilized as much as possible because the disposal of such a large quantity of fly ash is a serious environmental problem. The utilization of fly ash varies widely from country to country. The world average utilization amounts to approximately 16% of the total fly ash (Ahmaruzzaman, 2010).

In utilization of coal combustion fly ash the composition of the fly ashes is crucial. Therefore, the composition of coal combustion fly ash has been studied widely (Asokan et al., 2005; Belviso et al., 2015; Fytianos et al., 1998; Shaheen et al., 2014). For the handling and storage of fly ash also mechanical parameters are important. For both the particle size and the particle size distribution of coal fly ash measured results are available in the literature. Mass median diameters between 6.8 and 98 μm were reported (Chindaprasirt et al., 2011; Kutchko et al., 2006), while the maximum particle size is approximately 150–250 μm.

An essential parameter for the design of transport equipment and storage facilities for fine grained materials is their flowability. It depends on various material properties, for example the grain size, the grain size distribution, and the grain shape (Lumay et al., 2012; Schulze, 2006). The moisture content of the material also has considerable influence on the flowability because of the increasing influence of the liquid bridges between the particles and the resulting capillary forces (Emery et al., 2009; Plinke et al, 1994; Schulze, 1991) Therefore, an increased moisture content leads to reduced flowability.

In this study the influence of the moisture content on the flowability of coal combustion fly ash was investigated. The flowability at increased water content is important because the dust is often wetted to avoid dust generation during handling and storage of the material.

Materials and methods

The investigated fly ash sample was collected from a power plant using Polish hard coal as fuel. The fly ash from this power plant is separated from the off-gas by a three-field electrostatic precipitator. It is utilized as a milling additive in the cement industry. A fly ash sample of approximately 5 dm^3 was collected at the discharge system of the ESP of the off-gas de-dusting system. In the laboratory, the quantity of the collected fly ash sample was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Haver&Boecker HAVER RT, Quantachrome Micro Riffler).

In a first step the fly ash sample was dried in a compartment drier for twenty-four hours. For production of fly ash samples with different water content an Erweka AR 403/SW 1/S plough-share drum mixer was used where the dried fly ash was mixed with the appropriate amount of water. The

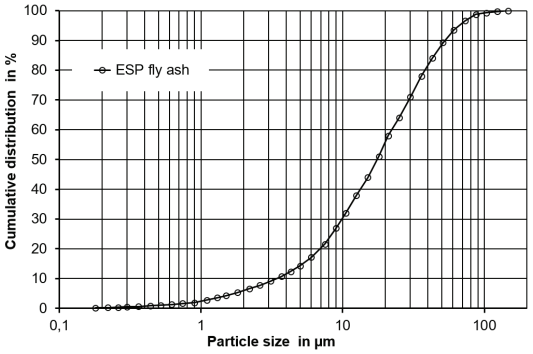

Fig. 1. Size distribution of the fly ash

Rys. 1. Rozkład wielkości uziarnienia popiołu lotnego

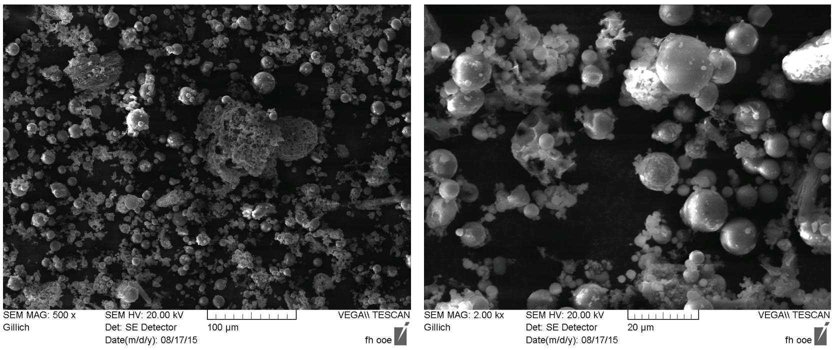

Fig. 2. Scanning electron microscope images of fly ash particles

Rys. 2. Obrazy ziaren popiołu lotnego ze skaningowego mikroskopu elektronowego

speed of the mixer was 300 rpm and the mixing time was 10 minutes. Afterwards, the moisture content of the samples was determined gravimetrically with a Sartorius infrared moisture analyser MA35M at 105°C.

The particle size distribution of the fly ash was measured using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS. The calibration of the instrument was checked with a Sympatec SiC-P600'06 standard.

Microscopic images of particles from the various size fractions were taken with a scanning electron microscope TESCAN, type VEGA LM.

The yield locus was determined using a Schulze RST-XS ring shear tester with a 30 cm³ shear cell. The bulk density of the material in dependence of the consolidation stress was also determined with the shear tester.

For a quantitative characterization of the flowability of a granular material the factor ff_c can be used, which is the ratio of the consolidation stress σ_1 to the unconfined yield strength σ_c (Schulze, 1996) The larger the value of ff_c, the better a granular material flows. The consolidation stress is equal to the major principal stress of the Mohr stress circle which is tangential to the yield locus and runs through the point of steady-state flow. The unconfined yield strength results from the stress circle which is tangential to the yield locus and runs through the origin (Jenike, 1964). The usual classification used to define flow behaviour consists of five categories: not flowing: $ff_c < 1$; very cohesive: $1 < ff_c < 2$; cohesive: $2 < ffc < 4$; easy-flowing: $4 < ff_c < 10$ and free-flowing: $10 < ff_c$ (Schulze, 1996). The flowability of a granular material often depends on the consolidation stress. For many powders better flowability will be achieved at a higher consolidation stress. This can be visualized best in a diagram showing the unconfined yield strength dependent upon the consolidation stress when the diagram also includes lines of constant ff_c ratio. Logarithmically scaled axes improve the representation of the results in the diagram (Lanzerstorfer, 2016).

Results and discussion

The particle size distributions of the fly ash is given in Figure 1. The mass median diameter was 18 µm. Thus, the size of the fly ash is within the reported size range.

Figure 2 shows scanning electron microscope (SEM) images of the fly ash. Most single particles have a rounded, nearly spherical shape. However, there are also some agglomerates and some particles with a different shape.

The unconfined yield strength dependent upon the consolidation stress is shown in Figure 3 for various values of the moisture content. Generally, the flowability decreases with increasing moisture content.

At a moisture content of 0.55% the fly ash was easy-flowing. Thereby, the flowability improved with increasing consolidation stress. At a moisture content of 0.95% the flowability was reduced (cohesive to easy-flowing) and at 2.25% the flowability was already very low (very cohesive to cohesive). At low values of the consolidation stress, a further increase in the moisture content had little influence on the flowability, while at higher values of the consolidation stress the flowability still decreased. Thereby, the effect of the improving flowability with increasing consolidation stress nearly diminished.

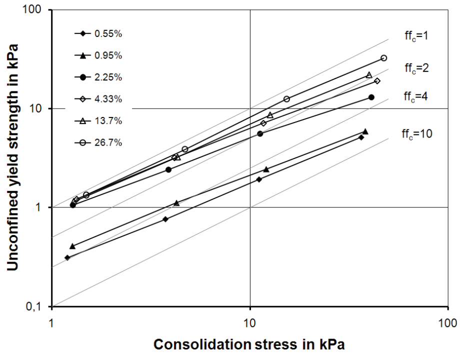

Fig. 3. Unconfined yield strength vs. Consolidation stress

Rys. 3. Nieskończona granica plastyczności w stosunku do naprężenia sumarycznego

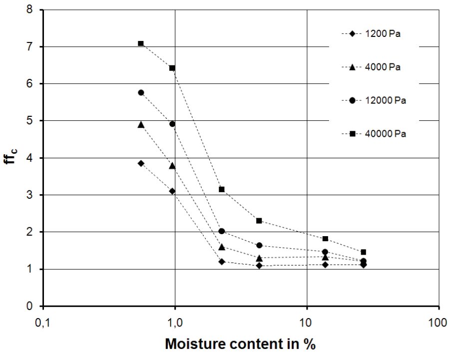

Fig. 4. Flowability as a function of the moisture content

Rys. 4. Sypkość jako funkcja wilgotności

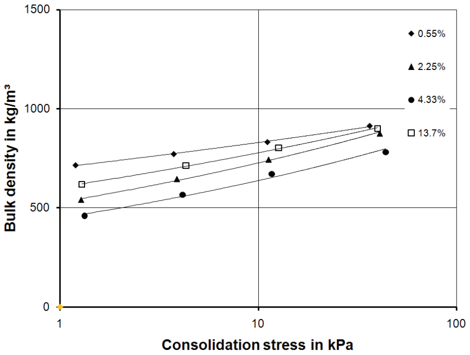

Fig. 5. Bulk density as a function of the consolidation stress for various values of the moisture content

Rys. 5. Gęstość nasypowa jako funkcja naprężenia dla różnych wartości wilgotności

Figure 4 shows the flowability as a function of the moisture content for various values of the consolidation stress. At low consolidation stress the flowability decreases rapidly with increasing moisture content. At the moisture content of 2.25% the minimum of ff_c was reached. A further increase of the moisture had little influence on the flowability. At the highest value of the consolidation stress the decrease in flowability was less steep. Thus, the minimum value of ff_c was reached at a higher value of the moisture content.

Generally, the bulk density of fine granular material increases with increasing consolidation stress (Lanzerstorfer, 2017). This was also observed for the investigated fly ash. At lower values of the moisture content the bulk density decreased with increasing moisture content. The minimum bulk density was measured at a moisture content of 4.33%. At the moisture content of 13.7% the bulk density was higher.

Conclusion

The measurements showed a significant influence of the moisture content on flow-relevant parameters of coal combustion fly ash. In the low moisture-content range of 0–3% the flowability decreased significantly with increasing moisture content, while at higher moisture content (>3%) the variation was rather small. The influence of the moisture content also strongly depends on the value of the consolidation stress.

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Płynność popiołu lotnego ze spalania mokrego węgla

Przy spalaniu węgla zawarte w nim minerały pozostają w postaci popiołu. Drobna frakcja popiołu opuszcza strefę spalania z gazem odlotowym, z którego jest oddzielana jako popiół lotny. W zależności od właściwości fizycznych i chemicznych można wykorzystać popioły lotne. Istotnym parametrem dla projektowania i eksploatacji urządzeń transportowych i magazynów materiałów drobnoziarnistych jest ich zdolność płynięcia. Zawartość wilgoci w materiale ma znaczący wpływ na zdolność płynięcia ze względu na rosnący wpływ mostków cieczowych między cząstkami i wynikającymi z nich siłami kapilarnymi. W pracy zbadano wpływ zawartości wilgoci na charakterystykę przepływu popiołu lotnego ze spalania węgla. Próbka popiołu lotnego została pobrana z odbiornika pyłu z elektrofiltra elektrowni z wykorzystaniem polskiego węgla kamiennego jako paliwa. Mediana średnicy ziarna popiołu lotnego wynosiła około 20 μm. Obrazy mikroskopowe pokazują, że większość cząstek to kule. Właściwości przepływu popiołu lotnego mierzono za pomocą testera ścinania pierścieniowego. Zawartość wilgoci w próbce zmieniano przez dodatek wody. Suchy popiół lotny charakteryzował się bardzo dobrymi właściwościami płynięcia, płynność ffc była w kategorii „łatwo płynący". Znaczny spadek płynności stwierdzono przy zwiększonej zawartości wilgoci. Dodatkowo zawartość wilgoci ma wpływ na gęstość nasypową popiołu lotnego. Zatem istotne dla przepływu parametry, które należy wziąć pod uwagę przy projektowaniu urządzeń do transportu i przechowywania drobnego materiału ziarnistego, pogarszają się wraz ze wzrostem zawartości wilgoci.

Słowa kluczowe: popiół lotny, spalanie węgla, wilgotność, sypkość

Non-Ferrous Metal Sorbents Based on Waste and Side Products of Mineral Benefication Plants

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Abstract

The saponite-containing product from the stage of process water clearing at benefication plant of the PAO Severalmaz was thickened using the electrochemical separation for use as sorbent of nickel and copper ions. The product features a high sorption capacity relatively the nickel and copper ions. It has been established that the sorption capacity can be enhanced by roasting the product at 750°C to 194 and 212 mg/g for the nickel and copper ions respectively.

An organomineral sorbent for nickel ions based on copper-nickel ore tailings of the JSC „The Kolskaya Mining and Metallurgical Company", thermally activated at 700°C, has been synthesized. The surface modification was performed by using the non-covalent immobilization of dimethylglyoxime.

Keywords: electrochemically modified saponite, sorption, thermal activation, metal ions, mine water, waste water

Introduction

For tailings ponds or waste rock piles exposed to atmospheric conditions, heavy metals (Ni, Cu) are often produced by oxidation of sulfide minerals (mainly pyrite and pyrrhotite), which also generates acid in the process (Plante, et al., 2010). Acid mine drainage (AMD) is an environmental problem that has drawn the attention of researchers in several countries around the world. This is mainly due to the presence of heavy metals in AMD, which could lead to degradation of both surface and ground water easily reach lakes, dams and rivers that are sources of water supply, making it unfit for human and animal consumption or crop irrigation (Masukume et al., 2014).

Treatment processes for metal contaminated industrial waters include chemical precipitation, extraction, ion exchange, adsorption and ultra-filtration. Clays, saponite, serpentine, overburden and tailings, containing chemically active minerals, are perspective materials for the development of highly effective sorbents for metal ions.

The present study was performed with saponite-containing product obtained using the electrochemical separation. When in aqueous medium, saponite forms a fine, gel-like suspension creating problems in operation of tailings facilities and hindering the close-loop circulation of process water. Experiments on saponite recovery from the process water of diamond mining plants are reported in works (Minenko, 2014; Chanturiya, et al. 2017) presenting a reagent-free electrochemical method for the pulp processing and equipment for the method's implementation (electrochemical separator). The apparatus incorporates realization of the processes of electrophoretic deposition of the saponite product at the anode and osmotic deposition of water at the cathode. The resulting concentrate (electrochemically modified saponite) is characterized by high concentrations of the solid phase (up to 620 g/dm3 of suspension), high contents of saponite and montmorillonite (up to 74.5 %) and lower concentrations of quartz and dolomite compared to the initial saponite-containing product(12% and 5%, respectively).

The most promising is the production of a modified sorbent based on waste from the mining industries. The increase in the absorptive capacity was achieved by fixing the reagent (dimethylglyoxime) on the of copper-nickel ore tailings (thermally activated at 700°C), namely, by impregnation.

Sorbents obtained by using method for the non-covalent immobilization have the advantages of covalently modified matrices (chemical, mechanical resistance, etc.), and do not have such disadvantages, as high labor intensity for the processes of modification and regeneration.

Materials and methods

Electrochemically modified saponite – concentrate of electrochemical separation from process water of the Arkhangelskaya kimberlite pipe (Minenko, 2014; Chanturiya, et al. 2017). The Lomonosov deposit of the Archangelsk diamondiferous province accommodates 10 kimberlite pipes. The anticipated volume of diamond-bearing ore and dump rock to be removed before reaching the open-pit mining limit is 300 mln t (Karpenko, 2009; Bezborodov, et al. 2003). Rock in the deposit is almost completely displaced by clay minerals, predominantly saponite, amounting to 90% in the vent facies (Karpenko, 2009).

The general formula saponite can be expressed as $NaMg_3[AISi_3O_{10}](OH)_2 \cdot 4H_2O$. Moreover, owing to the low charge of the layers the mineral can expand in water and has unique adsorption and ion-exchange properties caused by the presence of exchange cations. In addition, it is known that saponite, which in this product is electrochemically modified, has higher sorption characteristics in comparison with the

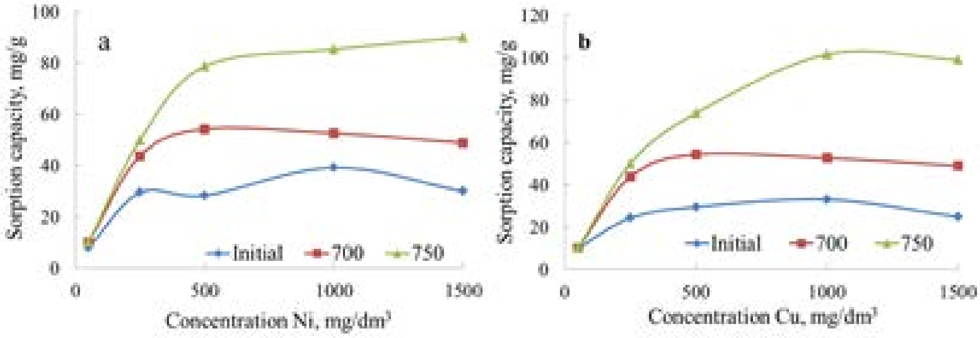

Fig. 1. Sorption isotherms of Ni(a), Cu(b) by saponite-containing products
Rys. 1. Izotermy sorpcji Ni (a), Cu (b) przez produkty zawierające saponit

Tab. 1. Kinetics of metals adsorption by electrochemically modified saponite and sintered saponite products
Tab. 1. Kinetyka adsorpcji metali przez elektrochemicznie modyfikowane saponity i spiekane produkty saponitowe

t, h	Initial			700°C			750°C		
	1:200	1:100	1:25		1:200	1:100	1:25		1:200
Sorption capacity relatively Cu, mg/g									
0.5	21.1	18.5	13.6	26.9	13.3	31.1	73.8	46.9	10.0
1	30.0	19.6	15.2	67.4	28.3	34.5	78.7	50.0	35.4
5	24.9	28.8	14.7	96.3	30.5	35.5	102.1	64.9	35.2
24	33.1	72.9	19.1	73.0	53.2	33.9	145.7	85.0	37.5
120	99.8	89.1	28.5	89.2	66.9	37.5	185.0	96.4	37.5
240	71.4	75.4	36.2	116.9	126.0	37.5	212.8	139.5	37.3
Sorption capacity relatively Ni, mg/g									
0.5	24.1	17.6	5.9	27.1	19.7	25.6	21.3	34.5	28.6
1	33.9	22.6	12.0	42.3	34.7	35.6	33.7	41.9	37.5
5	36.7	24.0	15.2	46.4	34.1	32.6	79.4	52.7	37.4
24	38.6	40.3	22.6	46.0	30.6	32.2	144.9	56.9	37.5
120	40.7	39.1	18.1	69.1	48.9	35.5	194.2	103.8	37.4
240	40.2	36.0	16.0	77.8	51.2	36.4	129.4	76.7	37.5

natural mineral. The sorption properties of the electrochemically modified saponite and its products sintered during 2 hours in the SNOL 6/11-B furnace at 700 and 750°C were investigated in batch conditions at the temperature of 20°C. This temperature range was selected after analysis of the results reported in work (Chanturiya, et al. 2014; Makarov, et al. 2005) dealing with structural modifications of dissimilar layered hydrosilicates and their sorption properties in the process of sintering.

The adsorbing solutions (further referred to as solutions) were the sulfate solutions of nickel and copper which are the main heavy-metal pollutants of natural waters in the Urals Mountains and North-West Russia. The metal concentrations in the solutions investigated were 50 to 1500 mg/dm³, which are the real concentrations in waste water affording to reveal and classify the new formations on the sorbents.

Creating the conditions for maximum saturation of the sorbent and complete (up to 99–100%) removal of heavy metal cations from solutions were based on analysis of the published data on the sorption capacity of clay minerals of the montmorillonite group (Esmail, 2016). In our experiments, the sorbent to solution ratio (further referred to as S:L) was varied from1:200 to 1:25; the exposure periods were 30 minutes to 10 days.

To obtain the organomineral sorbent, copper-nickel ore tailings of the JSC "The Kolskaya Mining and Metallurgical Company", consisting of serpentine (60%) and magnetite (13%), were used. The copper-nickel ore tailings were represented by the following chemical composition, %: SiO_2 37.39, MgO 28.29, Fe 18.10, Al_2O_3 3.73, CaO 2.71, TiO_2 0.945, Ni 0.19, Cu 0.06, Co 0.003. The tailing pond of the concentrating factory "Pechenga" ("The Kola MMC") was founded in 1965 in the town Zapolyarny. The reserves of copper-nickel ores tailings amount to 250 million tons, the annual growth is 7 million tons.

The copper-nickel ore tailings, thermally activated at 700°C, were modified by impregnation.

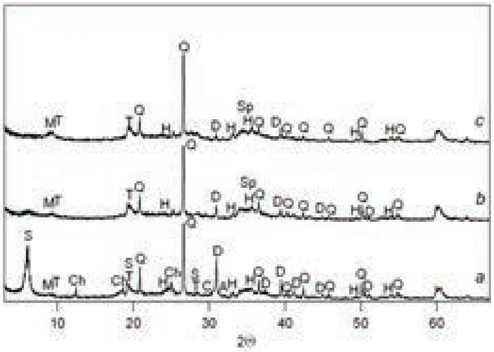

Fig. 2. XRD patterns of the sorbents after interaction with a nickel sulfate solution. Initial sorbent, exposure time of 5 days (a); sintered at 700°C, exposure time of 10 days (b); sintered at 750°C, exposure time of 5 days (c). S – saponite, Q – quartz, H – hematite, A – apatite, C – calcite, D – dolomite, M- mice, Ch – chlorite, T – talc, G – gypsum, Sp – spinel

Rys. 2. Analiza XRD sorbentów po interakcji z roztworem siarczanu niklu. Surowy sorbent, czas ekspozycji 5 dni (a); spiekany przy 700°C, czas ekspozycji 10 dni (b); spiekany przy 750°C, czas ekspozycji 5 dni (c). S – saponit, Q – kwarc, H – hematyt, A – apatyt, C – kalcyt, D – dolomit, M – myszy, Ch – chloryt, T – talk, G – gips, Sp – spinel

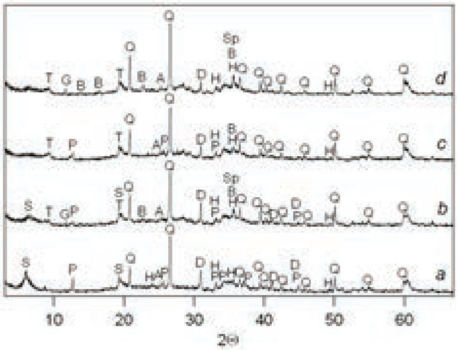

Fig. 3. XRD patterns of sorbents after reaction with a copper sulfate solution. Initial sorbent (a, 10 days); sorbent sintered at 700°C, (b, 10 days); sorbent sintered at 750°C (c, 5 days), and (d, 10 days). S – saponite, P – posnjakite, Q – quartz, H – hematite, A – apatite, D – dolomite, B – brochantite, T – talc, G – gypsum

Rys. 3. Analiza XRD sorbentów po reakcji z roztworem siarczanu miedzi. Początkowy sorbent (a, 10 dni); sorbent spiekany przy 700°C, (b, 10 dni); sorbent spiekany przy 750°C (c, 5 dni) i (d, 10 dni). S – saponit, P – posnjakit, Q – kwarc, H – hematyt, A – apatyt, D – dolomit, B – brochantyt, T – talk, G – gips

An alcoholic solution of dimethylglyoxime was placed into the reactor, and then a sample of the tailings was added. The temperature was varied from 50 to 90°C, the modifier consumption was from 2.5 to 30%, depending on the mass of the silicate matrix. The duration of the interaction was from 30 to 300 minutes. Experiments on the interaction of modified tailings with sulfate solutions containing nickel ions were carried out. In the experiments, the concentration of the nickel sulfate solution was 0.1 N.

The sorption of nickel ions was determined at various pH values: 1.64; 3.56; 4.01; 6.86; 9.18.

The ratio of S:L was 1:50. The interaction time was varied in 5, 15, 30, 60 minutes and 3, 6, 8, 24 hours, the ratio of S:L was 1:100.

The metal concentrations in solutions were determined using the atomic-absorption spectrometry (KVANT 2A spectrometer, "Cortec" LLC).

The phase composition of the solid products and newly formed minerals was determined using the XRD at a diffractometer X'Pert PRO MPD (Shimadzu) with Cu Kα radiation.

Results and discussion

Figure 1 demonstrates the relationships between the sorption capacity of saponite-containing products and the initial concentrations of $NiSO_4$ and $CuSO_4$ solutions at the solid to liquid ratio of 1:200 and the exposure time of 3 hours. It has been established that thermal activation of the electrochemically modified saponite enhances the sorption capacity. Interestingly, at low initial concentrations of the metals in solutions (down to 500 mg/dm^3) the sorption capacity of all the samples was observed to increase abruptly. Further increasing of initial concentration does not affect the sorption capacity of saponite-containing products, which suggests transition of the sorption process from diffusion to kinetic regime. Therefore, to achieve the maximum saturation of the sorbent with copper and nickel cations, we proceeded to experiment with solutions having the metal contents of 1500 mg/dm^3, and increased the exposure time to 10 days.

Table 1 presents the research results on variation of the sorption capacity of electrochemically modified saponite and products of sintered saponite with the S:L ratio and time of interaction to solution. For the initial electrochemically modified saponite, the maximum sorption capacity relatively the nickel and copper cations are 40.7 and 99.8 mg/g, respectively, and it is achieved after 5 days. On further interaction with solution the sorption capacity deteriorates probably as a result of developing/incipient destruction and resolution of the compounds newly formed on the sorbent.

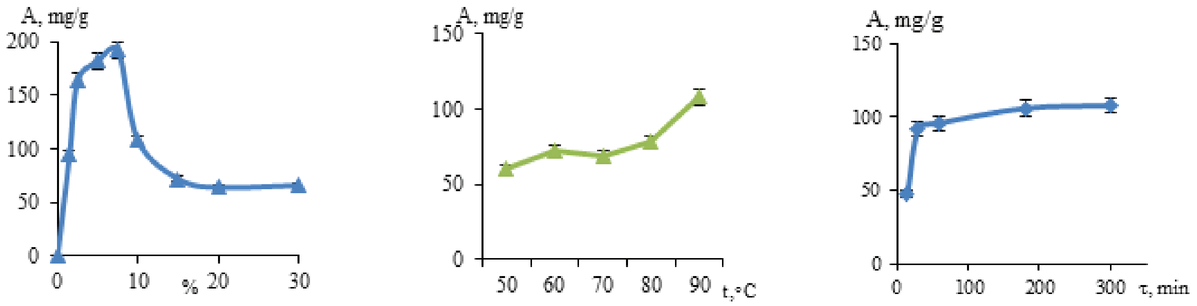

Fig. 4. Dependence of nickel ions sorption on the modifier concentration (a), on the reaction mixture temperature (b), on the interaction duration (c)
Rys. 4. Zależność sorpcji jonów niklu od stężenia modyfikatora (a), od temperatury mieszaniny reakcyjnej (b), od czasu oddziaływania (c)

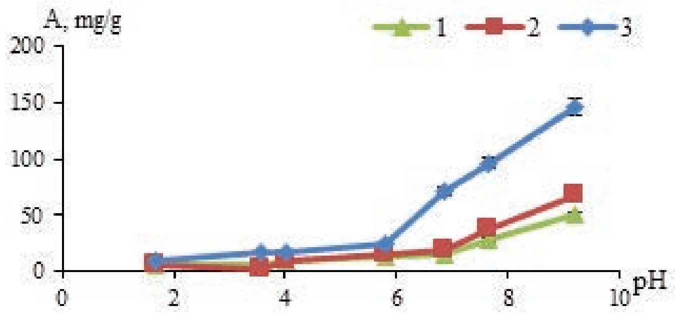

Fig. 5. Dependence of nickel ions sorption on pH medium. Initial tailings (1); tailings, thermally activated at 700°C (2); organomineral sorbent (3)
Rys. 5. Zależność sorpcji jonów niklu od odczynu pH. Odpady początkowe (1); odpady, aktywowane termicznie w 700°C (2); sorbent organomineralny (3)

The sorption capacity of electrochemically modified saponite to 77.8–126 mg/g via sintering; the level of solution purification was 94.7–100% after 5 days of exposure. The maximum sorption capacities relatively the nickel and copper cations of, respectively, 194.2 and 212.8 mg/g was observed on saponite samples sintered at 750°C at the ratios S:L= 1:200. By increasing the S:L ratioto1:25 the solution purification from copper and nickel cations achieved 100% already after 1 day of exposure to the sorbent.

It should also be noted that at less than 250 mg/dm³ metal concentrations in solutions the extraction of nickel and copper is 100% in less than 3 hours of interaction with the sorbent sintered at 750°C.

Thus, the electrochemically modified saponite is a good sorbent of nickel and copper ions and can be further improved by sintering at 700–750°C.

XRD studies of the sorbents maximally saturated with nickel suggest that the metal sorption on initial saponite follows the mechanism of cation exchange with metals cations distributing between the mineral structure packets. Moreover, a phase with spinel structure, probably containing nickel, has been recorded. Spinel also emerges after the nickel sulfate solution reacts with a product thermally activated at 700 and 750°C (Fig. 2, b, c). In these cases, saponite transforms to a layered talc-like phase which is likely to contain nickel in the inter-packet space.

The XRD of the sorbents saturated with copper to the maximum has shown the following changes in the phase composition, which suggests entraining of calcium and sodium from the interlayer space (Fig. 3; a). At the same time, these cations may be substituted both for copper cations and protons.

As a result of heat treatment at 700°C (Fig. 3; b) the saponite reflexes decreased sharply. Afterburning at 750°C saponite disappeared almost completely (Fig. 3; c, d); weak calcium reflexes indicated the onset of dolomite decomposition.

The new copper-containing phases were identified as basic sulfates insoluble in water. Reactions of the initial product and that sintered at 700°C produced posnjakite $Cu_4(SO_4)(OH)_6 \cdot H_2O$ (Fig. 3a, b); and brochantite $Cu_4(SO^4)(OH)_6$ was recorded for products sintered at 700 and 750°C (Fig. 3, c, d).

There is a slight dissimilarity between the phase composition of samples sintered at 750°C differing in reaction times with sulfate solution. Long exposure of the sintered product to the copper sulfate solution (10 days) has led to increasing of the reflex with d = 2.52 Å (2Θ = 35.5°), corresponding to phases with a spinel structure.

Figure 4 shows the sorption capacity for the synthesized sorbent depending on the modifier concentration, the temperature of the reaction mixture and duration of interaction. The rational parameters of the surface modification were determined: the temperature of the reaction mixture was 90°C, the duration of the interaction was 30 minutes, and the modifier weight amounted to 2.5–7.5%. Increasing the concentration of the modifier reduced the availability of functional groups and led to decrease in the sorption capacity. As a result of modification, the sorption capacity to nickel ions was increased substantially to 180–220 mg/g.

The influence of the initial pH value varying in the range from 1 to 10 on the sorption of nickel ions was studied. It should be noted that pH increase, beginning from 6, marks the considerable growth of nickel ions sorption (Fig. 5).

An important criterion while using a sorbent for water purification is the rate of sorption. Studying kinetics of the

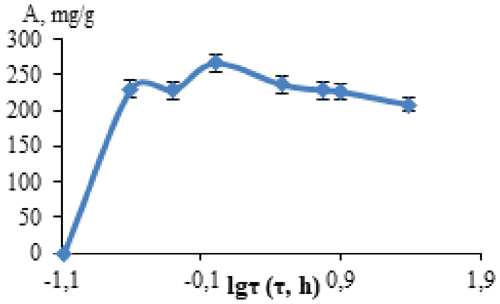

Fig. 6. Kinetics on the sorption of nickel ions by organomineral sorbent
Rys. 6. Kinetyka sorpcji jonów niklu przez sorbent organo-mineralny

nickel ions sorption by a modified sorbent showed the sharp increase within 5 minutes. The maximum value was achieved by contact for 30 minutes, then some desorption occurred (Fig. 6).

The results of the studies revealed that the surface modification significantly increased the sorption capacity for nickel ions to 220 mg/g, compared to thermally activated and initial tailings (38 and 28 mg/g, respectively, Fig. 2). The values obtained exceed the sorption capacity of sorbents, such as magnetite 1.25 mg/g (Martemyanov D. et al, 2013), glauconite 3.6 mg/g (Martemyanov D. et al, 2013), bentonite 35 mg/g (Somin, V. et al., 2014), brucite 95 mg/g.

Conclusion

This study is the first to substantiate and experimentally validate the following method for manufacturing from saponite-containing diamond-mining waste of sorbents with excellent cation exchange properties for effective treatment of process water from heavy metal cations.

Experiments have proved the feasibility of processing the electrochemically modified saponite for effective sorbents having an cation exchange capacity of over 200 mg/g, applicable in treating of process water from heavy metal ions to the MAC for fishing water reservoirs. The affinity of this sorbent towards metal ions could be arranged as follows $Cu^{2+} > Ni^{2+}$.

The modified sorbent based on copper-nickel ore tailings at the JSC "The Kolskaya Mining and Metallurgical Company" has high sorption capacity and can be proposed for purification industrial waters at the mining enterprises.

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Sorbenty metali nieżelaznych na bazie odpadów i produktów ubocznych z zakładów wzbogacania surowców

Produkt zawierający saponit z etapu oczyszczania wody technologicznej w zakładzie wzbogacania PAO Severalmaz został zagęszczony przy użyciu rozdzielania elektrochemicznego w celu zastosowania jako sorbent jonów niklu i miedzi. Produkt cechuje się dużą pojemnością sorpcyjną, w stosunku do jonów niklu i miedzi. Ustalono, że pojemność sorpcyjna może być zwiększona przez prażenie produktu w temperaturze 750°C do 194 i 212 mg/g odpowiednio dla jonów niklu i miedzi.

Zsyntetyzowano organo-mineralny sorbent dla jonów niklu oparty na odpadach z wzbogacania rud miedzi i niklu JSC „The Kolskaya Mining and Metalurgical Company", aktywowany termicznie w 700°C. Modyfikację powierzchni przeprowadzono stosując niekowalencyjną immobilizację dimetyloglioksymem.

Słowa kluczowe: saponit modyfikowany elektrochemicznie, sorpcja, aktywacja termiczna, jony metali, woda kopalniana, ścieki

Influence of Biogenic Acid on Concrete Materials

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Abstract

Microbial sulphur cycle in sewers evocate the serious problem in the area concrete corrosion, health related aspects and odour. These problems are primarily related to the release of bacterially produced hydrogen sulphide from wastewater to the atmosphere during sewage transports that dissolves in the condensate on the sewer crown. In the event sulphur-oxidizing bacteria oxidize the dissolved hydrogen sulphide and other sulphur compounds to sulphuric acid, which corrodes the concrete. The concrete gradually expands causing cracks and ruptures, loss of strength and overall decay of concrete.

The paper is focused on the investigation of the concrete specimens surface biodegradation study. From the viewpoint of concrete materials biodeterioration, mainly the bacteria sulphur- and sulphide-oxidising bacteria and sulphate-reducing bacteria are important and interesting. The role of bacteria mentioned above has been linked to the generation of the biogenic sulphuric acid resulting in corrosion process by dissolution of calcium containing minerals from the concrete matrices. The penetration of the corrosion was manifested by structural changes of concrete samples. The surface structure changes were by stereomicroscopy and atomic force microscopy (AFM) investigated.

Keywords: bacterially produced hydrogen sulphide, sulphuretum, biogenic sulphuric acid, concrete, AFM

Introduction

Corrosion in sewer systems by biologically produced sulphuric acid is a worldwide phenomenon and is considered to have a great economic impact (Sand, 1997). It is a consequence of a cyclic process caused by bacterial sulphur metabolism. Two types of bacterial metabolism sulphur compounds are involved in the cycle of sulphur in the environment. One is an anaerobic process in which anaerobic bacteria produce hydrogen sulphide. The other is an aerobic process in which the hydrogen sulphide is oxidised to elemental sulphur or sulphuric acid by aerobic bacteria. This biological cyclic process exists as a natural way for the cycling of sulphur compounds in the environment and may also exist in sewage collection systems. The bacterial population of this biological sulphur cycle is called "sulphuretum".

It involved mainly the sulphate-reducing bacteria (SRB) and sulphur- and sulphide-oxidising bacteria (SOB).

SRB are a unique and ubiquitous group of prokaryotic microorganisms (MO), found in a variety of anaerobic environmental niches such as soil, mud and sediments of freshwaters (rivers, lakes), thermal or no-thermal sulphur springs, sewage, mining waters from sulphide deposits, waters from deposits of mineral oil and natural gas and gastrointestinal tract of man and animals (Odom and Rivers Singleton, 1993). The most studied SRB are bacteria Desulfovibrio desulfuricans. The basic metabolic process of SRB is the anaerobic reduction of sulphates to hydrogen sulphide in which organic substrate (lactate, malate, etc.) or gaseous hydrogen is the electron donor and sulphate is the electron acceptor. Hydrogen sulphide consequently in the water reacts with the metals cations and forms the metallic sulphates of low solubility. It is the positive aspect of SRB, which is used in the area of treatment AMD (Tabak et al., 2003). In the case of sewage overcharge hydrogen sulphide enters the sewer atmosphere by volatilisation and dissolves in the condensate on the sewer crown. In addition hydrogen sulphide has reached the atmosphere it may react with oxygen to elemental sulphur, which is deposited the slime layer coating the walls. Hydrogen sulphide and sulphur are substrates for many SOB such as *Acidithiobacillus* thiooxidans, *Acidithiobacillus* neapolitanus and *Acidithiobacillus* intermedius. They will metabolise the hydrogen sulphide and sulphur to sulphuric acid, which corrodes the concrete.

SOB occurs in the sewage but predominantly represents autochthonous bacterial culture of sulphide deposits where it takes part on sulphide minerals oxidation and acid mine drainage (AMD) production (Johnson, 1995). The positive aspect of SOB in the environment and industry is bacterial leaching of sulphidic minerals and its concentrates and different wastes with the high content of sulphur compounds (Rawlings, 1997).

The general mechanism for the biogenic sulphuric acid caused corrosion of sewer systems was described many authors (King and Miller, 1971; Sand, 1997; Roberts et al., 2002 and others). The model depicting of biocorrosion of concrete pipes attributed to sulphuretum is given in Figure 1.

During the transport of raw sewage from the top of the sewage collection system to the treatment plants, the organisms in the sewage start to degrade the abundant organic compounds present in the raw sewage. This often results in a depletion of O_2 from the sewage. This result in the creation of anaerobic or anoxic conditions that allow the growth of SRB which grow only in the absence of O_2 and obtain energy by utilising small organic compounds or H_2 as energy sources and transferring the electrons produced to sulphate, thus reducing it to hydrogen

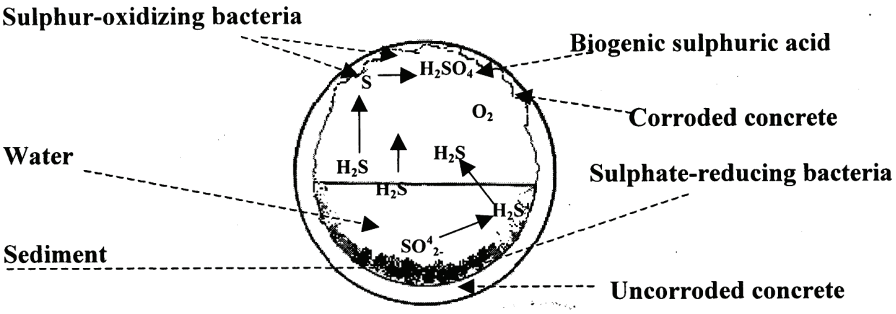

Fig. 1. Schematic representation of the sulphur-cycle occurring in sewer pipes [King and Miller, 1971 (adapted)]
Rys. 1. Schematyczne przedstawienie cyklu siarkowego występującego w rurach kanalizacyjnych [King and Miller, 1971 (dostosowany)]

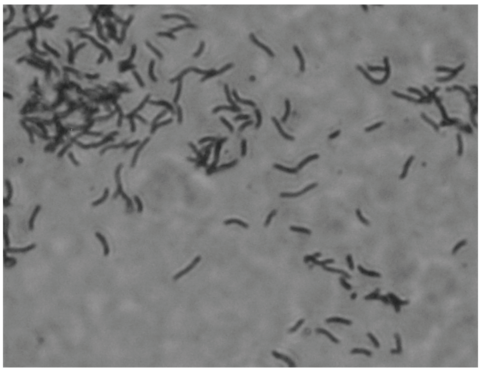

Fig. 2. Bacteria Desulfovibrio desulfuricans, isolated from the potable mineral water (Gajdovka spring, Slovakia)
Ryc. 2. Bakterie wyizolowane z pitnej wody mineralnej (źródło Gajdovka, Słowacja)

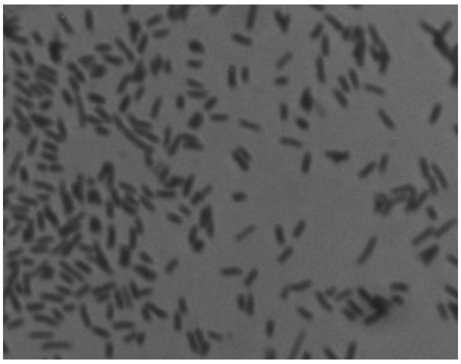

Fig. 3. Bacteria *Acidithiobacillus* thiooxidans, isolated from AMD from the shaft Pech (the old mine Smolník, Slovakia)
Ryc. 3. Bakterie *Acidithiobacillus tiooksydans*, wyizolowane z kwaśnego odcieku (AMD) z szybu Pech (stara kopalnia Smolník, Słowacja)

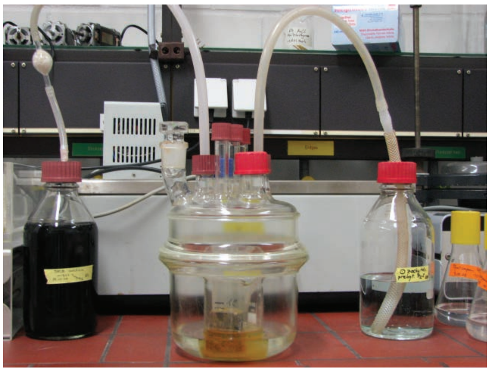

Fig. 4. The laboratory experimental system apparatus
Rys. 4. Laboratoryjne urządzenia pomiarowe

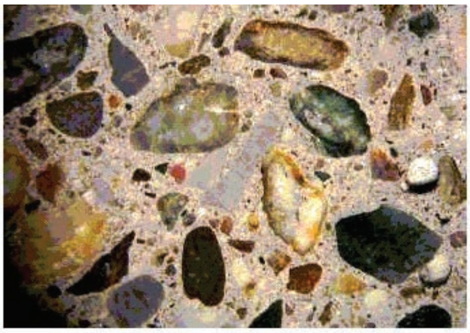

Fig. 5a. Smooth surface filling among aggregates before experiment Magnification of image 20 x 4.5
Rys. 5a. Wypełnienie powierzchni wśród agregatów przed eksperymentem. Powiększenie obrazu 20 x 4,5

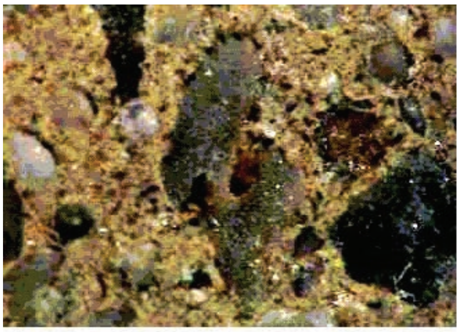

Fig. 5b. Considerable biodeterioration of concrete sample surface after 90 days. Magnification of image 20 x 4.5
Rys. 5b. Biodeterioracja powierzchni próbki betonu po 90 dniach. Powiększenie obrazu 20 x 4,5

sulphide. Well SRB grow in anaerobic conditions of the sediment and water that collects in the bottom of concrete pipes and hydrogen sulphide is produced. The sulphide produced eventually partitions into HS- and H_2S. H_2S is a gas and evolves into the headspace of the sewer pipes, reaching the crown of the pipe. The crown of the pipe is exposed to an aerobic environment that supports the growth of SOB.

The biodeterioration genesis has three stages: infection – creation of the permanent contact between MO and material; incubation – the period from the infection until the symptoms of biodegradation are visible or start causing a considerable technical damage to the material; manifestation – symptoms of biodegradation are clearly visible representing a technically significant damage to the material (Wasserbauer, 2000). The concrete deterioration after application of individual bacterial culture on the concrete samples by sulphuretum simulating was studied in our previous works (Harbulakova et al., 2008a,b). The changes of the concrete samples weight, the change of the pH and increased content of calcium and silicon in liquid phase were observed. The penetration of the corrosion is manifested by structural changes of concrete samples. The surface structure changes of corroded specimens can be investigated by many methods. The atomic force microscopy (AFM) can be used to image features with dimensions at the atomic scale up to approximately 100 μm and it reveals the surface topography with direct depth information (Denkhaus et al., 2006).

This paper is focused on the concrete surface structure changes study by microscopy methods.

Materials and methods

Bacteria and grow conditions

In the experiment, sulphate-reducing bacteria (SRB – Fig. 2) genera Desulfovibrio sp. and sulphur-oxidising bacteria (SOB – Fig. 3) genera *Acidithiobacillus* thiooxidans were used. SRB were isolated from the potable mineral water (Gajdovka spring, Košice, Slovakia) using Postgate's medium E and SOB were isolated from the acid mine water (the shaft Pech, Smolník, Slovakia) using the selective nutrient medium S according Waksman´s and Joffe´s by the plate dilution method.

Samples preparation

The original concrete specimens from real conditions were used for experiment. Concrete samples were tested according to the European Standards STN EN 206-1(2004): Concrete. The concrete were assessed on compression strength and categorized as class C 25/30. Concrete samples drilled by diamond apparatus were cut in triangle form with 5 cm in width and 1 cm thickness. Before experiments samples were sterilized in 70% ethanol and dried in an oven at 60ºC to constant weight.

Concrete biocorrosion

Concrete samples were put into reactor (Fig. 4) and inserted into two containers: the first was filled by acid mine drainage (AMD) and the second by distillate water (DV). The reactor was interconnected with the two flasks. One was filled by bacterial cultures SRB for the H_2S production. The second flask was filled by cadmium acetate solution for the H_2S capture. During 90 days concrete samples were every 7 days inoculated by SOB and was realized the change of nutrient medium for SRB cultivation too.

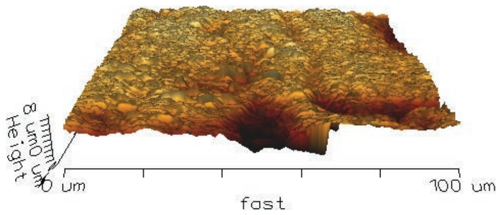

Fig. 6. Surface of concrete sample before experiment
Rys. 6. Powierzchnia próbki betonu przed eksperymentem

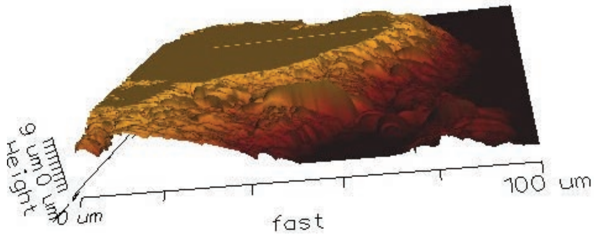

Fig. 7a. AMD immersed part of concrete sample
Rys. 7a. Część próbki betonu zanurzona w kwaśnym odcieku kopalnianym (AMD)

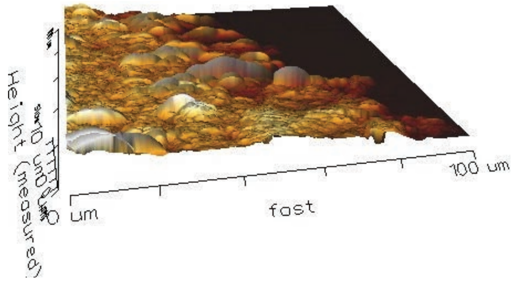

Fig. 7b. AMD not immersed part of concrete sample
Rys. 7b. Część próbki betonu nie zanurzona w kwaśnym odcieku kopalnianym (AMD)

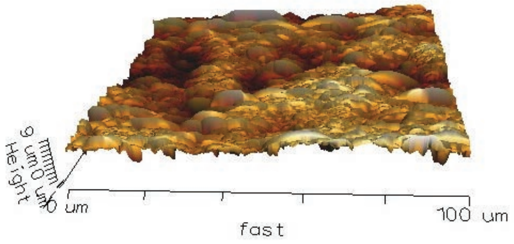

Fig. 8a. Immersed part of concrete sample taken out from DW
Rys. 8a. Zanurzona część próbki betonu pobranej z wody destylowanej (DW)

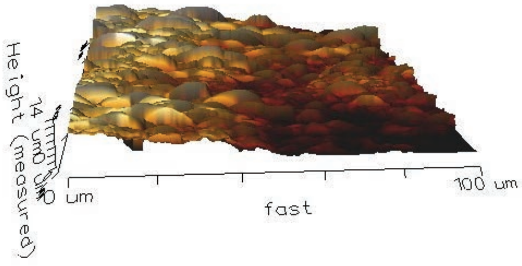

Fig. 8b. Non immersed part of concrete sample taken out from DW
Rys. 8b. Nie zanurzona część próbki betonu pobrana z DW

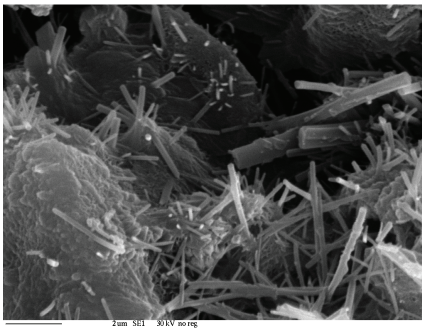

Fig. 9. Image of ettringit crystals precipitated on the concrete sample surface immersed into AMD captured by SEM
Rys. 9. Obraz kryształów etringitu wytrąconych na powierzchni próbki betonu zanurzonej w AMD zarejestrowanej przez SEM

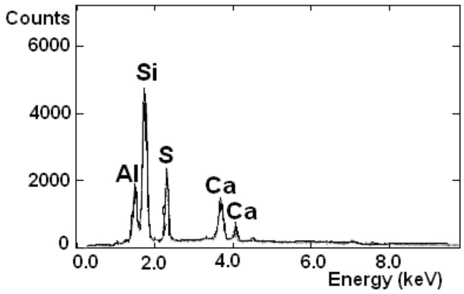

Fig. 10. EDS qualitative ettringite analysis
Rys. 10. Analiza jakościowa EDS etringitu

Methods

The disruption and damages of the concrete surface under sulphuric acid affect were investigated by stereomicroscopy, atomic force microscopy (AFM) and electron microscopy. Mineralogical stereomicroscope STM 723 ZOOM with the combination of digital camera Olympus – C-770 Ultra Zoom was used for upper (not immersed) part concrete samples study because of noticeable changes in structure of concrete. AFM (JPK Instruments, Germany) was used for both (immersed and not immersed) parts of concrete samples investigation. A NanoWizardII contant mode AFM was used to image the surface of concrete samples. For AFM imaging, silicon cantilever CSC 37 B (Micromash Estonia) with force constant 0.3 N/m, resonance frequency 37 Hz was used. Set point was 750 mV. Each AFM image consists of 512 by 512 pixels. The qualitative analyses of precipitates onto samples surface were investigated by scanning electron microscopy and energy depressive spectrometry (EDS) analysis.

Results and discussion

The considerable changes of concrete samples structure were observed by stereomicroscopy. Fig. 5a illustrates a surface of concrete specimen before experiment and Fig. 5b shows the visible surface changes after 90 days sulphuretum simulation.

For detailed study of concrete samples surface changes AFM method was used. In Fig. 6 the surface of concrete sample before experiment is shown. The surface is quite smooth, with the low roughness. After 90 days the both parts (immersed and non immersed) of concrete samples surface were by AFM observed. The differences between surface changes of lower (immersed) and upper (non immersed) parts of concrete samples were observed. The Fig. 7a and 7b represents the image of samples taken from AMD. On both figures is visible that the roughness increased and some aggregates were fallen out of concrete surface. The images of concrete samples surface taken out from deionised water are presented on Fig. 8a and 8b.

During the experiment the pH values of leachate were increasing up 7.03 (AMD) and 7.2 (DI water) because of calcium releasing. Depends on pH the lath-shaped crystals of ettringit ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) were on the surface observed by scanning electron microscopy and energy depressive spectrometry (EDS) analysis as shown on Fig. 9 and 10. The ettringite is secondarily produced under alkaline conditions after exposure to sulphate (Mori et al., 1992).

Conclusion

Experimental studies confirmed that visible changes of concrete samples surface structure were observed. Significant changes were observed mainly for concrete sample inserted in AMD because of sulphuric acid corrosion influence. More considerable structure changes were detected in not immersed part of both concrete samples because of direct microorganism application on the samples surface and absence of appropriate conditions for microorganisms grow (esspecially pH) in the liquid phase.

Crystals participated on concrete surface was identified as ettringite. According to literature (Mori et al., 1992) in range pH > 3 under strong alkaline conditions during hydratation, ettringite is formed in the corroded area.

Acknowledgements

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Wpływ kwasu biogennego na materiały betonowe

Cykl mikrobiologiczny siarki w wywołuje poważne problemy związane z korozją betonu a także dotyczące aspektów zdrowotnych i zapachu. Problemy te związane są przede wszystkim z uwalnianiem wytwarzanego przez bakterie siarkowodoru ze ścieków do atmosfery podczas transportu ścieków, który rozpuszcza się w kondensacie w instalacji kanalizacyjnej. W takim przypadku bakterie utleniające siarkę utleniają rozpuszczony siarkowodór i inne związki siarki do kwasu siarkowego, który powoduje korozję betonu. Beton stopniowo rozszerza się, powodując pęknięcia , utratę wytrzymałości i ogólny rozkład betonu.

Praca koncentruje się na badaniu badania biodegradacji powierzchni próbek betonu. Z punktu widzenia biodeterioracji właściwych materiałów, ważne są bakterie, głównie bakterie utleniające siarkę i siarczki oraz bakterie redukujące siarczany. Rola bakterii wspomnianych powyżej została powiązana z wytwarzaniem biogennego kwasu siarkowego, powodując proces korozji poprzez rozpuszczanie minerałów zawierających wapń z betonowych matryc. Penetracja korozji objawiła się zmianami strukturalnymi próbek betonu. Zmiany struktury powierzchni były badane za pomocą stereomikroskopii i mikroskopii sił atomowych (AFM).

Słowa kluczowe: wytwarzany przez siarkowodór, siarczek, biogenny kwas siarkowy, beton, AFM

Impact of Heavy Metals on Development of Metal Resistance in Soil Microbiota

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Abstract

Heavy metal pollution caused by anthropogenic activity is a great concern of the present days. Widespread use of substances containing metals inevitably lead to their deposition in soil affecting soil microbiota, which plays important role in maintaining soil functions. The aim of our study was to determine number of heavy metal resistant isolates acquired from the soil from heavy metal polluted area of dump near Hnúšťa. Soil samples were obtained from two collection sites (48° 36´ 4,47502´´ N, 19° 57´32,654´´ E and 48° 36´ 4,4634´´ N, 19° 57´ 32,67´´ E) and mixed together. The microorganisms used in this study were routinely cultivated and screened for resistance to different concentrations of four heavy metals – Zn (2–500 mg/l), Cu, Ni, Pb (all three metals tested at concentrations from 0,5 to 125 mg/l). Very high resistance against Cu, Ni and Pb even at the highest tested concentrations was found at majority of tested bacterial strains. Almost all 89 from 89 isolates show resistance against these metals at tested concentrations. Only in case of Zn we determined the MIC (minimal inhibitory concentration) – 125 mg/l. The results point out very high resistance pattern in soil bacteria.

Keywords: heavy metals, soil microbiota, metal resistance

Introduction

Environmental stress could be defined as a physiological response of individuals which can affect their wellbeing and performance. It is a force shaping evolution and adaptation in continuously changing environment and it is a characteristic of both – the stressed and the stressor (Bijlsma, 2005). Environmental stress is considered as a biological response to the physical parameters of the environment. Extrinsic stress that stems from changes in abiotic factors such as climate factors, temperature or chemical components, either man-made or naturally occurring, is regarded as the most important stress agent (Lindgren-Laurila, 2005; Sørensen et al., 2005). Rapidly growing human population causes major changes in the abiotic and biotic environment at a fast rate (Frankham, 2005).

Heavy metal pollution mainly caused by anthropogenic activity is widespread in the environment. Generally, heavy metals play a basic role in physiological and metabolic processes in humans, plants and microorganisms. Metals like Cu, Ni, Zn, Co and Cr act as micronutrients and are necessary in redox processes. The non-essential heavy metals like Cd, Pb, As, Hg or Ag have no biological importance to living organisms and are very toxic when present in the ecosystem (D´Amore et al., 2005). The occurrence of higher concentrations of heavy metals in the environment is a serious health problem due to their non-degradative property which enables them to be persistent in the nature for a long time with a long-term harmful effects on the ecosystem (Singh et al., 2011).

The natural population of soil microbiota is severely affected by the heavy metal pollution which can lead to the loss of bacterial species responsible for nutrient cycling what results in a negative effect on the functioning of the whole ecosystem. There are several soil physicochemical conditions which can strongly influence soil bacterial response to metal pollution. Soil texture, pH, organic matter content or clay content are main factors which affect metal toxicity and bioavailability (Azarbad et al., 2013).

Only a long-lasting exposure to the heavy-metal pollution results in the development of adapted microbial communities that can persist and survive in such habitat (Giller et al., 1998). It is believed that some microorganisms have evolved metal resistance shortly after the life begun because of the exposure to the toxic metals. And some microorganisms are believed to evolve metal resistance as a result of metal pollution exposure over the recent 50 years (Gomathy-Sabarinathan, 2010). To be able to survive under these toxic conditions of the environment, some bacteria have evolved several ways to withstand the potentially lethal conditions (Piotrowska-Seget et al., 2005). The resistance mechanisms developed by microorganisms include efflux pumps, permeability barriers, enzymatic detoxification, intra- and extra- cellular sequestration and reduction (Nies, 1999). Genetic determinants responsible for coding of these mechanisms are found in several bacterial strains. Most of them are plasmid encoded and show tendency to be specific for a particular metal, whereas others are more general and confer resistance to a variegation of metals (Gomathy-Sabarinathan, 2010). However, metal resistance genes and antibiotic resistance genes can be linked together if located on the same mobile genetic element in the cell what means that metal pollution may also sustain antibiotic resistance in microorganisms (Ghosh et al., 2000). The fact, that metal contaminated soil, in comparison to the non-metal contaminated soil, contain higher percentage of antibiotic resistant isolates have led to the conclusion, that metal pollution may play a part in increased bacterial antibiotic resistance through an indirect selection. Agricultural soils amended with metal containing fertilizers are considered a significant pool of antibiotic resistance genes in

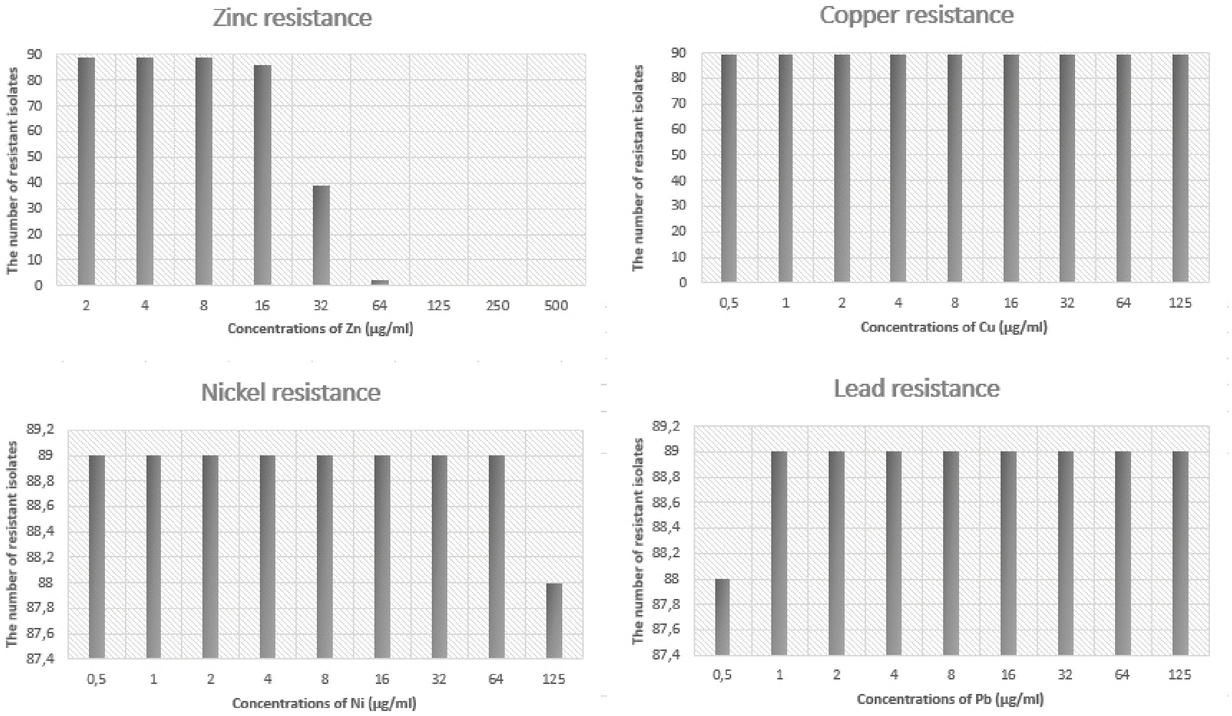

Fig. 1. The number of resistant isolates against zinc; copper; nickel; lead

Rys. 1. Liczba odpornych izolatów przeciwko cynkowi; miedzi; niklu; ołowiowi

the environment and a potential source of antibiotic resistance in bacterial pathogens infecting humans and animals (Alonso et al., 2001; Berg et al., 2005). Accordingly, accumulation of antibiotic resistance genes in soils and their assumed linkage to the metal resistance genes in soil microbiota are of concern. Hence, the main objective of this study was to determine the number of metal resistant bacterial isolates isolated from the metal contaminated soil of dump.

Materials and methods

Two soil samples (approx. 100g) were collected from the top layer (0–10 cm) at two collection sites located near the area of Hnúšťa (SK) (48° 36´ 4,47502´´ N, 19° 57´32,654´´ E and 48° 36´ 4,4634´´ N, 19° 57´ 32,67´´ E). In these sites, high concentrations of heavy metals have been accumulated for decades due to the mining activity. Both soil samples were mixed together thoroughly. 1g of the soil was suspended in 10ml PBS-T and intensively shaken for 30 minutes. Then, 50µl of serial 10-fold dilutions of soil suspensions were plated onto the TSA (Tryptic Soy Agar) agar plates which were cultivated at 25°C for 48 hours to determine CFU (colony forming units). Colonies of bacteria used for later metal resistance testing were selected based on their variable phenotype on TSA agar. Metal resistance testing of bacterial isolates obtained from the primary isolation was performed on MH (Mueller-Hinton) agar using the dilution method with the addition of metals- Zn, Cu, Ni, Pb. The metals were added to the medium in the form of water stock solution of their salts in an appropriate amount to the achievement of final concentrations of metal ions in the medium. The metal concentrations were as follows: Zn (2–500 mg/l), Cu, Ni, Pb (all three metals tested at concentrations from 0,5 to 125 mg/l). The plates were incubated at 25°C for 48 hours and then the growth of bacterial isolates was evaluated.

Results and discussion

In our experiment, we determined the number of bacterial CFU in metal contaminated soil after the 48 hours incubation of isolates of the primary isolation – 3.02x107. The count is approximately in accordance with the findings of Berg et al. (2005), who set CFU value of contaminated soil on 1.5x106 CFU. Based on the different phenotype of our colonies, we selected 89 bacterial colonies from these isolates to examine their metal resistance to heavy metals at variable concentrations.

All bacterial isolates exhibited very high resistance pattern (Figure 1) even at the highest concentrations of Ni, Cu and Pb- nearly all of them were resistant to all concentrations of these three metals, what is in accordance with the findings of Joshi (2013) who performed an experiment with the metal contaminated soil of industrial waste. Bacterial isolates obtained from this soil showed maximum tolerance to metals tested (Pb, Zn, Ni, Cu and others).

In our experiment, only the isolates growing on the medium amended with elevated concentration of Zn (concentration 125 mg/l and higher) showed sensitivity to this heavy metal. It could be caused by the fact, that some elements, like Zn, provide micronutrition for biochemical reactions as enzyme co-factors thus are essential for the cell (Bernier- Surette, 2013). In addition to this, Bernier and Surette (2013) also claimed, that bacterial responses to metals are concentration dependent- at higher concentrations they become toxic what can lead to cellular stress responses or even cell death. This statement was confirmed by our experiment in the case of Zn. In the case of other three metals tested, concentrations which were used in our research, was not high enough to demonstrate this tendency.

According to Spain and Alm (2003) zinc displays comparatively less toxic effect on bacterial cells in comparison with other heavy metals what is not in accordance with our results, because in our experiment zinc showed toxicity to bacteria at concentration 125 mg/l, whereas others heavy metals tested were not toxic to microorganisms even at higher concentrations.

However, there is one interesting fact, that all our isolates were of multi-resistant phenotype- to some extent they exhibited resistance against all four metals tested. All of the isolates were resistant to copper at all of its concentrations tested; 88/89 isolates showed resistance to nickel and lead at all of their concentrations tested, but resistance to zinc at different concentrations was variable- it ranged from 2 to 125µg Zn/ml.

Conclusion

The results proved very high resistance pattern in microorganisms isolated from contaminated soil of dump. Bacteria exposed to high concentrations of heavy metals in their natural habitat were forced to develop resistance mechanisms maintaining their fitness even under the stressful conditions of the environment. The widespread presence of metal resistance mechanisms is of concern because of the linkage between metal resistance genes and antibiotic resistance genes, what makes this issue interesting also from the medical point of view. Linkage and subsequent interspecific co-transfer these two groups of genes via the horizontal transport could become a serious health problem which can cause difficulties with the therapy of bacterial diseases in human.

Acknowledgements

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Wpływ metali ciężkich na rozwój odporności na zawartość metali w mikroflorze w glebie

Zanieczyszczenie metalami ciężkimi wywołane działalnością antropogeniczną jest wielkim problemem współczesności. Powszechne stosowanie substancji zawierających metale nieuchronnie prowadzi do ich odkładania się w glebie co wpływa na mikroflorę glebową, która odgrywa ważną rolę w utrzymywaniu funkcji gleby. Celem badań było określenie liczby izolatów odpornych na metale ciężkie pozyskanych z gleby z zanieczyszczonego obszaru składowiska metali ciężkich w pobliżu Hnúšťa. Próbki gleby pobrano z dwóch miejsc (48° 36' 4,47502'' N, 19° 57'32,654'' E i 48° 36' 4,4634''bN, 19° 57'32,67'' E) i wymieszano razem. Mikroorganizmy wykorzystane w tym badaniu były rutynowo hodowane i badane pod kątem odporności na różne stężenia czterech metali ciężkich: Zn (2–500 mg/l), Cu, Ni, Pb (wszystkie trzy badane metale w stężeniach od 0,5 do 125 mg/l). Bardzo wysoką odporność na Cu, Ni i Pb nawet przy najwyższych testowanych stężeniach stwierdzono w większości badanych szczepów bakteryjnych. Prawie wszystkie z 89 izolatów wykazują odporność na te metale w testowanych stężeniach. Tylko w przypadku Zn określiliśmy MIC (minimalne stężenie hamujące) = 125 mg/l. Wyniki wskazują na bardzo wysoki wzór oporności w bakteriach glebowych.

Słowa kluczowe: metale ciężkie, mikroflora gleby, odporność na zawartość metali

Study of Mechanisms Used by Algae to Decrease The Silver Toxicity in Aquatic Environment

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Abstract

In the study SEM, EDS, TEM and UV-vis analysis were used to investigate the biosorption, bioaccumulation and bioprecipitation/ bioreduction of silver by freshwater green alga Parachlorella kessleri *and to shed light on the reasons of biological silver nanoparticle production. When dead biomass of* P. kessleri *was used for silver removal, majority of silver (75%) was removed within 2 min. Biosorption was probably the main mechanisms responsible for Ag+ ions removal from aqueous solutions. However, when behaviour of living biomass in the presence of silver ions was studied, the decrease of silver concentration was slower (68% within 24 hours) with subsequent increase of silver concentration in the solution and extracellular formation of silver nanoparticles. The formed AgNPs exhibited a lower toxicity against tested organisms. Algal cells probably used the formation of nanoparticles combined with rapid biosorption as detoxification mechanisms against silver toxicity. Bioaccumulation inside the cells played only a minor role in the detoxification process.*

Keywords: silver, nanoparticle, detoxification, alga

Introduction

Although silver has a great reputation for its use in jewellery and coins, its primary use is industrial. Majority of silver, about 35% is used in electrical applications. Except of utilization in industry followed by utilization in jewellery and coins, silver is used in many various fields (Deschatre et al., 2015). However, nowadays we can see increasing utilization of silver in the form of silver nanoparticles because of their unique characteristics resulting in their application in various technologies such as solar energy absorption, catalyses of chemical reaction, surface enhancement Raman spectroscopy (SERS), biosensors, and many others. Silver's antibacterial qualities have applications that reach far beyond the medical world. Washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners all rely upon silver nanoparticles to sterilize up to 650 types of bacteria (Cantuaria et al., 2014). The total silver physical demand stood at about 33 thousand tons in 2014 and its supply was by 4.9% lower. Silver is known to be released to the environment through its industrial applications (Das 2010). Annually a minimum of 150 tons of produced silver enters the aquatic environment (Salunkhe et al., 2011).

Ionic silver is known as highly toxic to aquatic organisms, however recent studies have shown that the nano form of silver is more toxic and can cause damage in new ways. Even if the nanoparticle itself is not especially toxic, it increases the effectiveness of delivering silver ions to locations where they can cause toxicity (Fabrega et al., 2011). In the present time, considerable amount of nanosilver is used in various commercial products despite the fact that only very little is known about the environmental effects of their widespread use. On the other hand there is increasing amount of evidence that different organisms, their extracts or even exhausted cultivation media can be used for nanoparticles production. So it is visible that probably large group of biological molecules can be responsible for the silver reduction and nanoparticle formation. What means that organisms have already met with nanoparticles and they probably own mechanisms leading to nanoparticle toxicity elimination. So the aim of our work was to contribute to the study of silver nanoparticles fate in the environment and mechanisms which allow aquatic organisms to cope with the toxicity of silver ions. We have investigated three basic mechanisms – biosorption, bioaccumulation and bioreduction and their contribution to the silver removal or transformation in the presence of freshwater alga *Parachlorella kessleri*. These algae are commonly present in various aquatic environments so it is very probable that they have met with the silver ions and can be the part of biochemical routes resulting in its detoxification in the environment. We have compared the range of silver biosorption, bioaccumulation and bioprecipitation and their contribution to silver removal from environment and studied the differences in the toxicity of Ag+ ions and AgNP produced by algae so we would be able to contribute to the understanding of reasons of massive silver nanoparticle production in the biological environment.

As it is known biosorption is a process independent of metabolism, fast and reversible. Its mechanisms are generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface. Biosorption is mostly described in non-living cells however it can take place in living cells being the first, fast and reversible adsorption step operating within a much slower and complex overall bioaccumulation mechanism (Fomina, Gadd, 2014). Bioaccumulation is a process of intracellular metal accumulation taking part mostly in living organisms and depends on a variety of physical, chemical and biological mechanisms. It is slow process dependent on cell metabolism (Chojnacka, 2010, Kadukova, 2016). Bioprecipitation can

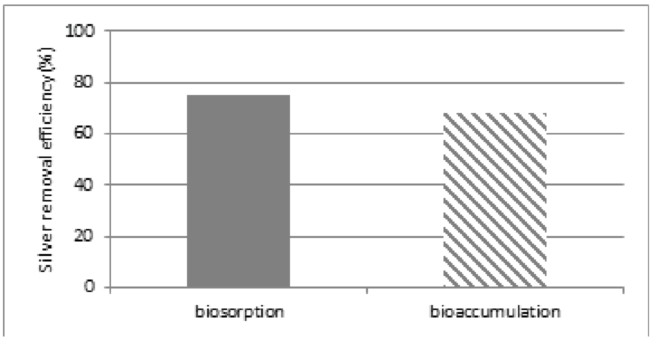

Fig. 1. Efficiency of silver removal by non-living (biosorption) and living (bioaccumulation) biomass of *P. kessleri*
Rys. 1. Efektywność usuwania srebra przez nieżywą (biosorpcję) i żywą (bioakumulację) biomasę P. kessleri

take place as metabolisms independent as well as metabolism dependent process resulting in production of precipitates in the cell environment or on the cell surface (Gadd, 2009).

Materials and methods

Biosorption experiments were performed using the same procedure as in previous studies with *P. kessleri* (Kadukova and Vircikova, 2005, Kadukova, 2016). Dried algal biomass (2 g/L) was placed in contact with $AgNO_3$ solution (80 mg/L) at room temperature and stirred magnetically for kinetic experiments. Equilibrium studies were conducted with initial silver concentrations in the range 5–850 mg/L. The pH values of solutions were adjusted to 5.0 (optimum value) by adding 0.1 M H_2SO_4 and 0.1 M NaOH solutions as appropriate. Three replicates were used in the study for both kinetic and equilibrium studies.

Samples were withdrawn at pre-determined time intervals (0, 2, 4, 6, 8, 10, 30, 60, 90, 120, 240, 480 and 1440 min, 2 and 4 days) for kinetic experiments and after 24 h for equilibrium experiments. The pH and redox potential were measured at the time of sample withdrawal using a GRYF 208L pH metre. Removed liquid samples were filtered through a membrane filter to determine the metal concentration using atomic absorption spectroscopy (Perkin Elmer model 3100 spectrophotometer). Sorption capacity q (mg/g) was calculated using the general equation which can be found elsewhere.

Bioaccumulation experiments were carried out similarly just living biomass of *P. kessleri* obtained after biomass filtration and consequent washing was used in the experiment. The volume of silver solution was adjusted so that the final cell concentration corresponded to 2 g/L of dry biomass. Solutions with the same concentrations as in the biosorption experiments were used for equilibrium studies and with the concentration 40 mg/L for kinetic studies. The amount of Ag accumulated by *P. kessleri* was calculated on a dry weight basis following the equation used for calculation of metal uptake by biosorption. To determine nanoparticle production UV–vis spectra of samples were recorded using an UNICAM UV4 UV/vis, dual beam spectrophotometer from 200 to 800 nm, operating at a resolution of 1 nm with quartz cells. As blanks, deionised water was used.

Results and discussion

The differences in silver ions biosorption and bioaccumulation are visible in the Fig. 1. When dead algal biomass was used 75% of silver was sorbed onto its surface within only 2 minutes. But in the presence of living cells the process was different. After addition of living biomass, the silver concentration showed an initial rapid decrease and remained roughly constant up to 24 h. A total decrease of silver concentration by 68% was observed. However, after 24 h the silver concentration in solution gradually increased up to 14 days. At the same time silver nanoparticles were produced in the solution. However, during the biosorption study reduction of silver into nanoparticles was not observed (Kadukova, 2016).

According to our previous studies (Kadukova et al., 2015, Kadukova, 2016) silver nanoparticles produced by alga *Parachlorella kessleri* were found to be less toxic not only for alga itself but also for other tested organisms in comparison with ionic silver. Thus, it is possible that nanoparticle production can be a part of detoxifying mechanism that alleviates the silver ion toxicity. The process of silver detoxification can take part in two steps:

1. The rapid binding of silver ions to the living algal biomass shortly after the biomass addition can be attributed to a metabolism-independent passive adsorption to the functional groups located on the cell surface
2. It is followed by active reduction either on the cell surface or in the solution later on.

The majority of silver taken up by the biomass was released back into solution. Although a gradual increase of total silver concentration was measured, the concentration of free silver ions remained constant for the whole process, suggesting that silver released back into solution was not only desorbed but probably reduced into metallic form (Kadukova, 2016).

According to the results, probably only a very small part of the silver ions (about 2%) was accumulated inside the cells. The majority (almost 50%) of the silver was reduced and nanoparticles were formed. Approximately 30% of silver ions remained in the solution.

Since the mechanism of biological nanoparticle synthesis has not yet been fully understood, there are many different hypotheses for their production. In the presence of algae it is probable that the huge amount of hydroxyl groups in the algal cell wall act as reductors of silver cations forming, in consequence, carbonyl groups. Following equation can be suggested to describe the process:

$$Ag^+ + R - OH \rightarrow Ag^0 + R = O + H^+ \quad (1)$$

Conclusion

It is known that silver is very toxic for microorganisms including algae. Although silver is easily precipitated in the environment there is still a portion that can be sequestered by organisms and transformed into silver nanoparticles. In our study we have found that in the presence of living algal cells silver ions were probably sequestered on the algal surface and gradually transformed into nanoparticles which are according to preliminary tests less toxic to algal cells in comparison with ionic silver and so production of silver nanoparticles can represent the detoxication mechanisms decreasing the silver toxicity in the environment. However, in the presence of non-living biomass silver was rapidly taken up by the biomass and remained sorbed onto algal surface without its transformation onto silver nanoparticles.

Acknowledgements

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Badanie mechanizmów stosowanych przez glony w celu zmniejszenia toksyczności srebra w środowisku wodnym

W badaniu wykorzystano analizę SEM, EDS, TEM i UV-vis do zbadania biosorpcji, bioakumulacji i bioprecypitacji/bioredukcji srebra przez słodkowodną zieloną algę Parachlorella kessleri *i rzucenia światła na przyczyny biologicznej produkcji nanocząstek srebra. Gdy do usunięcia srebra użyto martwej biomasy* P. kessleri*, większość srebra (75%) usunięto w ciągu 2 minut. Biosorpcja była prawdopodobnie głównym mechanizmem odpowiedzialnym za usuwanie jonów Ag+ z roztworów wodnych. Jednakże, gdy badano zachowanie żywej biomasy w obecności jonów srebra, spadek stężenia srebra był wolniejszy (68% w ciągu 24 godzin) z późniejszym wzrostem stężenia srebra w roztworze i zewnątrzkomórkowym tworzeniem nanocząstek srebra. Utworzone AgNP wykazywały mniejszą toksyczność wobec badanych organizmów. Komórki glonów prawdopodobnie wykorzystywały tworzenie nanocząstek połączonych z szybką biosorpcją jako mechanizmów detoksykacji przeciwko toksyczności srebra. Bioakumulacja wewnątrz komórek odgrywała tylko niewielką rolę w procesie detoksykacji.*

Słowa kluczowe: srebro, nanocząstka, detoksykacja, alga

The Experimental Estimation of The Elastic Modulus of a Fly Ash Based Trackbed Layer Under Cyclic Loading

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Abstract

In a railway track structure system, trackbed layers are designed to compensate for insufficient bearing capacity and/or water or frost resistance of natural soil. These, so called, 'capping layers' can be constructed from raw materials like sand or gravel or from industrial materials like asphalt or concrete. However, more environmentally and cost friendly alternatives have been studied in recent years. Fly-ash represents one such promising material and a trial section of a main line track with the capping layer made from a fly-ash-based mixture was constructed in Czech Republic in 2005. The performance of the capping layer in the section has been measured since. In this paper, results of the laboratory estimation of the elastic modulus under cyclic traffic-like induced loading are presented for the most recent group of samples. The results show that the elastic limit of the fly-ash-based material lies well above the stresses induced by railway traffic and that its behaviour is stable under the cyclic loading. This suggests that the mechanical properties of the material may not be determinative for the design of the layer and that the feasibility factors may take precedent. This in turn suggests that either the design strength of the material or the designed thickness of the layer may be possibly reduced.

Keywords: fly-ash stabilizer, trackbed, cyclic loading, elastic limit, elastic modulus

Introduction

A railway track structure is a system designed to provide vertical and horizontal support for passing railway vehicles. To this end, it utilises multiple elements but ultimately the whole system is built upon natural soil. When this soil is too weak to support the track structure or when the soil is susceptible to the ingress of water and/or freezing caused by low temperatures a special layer (called 'capping layer') needs to be designed atop of the natural soil (called 'subgrade') to protect it. This layer can be designed from raw materials, e.g., sand, gravel aggregate, or from industrial materials, e.g., asphalt, concrete. However, in recent years more cost and environmentally friendly alternatives have been studied. Fly ash, a by product of thermal power generation, represents one of the materials under focus. In the Czech Republic as soon as 2005 Lidmila (2005) studied feasibility of using fly ash material (pulverised fuel ash) for railway capping layers. His work culminated in designing and building of a trial section on a main railway line near Smiřice station. In the section, the fly-ash stabilizer capping layer was designed to protect subgrade bedrock consisting of clay limestone (weathered marlite), which is highly susceptible to frost. The trial section was finished in April 2005 and since then biannual measurements have taken place to investigate the behaviour of the track in real conditions. The investigation has consisted of in-situ Plate Load Tests and sample collection for further laboratory testing. First ten years of the research are described in Lidmila & Lojda (2015), Lojda et al. (2015) and Lojda et al. (2017).

Initially, the research focused on rheological changes of the material, e.g., changes in compressive strength, reference density or water content. However, recently the aim of the research has been expanded to investigate the behaviour of the material under dynamic traffic-resembled loading. This paper presents the results of the laboratory investigation into the dynamic behaviour of the fly-ash based material sampled from the capping layer of the trial section. The methodology of the experiment is discussed briefly and results for the first cohort of samples from year 2016 are presented.

Methodology

The aim of the research was to study the behaviour of the fly-ash material from the capping layer under dynamic traffic-resembled loading. A laboratory investigation to be performed on samples collected from the capping layer of the trial section was designed for the task. The samples were collected using core drilling technique, details of which can be found in Lidmila & Lojda (2015). Multiple samples were collected in Autumn 2016 with seven samples selected for the laboratory dynamic testing.

The testing apparatus consisted of a loading frame Inova Praha ZUZ 200 1350 with hydraulic actuator. The vertical deformation of the samples was measured by means of three absolute LVDT sensors of displacement Ahlborn FWA025T. The sensors were fixed to the sample using two metal rings in accordance with ČSN EN 13286-43. Ahlborn Almemo 2690-8A data logger was used for the experiment. The photo of the testing apparatus can be found on Figure 1.

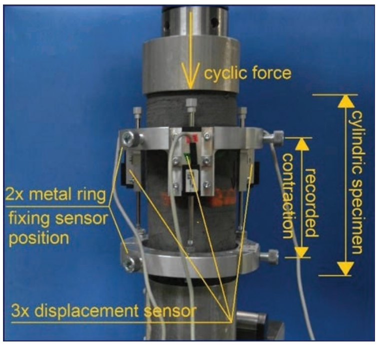

Fig. 1. Testing apparatus
Rys. 1. Aparatura badawcza

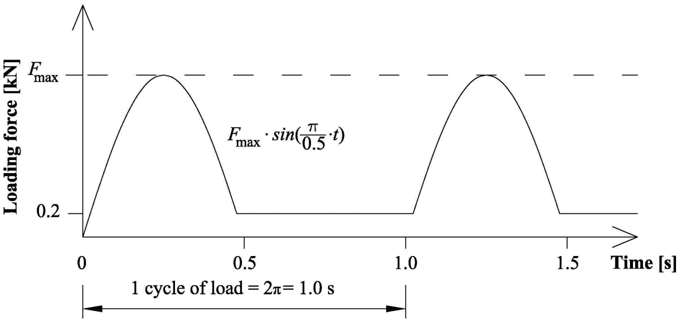

Fig. 2. Illustration of loading function (Lojda, Lidmila, Pýcha 2017)
Rys. 2. Ilustracja funkcji budowania (Lojda, Lidmila, Pýcha 2017)

Because no standard exists in the Czech Republic for testing of trackbed materials under dynamic traffic-resembled loading, a specific loading function was designed for the experiment. The design of the loading function followed recommendations provided in BS EN 13286-7 as closely as reasonably practicable while taking into consideration the limits of the testing apparatus. Hence, the loading function consisted of 0.5 s long loading impulse half-sine in shape followed by 0.5 s of null loading (see Figure 2). This function represented one cycle of loading. The complete loading of the sample then consisted of 500 cycles, applied in five steps, each step with different maximum applied force of 3 kN, 6 kN, 9 kN, 12 kN and 15 kN respectively. Details of the methodology can be found in Lojda et al. (2017).

For the discussion of the results, it is important to mention how the samples were treated with regards to their respective moisture contents. All samples were collected using the same technique as described above but their consequent treatment was different. Samples P3-2 and P3-3 were sealed in plastic containers immediately after drilling, preventing them from a loss of any moisture during transport and storage. The samples were taken out of the containers only immediately before the dynamic testing. Hence the moisture content of the samples P3-2 and P3-3 is expected to have been the natural moisture content of the capping layer material increased by some unknown amount of water which the samples likely absorbed during drilling. Samples P3-5, P3-6 and P3-8 were let to dry naturally in air until the changes in their mass stabilised. Finally, samples P2-1 and P2-2 were first dried in an oven and then re moisturised to achieve a water content of 35-40%, i.e., the natural water content of the fly-ash material in the capping layer. Aim of this artificial moisturising was to create samples with a moisture content close enough to that of the capping layer material as exists in situ, i.e., without the negative effect of the water ingress caused by the core drilling technique.

Results and Discussion

During the experiment, the applied force and the resulting deformation of the samples were recorded. This enabled to calculate the applied stresses and corresponding strains in the samples and to plot hysteresis loops for every sample and every step of loading, as shown on figures below. This form was chosen because hysteresis loops indicate the behaviour of the material under investigation, i.e., its linearity or nonlinearity, damping properties and ratchetting or shakedown behaviour.

Results for samples P3-2 and P3-3, which were both taken from the same measuring location on the trial section (profile P3) and which were prevented from drying, are presented on Figure 3. Results for samples P3 5, P3 6 and P3 8, taken from the same profile as samples P3 2 and P3 3 but allowed to dry naturally, are presented on Figure 4. Finally, results for samples P2 1 and P2 2, taken from different profile (P2) and artificially moisturised, are presented on Figure 5.

First, it can be seen that the results for sample P3-2 (Figure 3a) and sample P2 2 (Figure 5b) are invalid. The sample P3-2 seems to exhibit negative permanent strains in the fifth step of loading.

This was caused by the loosening of the screws fixing the two steel rings onto the sample during the fifth step of the loading. Hence, results for the fifth step of loading for sample P3 2 should not be considered valid because of the error in the apparatus. On the other hand, results of the sample P2 2 represent invalid results caused by a non homogeneity in the

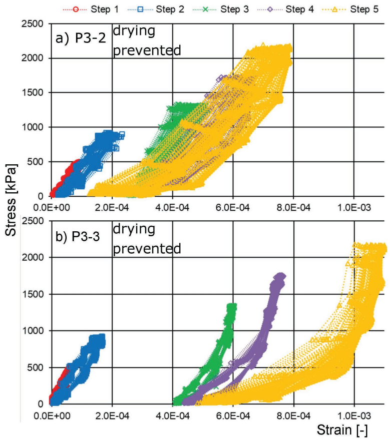

Fig. 3. Hysteresis loops for samples with prevented drying; a) sample P3-2, b) sample P3-3
Rys. 3. Pętle histerezy dla próbek z zapobieganiem suszeniu; a) próbka P3-2, b) próbka P3-3

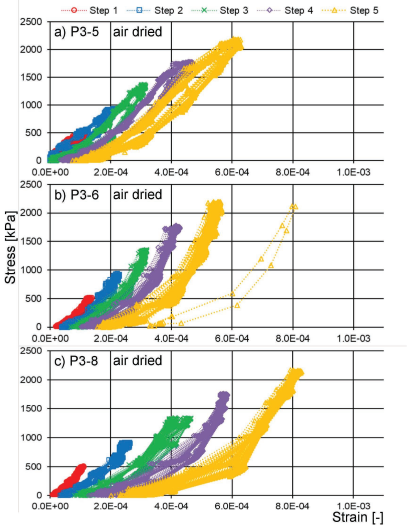

Fig. 4. Hysteresis loops for samples allowed to dry naturally; a) sample P3 5, b) sample P3 6, c) sample P3 8
Rys. 4. Pętle histerezy dla próbek pozostawionych do naturalnego wyschnięcia; a) próbka P3 5, b) próbka P3 6, c) próbka P3 8

material. It can be seen from Figure 5b that the sample exhibits extremely large strains even under low load. This was caused by a layer of slag formed across the whole diameter of the sample. The sample reached its strength limits during the fifth step of loading and collapsed. Hence, the results for sample P2 2 cannot be considered representative as well.

It can be seen from the remaining figures that the results are remarkably consistent across all samples, regardless of the moisture content. All samples exhibit close to purely elastic behaviour for the first two steps of loading, i.e., up to the loading of 1000 kPa, and then start to behave non linearly with hysteresis loops gaining typical convex shape (Pýcha 2016). However, it does not seem that loading limits were reached as all samples seem to exhibit shakedown behaviour even for the last step of the loading.

From the maximum applied stress and the maximum corresponding elastic strain it was possible to calculate elastic modulus E in every cycle of the loading. The results are summarised in Table 1, with n/v indicating that the results for a given sample and step of loading are not valid (see explanation above). The arrows represent changes in the values of elastic moduli in given cycles. It can be seen that for the first two steps the value of the elastic modulus either keeps constant or changes only slightly, which corresponds well with the assumption of a linear behaviour. For the other three steps, the value of the modulus increases significantly with the number of loading cycle in each step. This corresponds well with the assumption of shakedown behaviour. However, for the last three steps the elastic modulus does not have significant physical meaning because of the convex shape of the hysteresis loops and the non linear behaviour.

The average values of the elastic modulus are approximately 7000 MPa for samples with high water content and approximately 5500 MPa for samples with low water content, which corresponds well with the values obtained in the previous investigations with Impulse Excitation Method and Ultrasonic Method (Lidmila, Lojda 2015).

Conclusions

This paper presented research into the behaviour of fly ash based trackbed material under dynamic traffic resembled loading. During the investigation, laboratory testing of samples collected from a trial railway track section with a capping layer made of fly ash material was performed.

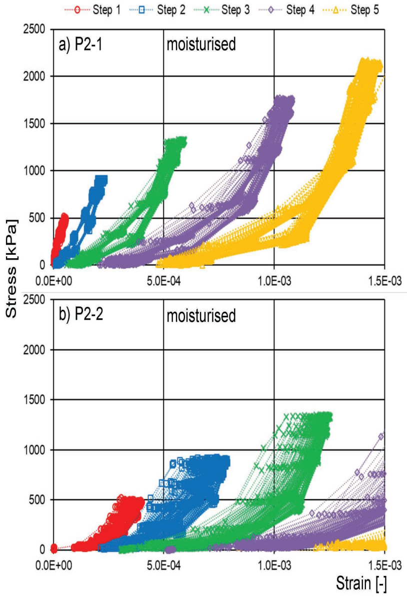

Fig. 5. Hysteresis loops for samples artificially moisturised; a) sample P2 1, b) sample P2 2
Rys. 5. Pętle histerezy dla próbek sztucznie nawilżonych; a) próbka P2 1, b) próbka P2 2

Tab. 1. Summary of elastic moduli in each loading step for different samples
Tab. 1. Podsumowanie modułów sprężystości w każdym etapie budowy dla różnych próbek

Sample	Water content	Elastic modulus of a sample *E* in a step in [MPa]				
		1	2	3	4	5
P3-2	Drying prevented	6500	6500→5500	n/v	n/v	n/v
P3-3	Drying prevented	8000	7000→6000	8000	6000→7000	4000→4500
Average		**7250**	**6750→5750**	-	-	-
P3-5	Air dried	5000→4500	4500	5000	5000	4500→5000
P3-5	Air dried	5000→6000	6000→7000	7000	7000	6500→7000
P3-8	Air dried	6000→7000	4500→5500	4000→5000	4000→5000	4000→5000
Average		**5300→5800**	**5000→5600**	n/a	n/a	n/a
P2-1	Moisturised	10,000	4500→5500	3000→3500	2000→3000	2000→3000
P2-2	Moisturised	n/v	n/v	n/v	n/v	n/v

The results shown that the material behaves linearly up to the load of 1000 kPa and non linearly with shakedown behaviour above that value. Hence, 1000 kPa can be considered the elastic limit of the fly ash trackbed material studied in this research (see Lojda et al, 2017, for details about the mixture used). This value was valid across samples with various moisture content. The value of 1000 kPa is significantly higher than most stresses induced in trackbed at the capping layer level below sleepers for even the highest train speeds. Hence, this suggests that the mechanical properties of the material are sufficient and that other properties, e.g., feasibility of construction, chemical consistency, economic factors, may take precedent during the design of a capping layer from the fly ash based material.

Acknowledgements

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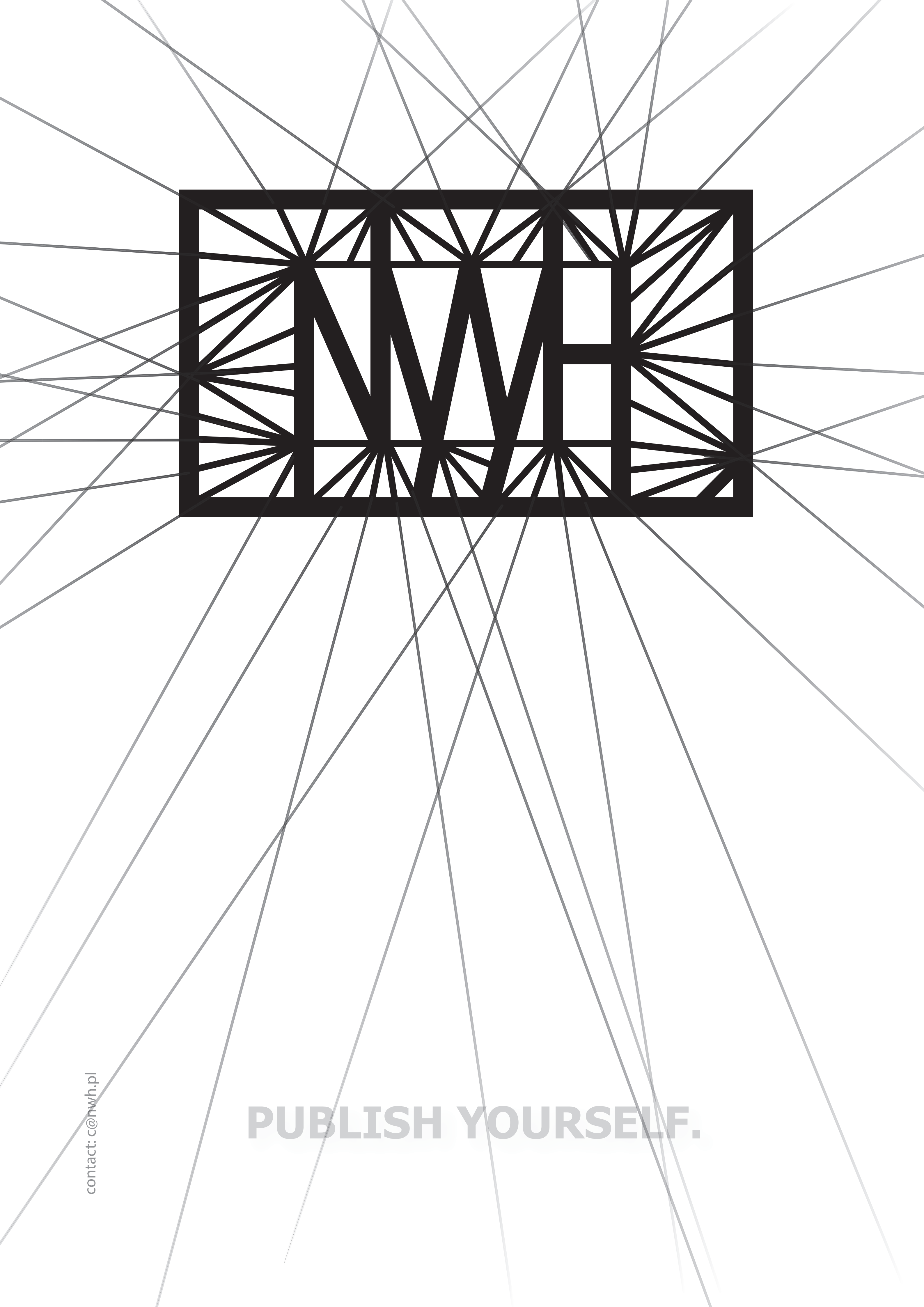
Eksperymentalna ocena sprężystego modułu warstwy nośnej na bazie popiołu lotnego w obszarze obciążenia cyklicznego

W systemie konstrukcji torów kolejowych warstwy nośne są zaprojektowane tak, aby kompensować niedostateczną nośność i/lub odporność na wodę lub mróz naturalnej gleby. Te tzw. warstwy zamykające mogą być zbudowane z surowców takich jak piasek lub żwir lub z materiałów przemysłowych, takich jak asfalt lub beton. W ostatnich latach badano alternatywy bardziej przyjazne dla środowiska i kosztów. Popiół lotny stanowi jeden z takich obiecujących materiałów, badania w Czechach prowadzono od 2005 r. Wykonano próbny odcinek głównego toru linii kolejowej z warstwą przykrywającą wykonaną z mieszanki na bazie popiołu lotnego. Wydajność warstwy przykrywającej w przekroju została zmierzona. W niniejszej pracy przedstawiono wyniki laboratoryjnej oceny modułu sprężystości przy obciążeniu indukowanym podobnym do ruchu cyklicznego dla najnowszej grupy próbek. Wyniki pokazują, że granica sprężystości materiału na bazie popiołu lotnego leży znacznie powyżej naprężeń wywołanych ruchem kolejowym i że jego zachowanie jest stabilne pod obciążeniem cyklicznym. Sugeruje to, że właściwości mechaniczne materiału mogą nie być decydujące dla konstrukcji warstwy i że materiał może być zastosowany. To z kolei sugeruje, że można albo zmniejszyć wytrzymałość projektową materiału, albo zaprojektowaną grubość warstwy.

Słowa kluczowe: stabilizator na bazie popiołu lotnego, warstwa nośna, obciążenie cykliczne, granica sprężystości, moduł sprężystości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Studies on Physicochemical Properties of Selected Apiproducts as Materials for Preparation of Protein Spheres

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Abstract

The main purpose of this work was to determine the impact of the location of bee apiaries in different parts of Poland on the physicochemical properties of selected bee honeys. Studies focused on the determination of the antioxidant properties of apiproducts. The water content in honeys as well as their pH values were also analyzed. Four types of honeys (honeydew, linden, buckwheat, acacia) originating from various parts of Poland were selected for the research. Based on the obtained results, it can be stated that the examined honeys differed in physicochemical properties, which was related to the differences in their chemical composition. All honeys tested showed antioxidant properties. It can also be found that the water content in analyzed products was related to their origin and variety. Analyzing pH measurements, it can also be observed that all tested samples were characterized by acidic properties.

Keywords: bee honey, antioxidant activity, DPPH, UV-VIS spectroscopy

Introduction

Currently, development of new drug carriers is observed. However, apart from efficiency of such drug systems it is also important to create such carriers that after release of drug will degrade into non-toxic substances that will not have a negative impact on environment. The toxic remains of applied carriers can be released during its degradation and can induce a cytotoxic effect. Therefore, a main objective of the presented research is to create an innovative carriers based on proteins derived from apiary products. Such a carrier will be modified using active substances such as anticancer drug. This solution will also affect the improvement of cancer treatment.

According to data from the National Cancer Registry over the past three decades, the number of cancer cases has doubled. Therefore scientists are looking for solutions that will improve the effectiveness of cancer treatment. In the standard methods of administering cancer drugs, their therapeutic possibilities are not fully exploited. Additionally, traditional methods of treatment often cause undesirable side effects. Moreover, in traditional treatment, the healing substance affects the entire body, and only a small part of it goes to the place affected by the disease or inflammation. Therefore intensive research conducted by scientists on the improvement of treatment methods led to the formation of carriers with specific properties. Due to the need of preparation of new, more effective drug delivery systems, the main objective of the research involves the development of innovative drug carriers based on proteins derived from apiary products. Such a carrier is characterized by a better ability to bind and release the drug compared to other carriers, degrades after fulfilling its role and is not toxic to the patient. Preparation of carriers has a low energy demand. There is no need of use of toxic reagents and any waste are not generated. Therefore two main advantages will be achieved: eco-friendly process of preparation as well as biodegradability of prepared carriers that don't affect adversely on the environment. The development of technology for the preparation of drug carriers based on proteins derived from apiary products is characterized by a high application potential.

Bee honeys from various parts of Poland and from various manufacturers constitute the research material for formation the above-mentioned carriers. The preliminary analysis of the physico-chemical properties of this material is necessary to select the appropriate honey for isolation of the protein fractions from it and to prepare polymer carriers. In this paper, description and analysis of the results of research works on selected bee honeys is resented. The following analyzes were conducted: refractometric determination of water content in selected apiproducts on the example of mel, analysis of the impact of honey type and its origin on water content, determination of honey antioxidative properties by spectroscopic technique using a DPPH radical (2.2 - diphenyl-1-picrylhydrazyl) and pH measurements of selected bee honeys over several weeks to check the impact of geographic origin and type of honey on pH values. During the measurements, the influence of the storage time of honeys on their pH values was also determined.

Materials and methods

In order to compare properties of selected apiproducts four types of honeys deriving from different parts of Poland were selected. Their type and origin is summarized in Table 1.

All chemicals applied in the research were at least of analytical reagent grade. DPPH and methanol were supplied by Sigma Aldrich.

Tab. 1. Types of analyzed honeys

Tab. 1. Rodzaje analizowanych miodów

Manufacturer	Region of Poland	Type of honey
Kosecki	North	Honeydew Acacia Buckwheat Linden
Gładys	Center	
Kószka	South	
Dutkowiak	West	

Tab. 2. Measurements of water content in honeys from the Kosecki company

Tab. 2. Pomiary zawartości wody w miodzie firmy Kosecki

Type of honey	Water content [%]		
	Measurement I	Measurement II	Measurement III
Honeydew	18.6	17.1	17.2
Buckwheat	19.5	18.1	17.9
Linden	18.5	17.3	17.2
Acacia	16.9	16.0	15.9

Tab. 3. Measurements of water content in honeys from the Gładys company

Tab. 3. Pomiary zawartości wody w miodzie firmy Gładys

Type of honey	Water content [%]		
	Measurement I	Measurement II	Measurement III
Honeydew	15.8	15.8	15.9
Buckwheat	18.1	18.2	19.0
Linden	17.8	17.9	18.2
Acacia	17.2	17.1	17.0

Tab. 4. Measurements of water content in honeys from the Dutkowiak company

Tab. 4. Pomiary zawartości wody w miodzie firmy Dutkowiak

Type of honey	Water content [%]		
	Measurement I	Measurement II	Measurement III
Honeydew	17.4	17.1	17.0
Buckwheat	18.4	18.4	18.5
Linden	18.1	18.0	18.3
Acacia	17.1	17.0	16.5

Tab. 5. Measurements of water content in honeys from the Kószka company

Tab. 5. Pomiary zawartości wody w miodzie firmy Kószka

Type of honey	Water content [%]		
	Measurement I	Measurement II	Measurement III
Honeydew	17.2	17.2	18.1
Buckwheat	17.8	17.7	18.2
Lindem	17.4	17.6	18.1
Acacia	17.9	17.8	18.6

Refractometric analysis of water content

The RHN1-ATC refractometer was used in the research. Before proceeding to the proper analysis of the water content, the device was calibrated using a calibration solution. Then, sample of analyzed honey was placed between two prisms and the refractometer was set towards daylight. After stabilization of the dividing line, the water content was read from the scale. Three measurements were conducted for each type of honey at 3-week intervals.

Analysis of pH values

The Multifunction meter CX - 701 multifunction apparatus was used for analysis. A sample of honey was placed in a clean container, and then the electrode of the device was immersed in it. Three measurements were made at 4-week intervals.

Analysis of antioxidant properties

During the study, analysis by means of the DPPH (1,1-diphenyl-2-picrylhydrazyl) radical in the form of an alcoholic solution was applied. The solution is characterized by a dark violet color with a maximum absorbance at a wavelength λ = 517 nm. The reaction scheme is peresented above.

In reaction with an antioxidant, DPPH captures electrons, forms a reduced form, and converts to a slightly yellow prod-

Tab. 6. Results of pH measurements for honeys from Kosecki

Tab. 6. Wyniki pomiarów pH dla miodów od Koseckiego

Type of honey	**pH value**		
	Measurement I	**Measurement II**	**Measurement III**
Honeydew	4.769	4.756	4.547
Buckwheat	3.866	3.873	3.595
Linden	4.090	4.094	3.724
Acacia	4.968	4.574	3.724

Tab. 7. Measurements of water content in honeys from the Kosecki company

Tab. 7. Pomiary zawartości wody w miodzie firmy Kosecki

Type of honey	**pH value**		
	Measurement I	**Measurement II**	**Measurement III**
Honeydew	4.989	4.967	4.715
Buchwheat	4.014	3.832	3.540
Linden	4.415	4.282	3.910
Acacia	4.681	4.424	4.042

Tab. 8. Measurements of water content in honeys from the Gładys company

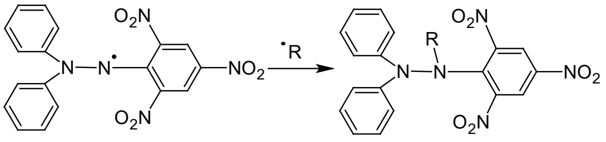
Tab. 8. Pomiary zawartości wody w miodzie firmy Gładys

Type of honey	**pH value**		
	Measurement I	**Measurement II**	**Measurement III**
Honeydew	4.606	4.615	4.600
Buckwheat	3.612	3.743	3.521
Linden	3.828	3.973	3.745
Acacia	4.692	3.690	3.941

Tab. 9. Results of pH measurements for honeys from Kószka

Tab . 9. Wyniki pomiarów pH dla miodów z Kószka

Type of honey	**pH value**		
	Measurement I	**Measurement II**	**Measurement III**
Honeydew	4.556	4.630	4.621
Buckwheat	3.863	3.692	3.725
Linden	3.925	4.080	3.950
Acacia	3.600	3.645	3.695



uct. These changes were monitored spectrophotometrically using a Biosens Spectrophotometer V-5100.

Results and discussion

Refractometric analysis of water content

Results of measurements of water content in honeys deriving from different parts of Poland are presented in Tables 2.–5. Three measurements at 3-week intervals were performed for each sample.

The percentage of water content in the tested honey samples ranges from 15.8% to 19.5%. The highest value was recorded for buckwheat honey from Kosecki, while the least amount of water contained honeydew honey from Gładys. The average water content in all honey was 17.6%. According to the Ordinance of the Minister of Agriculture and Rural Development, which specifies the requirements for the commercial quality of honey, the water content in nectar honey may not exceed 20%. For all tested samples, values below 20% were obtained.

In the case of honeys deriving from Dutkowiak, Kosecki and Gładys, the percentage of water varies depending on the variety of the tested honey. These differences are influenced by many factors, including a different source of floral nectar and the origin of honeys from different regions of the country, and thus other climatic conditions prevailing during the harvest. This dependence was not observed in case of honeys deriving from Kószka - similar values were obtained for each of the four types of honeys. However, honeys produced from the nectar of different flower species are characterized by different composition, therefore it is unlikely that such results were obtained. It can therefore be assumed that the original water content in these honeys exceeded certain norms and

Tab. 10. Antioxidant activity of analyzed honeys
Tab. 10. Aktywność przeciwutleniająca analizowanych miodów

Absorbance of control sample	Absorbance of tested sample	Manufacturer of analyzed honey	Type of honey	Antioxidant activity (A) [%]
0.6745	0.5452	Dutkowiak	Acacia	19.17
	0.5282	Gładys		21.69
	0.5868	Kosecki		13.00
	0.6454	Kószka		4.31
	0.3844	Dutkowiak	Buckwheat	43.01
	0.4848	Gładys		28.12
	0.3325	Kosecki		50.70
	0.5955	Kószka		11.71
	0.4793	Dutkowiak	Linden	28.94
	0.5212	Gładys		22.73
	0.4385	Kosecki		34.99
	0.5503	Kószka		18.41
	0.2144	Dutkowiak	Honeydew	68.21
	0.4361	Gładys		35.34
	0.3027	Kosecki		55.12
	0.4387	Kószka		34.96

it was intentionally changed to the value consistent with the regulation.

The water content for all honey changed over time. Differences were small, and way of sampling of honeys for testing could affect the change in the water content of the tested samples, because honey is characterized by hygroscopic properties, therefore in the case of exposure to the environment, some water could evaporate when the air was dry or absorbed in the case of space with high humidity. Such compounds as fructose (main sugar components of honey) present in honey are responsible for these properties. The fructose content depends on the honey variety, which affects different hygroscopic properties of the tested samples.

Measurements of pH values of analyzed honeys

Results of measurements of pH values of all analyzed honeys are presented below. Three measurements were carried out at 4-week intervals.

The pH values of the analyzed honeys are in the range from 3.521 to 4.989. It can therefore be concluded that all tested honey samples exhibit acidic properties. The lowest pH value was recorded for buckwheat honey from Dutkowiak, while the highest one was measured in case of honeydew honey from Gładys. The low pH of honey is mainly due to the presence of organic acids such as citric, gluconic and formic in analyzed honeys.

According to the obtained pH results, the lowest values were observed in case of the group of buckwheat honeys. All four samples, regardless of the manufacturer, were characterized by the lowest pH and thus the highest content of above-mentioned acids. This is probably related to the chemical composition of nectar obtained from buckwheat. On other hand, the highest pH values were recorded for honeydew honeys, while intermediate values for acacia and linden honeys. In the case of the majority of tested honeys, the decrease of the pH values over time was observed. The increasing acid reaction may result from the biochemical processes taking place in the product. The most important one is the process of oxidation of glucose (1) present in honey, proceeding in accordance with the following reaction:

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow C_6H_{12}O_7 + H_2O_2 \quad (1)$$

This process is related to the activity of the enzyme - glucose oxidase, which oxidizes glucose to the gluconic acid and H2O2. As a result of the reaction gluconic acid is formed, thus an increase in the amount of acids in the honey is observed, and therefore its lower pH value. As a result of a fact that honeys of different types originating from different parts of Poland are characterized by different enzymatic activity, differences in the dependence of pH decrease on storage time can be observed.

Analysis of antioxidant activity

Values of antioxidant activities of analyzed honeys were calculated using the following formula:

$$A = \frac{A_k - A_b}{A_k} \times 100\%$$

where:
A – antioxidant activity,
A_k – absorbance of control sample,
A_b – absorbance of analyzed sample.

The following measurement results were used for the calculations, taking into account the maximum absorbance value of the control sample and the test sample (measurement after 2 h and 15 min from the beginning of the reaction). The table below presents the calculated values of antioxidant activity.

Antioxidative activity of analyzed honeys ranged from 3.14% to 68.21%. The greatest efficiency of free radicals scavenging was determined for honeydew honey from Dutkowiak, while the smallest value was noted for the acacia honey from the Kószka company.

The obtained results can be analyzed in two ways - due to the producer and taking into account different varieties of honeys. In the first case, the best results were obtained for honeys from Dutkowiak, while the worst for honeys from Kószka, for which the antioxidant activity of any tested honey did not exceed 35%. The different properties of honeys from various producers are probably related to the various method of honey production and its storage. The origin of honey, that is the location of the apiary, is also important. Dutkowiak honey, which showed greater antioxidant capacity, came from the western part of Poland, whereas honey from Kószka from the south of the country.

Considering the different varieties of honeys, honeydew honeys proved to be the best in terms of antioxidant activity. Acacia honeys were characterized by the smallest values, in this group the maximum activity was 21%, while in the honeydew group it was 68%. Honeydew, buckwheat, linden and acacia honeys differ in their chemical composition, and thus have a different content of phenolic compounds and enzymes responsible for antioxidant properties.

Conclusion

Based on the conducted studies it can be concluded that the location of bee apiaries affects the physicochemical properties of selected varietal honeys, since the same variety of honey originating from different parts of the country in some cases has significantly different properties. Honey of different varieties are characterized by different physicochemical properties, i.e. different water content, different pH values and different antioxidant activity. The water content for all tested honeys meets the requirements relating to the commercial quality of honey, as the pH values of the tested honeys are in the range from 3.521 to 4.989.

Summing up the above conclusions, it can be concluded that the physicochemical properties of honey depend on both their variety, and hence the source of the floral nectar, on the producer and associated apiary location as well as on the method of production and storage of the apiproduct. Such material can certainly be used for the preparation of protein spheres, which in the current growth of medicine may give a broader look at the aspect of anti-cancer therapy. The fact of the properties of such carriers, depending on the proteins isolated from a given variety of honey, also seems to be very interesting.

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Badania właściwości fizykochemicznych wybranych pszczelich produktów ubocznych jako materiałów do wytwarzania sfer białkowych

Głównym celem tej pracy było określenie wpływu lokalizacji pasiek pszczelich w różnych częściach Polski na właściwości fizykochemiczne wybranych miodów pszczelich. Badania koncentrowały się na określeniu właściwości przeciwutleniających produktów api (pszczelich) . Analizowano również zawartość wody w miodzie, a także ich wartości pH. Do badań wybrano cztery rodzaje miodów (spadziowy, lipowy, gryczany, akacjowy) pochodzące z różnych regionów Polski. Na podstawie uzyskanych wyników można stwierdzić, że wytwarzane miody różniły się właściwościami fizykochemicznymi, co było związane z różnicami w ich składzie chemicznym. Wszystkie badane miody wykazały właściwości przeciwutleniające. Można również stwierdzić, że zawartość wody w analizowanych produktach była związana z ich pochodzeniem i odmianą. Analizując pomiary pH, można również zauważyć, że wszystkie badane próbki charakteryzowały się właściwościami kwasowymi.

Słowa kluczowe: miód pszczeli, aktywność antyoksydacyjna, DPPH, spektroskopia UV-VIS

Distribution of Antimony and Gold in Old Tailings and Heaps at the Milešov Locality (Příbram District)

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Abstract

Antimony ores were extracted and processed near the village of Milešov (Příbram district) for about twenty years in the second half of the 19th century. Large heaps and a small sludge pond were left behind after this period. In 1988, this locality was inspected and sampled in order to gather information about residual resources of gold and antimony. The original archive data from this survey were now studied again and interpreted using modern statistical and geostatistical methods. The interpolations methods chosen for this purpose were inverse distance weighting (IDW), simple kriging and geostatistical sequential Gaussian simulation (SGS). These procedures allowed for a much more accurate determination of the spatial distribution of the elements or substances studied. The results showed significantly higher volumes and a more accurate localization of the studied elements in both bodies (heap and tailings). This procedure can be considered as the basis of a new methodology for the assessment of similar objects.

Keywords: geostatistical methods, digital model, antimony ore mining, mining waste

Introduction

In the second half of the 19th century antimony ores were mined in the northern part of Milešov village, district of Příbram (Figure 1).

After the extraction and processing of ores, there left large heaps (Figure 2) and smaller sludge pond, which are almost untouched since the end of the operation.

In 1988, a detailed sampling was carried out and a final report with the calculation of the residual Au and Sb resources was finalised up (Mandík, 1988). All analyses and survey data are still available in archives.

At the end of the 20th century there was a worldwide increase in the consumption of mineral resources. The response to this trend has been the initiative "The Raw Material Initiative - Meeting our critical needs for growth and jobs in Europe", which defined a strategy for the future use of mineral resources. One of the pillars was also the recommendation to use secondary sources, represented by materials from the heaps and tailing ponds. The Task Force at the European Commission in June 2010 drafted the report "Critical raw materials for the EU", which included a list of so-called critical raw materials, including antimony (Sb), which was the main mined component at Milešov locality.

These facts led to try to re-interpret the original archive data using statistical and geostatistical methods.

Digital modeling of monitored elements spatial distribution

Modern statistical and geostatistical methods allowe to determine the spatial distribution of studied elements or substances with much greater accuracy. The first step in creating digital models of geological bodies is the processing of a digital terrain model. As a basis for the creation of the spatial model data from the 5th Generation Digital Model Relief (DMR 5G) of Czech Office for Surveying, Mapping and Cadastre (ČÚZK) was used. Consequently were created grids of heaps and tailing pond.

The reconstruction of the original surface at the site from the time of the exploration works was also solved. It has been shown that there is insufficient data in the available documentation to determine the morphology of the terrain at the time of sampling. Therefore, the current LIDAR data situation was taken into account for the creation of the model of these two bodies, knowing that in some places the terrain situation may have varied a little, but any differences would not have a significant impact on the results achieved.

A very important step was the consistent verification and correction of the input data. A number of incorrect data was found in the primary input data set from period of 1988 and it was necessary to edit them. The changes in data were mainly related to the unification of the reported values for the analysed elements (g, % and ppm), the correction of the coordinates of the exploration works and the addition of the Z (altitude) coordinates for all exploration work. From these data, a surface grid of the both bodies (heap and sludge pond) was created. The scope (delimitation) of both bodies was derived from the real situation in the field and from the location of the individual exploration work.

The corrected and completed input data was divided into 10 cm sections using the macro. The values of the technological parameters (contents) were located at the center of each section. For a heap it was total of 2028 sections and for sludge pond it was total of 822 sections. Such data has become the basis for their further treatment, i.e. data choices for creating horizontal and vertical cuts, statistical analysis, girding and visualization in 2D and 3D.

Fig. 1. Situation of the Milešov locality (top of the red arrow) in the map section (https://mapy.cz)
Rys. 1. Mapa sytuacyjna miejscowości Milešov (u góry czerwonej strzałki) w części mapy (https://mapy.cz)

Fig. 2. Front view at heaps from southwest
Rys. 2. Widok z przodu na hałdach z południowego zachodu

The process of statistical treatment and geostatistical structural analysis followed. The basic statistical processing of the technological parameters was performed in the Stanford Geostatistical Modeling Software (SGeMS). Due to different file formats, a special macro was created to convert input data into the SGeMS environment. Thus, histograms (graphical presentation of the data distribution using a column graph, where the height of the columns represent the frequency of the monitored quantity within a given interval) of Sb and Au for the heap and tailings were created. Further, a geostatistical structural analysis of the input data was carried out, describing the continuity, homogeneity, stationarity and anisotropy of the studied field. The above-mentioned SGeMS program was used to create experimental variogram (a discrete function calculated using a measure of variability between pairs of points at various distances) and selected theoretical variogram. The resulting variograms were used for the method of block kriging and geostatistical simulations.

Applied interpolation methods

Inverse Distance Weighting (IDW)

This method assumes that the value of the studied variable at the selected (random) point is statistically dependent on the values measured in its surroundings (Staněk, 2005). The effect of these surrounding values on the interpolated value decreases with the distance. Because of scarce sampling density, a relatively small amount of input data was available. The parameters for an ellipsoid of anisotropy and data selection was chosen 50 m in the X axis direction, 50 m in the Y axis direction and 2 m in the Z axis direction. Into the studied area was projected a regular grid and then 3D grids for Sb values and Au values, both limited by the surface. For this projection was used the Math module in the Voxler environment (http://www.goldensoftware.com/products/voxler).

In some parts of the heap there have also generated significant extrapolations due to the considerable extent of the ellipsoid and it may not necessarily correspond to reality. In the statistical comparison of the Sb and Au input values distribution and the values calculated for the 3D grid, the histograms show differences. The reason is low input data density and the limitation of both bodies by the terrain surface.

Ordinary Kriging (OK)

This spatial estimation method is based on the prerequisite of a zero mean value of the difference between the real and the estimated value of the monitored variable and minimal scattering of this difference. It gives the most accurate estimate of the mean value at a given domain, but unlike the input values, the scattering of the calculated values is minimal and calculated values are considerably smoothed (Remy et al., 2009).

The distribution of the input data for Sb and Au were considerably skew for both objects, so the transformation of the input data into the normal (Gaussian) distribution had to occur during the modeling process. Subsequently, the transformation of the calculated values of the blocks (3D grids) into the original distribution was performed. An ellipsoid of anisotropy and data selection with 50*50*2 m parameters was selected for this variant. The Sb and Au spatial grids were generated in the SGeMS environment and their geometry parameters were the same as for the IDW method.

For interpolation, it was necessary to create Sb and Au variograms for normal distribution of input data. Subsequently, the 3D grids Sb and Au were limited by the terrain surface.

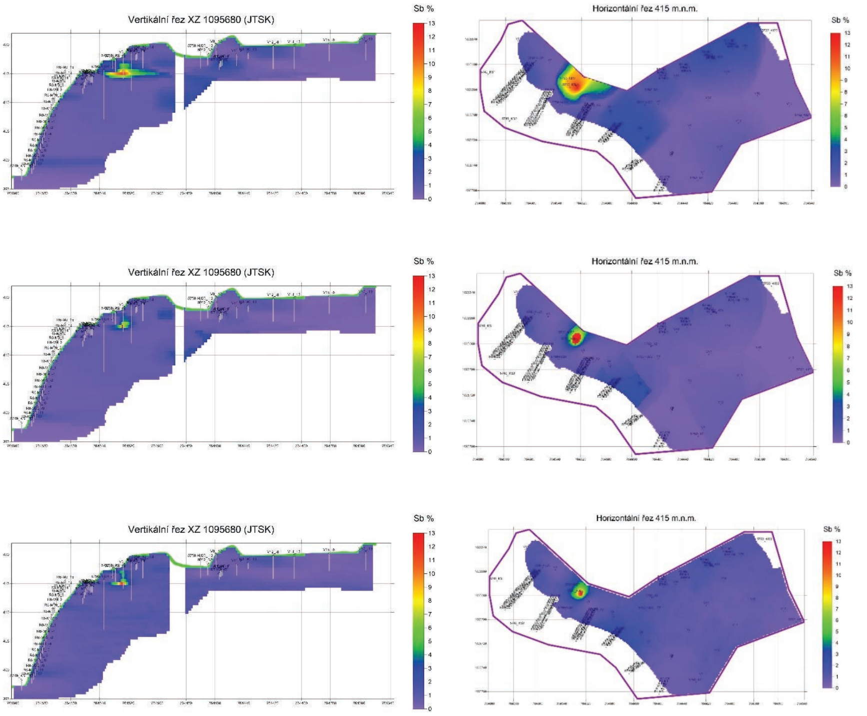

Fig. 3. Comparison of Sb distribution in vertical plane by chosen IDW, Kriging (OK) and SGSIM methods (on the left from top to bottom) and comparison of Sb distribution in horizontal plane by chosen IDW, Kriging (OK) and SGSIM methods (on the right from top to bottom)

Rys. 3. Porównanie rozkładu Sb w płaszczyźnie pionowej według wybranych metod IDW, Kriging (OK) i SGSIM (po lewej od góry do dołu) i porównanie rozkładu Sb w płaszczyźnie poziomej przez wybrane metody IDW, Kriging (OK) i SGSIM (po prawej od góry do dołu)

These grids of the monitored elements were converted to SGeMS, where a subsequent transformation of the calculated values of the blocks (3D grids) into the original distribution was done. The spatial 3D Sb and Au grids in the original distribution were converted by macros to be visualized in various ways.

Comparing the histograms of the distribution of the input and calculated Sb and Au values in the 3D grid we can observe the differences for all the monitored elements. This is caused again by the limitation of studied bodies by the surface terrain and due to low density of input data.

Sequential Gaussian Simulation (SGSIM)

SGSIM belongs to stochastic geostatistic methods. It allows calculating the values of a regionalized variable in the studied domain in that way, that the simulated values at the known measurement points (data sampling) exactly match the originally detected values (Goovaerts1 1997; Soares, 2001). In addition, the generated values have the same statistical distribution and the same variogram as the input values. Unlike kriging, the distribution of the input values coincides to the calculated values. Each of these implementations provides an equally probable possibility of unknown regionalized variable presentation.

For this variant, the same ellipsoid of anisotropy and data selection was chosen as in the previous method, i.e. 50*50*2 m. The same ware the variograms of the Sb and Au input data in the normal (Gaussian) distribution and the input parameters of 3D grid geometry was also the same.

For each element (Sb and Au) a hundred realizations were created, from which the mean value of blocks (E-type) was calculated. To convert data between different environments, special macros were created in Visual Basic for Applications. The spatial 3D grids Sb and Au in the original distribution were limited by the surface of the terrain and subsequently visualized in various ways.

Also in this case comparing the histograms of the distribution of the input values and the calculated values both of two elements shows very distinct differences. The reason is again a small density of input data and the limitation of both bodies by the terrain surface.

Comparison of achieved results

In the 1988 survey a total of 7 blocks were defined at this locality and reserves of Au and Sb were calculated as a cut method. In current mathematical models, spatial distribution of element contents is determined using 3D grids formed by regular blocks (segments). The number of segments varies with each of the used methods and depends on the selected parameters. The size of each block was 1 m * 1 m * 0.5 m and the volume of one block was 0.5 m^3. For digital processing and visualization of distributed elements, special software was developed for the use of Voxler (http://www.goldensoftware.com/products/voxler) and Surfer (http://www.goldensoftware.com/products/surfer) products by Golden Software (). The Voxler environment allows creation of different types of the input data visualization. The results of the Sb distribution within the heap in vertical plane (XZ 1095680) are shown in Figure 3 on the left and horizontal plane (415 m above sea level) are shown in Figure 3 on the right. We can see distinctly how differentially each method interprets the detected Sb anomalies.

The elements content estimation for each variant of the used models was calculated by the newly created program in

Tab. 1. Comparison of Au and Sb contents by particular methods
Tab. 1. Porównanie zawartości Au i Sb według poszczególnych metod

Used method	Au (kg)	Sb (t)
Vertical cuts (1988)	60,694	446,890
Inverse Distance Weighting	475,609	2523,444
Ordinary Kriging	397,933	2107,551
Sequential Gaussian Simulation	375,283	2491,144

Visual Basic. All the founded values of Au and Sb are shown in the Table 1 and they are compared with the results calculated by the cut method in 1988.

Although the same input data se was used, the amount of Au and Sb calculated by current geostatistical methods is significantly higher than the data obtained in 1988 by the cut method. For gold, the increase is almost seven times and the results of SGSIM and kriging are relatively close. For antimony, the increase is more than five times higher. Here, on the other hand, the most similar results are from the SGSIM and IDW methods.

Conclusion

This article presents the new concept for visualization of the monitored elements, their distribution and estimations of their content in the defined bodies. In this case, methods of Inverse Distance Weighting, Ordinary Kriging and Sequential Gaussian Simulation were used.

These results were compared to each other and to the data of the previous calculation made by the cut method. The volumes of studied elements were found to be almost six times higher than those calculated in 1988. The most realistic models are based on SGSIM, which is also the most modern method that eliminates some IDW and kriging negatives. However, if new exploration works could be done in greater density, more suitable localization and a wider range of analyses, the results would be much more accurate.

Calculations, visualization and creation of digital models have been applied to secondary anthropogenic objects, but can be also applied to primary geological bodies with natural deposition and distribution of elements.

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Rozkład zawartości antymonu i złota w starych osadnikach i hałdach w miejscowości Milešov (powiat Příbram)

Rudy antymonu były wydobywane i przetwarzane w pobliżu wioski Milešov (powiat Příbram) przez około dwadzieścia lat w drugiej połowie XIX wieku. Po tym okresie pozostały duże hałdy i mały staw osadowy. W 1988 r. miejscowość została poddana inspekcji i próbkowaniu w celu zebrania informacji o pozostałościach złota i antymonu. Oryginalne dane archiwalne z tego badania zostały teraz ponownie przeanalizowane i zinterpretowane przy użyciu nowoczesnych metod statystycznych i geostatystycznych. Metody interpolacji wybrane do tego celu to odwrotne ważenie odległości (IDW), prosty kriging i sekwencyjna geostatystyczna symulacja Gaussa (SGS). Procedury te pozwoliły na znacznie dokładniejsze określenie rozkładu przestrzennego badanych pierwiastków lub substancji. Wyniki pokazały znacznie wyższe objętości i dokładniejszą lokalizację badanych pierwiastkach w obu lokalizacjach (hałda i składowisko odpadów). Procedurę tę można uznać za podstawę nowej metodologii oceny podobnych obiektów.

Słowa kluczowe: metody geostatystyczne, model cyfrowy, wydobycie rud antymonu, odpady górnicze

Mechanochemical Reduction of Synthetic Sulphidic Copper-Bearing Minerals in an Industrial Scale

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Abstract

In this paper the mechanochemical reduction of binary sulphides chalcocite (Cu2S) and covellite (CuS) by elemental iron were investigated. The composition and properties of nano-powders prepared by high-energy milling were analyzed by X-ray diffraction, X-ray photoelectron spectroscopy and magnetic measurements. The XRD results showed that in case of chalcocite Cu2S the reaction takes place until 360 minutes, as no elemental iron, could be identified afterwards. In case of covellite CuS, after 480 minutes of mechanochemical reduction, a significant amount of non-reacted elemental iron could still be observed. The investigation of magnetic properties reveals significant decrease of saturation magnetization as a result of milling. XPS results showed a significant surface oxidation in both systems. Unlike the conventional high-temperature reduction of chalcocite and covellite, the mechanochemical reduction is fast and ambient temperature and atmospheric pressure are sufficient for its propagation.

Keywords: mechanochemistry, mechanochemical reduction, high-energy milling, sulphides

Introduction

Mechanochemical processing by high-energy milling is an innovative procedure that improves the efficiency of mineral processing via several factors, most importantly due to the formation of new surfaces and the creation of lattice defects (Tkáčová 1989, Baláž 2000a,b). In a typical technological process, the solid raw materials are transformed by liquid and/or gas phase reactions at high temperatures and pressures. The final products are then separated from the by-products, from the remaining starting materials and/or from the solvent. Very often, the final product is solid again (Boldyrev, 1998; Boldyrev and Tkáčová, 2000). Mechanochemical processing offers the possibility to simplify the entire technological process by avoiding operations in the gaseous and liquid states and to design the process according to the flowchart (Boldyrev, 1996a,b):

raw materials → solid state reaction → desired product

Among copper sulphides, covellite, CuS and chalcocite, Cu_2S are the most common. They are binary compounds of copper which contain the highest amount of copper from sulphide copper bearing minerals (Howard 1979, Goel 2014). Covellite (CuS) has wide range applications in photocatalysis, solar cells, sensors and as a cathode material in lithium chargeable batteries, etc. while, chalcocite (Cu_2S) is a p-type semiconductor having a band gap of 1.21 eV which is compatible for solar energy conversion, it can be used in solar cells, photocatalysts, biosensors and optoelectronic devices (Salavati-Niasari 2013, Yang 2014, Farhadi 2016, Sabah 2016, Cuevas 2016, Wu 2008, Zheng 2017). In addition to their unique properties, traditionally they are sources of copper in ores for metallurgical operations (Baláž 2002).

In this work, the processes of mechanochemical reduction of chalcocite and covellite with elemental iron at industrial scale conditions according to reactions (1, 2) were studied

$$Cu_2S + Fe \rightarrow 2Cu + FeS \qquad (1)$$

$$CuS + Fe \rightarrow Cu + FeS \qquad (2)$$

The aim of this paper is to illustrate effectiveness of so-called process of mechanochemical reduction in an industrial scale using industrial eccentric vibration mill (Fig.1) on example of two binary sulphides with elemental iron which led to production of nanocomposite Cu/FeS as an only product. Big advantage of using an industrial eccentric vibration milling in comparison to laboratory high energy milling is in the possibility of scaling-up the reduction and synthesis.

Materials and methods

Materials

For mechanochemical synthesis of covellite and chacocite copper (99% Merck, Germany) and sulfur (99% CG-Chemikalien, Germany) powders were used as elemental precursors. For mechanochemical reduction, mechanochemically synthesized copper sulphide covellite CuS (JCPDS 00-006-0464) or chalcocite Cu2S (JCPDS 72-1071) and elemental iron Fe (99% Winlab, Germany) were used as precursors. Iron was used as a reduction reagent.

Mechanochemical synthesis and reduction

Mechanochemical solid state reductions were performed in an industrial eccentric vibratory ball mill ESM 656−0.5 ks (Siebtechnik, Germany) working under the following conditions: 5 L steel satellite milling chamber attached to the main corpus of the mill, tungsten carbide balls with a diameter of 35

Fig. 1. Eccentric vibratory mill with attached closed satellite (left), open satellite filled with balls (right) (Baláž 2018)

Rys. 1. Mimośrodowy młyn wibracyjny z dołączonym zamkniętym satelitą (po lewej), otwarty satelita wypełniony kulkami (po prawej) (Baláž 2018)

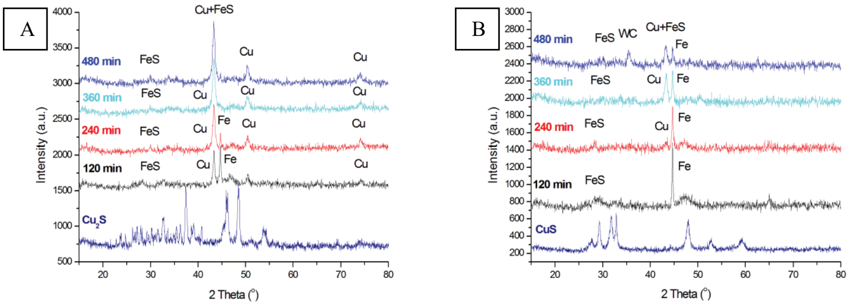

Fig. 2. XRD patterns recorded during mechanochemical reaction of covellite (Cu_2S) (A) and chalcocite (CuS) (B) with iron powder. The XRD patterns of starting Cu_2S and CuS are also provided.

Rys. 2.Widma XRD zarejestrowane podczas reakcji mechano-chemicznej kowelinu (Cu2S) (A) i chalkozynu (CuS) (B) z proszkiem żelaza. Przedstawiono również widma XRD stanu początkowego Cu_2S i CuS.

mm with a total mass of 30 kg, 80% ball filling, amplitude of the mill = 20 mm, rotational speed of the eccenter = 960 min^{-1}, argon atmosphere, 100 g of feed. The milling was performed for various times (t_M). In the case of mechanochemical synthesis of CuS and Cu_2S precursors, milling for 40 and 60 min, respectively, has been applied. In case of mechanochemical reduction of chalcocite Cu_2S and covellite CuS according to reactions (1) and (2), respectively, t_M 480 min has been applied. The amounts of corresponding sulphide and iron were calculated with respect to the stoichiometries of equations (1) and (2).

Characterization techniques

X-ray diffractometry (XRD)

The identification of phase composition was performed by XRD method with an X'Pert PW 3040 MPD diffractometer (Phillips, Germany) and D8 Advance diffractometer (Bruker Germany), both working in the 2θ geometry with Cu K_α (40kV, 40 mA) radiation.

Mass magnetization measurement

In order to obtain information on magnetic properties of the studied samples, mass magnetization was measured. The measurements were performed by using vibrating sample magnetometer (VSM) installed on a cryogen free superconducting magnet (Cryogenic Limited). The samples were measured in powder form packed in a specialized capsule. After the measurements, the magnetic moment values were divided by the sample mass, yielding the mass magnetization.

Photoelectron spectroscopy (XPS)

XPS measurements of samples were performed using XPS instrument SPECS equipped with PHOIBOS 100 SCD and non-monochromatic X-ray source. The survey surface spectrum was measured at 70 eV transition energy and core spectra at 20 eV at room temperature. All spectra were acquired at a basic pressure of 1 x 10^{-8} mbar with AlKα excitation at 10 kV (200 W). The data were analyzed by SpecsLab2 CasaXPS software (Casa Software Ltd). The spectrometer was calibrated against silver (Ag 3d). All samples showed variable degrees of charging due to their insulating nature. The problem was resolved by the calibration on carbon.

Results and discussion

In Fig. 2 A and B, XRD patterns of two systems (Cu_2S+Fe) and (CuS+Fe) are shown, respectively. In both cases the main peak corresponding to copper is overlapping with the troilite one. Therefore, the progress of the reaction can be traced mainly by observing the decrease of the intensity of main iron peak located at 2θ ~ 44°. For Cu_2S+Fe system, iron peak is no longer visible after tM 360 min, suggesting the completion of the reaction. However, for the CuS+Fe system, there is still a significant amount of iron visible after 480 min of milling, therefore we can conclude that reaction is still not completed.

In Fig.3, the dependence of mass magnetization on milling time t_M for both studied systems is given. Regarding the starting mixtures, the highest magnetization value was evidenced for (CuS+Fe) system and the lowest for (Cu_2S+Fe) system. In both cases, magnetization decrease with t_M, which correlates with the consumption of Fe in reactions. In the case of (Cu_2S+Fe) system reaction (1), the magnetization value after t_M 360 min and 480 min is around 10 Am²/kg, which con-

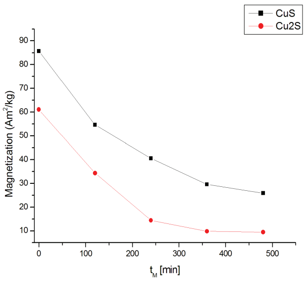

Fig. 3. Magnetization vs. tM for the reduction of chalcocite Cu₂S according to reaction (1) (red – circles), and that of covellite CuS according to reaction (2) (black – squares)
Ryc. 3. Namagnesowanie vs tM dla redukcji chalkozynu Cu₂S zgodnie z reakcją (1) (czerwone – kółka), a kowalinowej CuS według reakcji (2) (czarne – kwadraty)

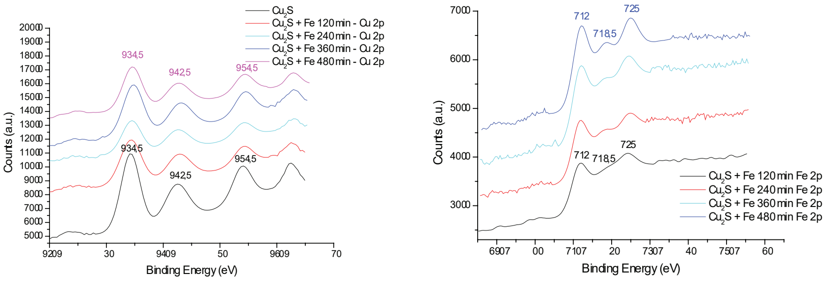

Fig. 4. High resolution XPS spectra of the mechanochemical reduction of chalcocite Cu₂S with elemental iron: A – copper 2p, B – iron 2p
Rys. 4. Widma XPS o wysokiej rozdzielczości mechano-chemicznej redukcji chalkozynu Cu₂S za pomocą żelaza pierwiastkowego: A – miedź 2p, B – żelazo 2p

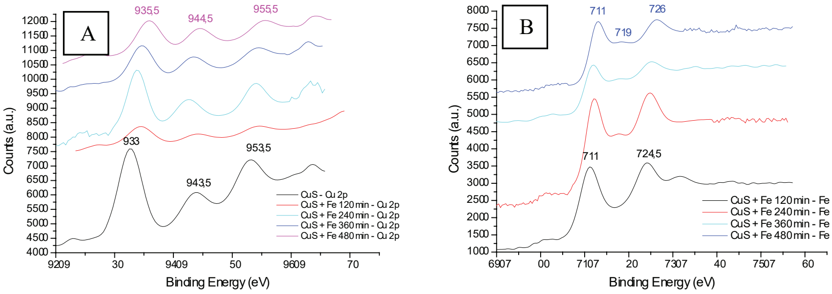

Fig. 5. High resolution XPS spectra of the mechanochemical reduction of covellite CuS with elemental iron: A – copper 2p, B – iron 2p
Rys. 5. Widma XPS o wysokiej rozdzielczości mechano-chemicznej redukcji CuS kowelinu z żelazem pierwiastkowym: A – miedź 2p, B – żelazo 2p

firms the observation from XRD that the reaction is almost completed already after t_M 360 min.

To compare of (Cu_2S+Fe) and (CuS+Fe) systems, the lowest value of saturation magnetization is observed in the first case for t_M=480 min, which correlates with Fig.2 (A). Regarding to the reaction (2) (covellite CuS reduction), the final value of saturation magnetization is higher, as the reaction did not proceed totally. This fact correlates with Fig.2 (B) where after t_M=480 min, elemental iron (Fe) is still observed.

X-ray photoelectron spectroscopy was used to elucidate the surface composition of the prepared powders after mechanochemical reduction of Cu_2S and CuS systems. High resolution spectra for Cu 2p and Fe 2p for both systems are shown in Figure 4 and 5 respectively.

In (Fig.4A) Cu 2p spectra at different t_M are shown for Cu_2S+Fe system. The detected signal for Cu in the spectrum for Cu_2S, are not in accordance with literature, concretely the observed peaks at 934.5 eV and 954.5 eV could hint to the oxidation of Cu_2S to $CuSO_4$ and copper oxides at the surface, which is a common phenomenon (Todd 2003). The peak at 944.5 eV could be present because of CuO formation on the surface (Parmigiani 1992). The Fe 2p spectra for (Cu_2S+Fe) system are shown in (Fig.4B). The observed peaks at 712 and 725 eV, could hint to the slight surface oxidation to Fe (III) (Grosvenor 2004, Idczak 2016), as according to the literature the oxidation state of Fe in FeS is (II) (Skinner 2003). A satellite peak located at 718.5 eV also provides a proof for the presence of iron in oxidation state (III) (Idczak 2016).

Fig.5A,B spectra of Cu 2p and Fe 2p at different tM are shown for (CuS+Fe) system. The detected signal for Cu in the spectrum for CuS, concretely the observed peaks at 935.5 and 955.5 eV are not in accordance with literature, due to presence of copper in oxidation state (II) (Ye 2015, Krylova 2009), which hints to the slight surface oxidation, as according to literature, the oxidation state of Cu in CuS, is (I) (Nduna 2014, Folmer 1980). A satellite peak located at 944.5 eV also provides a proof for the presence of copper in oxidation state (II) (YE 2015, Krylova 2009). The detected signals for Fe are shown in (Fig.5B), concretely the observed peaks at 711 and 726 eV, could hint to the slight surface oxidation of Fe (III) (Grosvenor 2004, Idczak 2016), as according to the literature the oxidation state of Fe in FeS is (II) (Skinner 2003). A satellite peak located at 719 eV also provides a proof for the presence of iron in oxidation state (III) (Idczak 2016). As the XPS measurements were not performed using argon sputtering, the surface impurities can significantly affect the results for both samples.

Conclusion

The mechanochemical reduction of chalcocite Cu_2S and covellite CuS with elemental iron as the reducing element was studied in this article. From the results we can conclude that mechanochemical reduction of both systems is possible. However, product is slightly oxidized on the surface due to high reactivity of produced nanoparticles. Our results suggest a possibility to perform chemical reduction without requirement of any high energy-consuming processes, e.g. in pyrometallurgy. This fact makes mechanochemical processing more environmental friendly and energy effective way for the treating of copper minerals in the partial production steps.

Acknowledgements

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Redukcja mechanochemiczna syntetycznych minerałów siarczkowo-miedziowych w skali przemysłowej

W artykule przedstawiono wyniki badań nad mechaniczno-chemiczną redukcję dwusiarczkowych chalkozynów (Cu2S) i kowelinu (CuS) przez żelazo pierwiastkowe. Skład i właściwości nanoproszków wytworzonych przez mielenie wysokoenergetyczne analizowano metodą dyfrakcji rentgenowskiej, rentgenowskiej spektroskopii fotoelektronowej i pomiarów magnetycznych. Wyniki XRD wykazały, że w przypadku chalkozynu Cu_2S reakcja zachodzi do 360 minut, ponieważ później nie można zidentyfikować żelaza pierwiastkowego. W przypadku kowelinu CuS, po 480 minutach redukcji mechaniczno-chemicznej, można było zaobserwować znaczną ilość nieprzereagowanego żelaza pierwiastkowego. Badanie właściwości magnetycznych ujawnia znaczne zmniejszenie podatności magnetycznej w wyniku rozdrabniania. Wyniki XPS wykazały znaczne utlenienie powierzchni w obu przypadkach. W przeciwieństwie do konwencjonalnej wysokotemperaturowej redukcji chalkozynu i kowelinu, redukcja mechano-chemiczna jest szybka, a temperatura otoczenia i ciśnienie atmosferyczne są wystarczające do jej propagacji.

Słowa kluczowe: mechanochemia, redukcja mechaniczno-chemiczna, mielenie wysokoenergetyczne, siarczki

Beneficiation of Talc-Magnesite Ore with Cu-Co Mineralization

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Abstract

Magnesite ore with a low chalcopyrite – cobaltite mineralization was subjected to a series of separations designed to evaluate the possible concentration of the two accessory minerals. Although the Cu-Co grade in the ore (> 0.01% Co, > 0.1% Cu) is significantly lower than the typical economic grades, content of the main valuable mineral for which the ore is mined and processed in combination with a listing of cobalt as a critical raw material, coupled with their higher price might compensate for the additional beneficiation stages. The ore was first crushed and subsequently classified to -100 μm and +100 -400 μm size fractions. The fine fraction was upgraded by froth flotation processing in laboratory froth flotation cell. The coarser fraction was processed in several separation stages including gravity separation on shaking table, magnetic separation and corona electrostatic separation. The same procedure was also repeated with a higher-grade sample as a verification of the procedures. Preliminary results suggest that the accessory minerals can be separated from the talc-magnesite ore and individual mineral concentrates with about 19% Co and 28% Cu were prepared. However, further work must be done to achieve desirable recoveries for the processing to be economically viable.

Keywords: mineral processing; cobalt; cobaltite; talc; beneficiation

Introduction

Classification of Cobalt as a Critical Raw Material (EUROPEAN COMMISSION, 2018) led to an increased interest in finding new possible sources of this metal. Increased production an also consumption of Co in recent years is mainly associated with increased demand for rechargeable batteries (nearly 80% of the annual consumption) and the forecast is that the trend will continue in the following years (USGS, 2018). According to the historical and latest US Geological Survey (USGS) numbers summarized in Figure 1, the overall trend of the mine production of Co seems to be positive. However, the production seems to have achieved its peak several years ago in 2015.

There are only two mines where Co-bearing minerals are considered primary valuable minerals – Bou-Azzer deposit in Morocco and Tenke Fungurume Mine in Democratic Republic of Congo (USGS, 2018). Cobalt is more commonly recovered as a by-product of other mineral processing activities, usually, it is associated with zinc, copper, nickel, silver, etc (RAO, 2014). Average ore grades range from 0.2 to 1%, accompanied by 1 to 3% Cu (MUDD et al., 2013).

Cobalt sulfide ores are usually beneficiated by froth flotation at acidic pH (~ 4) with xanthates, cobalt oxide ores at about pH 7.5 using nitrosonaphthol chelating reagents, while their combination can be used if the ore is partially oxidized. The high specific gravity of cobalt-bearing minerals (5.7–6.8) also allows the use of gravity-separation as the first step of concentration (RAO, 2014).

In this contribution recovery of Cu and Co bearing minerals from magnesite ore with low Cu and Co mineralization. Methods for the beneficiation of larger particles included gravity separation on shaking table, magnetic separation and corona electrostatic separation, while froth flotation method was tested for the fine fraction.

Materials and methods

Gravity concentration was carried out using the LY2100 shaking table (China) with a deck size of 2100*1050*850 mm and 1.1 kW motor power. 40 kg sample with 100 to 400 μm particles was used as a feed. Midlings resulting from the separation was mixed with fresh feed and there were thus only two final products of each step of gravity concentration on the shaking table.

Magnetic separation was conducted using dry high-intensity magnetic separator Mechanobr at 0.9 T. Corona electrostatic separation (Sturtevant, UK) was conducted at about 25 kV and 100 rpm. The sample was not heated during the test.

Froth flotation was carried out in a custom 3 l laboratory froth flotation cell. Fine fraction (-100 μm) of the ore was used. The test was carried out after at least 15 minutes of conditioning. The agitation speed of 1600 rpm and air flow rate of 4 l.min-1 was used in all tests. Variable flotation time was used during the tests – froth was scraped until it was no longer produced in considerable amounts.

Results and discussion

Flowsheets of the physical separation of the two different samples are shown in Figure 1 and Figure 2. Gravity separation of magnesite ore even with low Cu-Co mineralization is a suitable pre-processing method to produce preliminary Cu-Co concentrates. In a single operation, concentration factor (calculated as a ratio of the metal content in the concentrate and feed) of 10 and 12 was achieved for Co and Cu, resp. when processing the low-

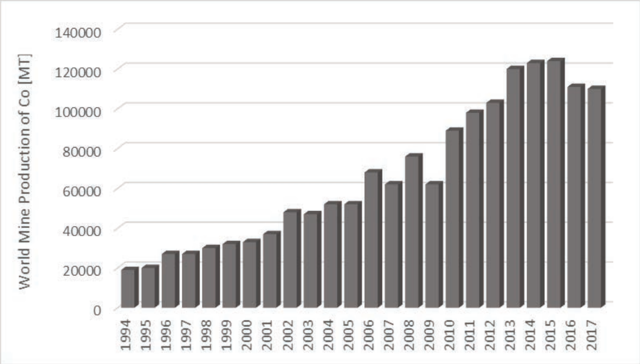

Fig. 1. World Mine Production of Cobalt over the years (USGS)
Rys. 1. Światowa produkcja kobaltu na przestrzeni lat (USGS)

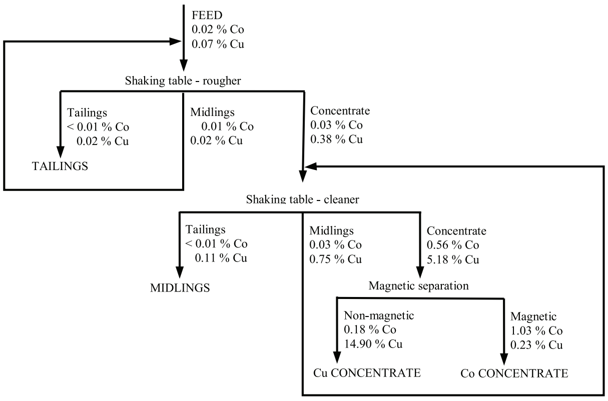

Fig. 2 Flowsheet of the processing of sample with lower Cu-Co content
Rys. 2 Schemat przeróbki próbki o niższej zawartości Cu-Co

grade ore with higher content of the metals (0.04 % Co, 0.57% Cu in the feed).

Two-stage gravity separation of the low-grade ore with lower metal content (0.02% Co, 0.07% Cu) resulted in a concentration factor of 28 and 38 for Co and Cu, resp. In both cases, Co content in the gravity concentrates with over 0.4% Co content achieved the grade of the usual primary cobalt ores. Copper content in the gravity concentrates with over 5% Cu severalfold exceeded the necessary grade.

Although the usual next step of mineral processing would be froth flotation of the concentrates (after grinding), two other physical separation methods were successfully tested. Further upgrading of the concentrate can be achieved using magnetic separation or a combination of magnetic and corona electrostatic separation. While magnetic separation alone (see Figure 2) was enough to produce a copper concentrate (non-magnetic product) with almost 15% Cu, cobalt concentrate (magnetic product) contained relatively low content of just over 1% Co. When an alternative approach of processing the gravity concentrate was used (see Figure 3) with corona electrostatic separation prior to magnetic separation, copper concentrate with over 22% Cu and cobalt concentrate with over 23% Co was produced. These results achieved with a sample of 100 to 315 μm suggested that the liberation of the valuable minerals is sufficient as both the theoretical Co content in cobaltite mineral and Cu content in chalcopyrite mineral is about 35%.

Although the overall recoveries of the valuable minerals during the laboratory tests aimed at testing the possibilities of physical separation methods were not high, this could be overcome by employing one or more stages of scavenging operations of the tailings and the midlings. It must also be noted that due to a low content of the Cu and Co minerals in the feed, processing of 40 kg of feed sample led to a preparation of only several grams of final concentrates.

For the fine fraction of the ore (-100 μm), froth flotation was tested. Three flotation tests were done – bulk Cu-Co flotation at lower 350 g.l^{-1} density and natural pH, bulk Cu-Co flotation at higher 700 g.l^{-1} density and natural pH and flotation at pH~4.5 (see Figure 6).

The result of the bulk Cu-Co flotation shown in Figure 4 suggested that chalcopyrite can be effectively recovered from the ore using a simple reagent scheme – only by using a xanthate collector (50 g.t^{-1} SIPX) and frother (20 g.t^{-1} MIBC). pH of the slurry was not adjusted and due to a large magnesite content in the ore, it was at around 8. This approach resulted in a production of concentrate with about 7.4% Cu content (concentration factor of over 90) in a single stage flotation with a recovery of chalcopyrite about 97%. However, no concentration of cobaltite was achieved. Also, the yield of the froth product was very low, only a little over 1%.

To avoid problems with froth scraping due to a low yield of the froth product, the higher slurry density of 700 g.l^{-1} was tested and the results are shown in Figure 5. While the dosage of the collector was kept constant at 50 g.t^{-1} in relation with the solids, the dosage of the frother was kept constant in terms of its concentration in the slurry and thus lowered to 10 g.t^{-1} (as the amount of the

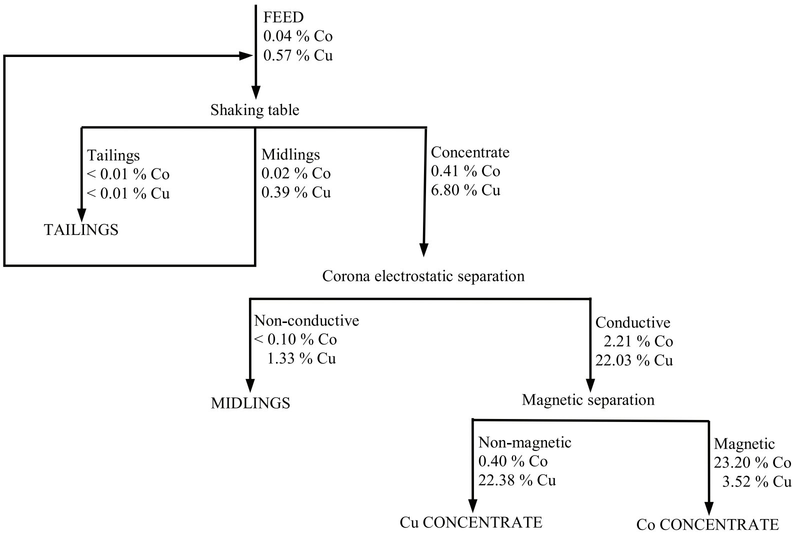

Fig. 3 Flowsheet of an alternative approach of processing used for the sample with a higher Cu-Co content

Rys. 3 Schemat alternatywnego podejścia do przeróbki rudy o wyższej zawartości Cu-Co

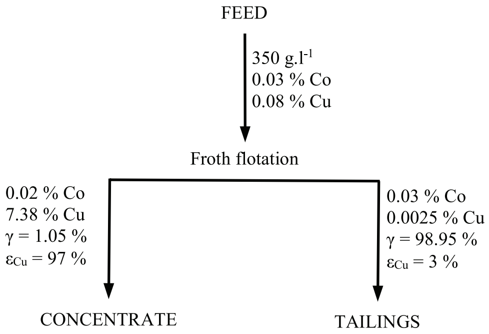

Fig. 4. Results of the bulk Cu-Co flotation

Rys. 4. Wyniki flotacji kolektywnej Cu-Co

solids in the slurry have doubled). Again, the test was conducted at natural pH.

Despite a slightly positive effect on the recovery of cobalt to concentrate, this has also significantly lowered the recovery of copper to concentrate (68% against 9 % in the previous test) as well as concentrate grade in terms of the Cu content (1.8% against 7.4%).

Third flotation test was aimed at the flotation recovery of cobaltite from the ore, which was expected to be highest in acidic conditions when using xanthate collectors. pH was therefore adjusted to about 4.5 and kept at that level during entire flotation. Other than that, the conditions were the same as in the previous flotation.

Results of the flotation shown in Figure 6, however, suggest, that not even adjustment of the pH increased the recovery of the Co to concentrate. By contrast, when compared with the results of the flotation using the same reagent scheme but natural pH (see Figure 5), Co content is even lower.

This suggests that the cobaltite found in the ore cannot be effectively recovered using SIPX collector. This might be due to a lower suitability of the collector as other xanthates – SEX (sodium ethyl xanthate) and PAX (potassium amyl xanthate) are usually used in these applications (RAO, 2014). However, the drop in the recovery in acidic conditions suggests that the cobaltite in the sample might be oxidized and flotation at natural pH using nitrosonaphthol chelating reagents might provide better results in terms of the Co recovery.

Overall, based on the preliminary results of the froth flotation processing it is advisable to test the bulk Cu-Co flotation at natural pH using a combination of xanthates and nitrosonaphthol reagents. It must also be noted that cleaning flotation aimed at the production of high-grade concentrate could not be tested due to the low yield of the froth product from rougher flotation.

Conclusion

Separation of Cu (chalcopyrite) and Co (cobaltite) from magnesite ore with low Cu-Co mineralization was tested. Gravity concentration was found to be a good method for preliminary concentration of the minerals (size fraction of 100 to 400 μm) and bulk concentrates with over 0.4% Co and over 5% Cu content was produced. When considering physical separation methods, it was found that using a combination of corona electrostatic separation and magnetic separation, individual mineral concentrates with relatively high metal content can be produced – over 22% Cu in the copper concentrate and over 23% Co in the cobalt concentrate. However, scavenging stages would have to be deployed to achieve satisfactory recoveries.

Fine fraction (-100 μm) was processed using froth flotation. By using of xanthate collector and frother (at natural slurry pH), recovery of Cu to concentrate of almost 97% was achieved at a grade of nearly 7.4% Cu in a single stage flotation. However, we were unable to concentrate Co (not even when pH of the slurry was adjusted to~4.5, which is reported to be the optimum). This

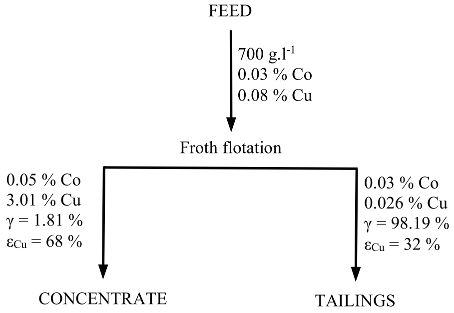

Fig. 5. Results of the bulk Cu-Co flotation with high slurry density

Rys. 5. Wyniki flotacji kolektywnej Cu-Co o wysokiej gęstości zawiesiny

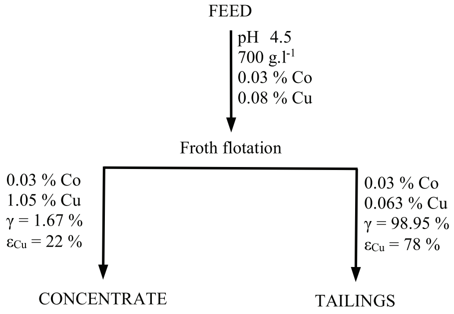

Fig. 6 Results of the flotation in acidic conditions

Rys. 6 Wyniki flotacji w warunkach kwasowych

was attributed to oxidation of the sample and use of a combination of xanthates and nitrosonaphthol collectors at natural pH was suggested in further tests.

Overall, a conclusion can be drawn that Co and Cu bearing minerals can be recovered by only using the physical separation methods from the supplied magnesite ore even when they are present only in small concentrations. Flotation was found to be a very promising method for the recovery of chalcopyrite. However, further tests must be conducted to find a suitable reagent regime for the recovery of cobaltite.

Acknowledgments

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Wzbogacenie rudy talku-magnezu z mineralizacją Cu-Co

Ruda magnezu o niskiej mineralizacji chalkopirytu – kobaltytu została poddana serii separacji mających na celu ocenę możliwego uzysku dwóch minerałów towarzyszących. Chociaż zawartość Cu-Co w rudzie (> 0,01% Co,> 0,1% Cu) jest znacznie niższy niż wartości opłacalne ekonomicznie, zawartość głównego cennego minerału (magnezytu) , dla którego ruda jest wydobywana i przetwarzana w połączeniu z zawartością kobaltu jako surowca krytycznego może zrekompensować koszt dodatkowych etapów wzbogacania. W pierwszym etapie rudę kruszono, a następnie klasyfikowano do frakcji o wielkości -100 μm i +100 -400 μm. Drobną frakcję poddawano flotacji pianowej w laboratoryjnej maszynce flotacyjnej. Grubsza frakcja była przetwarzana w kilku etapach, w tym separacja grawitacyjna na stole wstrząsanym, separacja magnetyczna i separacja elektrostatyczna. Ta sama procedura została powtórzona z próbką o wyższych zawartościach. Wstępne wyniki sugerują, że minerały towarzyszące można oddzielić od rudy talku i magnezytu i zyskano koncentraty mineralne z zawartością około 19% Co i 28% Cu. Jednakże konieczne są dalsze prace w celu osiągnięcia pożądanych uzysków, aby przetwarzanie było opłacalne ekonomicznie.

Słowa kluczowe: przeróbka minerałów, kobalt, kobaltyt, talk, wzbogacanie

Bacterial Leaching of Polymetallic Ores from Zlatý Chlum Locality

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Abstract

As for geology, Zlatý Chlum is a highly varied locality with frequent metaquarzit, amphibolite, quartz as well as deposits of sulphide ores. This work deals with the use of Acidithiobacillus ferrooxidans *to bioleach polymetallic ores (Cu, al, Zn, and Fe) from this locality. Leaching lasted for 5 weeks in a bioreactor that ensured optimal conditions for bioleaching. The results imply that the experiments were successful, leaching 54% of Fe, 28% of Cu and 47% of Al.*

Keywords: bacterial leaching, polymetallic ores, pyrite, chalcopyrite, Acidithiobacillus ferrooxidans, bioreactor

Introduction

Description of Zlatý Chlum locality

The processed samples originated from Zlatý Chlum, a hill in the Highlands of Zlaté Hory (Golden Mountains) approximately 2.5 km from the City of Jeseník in the Czech Republic. In terms of geology, it is an ore zone which has been in the centre of miners' interest for centuries. It is made up by a system of quartz lens and veins bound onto varied sequences of rocks, with prevailing mica schist, mica schist paragneiss with inserts of metaquartzit, lime silicate rocks, amphibolites and quartz. Gold occurs predominantly in quartz positions bound onto metaquartzit; it is less scattered in the surrounding rocks made up by granitite binary mica schist (garnets as large as 1 cm). It is pure gold, rarely inosculating with tellurides. The content of sulphides (pyrite, pyrrhotite, chalcopyrite) is lower than the content of the dominant rocks. Over 3.5 tons of gold was extracted in Zlatý Chlum. At present, the deposit is not mined due to the low metal content. [1]

Bioleaching

The process of bioleaching may be defined as the dissolution of minerals caused by direct or indirect action of diverse microorganisms. In the course of such processes, the natural flora of microorganisms consists of a mixture of acidophilic autotrophic bacteria. [2] Their role is to produce chemical agents vital for leaching. [3] It is a simple and effective method to recover metals from mineral raw materials, where conventional methods cannot be applied. The fundamental mechanism is the direct or indirect oxidation of sulphide ore. Through oxidation, metal releases into solution, from where it can be recovered using conventional chemical-physical methods. In this case, we aim to recover metals from sulphide minerals through the activity of bacteria of *Acidithiobacillus* genus, which convert insoluble metal sulphides into soluble sulphates. With regard to the character of the sample, we selected the most suitable species to leach sulphide ores, i.e. *Acidithiobacillus ferrooxidans*. [4,5,6]

Bacteria Acidithiobacillus

Acidithiobacillus is considered a biotechnologically and ecologically significant group of bacteria that is the most active in the dissolution of sulphides. It is Gram-negative, acidophilic, rod-like bacteria that thrive in acidic media of a low pH between 1.8 and 2.5. They gain energy from the oxidation of sulphur and reduced sulphur compounds, or via the oxidation of bivalent iron and hydrogen. Considering their metabolic properties, they are suitable to process mineral and electronic waste, and for the desulphurisation of gas and coal. A negative aspect of the metabolic activities of the bacteria is biocorrosion due to the production of sulphuric acid. As for their physiological and morphological characteristics, it shows that *Acidithiobacillus* genus contains at least seven species, e.g. *Acidithiobacillus ferrooxidans*, *Acidithiobacillus ferridurans*, *Acidithiobacillus ferrivorans* and *Acidithiobacillus ferriphilus*, *Acidithiobacillus thiooxidans*, *Acidithiobacillus caldus* and *Acidithiobacillus albertensis*. [7,8]

Acidithiobacillus is a group of microorganisms important for the dissolution of copper, zinc, iron and arsenic from diverse ores, sediments and waste [9]. Their genes determine the transport routes of nutrients, including K, P and Fe, which are vital for the intercellular balance as well as elimination of toxic elements, such as Hg, Pb, As, Cr, Cd and Ag. [10]

Tab. 1. Results of X-ray diffraction

Tab. 1. Wyniki dyfrakcji rentgenowskiej

Name of mineral	**Chemical formula**	**Content (%)**
Quartz	SiO_2	85.38
Sphalerite	ZnS	0.14
Chlorite	$(Mg,Fe)_6\ (Si,Al)_4O_{10}\ (OH)_8$	1.36
Chalcopyrite	$CuFeS_2$	2.31
Albite	$NaAlSi_3O_8$	5.94
Orthoclase	$KAlSi_3O_8$	2.30
Pyrite	FeS_2	1.47
Galenite	PbS	0.73

Tab. 2. Leaching of Al

Tab. 2. Ługowanie Al

Leaching time	**Metal concentration (%)**	**Recovery of metal (%)**
Input	2.1301	
1. week	1.2059	43.39
2. week	1.1928	44.01
3. week	1.1893	44.64
4. week	1.1406	46.46
5. week	1.1229	47.29

Tab. 3. Leaching of Fe

Tab. 3. Ługowanie Fe

Leaching time	**Metal concentration (%)**	**Recovery of metal (%)**
Input	2.51	
1. week	2.48	1
2. week	2.15	14.17
3. week	1.75	30.05
4. week	1.44	42.27
5. week	1.14	54.41

Tab. 4. Leaching of Cu

Tab. 4. Ługowanie Cu

Leaching time	**Metal concentration (%)**	**Recovery of metal (%)**
Input	2.343	
1. week	2.030	13.35
2. week	1.844	21.29
3. week	1.801	23.10
4. week	1.685	27.15
5. week	1.651	28.08

Materials and Methods

The samples come from Zlatý Chlum. Subsequently they were processed in the laboratory of the Department of Environmental Engineering at VŠB-TU Ostrava using a vibrating attrition mill. The samples were ground to the grain size fraction -0.063 mm.

The mineralogical composition analysis of the samples was carried out. An X-ray diffraction analysis was done in the laboratories of the Department of Geological Engineering at VŠB-TU Ostrava. The measurements were carried out on a modernized, fully automated diffractometer URD-6 (Rich. Seifert-FPM, SRN). The following phases were identified in the samples in question: quartz, chlorite, chalcopyrite, albite, pyrite. (See Table 1).

Methodology of bacterial leaching

For the bioleaching process, we prepared 9K medium according to Silverman and Lundgren, in which *Acidithiobacillus ferrooxidans* was cultivated.

The leaching process took place in New Brunswick BIOFLO®&CELLINGEN® 310 (Figure 1). Having sterilized the bioreactor, 500 g of sample from Zlatý Chlum at 100% grain size under 0.063 mm and 10 litres of 9K medium free of $FeSO_4$ were inserted inside the bioreactor. After one-hour stirring and homogenization of the suspension, a bacterial culture of *Acidithiobacillus ferrooxidans* in the amount of 880 ml was introduced into reactor. A pre-cultivated culture of *Acidithiobacillus ferrooxidans* from the Institute of Microbiology in Brno was applied.

The bioreactor New Brunswick BIOFLO®&CELLINGEN® 310 is a glass vessel of 14 l. To make the bioleaching process most effective and yielding, it is vital to

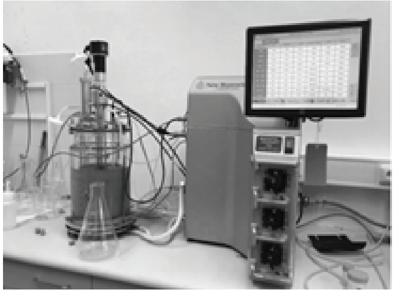

Fig. 1. Bioreactor Bioflo 310
Fig. 1. Bioreaktor Bioflo 310

ensure optimal conditions for the growth of bacteria. The bioreactor Bioflo 310 is able to maintain constant pH of the environment, temperature, degree of aeration, concentration of CO_2 and O_2, and rate of agitation.
Conditions:

- Dissolved O2:100/l
- Temperature: 30°C
- pH: 1.8
- Agitation: 150 RPM
- Leaching time: 5 weeks

The samples were leached for 5 weeks. In the course of leaching, samples were drawn after the 1st, 2nd, 3rd, 4th and 5th week. All the samples were washed in 0.1.mol HCl and later in distilled water to stabilize pH. The drawn samples were analysed using a portable spectrometer Dynamic XRF DELTA PROFESSIONAL by BAS Rudice s.r.o. In the course of experiment, the colour of the leached sample changed. At the start, the colour was dark brown and it became lighter during the experiment, which was likely caused by the highly acidic environment.

Results and discussion

The results showed that the application of ATF bacteria disrupted the strong sulphidic bonds and led to the release of metals into the solution. We observed the following metals of interest: Al, Fe, and Cu. We also observed leaching of sphalerite (ZnS), but with regard to its trace concentrations measured by the X-ray spectrometer, we did not determine it further.

Leaching of Al

At the input, aluminium was at 2.13%. In the first week of leaching there was a rapid decrease in Al by 43.39 %. In the following weeks, aluminium release continued, but in a less striking speed. From the second to the fifth week, the decrease ranged around 4% (see Table 2). The aluminium recovery after five weeks was 47.29%. It may thus be stated that aluminium may successfully be leached in a bioreactor using the bacterial strain of *Acidithiobacillus ferrooxidans*.

Leaching of Fe

The feed percentage of Fe in the sample was 2.51 %. During the first week of bacterial leaching, no leaching bacterial activity was observed. It appears that the bacteria were adapting to the environment and they replicated and grew slowly. As a result, only 1% of Fe passed into the solution (Table 3). In the second week of bioleaching, there was a prominent increase in Fe release amounting to 14.17%. In the following weeks (third to fifth) the metal recovery grew gradually. In the third week the recovery of Fe was 30.05%, in the fourth it was 42.27% and 54.41% in the fifth.

Leaching of Cu

The input percentage of Cu in the sample was 2.343 %. In the first week of leaching in the BioFlo 310, the metal content of Cu decreased to 2.03%, which corresponds to a Cu recovery of 13.35%. In the following weeks, there was a gradual decrease in the sample metal content. After the second week, the solution was enriched by 21.29 % of Cu. In the third to fifth weeks, the copper content dropped to 1.651%, which corresponds to the overall copper recovery of 28.08%. (Table 4).

Conclusion

The samples were drawn from the locality Zlatý Chlum, in the Czech Republic. Bacterial leaching was carried out under pilot-plant conditions in a bioreactor New Brunswick BIOFLO®&CELLINGEN® 310 using the bacterial strain of *Acidithiobacillus ferrooxidans*. This strain was selected for its fitness for the sample in question. The drawn samples were ground below 0.063 mm grain size, mixed with Silverman 9K medium and leached with the bacteria in the bioreactor.

The experiment lasted for 5 weeks (35 days) under optimal conditions set for the bioreactor. With regard to the mineralogical composition of the sample, we observed the following metals: Al, Fe, and Cu. The most striking was the course of iron leaching, during which only 1% leached in the first week, followed by a rapid increase to 54% in the weeks after. Copper leaching was gradual and the overall copper recovery was 28%. Aluminium also showed interesting results as it had a recovery of 43% in the first week of leaching, which increased to 47% in the weeks to come. It may thus be stated that bacterial leaching of low-grade ores, as this was the case, has its advantages and may successfully be used as an alternative extraction method, particularly to recover Fe. The disadvantage is the duration of the leaching process.

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Bakteryjne ługowanie rud polimetalicznych z miejscowości Zlatý Chlum

Geologicznie Zlatý Chlum jest bardzo zróżnicowanym złożem z częstymi meta- kwarcytami, amfibolitami, kwarcem oraz polimetalicznymi rudami siarczkowymi. Artykuł dotyczy zastosowania bakterii Acidithiobacillus ferrooxidans do ługowania bakteryjnego rud polimetalicznych (Cu, Al, Zn i Fe) z tej miejscowości. Ługowanie trwało 5 tygodni w bioreaktorze, który zapewniał optymalne warunki do bioługowania. Wyniki pokazują, że eksperymenty zakończyły się powodzeniem, uzyskano stopień wyługowania 54% Fe, 28% Cu i 47% Al.

Słowa kluczowe: ługowanie bakteryjne, rudy polimetaliczne, piryt, chalkopiryt, Acidithiobacillus ferrooksydans*, bioreaktor*

Safety of Infrastructure Operation in New Climate Conditions

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Abstract

The reliability of infrastructure buildings is a basic prerequisite for utility values of built-up in towns and municipalities areas. It creates the prerequisites for the long-term sustainability of the housing stocks of humans and, at the same time, is a condition for the region industrial base development. This reality is perceived by the public as an obvious standard which is a part of human life. However in the reality this is a very complex mechanism that can be severely disturbed in various conditions and situations. To prevent these situations from happening in practice it is imperative that state, government and different infrastructure types know the security risks that have a potential to change natural and operational environment and are ready to eliminate them.

The following article deals with these issues, how to recognize the threat of an imminent emergency or critical situations and which resources are needed to increase the infrastructure reliability.

Keywords: reliability, security, infrastructure, risk, emergency, risk elimination, system immunity

Introduction

The current European human population knows no longer its environment other than benefits that national infrastructure provides to its citizens. In most non-European countries, however the real living conditions are completely different.

Infrastructure environment is not a natural stable phenomenon but a human variant of life which is not only necessary to maintain but also to develop further. Infrastructure maintenance and development must not be natural but have to respect the full range of rules that respect the natural environment and human needs. Immediate human needs and interests must not be preffered to balanced states. Humanity in today´s technologically advanced countries since the 19th century has not respected the number of natural laws or underestimated their signifikance. Consequences are now beginning to show up in secondary phenomena in their own natural environment, aquatic ecosystems and also in infrastructure, its reliability and the safety of operating systems.

Now the time occures when part of mistakes will need to be remedied and change the overal approach to the use of the natural environment. As mentioned in this article some mistakes are only a regional character and a negative scope. Others are beginning to manifest themselves on a global scale which can be reduced bz a global approach to solving the problem. With their concurrent action, without solutions, they may not only affect the current living conditions of the people in the coming years but also have a serious to critical negative impact on flora and fauna worldwide and consequently may appear in the social society sphere [1]. In addition to aspects above it will also affect the reliability and safety of different operation types of public and private infrastructure.

Infrastructure and its impact on the function of the economically and industrially used area

The infrastrucutre of technologically advanced states in the world consits of a numer of object and technical line structures in particular the energy supply, drinking water and wastewater drainage to the recipients. Their incorporation in territorialunits has a fundamental geostrategic significance not only in a standard environment but also in extraordinary events or crisis situations. They have a potential to incriese or mitigate consequences of these extraordinary events possibly with the appropiate composition to prevent these negative phenomena.

Without the operational reliability and basic infrastructute function it is not possible to develop the economic aktivity of the built-up areas in the regions and to improve the newly created environment.

The basic infrastructure consists of the following tecnical and operating systems:

- residental public and private buildings,
- technical infrastructure of territorial unit (natural gas, electricity, drinking water, sewage),
- transport infrastructure (roads, railway communications),
- medical facilities (hospitals, medical instituitions),
- industrial objects (production and storage facilities),
- industrial zones,
- business zones.

The facilities and building are changing over time. It has been changing not only their basic parametres but also their reliability and usability for their primary purpose. In the case of general constructions in particular the changes are slow and so called comestic, the construction of the technical infrastructure during its lifetime often loses its initial performance parametres. These parametres can seriously endanger general city stability, municipalities, industrial base and broader concepts and also citizen security.

Fig. 1. Flooded area due to flood in 1997 [2]
Rys. 1. Zalany teren w związku z powodzią w 1997 r. [2]

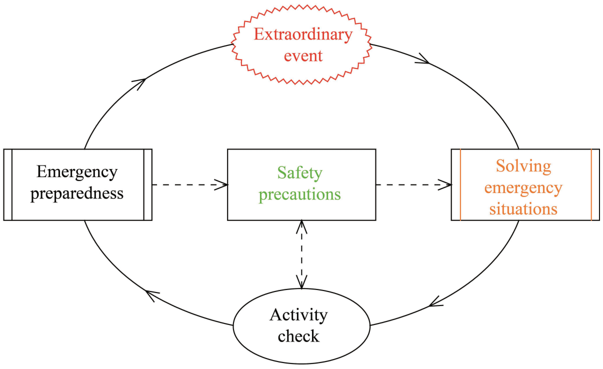

Fig. 2. Emergency management concept in the Czech republic [3]
Rys. 2. Koncepcja zarządzania kryzysowego w Republice Czeskiej [3]

Security threats to infrastructure in new climatic conditions

As clear from the previous chapter in this article, the general urban funcionality and operability are conditioned by reliability of thecnical infrastructure. Despite technical progress however technical infrastructure can not achieve 100% system realiability and security of energy supply or drinking water. These systems can affect two fundamental factors which have a potential to shut down for a different time:

- natural influences,
- anthropogenic events.

These events occurance is dependent on the geological and natural conditions in which the infrastructure is located in and at the same time on the technical adaptation of infrastructure facility concerned to handle difficult natural changes or anthropogenic events. With the upcoming climate change it is not only possible to increase the natural incidents number but also to increase intensity of the secondary anthropogenic emergencies impact in the affected area.

Natural influences

In the whole range of occurance possibilities an extraordinary event with a natural character with an extremely negative impact on the useful environment of bulit-up areas and its infrastructure are floods, see in Fig. 1.

Floods, climatic and hydrological droughts will be almost certainly major threats in 21st century global climate threat. They will fundamentally influence the whole range of human activities and infrastructure facilities. Without a sufficient preventive preparation for their preparation, the consequences will increase in many cases and accumulate at the same time.

Anthropogenic events

Anthropogenic events themselves have often far-reaching negative impacts on human health and people´s lifes. However in many industrial activities they have also a potential to endanger the environment. This is particulary the case for aquatic ecosystems in which during the emergencies events with chemical leakage into receptacles or flooded soil layers, serious natural and safety damage can occure. These are in particular the following threats:

- groundwater or surface contamination
- temporary decommissioning of drinking water sources,
- serious damage to the environment, fauna and flora in the river basin,
- ampflication of abovementioned extraordinary events with the simultaneous hydrological drought.

If a person has limited possibilities to influence the occurrence of extraordinary events or crisis situations caused by natural influences, then creating sufficient preventive conditions to minimize the consequences of threats to anthropogenic events is in the human power.

Elimination of natural and anthropogenic risks

The theoretical elimination issue of natural and anthropogenic threats is currently relativem sophisticated. However

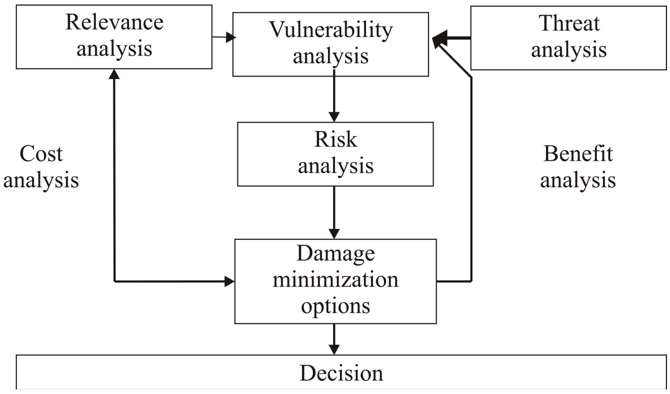

Fig. 3. Basic risk management scheme [5]
Rys. 3. Podstawowy schemat zarządzania ryzykiem [5]

its implementation in practice must be based on at least the following aspects:

- actual risks detailed analysis,
- thought maps for their elimination in space,
- crisis plans elaboration for public administration,
- developing crisis preparedness plans for infrastructure operators.

If these principles are appropriately incorporated into safety measures, see Fig. 2, an acceptable outcome can be obtained when an emergency or a crisis situation arises.

In the practice, a two-phase or three-phase model is used. The initial two-phase model (emergency preparedness, emergency situation) in real is then decomposed into a three-phase model (protection, response, recovery). Together with technical procedures, threats and risk management are accompanied by ethical issues [4]. At the same time it is necessary to maintain a sequence of steps and actions as part of activities to reduce extraordinary events consequences, see Fig. 3.

In assesing the continuity of the territory technical infrastructure it is appropiate among other measures to consider in addition to other measures, the ration of expected negative impacts arising from human factor failures or technological disasters and natural events effects and also the risk of crisis emergence.

Due to the dynamic scinetific knowledge development of new equipment and technologies, it is always necessary to consider whether the taken measures are only temporary or in line with a long-term development trends. One of these considerations may also be the search for new routes and resilence ways of regional infrastructure systems [6].

Finding new ways to increase resilence of regional infrastructure operating systems

Scientific knowledge has a fundamental importance in further long-term area sustainability and its environment. Together with the technical and industrial base development they have a potential to create defense systems that reduce current security risks [7]. However it is always appropriate for science and technology to respond to other stimuli that can be the part of security development after initial analysis. One of these ways can be solve by the following issues:

- approach changing to solve past ecological faults in the sustainability of water precipitation in areas threatened by hydrological drought
- deactivating ways to a large part of melioration structures,
- new types development of climate change monitoring systems not surface and underground water reserves, especially in vulnerable areas of meteorological drought.

The above mentioned research and searching for new routes based on scientific risk analyses while maintaining a link to the potential of technology development can reduce a considerable part of security threats in a relatively short time period. At the same time preventing new threats emerging in individual world regions can set in.

Conclusion

Given that the advent of climate change in 21st century is already proven it is necessary to adapt to that situation. It must not be a passive approach but an active solution to eliminate threats consequences. One of the ways in which approaches and remedies can be accessed is also suggested in this article. Its structure is based on long-term studies of the article author subject and their solution in practice. Perhaps the article will bet he next successive solution in coming years.

Acknowledgments

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Bezpieczeństwo eksploatacji infrastruktury w nowych warunkach klimatycznych

Niezawodność budynków infrastruktury jest podstawowym warunkiem wartości użytkowej zabudowy w miastach i gminach. Niezawodność tworzy warunki wstępne dla długoterminowej stabilności zasobów mieszkaniowych ludności, a jednocześnie jest warunkiem rozwoju bazy przemysłowej regionu. Ta rzeczywistość jest postrzegana przez opinię publiczną jako oczywisty standard, który jest częścią ludzkiego życia. Jednak w rzeczywistości jest to bardzo złożony mechanizm, który może być poważnie zakłócony w różnych warunkach i sytuacjach. Aby zapobiec takim sytuacjom w praktyce, konieczne jest, aby państwo, rząd i różni operatorzy infrastruktury znali zagrożenia dla bezpieczeństwa, które mogą podlegać zmianom przez zmiany w środowisku naturalnym i być gotowymi na ich wyeliminowanie.

Artykuł dotyczy tych zagadnień, dotyczących rozpoznawania zagrożeń wynikających z sytuacji awaryjnych lub sytuacji krytycznych oraz określenia jakie zasoby są potrzebne do zwiększenia niezawodności infrastruktury.

Słowa kluczowe: niezawodność, bezpieczeństwo, infrastruktura, ryzyko, awarie, eliminacja ryzyka, odporność systemu

Adsorption Characteristics of Combined Sulfhydryl Collector on Chalcopyrite and Arsenopyrite in Flotation of Complex Gold Ores

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Abstract

The paper presents the results of experimental study of the adsorption properties of the combined sulfhydril collecting reagent – a mixed solution of sodium diethyl-dithiocarbamate (DEDTC) and oxypropyl diethyl-dithiocarbamate ester (OPDTC) towards chalcopyrite and arsenopyrite with a view to its application as a selective collector of Au-containing sulfide minerals in flotation of complex refractory ores. Combined diethyl-dithiocarbamate solution (DEDTCc) incorporated a fixed content of anionic and non-ionic components (DEDTC:OPDTC = 1:1) and occurred variable hydrophobic effect on the surface of the basic gold-bearing sulfide minerals – chalcopyrite and arsenopyrite.

The mechanism of adsorption of the components of combined collector on the surface of chalcopyrite and arsenopyrite was identified to form characteristic molecular shape of adsorbed collector convex neoplasms and sinter chemically adsorbed film of the reactant, which is firmly anchored on the surface. The newly formed phase of the adsorbed reagent did not dissolve in water at a subsequent washing. In this case, the phase of nonionic ester OPDTC was partially removed by water and the residual adsorbed droplets changed their shape and became flatter. By X-ray microanalysis C and O bands relating to the structure of the combined DEDTCc were identified on the surface of arsenopyrite and chalcopyrite. The original technic for analyzing the liner dimension of surface images with an application of scanning laser microscopy and the software of the Analyzer was developed and the authors succeeded to provide a quantitative evaluation of the adsorption of DEDTCc on the surface of chalcopyrite and arsenopyrite.

Keywords: flotation, selective collector, gold ores

Introduction

The recovery of gold and the other precious metals from complex refractory ores that are characterized by low content of valuable components and fine impregnation of gold highly depends upon the flotation reagent modes. It may be improved by creating new combinations of novel selective reagents and conventional collecting agents providing durable hydrophobic coating on the surface of extracted minerals [1].

In IPKON RAS the novel complex collecting reagents, including modified diethyldithiocarbamate (DEDTCc) have been developed and tested for flotation extraction of sulfide minerals with emulsion gold impregnation. DEDTCc reagent is a composition which incorporates nonionic dithiocarbamic acid thioester (OPDTC) in addition to the ionic form of the main component - diethyldithiocarbamate (DEDTC) [2, 3]. There have been identified in the previous flotation and adsorption tests that nonionic OPDTC component is capable of forming a hard water-soluble gold compound on the surface of gold-containing arsenopyrite and pyrite in flotation conditions, providing selective hydrophobic coating and better floatability of gold-bearing sulfides. Introducing OPDTC nonionic component into the composition of a modified collector solution improves the conditions for its dissolution in the aqueous phase and provides better contact with the mineral surface.

A method for producing modified DEDTC solution has been developed in IPKON RAS by senior research associate Ivanova T.A., PhD [3, 4]. The method is based on the treatment of the low concentrated DEDTC solution by propylene hydrochloride to obtain a homogeneous solution of OPDTC and DEDTC in a certain ratio of the components of the solution directly before introduction into the flotation process.

The application of this reagent in a combination with xanthate and organic depressor made it possible to increase the selectivity of the separation process between auriferous pyrite and arsenopyrite, and reduce the arsenic content in the Au-pyrite concentrate [2, 5].

Due to the fact, that the choice of the optimal conditions for the formation of the hydrophobic layer of the collector on the surface of gold minerals is a determining factor in improving the recovery of precious metals from refractory ores, a detailed study of the nature of its adsorption on the surface of sulfide minerals has been performed. Arsenopyrite, which is the main gold-bearing sulfide mineral in refractory sulfide ores, and chalcopyrite – analogue of activated by copper salts arsenopyrite have been analyzed. As a result, DEDTCc adsorption on the surface of auriferous arsenopyrite and pyrite tested by UV spectroscopy was found, and the selectivity of DEDTCc compared to conventional DEDTC and xanthate flotation of gold-bearing sulfides was proved.

In this paper, analogue DEDTCc has been tested in adsorption and flotation conditions of chalcopyrite and arsenopyrite. DEDTCc was obtained by adding OPDTC into solution of DEDTC in the ratio 1: 1.

Tab. 1. The chemical composition of the mineral samples

Tab. 1. Skład chemiczny próbek minerałów

Minerals	Content, %						
	Fe	S	As	Cu	Oxides	Others	Au, ppm
Arsenopyrite	29.7	19.3	40.5	0.04	10.4	<0.1	15
Chalcopyrite	28.1	28.3	-	26.4	15.4	1.8	40

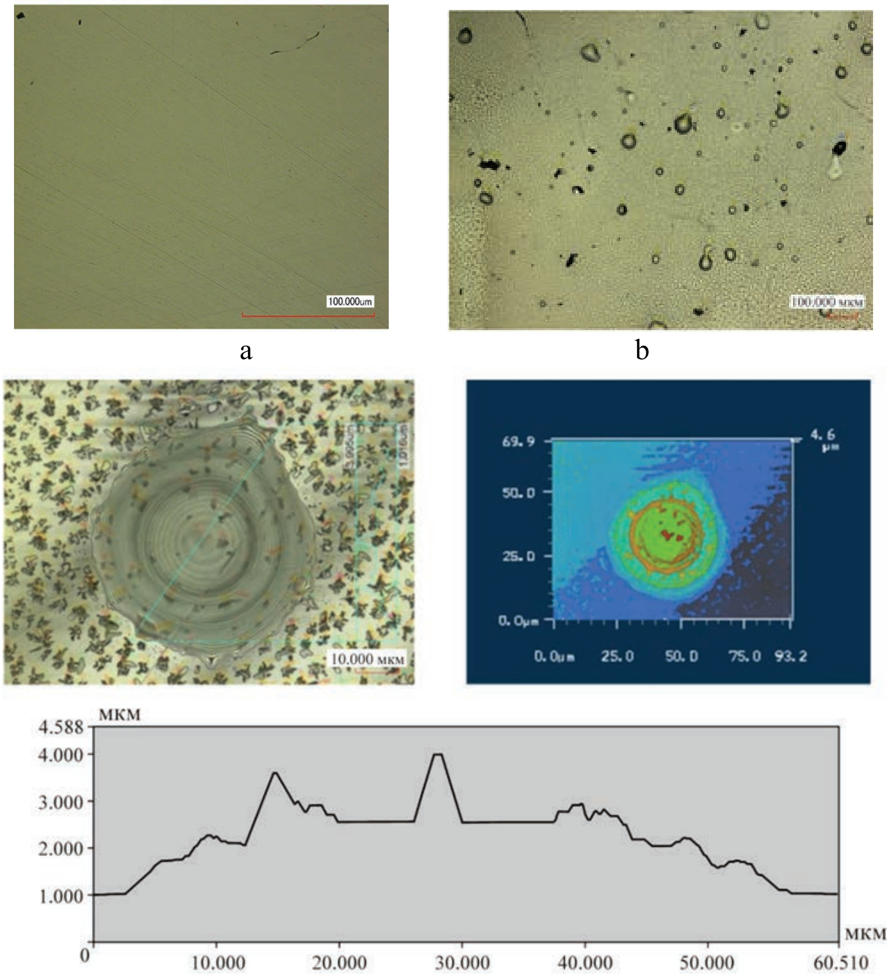


Fig. 1. Image of polished chalcopyrite before (a) and after DEDTCm treatment (P = 100 mg / l) (KEYENCE) (b) and the height of the surface roughness (the height of the connection layer, a foothold on the surface of the section) (c, Label 10 microns)

Rys. 1. Obraz szlifu chalkopirytu przed (a) i po adsorpcji DEDTCm (P = 100 mg / l) (KEYENCE) (b) i wielkość chropowatości powierzchni (wysokość warstwy łączącej, przyczółek na powierzchni sekcji) (c, Etykieta 10 mikronów)

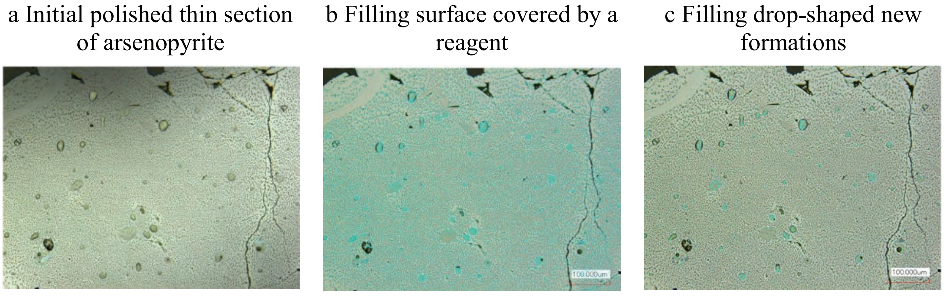
Materials and Methods

Mineral fractions of chalcopyrite and arsenopyrite were selected from samples of gold ore. The chemical composition is shown in Table 1.

Newly formed films of combined collector DEDTCc on polished sections of minerals (10x10x2 mm in size) were studied on analytical scanning electron (LEO 1420VP + INCA Oxford 350), and a laser microscope (KEYENCE VK-9700 with 1 nm resolution). Research methods are optical, confocal laser, analytical electronic, scanning probe microscopy, UV-spectrophotometry of reagent solutions, flotation of minerals. The KEYENCE scanning laser microscope with the surface analysis module VK-9700 enables making a non-contact measurement of the roughness of the surface of minerals and thus determining the height and size of the new formations obtained as a result of interaction with the reagents. The electronic microscope with energy-dispersive microanalyzer LEO-1420 VP INCA-350 allows determining the elemental composition of micro- and nanophases of reagents on the surface of minerals. UV-spectrophotometry was used to analyze the DEDTCc concentration in aqua phase of mineral suspension before and after contact with ground fractions (-0.1 + 0.063 mm) of chalcopyrite and arsenopyrite. The liquid phase was decanted after centrifugation and the residual concentration of the components of DEDTCm was analyzed by spectrophotometer SHIMADZU-1700.

Results and Discussion

The images of polished sections of chalcopyrite on analytical scanning electron (LEO 1420VP + INCA Oxford 350) and laser microscope (KEYENCE VK-9700 with 1 nm resolution) have shown that after contact with the DEDTCc solution characteristic molecular shape of adsorbed collector appeared (Fig.



a Initial polished thin section of arsenopyrite

b Filling surface covered by a reagent

c Filling drop-shaped new formations

Mineral surface area, µm^2	Surface area covered by a reagent, µm^2	Percentage of coverage by a reagent, %
499405	108091	21.6
	Drop-shaped new formations 14469.525	2.9

Fig. 2. Determining the surface area of the polished thin section of arsenopyrite coated with the DEDTCc reagent. Laser microscope KEYENCE VK-9700. Magnification of 20X

Rys. 2. Określenie pola powierzchni wypolerowanego cienkiego szlifu arsenopirytu pokrytego odczynnikiem DEDTCc. Mikroskop laserowy KEYENCE VK-9700. Powiększenie 20X

1). One can see the convex neoplasms that formed chemically adsorbed films of the reactant, which firmly anchored on the surface and did not dissolve in water at a subsequent washing.

Newly formed discrete sinter multi-phase of reactant had round shape with a diameter of 0.1 to 55 microns (Fig. 1c). Non-contact measurement of surface irregularities formed on the scanning microscope, helped to estimate the height of detected tumors, which was h = 0.1 - 0.4 mm for small phase (diameter 0.1–1.0 mm) and h = 0.65–1.85 microns to the larger formations (diameter up to 55 microns).

On the surface of arsenopyrite one could enjoy the very similar newly formed phase of the reagent after its contact with the mineral, but a little bit smaller in size and concentration (Fig. 2). Very close to round shape, a diameter of films is 0.1 to 34 microns and the height of detected tumors is about h = 0.1–0.4 mm for small phase (diameter 0.1–1.0 mm) and h = 0.65–1.65 microns to the bigger formations (diameter up to 34 microns).

In both cases, the phase reactant of nonionic component was partially removed by water and the droplets became flatter. By X-ray microanalysis, C and D picks were identified on the surface of arsenopyrite and chalcopyrite relating to the structure of the combined reagent. The different character of the adsorption phase of the combined reagent components could be explained by the chemical and the physical adsorption of combined collector. Nonionic component is attached to a mineral in the form of drop-shaped sinter tumors with a well-defined circular shape, with a diameter of 0.1 to 27.4 microns and a maximum height of 0.65 to 1.85 microns. Chemically adsorbed anionic DEDCT formed the new phase of irregularly shaped size 63–100 mm and a thickness of 10–20 microns. A combination of both phases on the surface of the sulfides is favorable for efficient flotation of associated gold from refractory ores.

In the course of the research, an original technique was developed to quantify the adsorption of DEDTCc on the surface of sulfide minerals in flotation conditions. The originality and novelty of the approach to the study of thin reagent films on the surface of mineral surfaces is to compare the numerical measurements of the unevenness of the relief of a mineral before and after a contact with the reagent solutions.

An analysis of the surface condition of sulfide minerals before and after contacting with reagent solutions is carried out using a KEYENCE VK-9700 confocal laser scanning microscope. This microscope enables making color images, conducting non-contact measurements of high definition. The shortwave laser and white light source are used simultaneously for lighting. The use of a laser beam allows the user to obtain the most accurate images of the surface relief of the object under study, as well as to perform numerical measurements of the unevenness of the relief.

Non-contact measurements were carried out by obtaining three-dimensional coordinates of the points of the sample surface relief by laser scanning. To display objects along three coordinates, a virtual manipulator and a computer mouse are used. The microscope is equipped with a revolver system of Nikon lenses, using which the researcher can adjust the magnification in the range 10X–150X. Observation and imaging is performed using the VK-Viewer software.

Measurements of the areas of the newly formed phases of the reagent on the surface of mineral polished sections were performed using the VK-Analyzer software on the basis of a color image by filling the object's selected area with a selected gradient. In other words, either the layer of the adsorbed reagent or the surface free from the reagent is highlighted in color, and the corresponding area is measured. The adsorption of the reagent according to the developed method is assessed by the degree of coverage of the surface of a mineral with a reagent (Fig. 2).

The measurements made at several fields of view (with an increase of 20X) showed that 21.6% of the arsenopyrite surface was covered by the DEDTCc reagent. The area occupied by the droplets in the neoplasms that may be presented by physically adsorbed OPDTC ester or disulfide DEDTC2, estimated 2.9% of the total area of the reagent coating (Fig. 2).

The measurements of the adsorption layer of the combined diethyl dithiocarbamate on the surface of chalcopyrite and arsenopyrite at several sites of the field showed that the degree of coverage of the surface of arsenopyrite by the DEDTCc reagent is 3 times lower than chalcopyrite, and is 21.6–27% (for chalcopyrite – 65–72,2%), which can provide preferential flotation of chalcopyrite compared to arsenopyrite into the con-

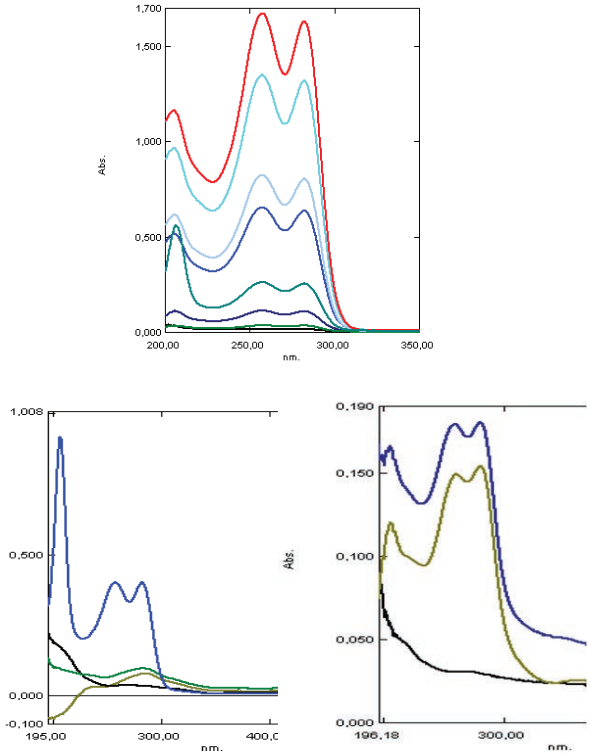


Fig. 3. UV-spectra of DEDTC initial solution (concentration 0,56–28 mg/l) (a), liquid phase of chalcopyrite suspension after DEDTC treatment (C = 10 mg/l) (b) and arsenopyrite suspension after DEDTC treatment (C = 5 mg/l) (c)

Rys. 3. Widma UV roztworu początkowego DEDTC (stężenie 0,56–28 mg / l) (a), faza ciekła zawiesiny chalkopirytu po obróbce DEDTC (C = 10 mg / l) (b) i zawiesina arsenopirytu po DEDTC leczenie (C = 5 mg / l) (c)

centrate. The total area of the tumors in the form of drops that characterize the physically sorbed component of the solution (OPDTC or DEDTC2) on the arsenopyrite was 2.9% of the total area of the coating reagent.

The predominant adsorption of DEDTCc on the chalcopyrite was quantified by UV spectroscopy of the liquid phase of mineral suspensions before and after contact of minerals with the reagent according to the difference between the initial and residual concentrations of DEDTC. Fig. 3 demonstrates UV spectra of the initial solutions of DEDTC at different concentrations (from 0.56 to 28 mg/l), on which the calibration curve was constructed, and spectra of the liquid phase of mineral suspensions after contact of the reagent with minerals are presented. By changing the optical density at the characteristic wavelengths of 257 and 282 nm, the residual concentration of the reagent and the adsorption of the reagent on the mineral were calculated. The residual concentration of DEDTCc in arsenopyrite suspenssion was 78–87% of initial concentration and adsorption was 0.02–0.04 mg/g. In the same experimental conditions the residual concentration of DEDTCc in chalcopyrite suspenssion was 19–24% of initial concentration and adsorption was 0.15–0.16 mg/g.

Conclusions

On scanning microscope from KEYENCE VK-9700 analyzer the formation of the adsorbed layer and the dimensions of newly formed phases of the combined collector DEDTCc, anchored in the surface of chalcopyrite and arsenopyrite under flotation conditions have been determined experimentally. Different newly formed phases on the surface of chalcopyrite and arsenopyrite indicated the chemical and physical nature of adsorption of the components of combined DEDTCc – anionic DEDTC and non-ionic OPDTC, respectively.

Nonionic OPDTC reagent fixed on the surface in the form of sinter drop-like neoplasms having clearly defined circular shape with a diameter of 0.1 to 27.4 microns and a maximum height of 0.65 to 1.85 microns. Combined DEDTCc formed irregularly shaped phase size 63–100 microns and a thickness of 10–20 microns, characterized by adsorption OPDTC neoplasms, which obviously explained c.

During the research it was established that for the selective separation of copper and arsenic sulfide minerals into concentrates of different kinds, it is possible to use combined DEDTCc capable to be selectively adsorbed on the chalcopyrite surface rather than on arsenopyrite. Using the laser KEYENCE VK-9700 and electronic LEO-1420 VP INCA-350 microscopy methods, it has been established that the film of a combined DEDTCc was not washed off with water and fixed firmly enough on the surface of the polished sections of chalcopyrite.

The measurements of the adsorption layer of the combined diethyl dithiocarbamate on the surface of sulfide minerals at several sites of the field showed that the degree of coverage of the surface of arsenopyrite by the DEDTCc reagent is 3 times lower than chalcopyrite, which can provide preferential flotation of chalcopyrite compared to arsenopyrite into the concentrate.

Acknowledgments:

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Charakterystyka adsorpcji kombinowanego kolektora sulfhydrylowego na chalkopirycie i arsenopirycie w flotacji złożonych rud złota

W pracy przedstawiono wyniki badań eksperymentalnych właściwości adsorpcyjnych kombinowanego odczynnika zbierającego sulfhydryl – mieszanego roztworu dietyloditiokarbaminianu sodu (DEDTC) i estru oksypropylodietyloditiokarbaminianowego (OPDTC) w kierunku chalkopirytu i arsenopirytu w celu jego zastosowania selektywny kolektor minerałów siarczkowych zawierających Au w flotacji złożonych rud ogniotrwałych. Połączony roztwór dietylo-ditiokarbaminianu (DEDTCc) zawierał stałą zawartość składników anionowych i niejonowych (DEDTC: OPDTC = 1: 1) i zaobserwowano zmienny efekt hydrofobowy na powierzchni podstawowych minerałów siarczkowych niosących złoto - chalkopirytu i arsenopirytu.

Mechanizm adsorpcji składników kombinowanego kolektora na powierzchni chalkopirytu i arsenopirytu został zidentyfikowany jako charakterystyczny skład molekularny adsorbowanego kolektora chemicznie zaadsorbowanych cząsteczek reagenta, który jest mocno zakotwiczony na powierzchni. Nowo utworzona faza zaadsorbowanego odczynnika nie rozpuszczała się w wodzie podczas kolejnego płukania. W tym przypadku faza niejonowego estru OPDTC została częściowo usunięta przez wodę, a resztkowe zaadsorbowane kropelki zmieniły swój kształt i stały się bardziej płaskie. Za pomocą mikroanalizy rentgenowskiej zidentyfikowano pasma C i O dotyczące struktury połączonego DEDTCc na powierzchni arsenopirytu i chalkopirytu. Opracowano oryginalną technikę analizy wymiaru liniowego obrazów powierzchni za pomocą skaningowej mikroskopii laserowej i oprogramowania analizatora, a autorom udało się określić ilościową ocenę adsorpcji DEDTCc na powierzchni chalkopirytu i arsenopirytu.

Słowa kluczowe: flotacja, selektywny kolektor, rudy złota

Transport of Organic Dyes in Systems Containing Humic Acids

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Abstract

This work is focused on transport organic dyes in systems containing humic acids as active reaction agent. Methylene blue was used as a model organic dye which can behave as pollutant and influence many processes in nature. Transport of pollutants in nature is strongly affected by interactions with humic acids or natural organic matter. Their influence is dependent on affinity of pollutant to content and strength of active binding sites. Two different humic samples are used in this study in order to compare their properties on transport of organic dye. Both humic acids are used in original extracted form as well as in the form of samples with selective blocked functional groups.

Keywords: humic substances, diffusion cells, methylene blue, ionic compound, diffusion

Introducion

Humic substances represent a wide range of organic compounds generated by gradual decomposition of plant residues and dead organisms in ecosystems. They are among the most widespread compounds in the world that contain a huge amount of carbon in its structure. Information and knowledge about them are still limited, thereby offering an opportunity for further research. Humic substances create an important part of soil organic matter, involved in soil self-cleaning, soil retention, buffer capacity soil and CO_2 binding in it. Industrial production, agriculture and other human activities bring a lot of pollution into nature. These pollutions are not only getting to the surface and ground water, but also to the soil and air. Therefore, it is important to understand the mechanisms of transport of pollutants, their interactions with soil organic matter and potential immobilization in nature.

Teams from all over the word deal with the binding of various pollutants to humic substances.

The interaction possibilities can be different: ion exchange, hydrogen bridge formation, coulombic interactions, hydrogen bridges, van der Waals interactions, hydrophobic interactions, etc. in Klučáková et al. (2014a) and Sedláček et al. (2013). These interactions and binding strength are strongly influenced by physical-chemical parameters such as pH, ionic strength, humectant concentration or temperature.

All these parameters can have important influence on the bioavailability of given pollutant and its further functioning in nature.

Main aim of this work is to study the transport of methylene blue through a membrane in a solution containing humic acids and their interactions. In order to investigate the interactions in detail, humic acids with selective blocked functional groups were used for the comparison. Due to methylation of carboxyl groups, which are mainly responsible for coulombic interactions between negatively charged carboxyl and cationic charged organic pollutant, was observed way of binding.

The methylene blue was chosen as a model organic dye due to its similar to many herbicides and pesticides commonly used in agriculture.

Material and Methods

Two different humic acids were used in this study. The first one, (HA1) was Leonardite standard of humic acids (1S104H) purchased from International Humic Substances Society (for its characterization see http://humic-substances.org). Other sample, (HA2) was extracted from lignite mined in the Czech Republic and characterized previously e.g. in Klučáková et al. (2014b) and Klučáková et al. (2016).

Sample HA1 was methylated with trimethylsilyldiazomethane by means of method described in Klučáková et al. (2014a, 2016). It was designated as mHA1. Methylated humic acids as well as original samples were characterized by means of FT-IR spectrometry (Nicolet iS50) and elemental analysis (EURO EA Elemental Analyzer).

Two different concentrations of humic acids (50 and 100 mg/L) and one concentration of methylene blue were used and all solutions were prepared in phosphate buffer (pH = 7).

The PrermeGear diffusion cells were used for the experiment. A dialysis membrane Spectra/Por® (Spectrum laboratories, Inc. MWCO: 3,500 kDa) was placed between diffusion cells to separate the solution of humic sample from the solution of methylene blue. A small magnetic stirrer was placed into the small space at the bottom of each dialysis cell the need to place in a small space at the bottom of the cells. Cell connection was secured by side clamps to ensure that cells are perfectly fixed. The absorbance at 665 nm (Hitachi U-3900H) was monitored during the experiment and concentration of methylene blue was calculated using calibration curve.

Results and Discussion

The basic characteristics of used humic samples are shown in Figure 1 and Table 1. It can be seen, the methyla-

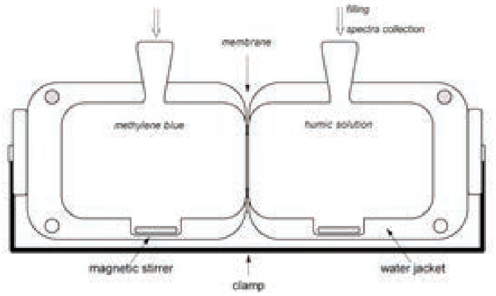

Fig. 1. Scheme of diffusion cells
Rys. 1. Schemat komórek dyfuzyjnych

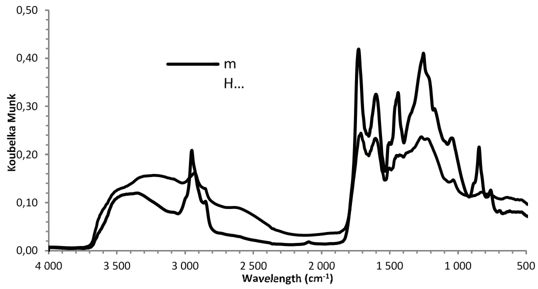

Fig. 2. FT-IR spectra of HA1 (full line) and mHA1 (dashed line) measured using DRIFT method
Rys. 2. Widma FT-IR HA1 (pełna linia) i mHA1 (linia przerywana) mierzone metodą DRIFT

tion of functional groups resulted in changes of FT-IR spectra characteristic for esters. The intensity of the broad peak at around 3500 cm^{-1} was decreased by methylation and the shallow band at 2580 cm^{-1} was completely absent. The absorption band corresponding to C=O stretching was shifted to higher wavenumbers after methylation (from ~1720 cm^{-1} to ~1735 cm^{-1}) and its intensity was increased. The observed changes in spectra caused by methylation corresponded with our results published previously Klučáková et al. (2014a, 2015).

The replacement of H+ ion by $-CH_3$ group in carboxylic functional groups was expressed in changes in the humic elemental composition. The ratio between carbon and hydrogen decreased and the ratio between carbon and oxygen increased as a consequence of the methylation. The contents of sulfur and nitrogen was very low, therefore their role in humic interactions can be neglected in this case.

In Figure 3, the example of experimental data is shown. The dye concentration decreased gradually in the donor cell as a result of its transport through membrane into the acceptor cell. Assuming that whole amount of dye transported through membrane interacts with humic acids, the decrease of its concentration should be equal to the amount of methylene blue bound to humic acids. The obtained decreases for all used humic samples are in the Table 2. The amount of methylene blue transported through membrane decreases with increasing initial concentration of humic acids in the acceptor cell. Simultaneously, this amount is lower in the case of humic acids with methylated carboxyl groups.

It can be seen can be seen, the concentration of methylene blue in the acceptor cell gradually increases (Figure 3). It means that some dye in the acceptor cell is unbound and mobile. As it was shown in our recent works Sedláček et al. (2013), Klučáková et al. (2014a,2015), the equilibrium between humic acids and reactant can establish and ions are bound in humic structure with different strength. Our experimental arrangement involves two equilibriums. At first, it is the equilibrium between donor and acceptor cells.

If we assuming that big humic molecules cannot be transported through membrane, so called Donnan equilibrium is established. Another equilibrium is established between free mobile and bound methylene blue. A general description or mathematical solution of our experiment is not easy. In addition, the situation can be more complex, e.g. equilibriums between dye particles bound to humic acids with different strengths can exist or some fractions of humic acids are able to move through the membrane. Many simplifying assumptions have to be accepted in order to make a mathematical model of the situation in our experimental arrangement.

On the other hand, our experiments can simulate some processes occuring in nature and our data from this experiment can improve our knowledge of interactions between natural organic matter and organic dyes. It was confirmed that the transport of pollutants in nature is strongly affected by the reactivity of humic substances. In general, leonardite humic standard contains much more carboxylic functional groups in comparison with the humic acids extracted from lignite (Klučáková et al., 2015). It caused positive influence on the concentration decrease of dye in the donor cell. The blocking of these binding sites caused a decrease of driving force of the dye transport through membrane as a result of the changes in experiment conditions (Figure 4). The blocked carboxylic groups cannot dissociate and bind dye ions but the interactions between hydrophobic humic structures and aromatic methylene blue can be more applied.

Tab. 1. Elemental composition of used humic samples (normalized on dry ash free mass)
Tab. 1. Skład pierwiastkowy badanych próbek humusowych (znormalizowany do suchej masy wolnej od popiołu)

sample	C (% at.)	H (% at.)	O (% at.)	N (% at.)	S (% at.)	C/H	C/O
HA1	48.1	33.2	17.7	0.8	0.2	1.45	2.72
mHA1	45.5	37.9	15.9	0.6	0.1	1.20	2.86
HA2	38.6	38.5	22	0.8	0.1	1.00	1.75

Tab. 2. Decrease of dye content in donor cell normalized on humic mass (number 1 means initial humic concentration 50 mg/L, number 2 100 mg/L)
Tab. 2. Zmniejszenie zawartości barwnika w komórce donora znormalizowanej (liczba 1 oznacza początkowe stężenie humusowe 50 mg/l, liczba 2 100 mg/l)

sample	decrease (g/g)	
	1	2
HA1	1.92 ± 0.01	0.99 ± 0.01
mHA1	1.63 ± 0.01	0.90 ± 0.01
HA2	1.60 ± 0.03	0.96 ± 0.02

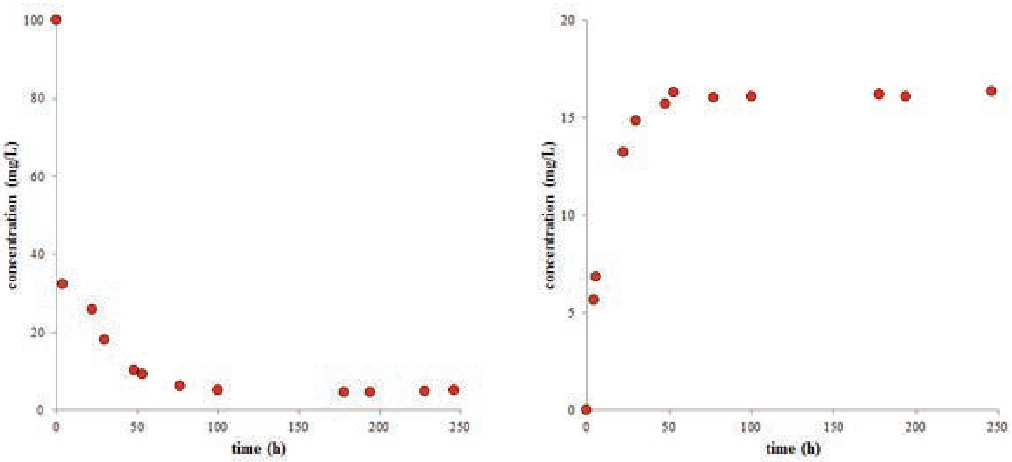

Fig. 3. Time development of concentration of methylene blue in donor (left) and acceptor (right) cell (HA2 with initial concentration 100 mg/L)
Ryc. 3. Zmiana w czasie stężenia błękitu metylenowego w komórce donora (po lewej) i akceptorze (po prawej) (HA2 o początkowym stężeniu 100 mg/l)

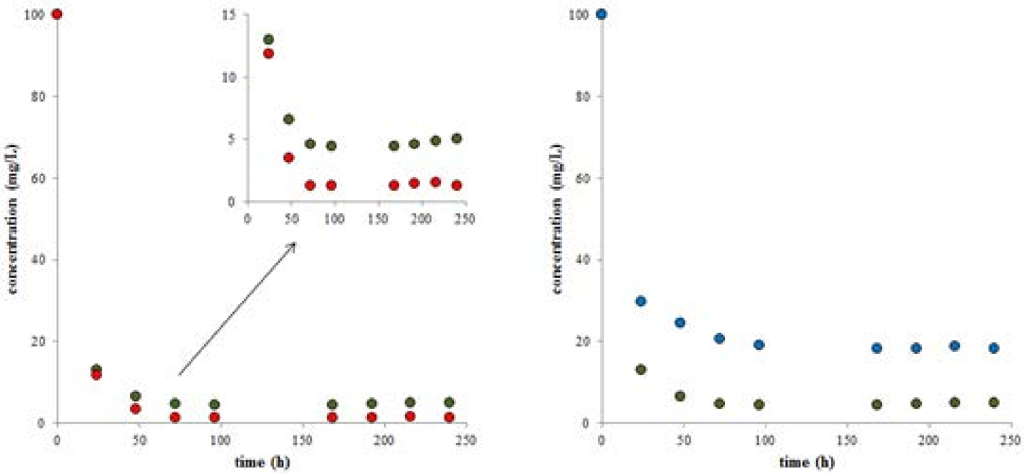

Fig. 4. Time development of concentration of methylene blue in donor cell: HA1 with initial concentration 50 mg/L (green), HA1 with initial concentration 100 mg/L (red), mHA1 with initial concentration 50 mg/L (blue)
Ryc. 4. Zmiana w czasie stężenia błękitu metylenowego w donorze: HA1 o początkowym stężeniu 50 mg/l (zielony), HA1 o początkowym stężeniu 100 mg/l (czerwony), mHA1 o początkowym stężeniu 50 mg/l (niebieski)

Conclusion

Main aim of this work was to study the transport of methylene blue through a membrane in a solution containing humic acids. Two different humic acids were used in this study. The first one, (HA1) was Leonardite standard of humic from International Humic Substances and sample (HA2) was extracted from lignite mined in the Czech Republic. Carboxyl groups are mainly responsible for coulombic interactions between negatively charged carboxyl and cationic charged organic dye (methylene blue). Due to methylation of carboxyl groups of humic acids were selectively blocked functional groups (mHA1).

The replacement of H+ ion by –CH3 group in carboxylic functional groups was expressed in changes in the humic elemental composition and the methylation of functional groups resulted in changes of FT-IR spectra characteristic for esters.

During experiments the concentration of methylene blue in the acceptor cell gradually increases and decrease of dye content in donor cell was measured. It means that some dye in the acceptor cell was unbound and mobile. There was the equilibrium between donor and acceptor cell if big humic molecules cannot be transported through membrane, so called Donnan equilibrium was established. There was equilibrium established between free mobile and bound methylene blue as well.

Leonardite humic standard (HA1) contains much more carboxylic functional groups in comparison with the humic acids extracted from lignite (HA2). It caused positive influence on the concentration decrease of dye in the donor cell. The blocked carboxylic groups (mHA1) cannot dissociate and bind dye ions but the interactions between hydrophobic humic structures and aromatic methylene blue can be more applied.

Acknowledgments

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Transport barwników organicznych w układach zawierających kwasy huminowe

Niniejsza praca koncentruje się na transporcie barwników organicznych w systemach zawierających kwasy huminowe jako środek aktywny. Błękit metylenowy wykorzystano jako modelowy barwnik organiczny, który może zachowywać się jak substancja zanieczyszczająca i wpływać na wiele procesów w przyrodzie. Na transport zanieczyszczeń w przyrodzie silnie wpływają interakcje z kwasami huminowymi lub naturalną materią organiczną. Ich wpływ zależy od powinowactwa substancji zanieczyszczającej do zawartości i siły aktywnych miejsc wiązania. W badaniu tym zastosowano dwie różne próbki humusowe w celu porównania ich właściwości w transporcie barwnika organicznego. Oba kwasy humusowe stosuje się w oryginalnej postaci ekstrahowanej, jak również w postaci próbek z selektywnie zablokowanymi grupami funkcyjnymi.

Słowa kluczowe: substancje humusowe, komórki dyfuzyjne, błękit metylenowy, związek jonowy, dyfuzja

Monitoring of Indoor Ultrafine Particulate Matter at the Sites of the Czech Armed Forces

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Abstract

Ultrafine particles and nanoparticles in the air are evaluated as a risk factor for the development of respiratory and other health symptoms due to their inhalation from the ambient air. The Czech Army professionals are expected to have frequent presence in a polluted environment and regular exposure to air with increased concentration of airborne pollutants. The report evaluates the presence of ultra-fine particles (in the range of about 7.6–299.6 nm) in rooms often used by soldiers during their working hours when they are not deployed. The purpose is to assess whether the presence of troops in these workplaces is safe and does not pose a risk of adverse health effects in itself. Testing took place in three military rooms (classroom 1, classroom 2 and exercise flight simulator room). Seven samples of air were analysed in time by the scanning mobility particle sizer in succession. Mean particle concentrations were found at 1.79×10^4, 7.53×10^3 and 8.39×10^3 $N\cdot cm^{-3}$ for the classroom 1, classroom 2 and exercise flight simulator room. Conclusions of the research have shown that particle concentrations in the places of the Czech Army can reach values that border the immission limits stated by the World Health Organisation.

Keywords: ultrafine particle, indoor air, air quality, health risk

Introduction

Some pollutants are naturally occurring since time immemorial, and their amount is usually increased by human activity. This type of pollutants also includes ultrafine particles (UFP) of less than 100 nm (Viana et al., 2015), which are released into the atmosphere mainly by various types of combustion, transport, industrial activity, etc.

Health Risks from Inhalation of Ultrafine Particles

Particle size is critical for nanoparticle penetration and deposition in the respiratory tract. The finest submicrometric fraction of the particles passes through the lungs (Ministry of the Environment, 2015). Nanoparticles, especially those smaller than 30 nm, cause oxidative stress and are the most dangerous form of air pollution. The surface properties of nanoparticles, including their surface charge, play an important role in this process because UFP exhibit high activity in the lungs (Večeřa et al., 2012).

Immission Limits of Ultrafine Particles in the Air

Nanoparticles in the air are referred to as so-called particulate matter (PM). For example, the World Health Organization (WHO) recommends that a quantity of nanoparticles smaller than 2.5 µm (PM2.5) in the atmosphere is at a maximum level of 10 $\mu g.m^{-3}$ per year and not more than 25 $\mu g.m^{-3}$ per 24 hours (WHO, 2005). In the Czech Republic, air quality is assessed on the basis of requirements of Act No. 201/2012 Collections, on air protection. Here is a requirement for a maximum permissible PM2.5 limit of 20 $\mu g.m^{-3}$ per year (Czech Republic, 2012).

Air Quality Inside Buildings of Military Departments

UFP exposures inside buildings are often divided into two parts that differ significantly in composition, time regime and their relation to patterns of human activity in time. The first part refers to particles from outside air that can significantly affect PM levels inside buildings and transport-related microenvironments. The second part refers to particles from internal sources that have the potential to generate very high levels of PM that do not correlate with external levels of particles on a temporary basis (McAuley et al., 2010; Morawska et al., 2013).

Czech Armed Forces (CAF) belong among the components of the Integrated Rescue System, whose personnel is at risk of higher UFP loads from the air. In military environments, air pollution is often caused by using combat techniques and weapons, combat vehicles, guns, and a number of special weapons and military equipment in field conditions. In these activities, a large amount of airborne particles is released (Nindl et al., 2013).

The state of health protective equipment used against inhalation of pollutants and the safety and protection of soldiers' health is a topic closely monitored. In particular, efforts are made to avoid excessive pollution by air pollutants even in situations where these persons do not directly participate in their own field activities. The aim of this paper is to propose a comprehensive image of the burden of selected interior spaces of military buildings with ultra-fine particles in the range of 7.6–299.6 nm. On the basis of these data, it will be possible to assess whether the presence of exposed professionals in these workplaces is safe and does not in itself pose a risk of adverse health effects.

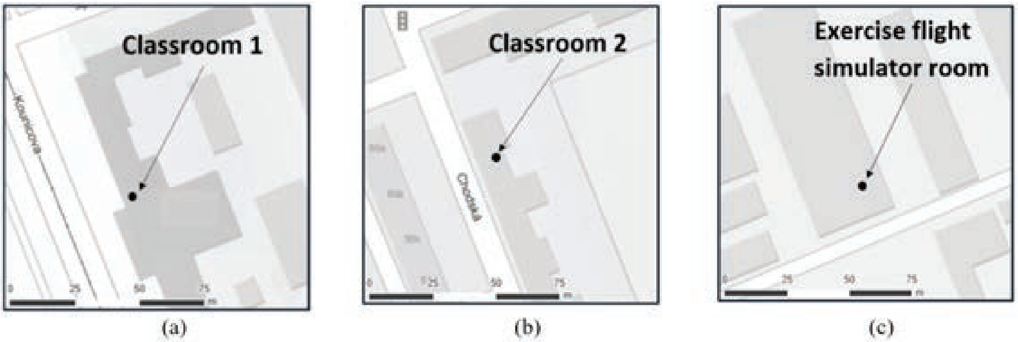


Fig. 1. Illustration of the sampling places in the examined buildings: (a) classroom 1, (b) classroom 2, (c) flight simulator room (source: own)
Rys. 1. Miejsca pobierania próbek w badanych budynkach: (a) klasa 1, (b) klasa 2, (c) sala symulatora lotu (źródło: własne)

Methods

The methods used for the evaluation of selected indicators were introduced at the Institute of Analytical Chemistry of the Academy of Sciences of the Czech Republic. The numerical concentrations of UFP aerosol particles were measured in the interior of the three rooms of military departments (classroom 1, classroom 2 and exercise flight simulator room). All buildings are located in the suburban part of Brno (Czech Republic). The scanning mobility particle sizer (SMPS, model 3936L72, TSI) was used to measure the particle size ranged from 7.6 nm to 299.6 nm. In all cases, measurements were made in empty room oriented to a high-traffic street. Seven samples of air were immediately analysed in succession (one sample time was approximately 5 minutes, so the total measurement time in one school was approximately 35 minutes). All doors and windows in rooms were closed during the measurement. Illustrations of measured rooms are in the Figure 1.

Experimental Part

Because research studies suggest (McAuley et al., 2010) that sources of nanoparticles from the external environment (in the first instance the traffic situation) have a great influence on the concentrations inside the adjacent buildings, the characteristics of the nearest UFP sources from heavy traffic are given in the Table 1. For this purpose, dimensionless coefficient K was calculated, where a is the traffic intensity of the nearest thoroughfare [number of vehicles per day], e is Euler's number and x is the distance of the nearest frequent thoroughfare [in 100 m]:

$$K = \frac{a}{e^x}$$

Description of Meteorological Conditions at the Time of Measurement

The highest values of pollutant concentrations are usually achieved during unfavorable dispersion conditions outside the transport sites (Ministry of Environment, 2015; Morawska et al., 2013). For each room investigated, the values of the basic meteorological indicators that were reported in Brno at the time of the measurements were subsequently surveyed in the archive (see Table 2).

Statistical Evaluation of Results

To evaluate the signal from the SMPS, Aerosol Instrument Manager (TSI, 2010) was used to calculate the particle size distribution by dividing the particle size range into 64 identical channels. In addition, the total number of particles C_N [$N·cm^{-3}$] was calculated, where n is the total number of channels and C_i [$N·cm^{-3}$] is the number of particles in the i-th channel:

$$C_N = \sum_{i=1}^{n} C_i$$

The total particle volume V [$nm^3·cm^{-3}$], where Ri is the radius of the particles measured in the i-channel was then estimated.

$$V = \frac{4}{3}\pi \sum_{i=1}^{n} R_i^3 C_i$$

Furthermore, on the basis of measured data, approximate total mass concentration of particles C_M [$\mu g·m^{-3}$] according was estimated. In this equation, ρ stands for average:

$$C_M = V\rho$$

The corresponding value of particle density ρ = 1.5 g·cm-3 to urban aerosol from various studies was used (Zhao, et al., 2016).

Results

The measured results are presented in Table 3 that summarizes the main data and statistical calculations of measured UFP in the examined rooms. The highest particle volume was measured in the exercise flight simulator room (7.93·109 $nm^3·cm^{-3}$). The particle volume acquired in military classroom 2 and classroom 1 was 2.22·109 and 3.98·109 $nm^3·cm^{-3}$.

Acquired results show different values of the nanoparticles in the monitored spaces within the distinct sites of the Czech Armed Forces. At the CAF classroom 1, the average concentration was detected at 1.79×10^4 $N·cm^{-3}$, which corresponds to the average weight of the nanoparticles at the level of 5.97 $\mu g·m^{-3}$ of air. Mean particle diameter of nanoparticles was at the size of about 36.61 nm as the lowest observed diameter within the tested rooms.

In the classroom 2, the average nanoparticle concentration measured was 7.53×10^3 $N·cm^{-3}$, which corresponds to the average weight of nanoparticles at the level of 3.32 $\mu g·m^{-3}$. Mean particle diameter of nanoparticles was at the mean size of 41.97 nm.

In the exercise flight simulator room, the average nanoparticle concentration measured was 8.39×10^3 $N·cm^{-3}$,

Tab. 1. Characteristics of investigated CAF rooms during air sampling (source: own) [Note: SE – southeast; NW – northwest; N – north; *) RNDr. Jiří Huzlík, PhD. Transport Centre in Brno [interview], 2012; **)Traffic Slope 2016 – Transport Research Centre, 2016]

Tab. 1. Charakterystyka badanych pomieszczeń CAF podczas próbkowania powietrza (źródło: własne) [Uwaga: SE – południowy wschód; NW – północny zachód; N – północ; *) RNDr. Jiří Hužlík, PhD. Transport Center w Brnie [wywiad], 2012; **) Nachylenie ruchu 2016 – Centrum Badań Transportu, 2016]

Tested rooms	Description of the sampling place	Usual activities performed inside the tested rooms	Description of the building	Distance, location and traffic intensity of the nearest known thoroughfare	K
Classroom 1	Room on the 1st floor, with the size about 50 m^2, unventilated	Theoretical teaching of military students	Five floor Public Military School, built in 1936–1937	260 m, SE, 17 000 vehicles per day in average $^{*)}$	1262.65
Classroom 2	Room on the 2nd floor, with the size approximately 50 m^2	Theoretical teaching of military students	Three floor Public Barracks, built in 1904	805 m, NW, 30 066 vehicles per day in average $^{**)}$	9.59
Exercise flight simulator room	Hall on the ground floor, with the size approximately 200 m^2	Practical training of military students in handling with military aircraft technology	Two floor Public Barracks, built in 1927	560 m, N, 45 682 vehicles per day in average $^{**)}$	168.93

Tab. 2. The values of the basic meteorological indicators recorded in Brno at the time of measurement at the monitored sites of CAF (source: Meteocentrum.cz, 2018) [Note: T_{atm} – air temperature, T_{dp} – dew point temperature, P_{atm} – atmospheric pressure, w – wind speed, PWD – prevailing wind direction, N – north, E – east, NE – northeast]

Tab. 2. Wartości podstawowych wskaźników meteorologicznych zarejestrowanych w Brnie w czasie pomiaru w monitorowanych miejscach CAF (źródło: Meteocentrum.cz, 2018) [Uwaga: T_{atm} – temperatura powietrza, T_{dp} – temperatura punktu rosy, P_{atm} – atmosfera ciśnienie, w – prędkość wiatru, PWD – dominujący kierunek wiatru, N – północ, E – wschód, NE – północny wschód]

	Date and time	T_{atm} [°C]	T_{dp} [°C]	P_{atm} [hPa]	w [km·h^{-1}]	PWD
Classroom 1	18.1.2018 10:00	-1	-4	1008	7	N
Classroom 2	18.1.2018 9:00	-1	-3	1008	9	NE
Flight sim. room	25.1.2018 8:30	-1	-2	1024	11	E

Tab. 3. Acquired concentrations of particles (source: own) [Note: NA – not measured]

Tab. 3. Stężenia cząstek (źródło: własne) [Uwaga: NA – nie mierzone]

Ci [N·cm^{-3}] / Mi [μg·m^{-3}]	Flight simulator room	Classroom 2	Classroom 1
1. measure	7029.74 / 11.91	6064.23 / 3.15	16400.62 / 5.78
2. measure	8053.28 / 11.89	6186.8 / 3.18	16054.02 / 5.78
3. measure	8499.84 / 11.79	6575.07 / 3.24	17356.14 / 5.87
4. measure	8750.78 / 11.91	7626.17 / 3.34	17825.85 / 6.10
5. measure	8982.19 / 12.00	8348.68 / 3.37	19123.94 / 6.01
6. measure	8812.34 / 12.00	8546.88 / 3.50	20484.68 / 6.26
7. measure	8621.25 / 11.76	9393.46 / 3.48	NA
C_N [N·cm^{-3}] / C_M [μg·m^{-3}]	8392.77 / 11.89	7534.48 / 3.32	17874.21 / 5.97
Average std. deviation [%]	30.77	46.19	128.54
V [nm^3·cm^{-3}]	$7.93 \cdot 10^9$	$2.22 \cdot 10^9$	$3.98 \cdot 10^9$

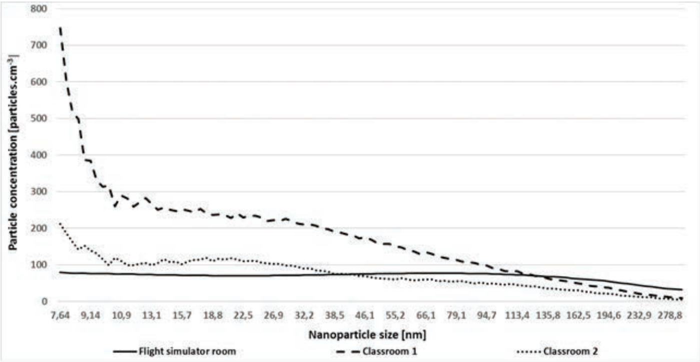
which corresponds to the average weight of nanoparticles at the level 11.89 μg·m^{-3}. This is probably because there was a higher number of larger particles with the mean diameter about 100 nm. Mean particle diameter of nanoparticles was at the size of about 70.01 nm.

Discussion

Due to easy permeability of UFP smaller than 30 nm through respiratory tract, they may increase health risks more easily in comparison with other tested rooms (Večeřa et al., 2012). Highest levels of such particles were found in the classroom 1. However, amount of particulate matter in the air of flight simulator room (11.89 μg·m^{-3}) exceeded the limit recommended by the WHO (maximum annual mean of $PM_{2.5}$ on the level of 10 μg·m^{-3}). In the case that in the air of the flight simulator room are achieved similar values of UFP particles regularly, long-term inhalation of such air may pose a health risk (WHO, 2005). Figure 2 shows mean C_i values of performed measurements ordered by their size for tested rooms.

Acquired data are in accordance with the calculated coefficient K, which was the highest in the classroom 1 (1262.65), suggesting that frequent traffic in the nearest surroundings contributes to high number concentrations of ultrafine particles in classroom 1. Regarding research studies focused on the traffic as the main source of nanoparticles with sizes lower than 100 nm (Gong et al., 2009), our results indicate that the main source of UFP in classroom 1 is related to the frequent traffic (number of particles increased with the decreasing size of particles in general). In the classroom 2 and

Fig. 2. The concentration of nanoparticles in the tested military rooms (source: own)
Rys. 2. Stężenie nanocząstek w badanych pomieszczeniach wojskowych (źródło: własne)



exercise flight simulator room, with the coefficients K 9.59 and 168.93 respectively, the traffic was the probably source of nanoparticles to a lesser extent.

Conclusion

The paper monitored the presence of UFP in the size range from 7.6–299.6 nm in rooms often used by troops of the Czech Armed Forces (classroom 1, classroom 2 and exercise flight simulator room). The general characteristics (average particle count, mean standard deviation, corresponding mass and size distribution) were evaluated and consequently statistically evaluated (mean particle diameter, total particle number and mass concentration, particle surface, specific surface area and particle volume). Average particle counts of 1.79×10^4, 7.53×10^3 and 8.39×10^3 $N\cdot cm^{-3}$ were determined for the classroom 1, classroom 2 and exercise flight simulator room. This concentrations correspond to the mean particle weight of 5.97, 3.32 and 11.89 $\mu g\cdot m^{-3}$ for the classroom 1, classroom 2 and exercise flight simulator room. The concentration found in flight simulator room border with the immission limit stated by the WHO (maximum annual mean of $PM_{2.5}$ particles is recommended to be lower than 10 $\mu g.m^{-3}$). Such concentrations may pose a health risk when inhaled for a long time. However, the measured range did not include other particle sizes than 7.6–299.6 nm. Therefore, it is possible to expect that the number of particles smaller than 2.5 μm was higher than we found. Moreover, duration of our measurements was 35 minutes and UFP at the annual horizon is unknown. Expert studies focused on the occupational health symptoms of troops highlighted that military staff should increase the use of breathing masks in all hazardous situations as much as possible (Nindl et al., 2013).

Acknowledgements

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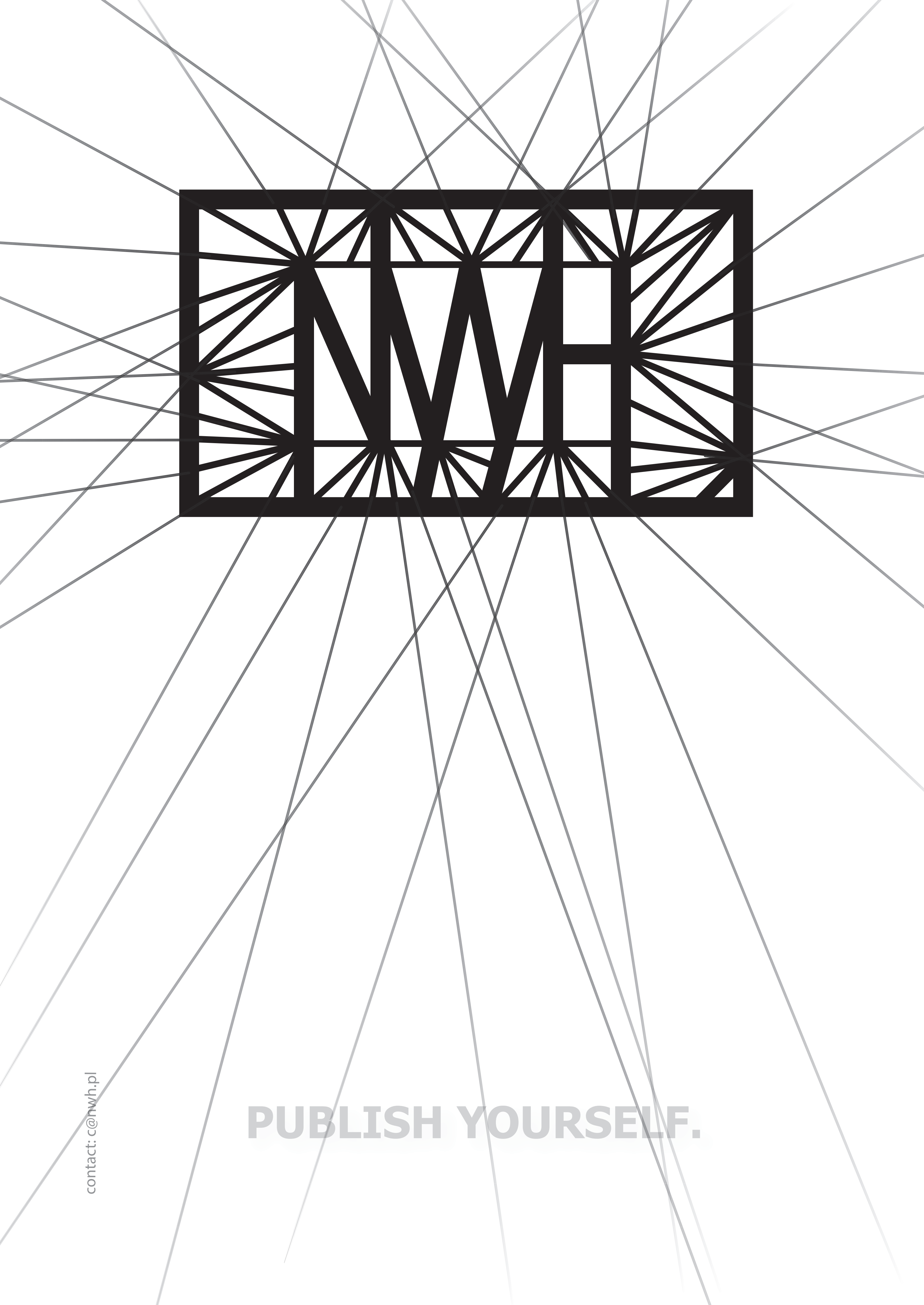
Monitorowanie ultradrobnych cząstek w pomieszczeniach na terenach czeskich sił zbrojnych

Najdrobniejsze cząstki i nanocząsteczki w powietrzu są oceniane jako czynnik ryzyka dla dróg oddechowych i innych objawów zdrowotnych spowodowanych ich wdychaniem z otaczającego powietrza. Oczekuje się, że specjaliści z czeskiej armii będą często obecni w zanieczyszczonym środowisku i będą regularnie narażeni na kontakt z powietrzem o zwiększonej koncentracji zanieczyszczeń. Raport ocenia obecność ultradrobnych cząstek (w zakresie około 7,6–299,6 nm) w pomieszczeniach często używanych przez żołnierzy w godzinach pracy. Celem jest ocena, czy obecność wojsk w tych miejscach pracy jest bezpieczna i sama w sobie nie stwarza ryzyka negatywnych skutków zdrowotnych. Testowanie odbyło się w trzech pomieszczeniach wojskowych (sala 1, sala 2 i sala do ćwiczeń). Siedem próbek powietrza analizowano w czasie przez separator cząstek. Stwierdzone średnie stężenia cząstek 1,79 × 104, 7,53 × 103 i 8,39 × 103 [N · cm^{-3}] w sali lekcyjnej 1, klasie 2 i sali do ćwiczeń. Wnioski z badań wykazały, że stężenia cząstek w wybranych pomieszczeniach czeskiej armii mogą osiągnąć wartości graniczące z limitami imisji podanymi przez Światową Organizację Zdrowia.

Słowa kluczowe: ultradrobne cząstka, powietrze w pomieszczeniach, jakość powietrza, ryzyko dla zdrowia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Nano-design of Zeolites Biomass Wastes Valorization: Dehydration of Lactic Acid into Acrylic Acid

Izabela KURZYDYM, Izabela CZEKAJ[1)]

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Abstract

The valorization of waste from biomass currently arouses great interest. In the present study we concentrate on the design of innovative BEA zeolite catalysts with applied metal nanoparticles - copper, vanadium and manganese for the dehydration of lactic acid to acrylic acid. The ab initio method based on density functional theory (DFT) was used to calculate the electron structure of the analyzed molecules. The non-local generalized gradient corrected functionals GGA-RPBE was used to in order to account for electron exchange and correlation. The cluster model was represented by a hierarchical zeolite $M_2Al_2Si_{12}O_{40}H_{22}$ *(M = Cu, V, Mn). The stabilization of the* $M\text{-}O_b\text{-}M$ *dimer complex in the hierarchical structure of BEA, mechanism of adsorption of lactic acid on BEA zeolite with applied metal dimers and formation of acrylic acid on these zeolites were investigated. The examined metals form stable dimers interconnected by a bridge oxygen (Ob). Adsorption of lactic acid takes place in the vicinity of a dimer of* $M\text{-}O_b\text{-}M$*. The dehydration of lactic acid to acrylic acid in all cases consists in the separation of the hydroxyl group and creating a connection with a metal center of dimer and disconnection of a single hydrogen atom from the methyl group and its interaction with bridge oxygen of dimer.*

Keywords: DFT method, metalic nanoparticles, lactic acid dehydration, acrylic acid

Introduction

Major challenge of society research is to build fuels and chemical intermediates from available and renewable materials that do not compete with food crops for water or fertilizer (Pacala et al.,2004). The urgent needs for a more sustainable production of chemicals from renewable feedstock, like biomass, have caused intensive research efforts in search for novel porous nano-materials (Corma et al., 2007). Such materials may combine high catalytic activity, selectivity and a long-term stability by controlling their structure, porosity and functionalities. Knowledge about catalysts molecular structure and reaction mechanism is necessary to design and synthetize optimal materials. Due to ability to catalyze many types of hydrocarbon reactions as well as due to specific structure of active sites zeolites are ideal candidates for the production of chemicals from biomass, e.g. dehydration reactions (Rinaldi et al., 2009, Stöcker et al., 2008). Additionally, zeolites are effective three dimensional supports for active nanoparticles as well as there are flexible for metal exchange inside framework.

Acrylic acid is currently used as a starting material to produce many chemicals and polymers for example in the textile industry (Xu et al., 2006). At the present time acrylic acid is produced in a two-step reaction by partial oxidation of propylene (Lin, 2001). Due to the increased use of renewable sources, the production of acrylic acid as a result of dehydration of lactic acid is an attractive alternative.

In the present part of study, we are interested in designing a new approach for the synthesis of acrylic acid from lactic acid over zeolite catalysts. The theoretical modeling of lactic acid dehydration would help in further development and synthesis of zeolite with declare structure, e.g. proper metallic nanoparticles in the zeolite frame.

Computational method

The ab initio method based on density functional theory (DFT) was used to calculate the electronic structure of the analyzed molecules (StoBe code). The exchange and electron correlation is taken by using for the calculation of the generalized non-local functional GGA-RPBE (Pardew et al., 1996; Hammer et al., 1999). The use of extended Gauss functions allowed for the presentation of all Kohna-Sham orbits by a linear combination of atomic orbitals (LCAO's) (Lebanowski, Anzelm, 1991; Godbout et al., 1992). The Mulliken population analysis for a detailed analysis of the electron structure (Mulliken, 1955), and the Mayer procedure to interpret the rows of bonds was used (Mayer, 1983; Mayer, 1987). In the studies of stabilization of dimeric M-O-M complexes we based on previous theoretical studies on iron dlimers in the ZSM-5 framework (Czekaj et al., 2013).

Results and discussion

The stabilization of dimer complexes M-Ob-M (where M=Cu, V, Mn) on the BEA zeolite surface obtained by simulation of hierarchization in the alkaline environment was investigated (Figure 1). All analyzed structures revealed stabilization of the dimer around the aluminum and oxygen atoms in the BEA zeolite structure. This indicates a strongly active acid center on the aluminum atom. Stable dimers are formed by connection of metal atoms witch bridge oxygen. Bond lengths between the metal atoms and bridge oxygen atom are slightly different depending on the element and are equal: for

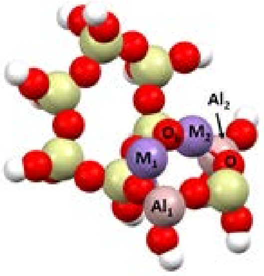

Fig. 1. Metal dimer M-Ob-M (where M= Cu, V or Mn) in the hierarchical BEA zeolite
Rys. 1. Dimer metaliczny M-Ob-M (gdzie M = Cu, V lub Mn) w hierarchicznym zeolicie BEA

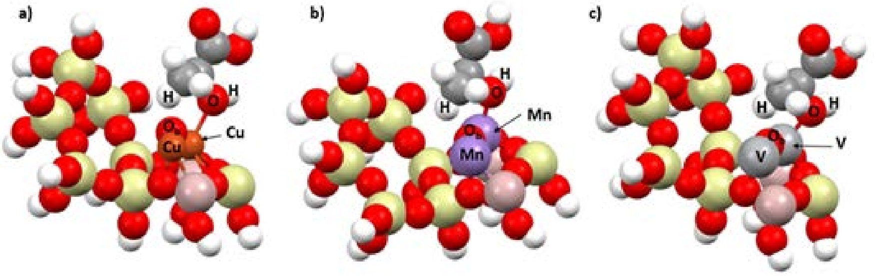

Fig. 2. Hierarchical model of BEA zeolite with a metallic dimer and adsorbed lactic acid a) Cu, b) V, c) Mn
Rys. 2. Hierarchiczny model zeolitu BEA z dimerem metalicznym i zaadsorbowanym kwasem mlekowym a) Cu, b) V, c) Mn

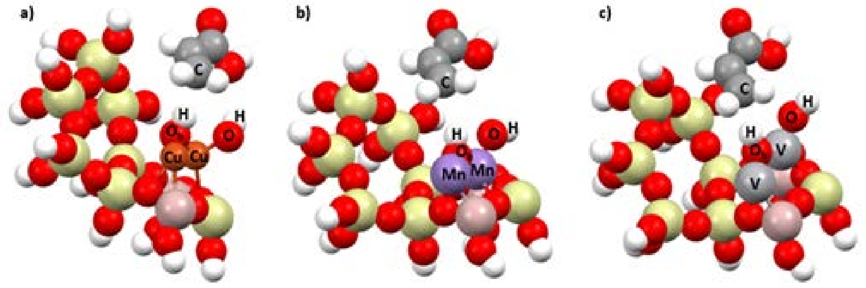

Fig. 3. Hierarchical model of BEA zeolite with a metallic dimer and desorbed acrylic acid a) Cu, b) V, c) Mn
Rys. 2. Hierarchiczny model zeolitu BEA z dimerem metalicznym i desorbującym kwasem akrylowym a) Cu, b) V, c) Mn

Cu – 1.81 and 1.86 Å, V – 1.76 and 1.77 Å, Mn – both 1.68 Å. Despite these small differences, the mechanism of dimer deposition on BEA zeolite is basically the same. A strong correlation between vanadium and manganese metallic centers was also demonstrated (bond order Mn-Mn 1.90 and V-V 1.88) while in copper these interactions are negligible and around 0.17 for Cu-Cu.

The next step of the analyzed mechanism of dehydration of lactic acid to acrylic acid is the adsorption of lactic acid on the metallic dimer deposited on the surface of the BEA zeolite (Figure 2). It can be seen that lactic acid interacts via its hydroxyl group of α-carbon with the metallic center of the dimer. Bond order between oxygen of hydroxyl group and the metallic center are equal: for Cu-O 0.14, Mn-O 0.24 and V-O 0.29. The single hydrogen atom of methyl group also participates in the lactic acid adsorption process. It interacts with the bridge oxygen of the dimer. In all cases the bond order between hydrogen and bridge oxygen is about 0.01–0.05.

The last step of dehydration is the desorption of acrylic acid (Figure 3). Visualization of results allows us to state that the water molecule separates from lactic acid in the form of two hydroxyl groups at metal dimer. The first hydroxyl group attaches to the metallic center, while second hydroxyl group is formed at bridge position between metal centers of dimer. The bond between β-carbon of acrylic acid and the hydrogen of bridge hydroxyl group is broken. This indicates the complete formation of acrylic acid and its desorption from the BEA zeolite surface. The bond order of the formed hydroxyl group H-Ob is about 0.6 for each dimer. In contrast, the hydroxyl group attached to the metallic center shows the following bonds order between metal and oxygen: Cu-OH 0.73, Mn-OH 1.12, V-OH 1.07. After desorption, the dimers occur in a hydrated form.

Analyzing the length of bonds between individual atoms, we can notice that the attachment of a hydroxyl group and a single hydrogen atom to the dimer causes structural changes of metal dimer. Mainly, the metal-bridge oxygen bond lengthen by 0.15-0.2 Å (Figure 4). The interaction of the hydrated form of the dimer with acrylic acid is negligible. The newly formed hydroxyl groups have the lengths of bonds typical for these types of moieties (about 1Å).

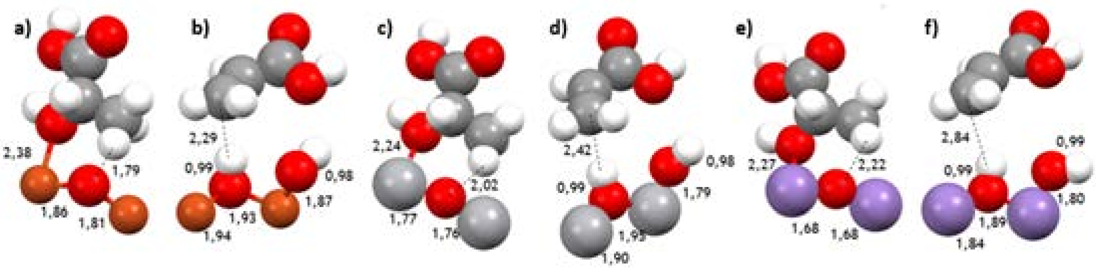

Fig. 4. Structure of lactic acid and acrylic acid: a) LA with Cu_2O dimer, b) AA with Cu_2O dimer, c) LA with V_2O dimer, d) AA with V_2O dimer, e) LA with Mn_2O dimer, f) AA with Mn_2O dimer

Rys. 4. Struktura kwasu mlekowego i kwasu akrylowego: a) kwas mlekowy z dimerem Cu_2O, b) kwas akrylowy z dimerem Cu_2O, c) kwas mlekowy z dimerem V_2O, d) kwas akrylowy z dimerem V_2O, e) kwas mlekowy z dimerem Mn_2O, f) kwas akrylowy z dimerem Mn_2O

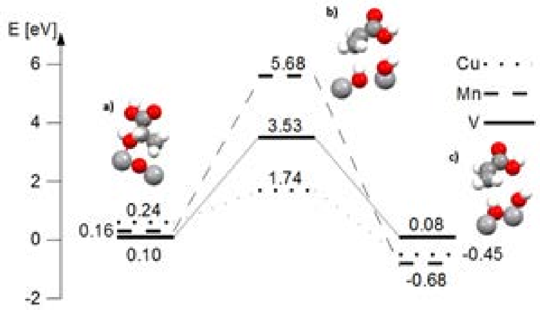

Fig. 5. Energy diagram of lactic acid dehydration into acrylic acid over dimeric M-O_b-M complex in the BEA zeolite, where M= Cu, V, Mn, a) lactic acid adsorption, b) intermediate stage, c) desorption of acrylic acid

Rys. 5. Schemat energetyczny odwodnienia kwasu mlekowego do kwasu akrylowego nad dimerycznym kompleksem M-O_b-M w zeolicie BEA, gdzie M = Cu, V, Mn, a) adsorpcja kwasu mlekowego, b) etap pośredni, c) desorpcja kwasu akrylowego

The energies of individual steps of lactic acid dehydration were also analyzed (Figure 5). The first step illustrates the energy required for the adsorption of lactic acid on the surface of the catalyst (Figure 5a). The lowest energy has adsorption on vanadium dimer (0.10 eV). In all cases this step is slightly endothermic and the energies are comparable. The next step is a transitional state consisting in the formation of acrylic acid (Figure 5b). This reaction is strongly endothermic and the energies are varied depending on the metal in the dimer. The highest energy is shown for manganese dimer (5.68 eV), the lower for vanadium dimer (3.53 eV) and the lowest in case of copper dimer (1.74 eV). The last step is the desorption of acrylic acid (Figure 5c). This step is exothermic for manganese and copper dimer (-0.68 and -0.45 eV), and endothermic for vanadium dimer (0.08 eV). Comparing the energy barriers, it can be concluded that the most energy-efficient catalyst would be BEA zeolite with an embedded copper dimer.

Conclusion

The hierarchical structure of the BEA zeolite has been considered, which allowed the analysis of the reaction directly on the surface of the BEA catalyst. The metal M-Ob-M dimers (M=Mn, Cu, V) have been found to be stable above oxygen bound with aluminum centers of BEA zeolite. The geometric compatibility of the metallic dimers and lactic acid allows for the proposed direct dehydration mechanism, where the oxygen center of the hydroxyl group of the α-carbon interacts with the metal center of the dimer and hydrogen is subtracted from the β-carbon and bound with the bridge oxygen of the metal dimer. The most energy-efficient catalyst would be BEA zeolite with an embedded copper dimer.

Acknowledgement

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Abstrakt

Waloryzacja odpadów z biomasy cieszy się obecnie dużym zainteresowaniem. W niniejszych badaniach koncentrujemy się na projektowaniu innowacyjnych katalizatorów zeolitowych BEA z nanocząstkami metali - miedzi, wanadu i manganu w celu odwodnienia kwasu mlekowego do kwasu akrylowego. Metoda ab initio oparta na teorii funkcjonalności gęstości (DFT) została wykorzystana, przy użyciu nielokalnego funkcjonału korelacyjno-wymiennego GGA-RPBE, do obliczenia struktury elektronowej analizowanych cząsteczek. Hierarchiczny zeolite BEA był reprezentowany przez model klasterowy $M_2Al_2Si_{12}O_{40}H_{22}$ *(M = Cu, V, Mn). Badano stabilizację dimeru* $M\text{-}O_b\text{-}M$ *w hierarchicznej strukturze BEA, mechanizm adsorpcji kwasu mlekowego na zeolicie BEA z zastosowanymi dimerami metali i tworzenie kwasu akrylowego na tych zeolitach. Badane metale tworzą stabilne dimery połączone wzajemnie tlenem mostkowym* (O_b)*. Adsorpcja kwasu mlekowego odbywa się w pobliżu dimeru* $M\text{-}O_b\text{-}M$*. Odwodnienie kwasu mlekowego do kwasu akrylowego we wszystkich przypadkach polega na oddzieleniu grupy hydroksylowej i utworzeniu połączenia z jednym z metali dimeru i odłączeniem pojedynczego atomu wodoru od grupy metylowej kwasu mlekowego i jego oddziaływaniem z tlenem mostkowym dimeru.*

Słowa kluczowe: metoda DFT, nanocząstki metaliczne, odwodnienie kwasu mlekowego, kwas akrylowy

The Analysis of The Process of Barley Grain Separation from Undesirable Particles

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Abstract

The article focuses on the intensification of raw barley grains initial purification and separation processes before the subsequent processing in the area of brewing. Above all, it deals with the physical and mechanical concepts of the purification and separation of qualitatively satisfactory grains from undesirable impurities, e.g. coarse impurities, as the prevention from the potential damage of milling and scrapping facilities. Four different cultivated barley species were tested within the study. Physical and mechanical parameters were determined in all samples, for instance powder density, angle of internal friction and external friction angle with steel contact material, particle size distribution and morphology. The first results of measuring revealed the difference in the quality of initial entering component of barley grains before the purification process compared to the output quality of grains after machine purification and separation processes in the facilities determined for the subsequent grain storage. As a result of the non-effective process of separation, the final quality of the product, i.e. the beer, may be affected by the qualitative parameters of partial processes involved in treating barley grains.

Keywords: barley, angle of internal friction; separation; qualitative parameters

Introduction

Especially grown types of malt barley grains are used in the food industry, especially in brewing, where they are one of the most important ingredients used in beer production. The effort to objectively and comprehensively illustrate the malting quality of varieties of barley has led to the creation of different assessment systems and procedures. At present, the malting quality of barley varieties is evaluated according to the "malting quality indicator", which was based on the requirements of the processing industry. The key indicators of quality malting barley are especially germination and germination energy. A very important feature is nitrogen content - protein and starch content. Important quality criteria are further mechanical features such as the proportion of grains of 2.5 mm above the screen, at a base value of 80% at baseline and 20% in the size of 2.8 mm. Malting barley should not contain any waste - dry and undeveloped grains which pass through a sieve size 2.2 mm [1,2]. When barley is picked up by growers, the malt house performs a basic analysis that determines the quality for classification, but also whether barley may be specially treated. Pre-treatment, cleaning and storage in silos are then carried out. The pretreatment leads to the removal of dust, light parts and metal parts. The cleaning takes place in two stages, first in the first conical cylinder, the coarse impurities are separated from a mixture of material that passes through the conical cylinder. In the second stage, barley is separated from fine particles of impurities, barley grains, and round grains of weeds, which overflow through the trimer - cylinder, the jacket of which is provided on the inner side with pocket-shaped pits with a diameter of 6.5 mm. The attachments are then transferred by means of the auger to the collecting point where they are conveyed to the sacking socket. Separated barley is lifted above the cylinder axis at the end of the cleaning and drops to the collecting point by sliding, at this stage the last product separation from the finest air extraction particles takes place. Grading of barley grains by size has technological significance to achieve uniform soaking, germination and obtaining perfectly homogeneous malt [3]. It is clear that his detailed analysis will help to understand the basic principles and to find critical places with the possibility of innovation.

Experiments and Methods

Material

In our case, malted barley was chosen as the material evaluated, and 4 varieties of specially brewed brewer's barley grown in the Czech Republic – Moravia region were selected. These barley samples were taken from silos. These are the species called Malz, Sebastian, Francin and KWS Irina, where the basic quality parameters - humidity in the range of 13–13.2%, overflow of the overfill fraction 2.5 mm in the range 91.6–95.5% were determined upon receipt. %, 2.2 mm sub-saturation fraction from 4.5–7.3 wt. %, germination in total 99%.

Powder density

A sample of barley of specified weight was poured into the measuring cylinder and the apparent volume value was

Tab. 1. Parameters of powder density, angle of repose, flow characteristics based on the Hausner ratio (HR) and the Carrs index (CI)
Tab. 1. Gęstość proszku, kąt tarcia wewnętrznego, charakterystyki przepływu w oparciu o współczynnik Hausnera (HR) i indeks Carrsa (CI)

Barley's sample	**Powder density [kg.m^{-3}]**	**Angle of repose α [°]**	**CI [%]**	**HR [-]**	**Flow**
Malz before	656.3	25.6	3.4	1.03	excellent
Malz after	676.6	17.6	5.8	1.06	excellent
Sebastian before	627.1	21.8	9.6	1.11	excellent
Sebastian after	669.4	15.6	8.7	1.10	excellent
Francin before	669.4	19.2	9.6	1.10	excellent
Francin after	707.7	18.6	9.1	1.10	excellent
KWS IRINA before	638.5	18.2	10.0	1.10	excellent
KWS IRINA after	659.1	16.4	8.7	1.10	excellent

Tab. 2. Parameters of the external and internal friction angles
Tab. 2. Parametry zewnętrznego i wewnętrznego kąta tarcia

Barley's sample	**Angle of internal friction [°]**	**Angle of external friction [°]**	**Classification of flowability**
Malz before	29.1	11.1	Free flowing
Malz after	30.5	8.2	Free flowing
Sebastian before	31.3	10.9	Free flowing
Sebastian after	31.7	8.8	Free flowing
Francin before	29.9	9.6	Free flowing
Francin after	30.7	8.5	Free flowing
KWS IRINA before	29.9	9.7	Free flowing
KWS IRINA after	30.4	9.3	Free flowing

Tab. 3. Parameters of particle size distribution, particles'sphericity (SPHT3), width/length ratio (b/l3)
Tab. 3. Parametry rozkładu wielkości cząstek, sferyczność cząstek (SPHT3), stosunek szerokości do długości (b/l3)

Barley's sample	**Malz before**	**Malz after**	**Sebastian before**	**Sebastian after**	**Francin before**	**Francin after**	**KWS IRINA before**	**KWS IRINA after**
D_{10} [mm]	3.05	3.04	3.04	3.02	2.92	3.00	3.00	3.03
D_{50} [mm]	3.70	3.67	3.62	3.59	3.54	3.56	3.69	3.67
D_{90} [mm]	4.22	4.17	4.08	4.05	4.05	4.06	4.29	4.21
$SPHT_3$	0.69	0.71	0.71	0.73	0.73	0.74	0.71	0.72
b/l_3	0.49	0.50	0.51	0.52	0.52	0.53	0.50	0.51

subtracted. Powder density was determined by weight and apparent volume [4, 5]. The barley sample was evenly dispensed from the hollow cylinder to a conical-shaped horizontal surface. The powder angle was determined as the largest angle, which forms the horizontal surface and the surface line of the cone formed by the embedded barley sample. The powder angle was determined as a tagengs angle equal to the height of the cone and the radius of the cone.

Angle of internal friction and wall friction

The principle of measuring the shear properties of powder materials consists of loading the volume of the powder mass where the masses by normal load of the preset size and the subsequent displacement of the powder layer in a direction perpendicular to the normal load. The shear stress will result from the friction between the particles, which is detected. Specifically, the force required to overcome shear forces occurring between the particles due to the action of normal force is measured. These forces are further recalculated to the stress [6,7]. Measurement of angles of internal and wall friction was performed on Schulze Ring Shear Tester RST-01 (Wolfenbuttel, Germany), where the principle of measuring these parameters is the use of rotational motion [8].

Granulometry and particle shape

To measure the size and shape of grains of free-flowing powder materials an Camsizer optoelectronic device consisting of a planar light source, feeder, measured material, two CCD cameras for bulk images, a cleaning unit, and a PC with an evaluation program were used. Powder material particles overlap the end edge of the vibrating trough, rotation occurs during fall. Rotating particles pass through the instrument through the measuring space - images are generated using one or two CCD cameras and then analyzed. The granulometric analysis of the test material is generated automatically from the frames obtained.

Results and Discussion

Mechanical and physical parameters

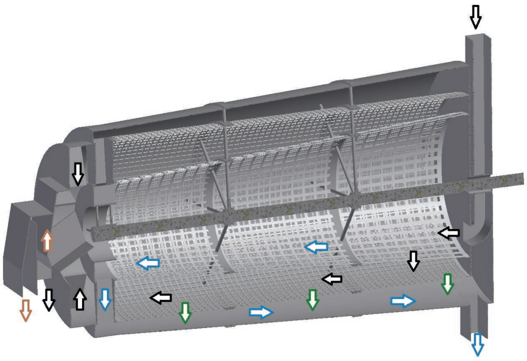

Fig. 1. Proposal for the innovation of the separation process
Rys. 1. Propozycja innowacji procesu separacji

The flow properties were first determined for unpurified raw state samples and for samples after cleaning. The resulting values of powder densities, the angle of repose, CI (Carrs index) and HR (Hausner ratio) [9] for test samples are shown in Tab. 1.

The results show that the values for unpurified samples are different in all measurements, but the mass flow rate as a whole is identical when compared to the Hausner ratio (HR) and Carr's index (CI). It can be stated that the purity of the test materials does not significantly affect their flow properties. The flow pattern was defined as excellent for all cases. The specified parameters of the wall and internal friction angles are summarized in Tab. 2. From the results of the measured values, it is clear that the values of the internal friction angles are slightly smaller than the values for the samples of the cleaned. It is likely that the unpurified material contains fine dust or other fine impurities that contribute to reducing friction. The external friction angle is higher for uncleaned samples than for the cleaned ones. From the flowability point of view, the same conclusion as in density measurements was reached, ie. the degree of purity of the accepted barley in the tested cases does not significantly affect their flowability.

In terms of particle size measurement, it is possible to see the difference in b/l3 - width/length ratio. This ratio is greater for cleaned grains than for uncleaned (Tab. 3). It is further apparent substantial difference in the parameters of sphericity $SPHT_3$ when this parameter is also always greater at the purified grains than in untreated grains.

Separation process

On the basis of the determined characteristics, it was found that the critical process of separation is not the mechanical cleaning process itself, but the removal of impurities from the technological line. Consequently, the conical shape of the discharge drum has been proposed in which the rough material is displaced along with fine impurities as shown in Fig. 1.

The mixture of material enters the upper part of the cleaner shown in Fig. 1 with a black arrow, this arrow further showing the direction of travel of the resulting barley product. In the first stage, the mixture is separated from coarse impurities by a conical roller, and the remaining material blends into the second cleaning step, perforated by the drum, where barley is separated from fine impurities. Fine impurities fall through the drum, as shown by the green arrow, and mix with coarse particles in the last drum, and the mixture is taken out for recycling. The barley, free of coarse and fine impurities, is lifted above the cylinder axis at the end of the cleaning and drops into the collection point by slipping. At this stage, a brown arrow shows the last separation of the product from the finest particles by air extraction in Fig. 1.

Conclusion

The objective of this work was to analyze the process of separation of barley grains from undesirable particles, such as admixtures of clay, stones, metal particles, grass, but also damaged and small grains. Evaluation was conducted in four different areas, where four kinds of barley grain samples were compared, which were taken in primary unpurified form with samples that underwent a purification and separation process. Despite the fact that there are different types of brewery barley varieties, a certain phase appeared in our measurements, as evidenced by the recorded values. From the established characteristics it was found that the critical point of separation is not the mechanical cleaning process itself, but the removal of impurities from the technological line. Consequently, the conical shape of the draining drum has been designed, in which the rough material is displaced along with fine dirt.

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Analiza procesu oddzielania ziarna jęczmienia od zanieczyszczeń

Artykuł koncentruje się na intensyfikacji wstępnych procesów oczyszczania i separacji surowych ziaren jęczmienia przed dalszym przetwarzaniem w procesie warzenia piwa. Przede wszystkim zajmuje się fizycznymi i mechanicznymi koncepcjami oczyszczania i oddzielania jakościowo zadowalających ziaren od niepożądanych zanieczyszczeń, np. gruboziarniste zanieczyszczenia, zapobiegające potencjalnym uszkodzeniom urządzeń do mielenia oddzielania zanieczyszczeń. W ramach badań przetestowano cztery różne gatunki jęczmienia. We wszystkich próbkach określono parametry fizyczne i mechaniczne, na przykład gęstość proszku, kąt tarcia wewnętrznego i kąt tarcia zewnętrznego ze stalowym materiałem kontaktowym, rozkład wielkości cząstek i ich morfologię. Pierwsze wyniki pomiarów ujawniły różnicę w jakości ziaren jęczmienia przed procesem oczyszczania w porównaniu z jakością wyjściową ziaren po oczyszczeniu. W wyniku nieefektywnego procesu separacji na jakość końcową produktu (piwo) mogą wpływać parametry jakościowe kolejnych procesów związanych z obróbką ziaren jęczmienia.

Słowa kluczowe: jęczmień, kąt tarcia wewnętrznego, separacja, parametry jakościowe

Recycling of Spent Hydrodehalogenation Catalysts – Problems Dealing with Separation of Aluminium

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Abstract

Our study is focused on utilization and recycling of copper and nickel applicable for reductive degradation of tetrabromobisphenol A (TBBPA), the high use brominated flame retardant for printed circuit boards. Deactivated and/or poisoned hydrodebromination catalysts are produced by reductive destruction of brominated phenol (TBBPA) dissolved in alkaline aqueous solution using Raney Al-Ni and/or Devarda´s Al-Cu-Zn alloys. Spent metallic slurry is treated with aqueous sulfuric acid to dissolve residual aluminium and/or zinc and decanted residual metal is subsequently treated under oxidation conditions and dissolved in excess of mineral acid by co-action of oxidant. The corresponding metal salt is separated from corresponding leachates containing excess of acid by evaporation and recycling of volatile components. Obtained copper or nickel salts were used as sources of Raney type hydrodebromination catalysts produced for in-situ by action of $NaBH_4$.

Keywords: Raney nickel; copper; tetrabromobisphenol A; hydrometallurgy; borohydride; reduction

Introduction

In sustainable system for use of materials, not only the production of goods needs to be sustainable, but also the management of residues and wastes (Gutknecht et al., 2017).

Copper is with high recovery priority, followed by nickel, aluminum, tin, lead, zinc and other (Wu et al., 2017).

Owing to the current rapid development of electronic technology, electrical and electronic equipment, for example printed circuit boards (PCBs), have a shorter life span compared to products produced in the past. The resultant short life spans of electrical and electronic equipments have generated large amounts of waste, known as e-waste. Useful components can be recovered from e-waste to save resources. This is because e-waste from PCBs has a high metal content. Waste PCBs contain approximately 70% nonmetals, 10% of copper and 20% of another metals (Xiu et al., 2014).

However, the PCBs exhibit complex multilayered metal-woven glass fiber structure which is reinforced by brominated epoxy resin containing 15–20 wt% of flame retardants (Ghosh et al., 2015).

The main structural part of brominated epoxy resins is tetrabromobisphenol A (TBBPA), which is the highest production volume brominated flame retardant. The primary use of TBBPA is as a reactive flame retardant in resins for PCBs (Malkoske et al., 2016).The occurrence of TBBPA can behave as precursor in the formation of highly stable and toxic poly- brominated dibenzo-p-dioxins and benzofurans (PBDD/Fs) (Tang et al., 2014).

Given that brominated flame retardant materials in e-waste plastics have been the major impediment for recycling treatment, chemical recycling has been proposed as an environmentally friendly method of recycling e-waste plastics for clean fuels production or chemical feedstocks (Ma Ch. et al., 2016).

Catalytic hydrodehalogenation is usually used to dispose waste halogenated compounds. The experiments of Shen and Sun (2009) proved that metal salts, $FeCl3$, $NiCl2$, $CoCl2$, $CuBr$ and some iron complexes with benzimidazole ligand are efficient catalysts for hydrodebromination of bromoarenes under mild reaction conditions of room temperature and $N2$ atmosphere with two equivalents of Grignard reagents (Shen and Sun, 2009).

Moreover, Raney Al-Ni and Devarda´s Al-Cu-Zn alloys also displayed high dehalogenating aktivity in alkaline aqueous solution under room temperature and ambient pressure. (Weidlich T. et al., 2013).

However, the described Al-Ni or Al-Cu-Zn based hydrodebromination method produces copper or nickel slurry (spent Cu or Ni) as solid product with substantially reduced activity for further hydrodebromination. These slurries are simply separated by sedimentation of obtained reaction mixture. These slurries contain around 20 wt. % of unreacted aluminium and 80 wt. % of copper or nickel which are economically valuable metals. In addition, these metals are common components of PCBs. The potential recovery of Cu and Ni from spent hydrodebromination catalysts by simple and cost effective technique helps to solve the economy of the above mentioned remediation process. In addition, at least part of copper and nickel from waste PCBs could be utilized in hydrodebromination of brominated aromatic flame retardants.

Due to these reasons, attempts to recover copper and nickel applicable for hydrodebromination from separated metallic slurries were studied.

Materials and methods

The removal efficiency of reductive debromination of TBBPA was quantified by analysis of AOX content according to the Environmental Protection Agency (EPA Method 1650).

Aqueous alkaline 2.5 mM TBBPA solution was prepared by dissolution of 1.36 TBBPA (Sigma-Aldrich Co.) in 1 liter of 0.1M aq. NaOH solution. The measured AOX content is 425 mg L^{-1}.

Tab. 1. Content of sulfuric acid and metals before and after leaching

Tab. 1. Zawartość kwasu siarkowego i metali przed i po ługowaniu

Description of aq. solution	Concentration (wt %)	Metal concentration (mg L^{-1})	
	H_2SO_4	Ni	Al
Leachate Ni1 (13wt% H_2SO_4)	13	2666	1416
Leachate Ni2 (hot 13wt% H_2SO_4)	13	2655	1307
Leachate Ni3 ($K_2S_2O_8$/H_2SO_4)	32	1455	384
Leachate Ni4 (recycled aq.$NiSO_4$)	-	7362	3764

Tab. 2. Content of sulfuric acid and metals before and after leaching

Tab. 2. Zawartość kwasu siarkowego i metali przed i po ługowaniu

Description of aq. solution	Concentration (wt%)	Metal concentration (mg L^{-1})		
	of acid	Cu	Al	Zn
Leachate Cu1 (13wt% H_2SO_4)	13	1.0	345.4	187.9
Leachate Cu2 (hot 13wt% H_2SO_4)	13	0.2	2570.0	220.0
Leachate Cu3(H_2O_2/35 wt %HCl)	17	3928	7	30
Leachate Cu4 (recycled aq.$CuCl_2$)	-	10715	1.2	0.1

Application and recycling of Ni-based debromination catalyst

Debromination of TBBPA using Raney Al-Ni alloy

Raney Al-Ni alloy (410 mg, Sigma-Aldrich) was added into the 100 mL of alkaline aqueous 2.5 mM TBBPA solution, 150 mL of 0.1 M aqueous NaOH was added and the obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX=2.38 mg L^{-1}) which indicates 98.6% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Ni catalyst was collected and stored under water.

1. Leaching of Al from spent Raney nickel catalyst in 13 wt% H_2SO_4

The slurry of spent nickel catalyst collected from five debromination experiments described above was filtered by suction and dried on air. 3.0 grams of wet Ni cake was mixed with 200 mL (217.2 g) of 13 wt. % H_2SO_4 (density 1.086 kg L^{-1}) under stirring and the obtained slurry was agitated about 15 hours, insoluble part was separated by sedimentation and 50 mL of liquid phase was filtered (Leachate Ni1). Obtained leachate Ni1 was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The compositions of leachates are described in Table 1.

The remaining reaction mixture (150 mL) was heated 60 minutes at 100°C, filtered and filtrate was diluted to exact 200 mL using deionized water (Leachate Ni2) and analysed by ICP-OES.

2. Leaching of Ni from spent Raney nickel catalyst in 32 wt% H_2SO_4 by co-action of $K_2S_2O_8$

To the insoluble part, 540 mg of $K_2S_2O_8$ (2 mmol) was added, dissolved by addition of 40 mL of deionized water and mixed with 10 mL (19.4 g) of concentrated sulfuric acid. The obtained suspension was heated for 16 hours at 100°C. The obtained solution was cooled, the volume was adjusted to 100 mL using distilled water (leachate Ni3). Obtained solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The composition of leachate 3 is described in Table 1.

3. Separation $NiSO_4$

Crystalline $NiSO_4$ was isolated from leachates 1–3 (300 mL) by evaporation of excess water at 140°C using oil bath (248.3 g of distillate was obtained) and subsequent separation crystals obtained by cooling of distillation residue at room temperature by suction. The green crystalline product was dissolved in deionized water, adjusted to 100 mL using deionized water and analysed by ICP-OES (leachate Ni4).

Debromination of TBBPA using recycled Ni:

$NaBH_4$ (0.8 g, 20 mmol) was dissolved in 100 mL of 0.1M aqueous NaOH solution. To this solution was added dropwise 50 mL of obtained leachate 4 (recycled Ni in the form of $NiSO_4$ solution) during 5 minutes and 50 mL of alkaline 2.5 mM aqueous TBBPA solution. The obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX= 18.3 mg L^{-1}) which indicates 83% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Ni catalyst was collected and stored under water for further recycling. Obtained filtrate was acidified using 13 wt% H_2SO_4 to pH=6.2±0.2 and flocculated $Al(OH)_3$ was removed by filtration.

Application and recycling of Cu-based debromination catalyst

Debromination of TBBPA using Devarda´s Al-Cu-Zn alloy

Devarda´s Al-Cu-Zn alloy (800 mg, Sigma Aldrich Co.) was added into the 100 mL of alkaline aqueous 2.5 mM TBBPA solution, 150 mL of 0.1 M aqueous NaOH was added and the obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX=6.43 mg L-1) which indicates 96.2% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Cu catalyst was collected and stored under water. Obtained filtrate was acidified with leachate Cu2 (see Table 2) to pH=6.2±0.2 and flocculated $Al(OH)_3$ was removed by filtration.

1. Leaching of Al and Zn from spent Devarda´s alloy in 13 wt% H_2SO_4

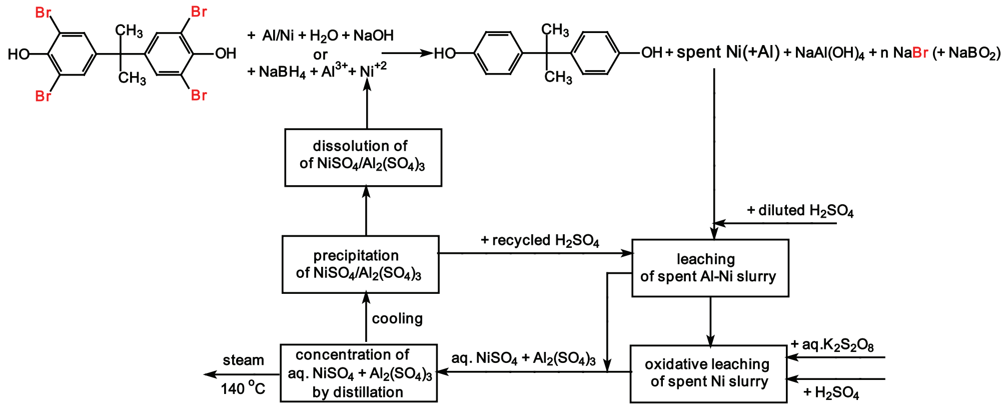

Fig. 1. Scheme of TBBPA hydrodebromination with subsequent recycling of spent Ni catalyst
Rys. 1. Schemat hydrodebrominacji TBBPA z późniejszym recyklingiem zużytego katalizatora Ni

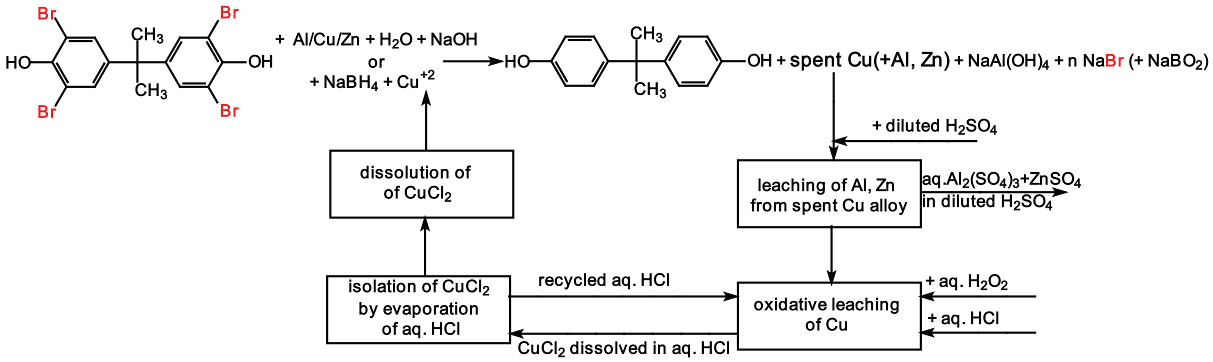

Fig. 2. Scheme of TBBPA hydrodebromination with subsequent recycling of spent Cu catalyst
Rys. 2. Schemat hydrodebrominacji TBBPA z późniejszym recyklingiem zużytego katalizatora Cu

The slurry of spent copper catalyst collected from three debromination experiments described above was filtered by suction and dried on air. 3.0 grams of wet Cu cake was mixed with 200 mL (218.3 g) of 13 wt. % H_2SO_4 (density 1.086 kg L^{-1}) under stirring and the obtained slurry was agitated about 15 hours, insoluble part was separated by sedimentation and 50 mL of liquid phase was filtered (Leachate Cu1). Obtained leachate 1 was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The compositions of leachates are described in Table 2.

The remaining reaction mixture was heated 60 minutes at 100°C under stirring, filtered and filtrate was diluted to exact 200 mL using deionized water (Leachate Cu2) and analysed by ICP-OES.

2. Leaching of Cu from spent Devarda´s Al-Cu-Zn catalyst in 17 wt% HCl by co-action of H_2O_2

To the insoluble part, 25 mL (30 g) of 35 wt% aq.HCl was added and 11 mL (12 g) of 33 wt% H_2O_2 diluted with 18 mL of deionized water was added dropwise and subsequently stirred 60 minutes at 70°C. The obtained green solution was cooled, the volume was adjusted to 200 mL using distilled water (Leachate Cu3). Obtained solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The composition of leachate 3 is described in Table 1.

3. Separation of $CuCl_2$

Crystalline $CuCl_2$ was isolated from leachate 3 (195 mL) by evaporation of excess water at 120°C using oil bath (178.7 g of distillate was obtained) and subsequent suction of precipitated crystals obtained by cooling of distillation residue at room temperature. The green crystalline product was dissolved in 100 mL of deionized water and analysed by ICP-OES (Leachate Cu4).

Debromination of TBBPA using recycled Cu:

NaBH4 (0.8 g, 20 mmol) was dissolved in 100 mL of 0.1M aqueous NaOH solution. To this solution was added dropwise 50 mL of obtained leachate Cu4 (recycled Cu in the form of CuCl2 solution) during 5 minutes and 50 mL of alkaline 2.5 mM aqueous TBBPA solution. The obtained suspension was stirred at room temperature overnight. After filtration, the content of AOX in filtrate was measured (AOX= 0.703 mg L^{-1}) which indicates 99.3% removal efficiency of adsorbable organically bound halogen. The filter cake containing spent Cu catalyst was collected and stored under water for further recycling. Alkaline filtrate was acidified with leachate Cu2 (see Table 2) to pH=6.2±0.2 and flocculated Al(OH)3 was removed by filtration.

Results and discussion

Both spent nickel and copper catalysts were produced by reductive destruction of harmfull tetrabromobisphenol A

(TBBPA, commonly used as flame retardant for PCBs) in model waste water using Raney Al-Ni or Devarda´s Al-Cu-Zn alloy as reductant at room temperature, ambient pressure in diluted NaOH solution (Figure 1 and 2). Slurry of used Ni (or Cu) catalyst was separated by filtration and treated using hydrometallurgical technique. Obtained aqueous phase from hydrodebromination steps were neutralized and treated with flocculation using dissolved aluminium salts.

The recycling procedure for spent Ni catalyst consists of three steps. At first, most of residual aluminium content and part of Ni in separated nickel slurry (spent Raney Ni) was dissolved in excess of diluted sulfuric acid and remaining insoluble part (metallic Ni) was subsequently dissolved in $K_2S_2O_8/H_2SO_4$ mixture. Both leachate were collected and crystalline $NiSO_4$ was isolated by concentration of leachates (evaporation of excess of water). The isolated green product was dissolved in 50 mL of deionized water, analysed by ICP-OES, and used in debromination step.

Nonselective leaching of collected spent nickel catalyst obtained from hydrodebromination of TBBPA described above was carried out using excess of 13 wt. % aqueous sulfuric acid and subsequent action of 32 wt. % sulfuric acid by co-action potassium peroxosulphate under reflux overnight (see Figure 1). The composition of leachates are depicted in Table 1.

It is desirable to recycle excess of used sulfuric acid from leach liquors due to the environmental and economic reasons. This is possible by use of diffusion dialysis (Bendova and Weidlich, 2018) or by evaporation of excess water and recycling of H_2SO_4 separated from precipitated salts. The separated H_2SO_4 (filtrate) could be recycled in Ni leaching step.

The separated mixture of $NiSO_4/Al_2(SO_4)_3$ salts was used as a source of Ni catalyst for hydrodebromination of TBBPA using excess of $NaBH_4$. However, as we tested, mixture of NiSO4 contaminated with $Al_2(SO_4)_3$ is not suitable source of Ni catalyst applicable for complete hydrodebromination of TBBPA.

Spent Cu catalyst recycling procedure consists of three steps. Separation of Cu and electropositive Al and Zn from spent catalyst slurry is quite selective using 13 wt. % sulfuric acid (see Table 2). High selectivity enables separation of $Al_2(SO_4)_3$ and $ZnSO_4$ in diluted H_2SO_4 and this leachate is suitable as neutralization/flocculation agent for alkaline filtrate obtained in hydrodebromination step. Subsequent leaching of remaining Cu slurry using aqueous HCl and H_2O_2 enables very effective dissolution of Cu. Produced CuCl2 was isolated simply by distillation of aqueous HCl. In addition, distilled aqueous HCl is simply recyclable in another Cu leaching step.

Prepared aqueous solution of recycled $CuCl_2$ in co-action of excess $NaBH_4$ was discovered as very effective hydrodebromination agent.

Conclusions

In conclusion, waste TBBPA is simply debrominated using Al-Ni or Al-Cu-Zn alloys. However, application of Cu-based catalyst is much more favourable due to its simple recycling by hydrometallurgical re-working and due its possible simple availability from recycled waste PCBs. Potentially, hydrometallurgical separation of Cu from spent PCBs with subsequent utilization of obtained $CuCl_2$ in hydrodebromination of waste flame retardant TBBPA produced by hydrolytic treatment of PCBs based epoxy resins enables safe, cheap and simple destruction of harmful TBBPA and production of metallic Cu.

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Recykling zużytych katalizatorów hydrodehalogenacji – problemy z separacją aluminium

Nasze badania koncentrują się na wykorzystaniu i recyklingu miedzi i niklu stosowanym do redukcyjnej degradacji tetrabromobisfenolu A (TBBPA), wysokowydajnego bromowanego środka zmniejszającego palność płytek obwodów drukowanych. Dezaktywowane i/lub zuzyte katalizatory hydrodebromowania wytwarza się przez redukcyjne zniszczenie bromowanego fenolu (TBBPA) rozpuszczonego w alkalicznym roztworze wodnym przy użyciu stopów Al-Cu-Zn Raneya Al-Ni i/lub Devarda. Zużyta metaliczna zawiesina jest traktowana wodnym roztworem kwasu siarkowego w celu rozpuszczenia resztkowego aluminium i/lub cynku, a zdekantowany pozostały metal jest następnie obrabiany w warunkach utleniania i rozpuszczany w nadmiarze kwasu mineralnego przez współdziałanie utleniacza. Odpowiednia sól metalu jest oddzielana od odpowiednich odcieków zawierających nadmiar kwasu przez odparowanie i zawracanie lotnych składników. Otrzymane sole miedzi lub niklu zastosowano jako źródła katalizatorów hydrodebromowania typu Raneya wytworzonych in situ przez działanie $NaBH_4$.

Słowa kluczowe: nikiel Raneya, miedź, tetrabromobisfenol A, hydrometalurgia, borowodorek, zmniejszenie

Size Distribution of Particulate Matter in Indoor Environment During Nanomaterial Paint Application

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Abstract

Due to the increasing production and development of nanoparticles, it has become necessary to control the exposure to ultrafine particles (aerodynamic diameter < 0.1 μm) when handling nanopaints. The paper deals with the number and mass distribution of particulate matter (PM) in an indoor environment before, during and after the application of paint Protectam FN containing titanium nanoparticles. The size distribution determination was performed by the electrical low-pressure cascade impactor (ELPI$^+$) in the range from 0.006 μm to 9.93 μm. The highest number of particles was observed in the range from 0.006 to 0.0175 μm. The particulate mass concentration ranging from 0.0175 to 0.0307 μm did not represent more than 0.5% of the sum of PM10 during the individual measurements. The particle mass concentration increased in the range of 0.0175 to 0.0307 μm, after application of the coating nanopaint Protectam FN, but it was observed that the total number of particles has decreased. During the days following the application of the nanopaint, the mass concentration in this grain size class was significantly reduced.

Keywords: nanopaint, indoor environment, particulate matter, nanoparticles, ELPI$^+$

Introduction

The indoor air quality can influence decisively human health. People are spending indoor up to 80–90% of the time. The indoor sources of particulate matter (PM) are commonly classified according to the activities of building users. The walking generates a substantial large number of particles larger than 1 μm. On the other hand, fine-grained particulate matter can be typically generated during a lot of activities as cooking and heating using a fireplace, tobacco smoking, vacuum cleaning and so on (Hussein et al., 2006; Lappalainen et al., 2013; Bo et al., 2017). Emissions from building materials, consumer products, and printers can also be significant sources of PM indoor (Lappalainen et al., 2013). Hussein et al., 2005 investigated the relationship of indoor-to-outdoor PM with the effects of indoor activities on the number size distributions of PM. The particles come from outdoor sources during the absence of indoor sources. The maximum penetration PM was found for particles with diameter 0.1–0.4 μm.

The mean value of the indoor/outdoor values was 0.36 for ultrafine particles (diameter < 0.1 μm) and 0.60 for PM > 0.1 μm (Hussein et al., 2005). Penetration of particles from outdoor to indoor environment of a building can reach up to 100%. It is most significant for particles of the size from 0.1 to 1 μm. Particles PM < 0.1 μm a PM 2.5–10 μm usually dominate in indoor environment (Schneider, 2008).

Resuspension of dust particles in an indoor environment of buildings is caused by usual activities (cleaning, walking). It decreases with decreasing particle size, for particles of the size < 1 μm it is not essential. Schneider (2008) reports that resuspension concerns the particles of the size from 2.5 to 10 μm. In the indoor air (office rooms), mean number of these particles was 1900 per litre, while the mean number of particles ≥ 5 μm was 20 particles per litre (Lappalainen et al., 2013). The number of particles varies from low values (< 10^3 particles/cm^3) in particularly clean indoor rooms to high values (> 10^6 particles/cm^3) in the presence of intense sources of PM (Bo et al., 2017). The mass concentration of $PM_{2.5}$ in office rooms ranged between 4.7 and 37.6 μg/m^3, the median value was 11.7 μg/m^3. The mass concentration of $PM_{2.5}$ varied between 2.6 and 31.2 μg/m^3 in the 20 office buildings (Europe) (Szigeti et al., 2017).

Particles in indoor rooms can contain contaminants, bacteria, and other harmful substances. Nano-coatings can offer protection from pollutants, bacteria etc. (Koivisto et al., 2018). Nano-coatings are highly transparent layers of metals, ceramics or polymers, with typical size below 100 nm. Photocatalytic materials remove various air pollutants under UV-light illumination. Especially the photoactive materials based on TiO_2 can enable photocatalytic reaction under visible light. These reactions increase the efficiency of photocatalytic oxidation and the using of photocatalytic applications in indoor. Photocatalytic oxidation of materials based on TiO_2 generates free radicals. Due to these properties, photocatalytic surfaces are self-cleaning, antimicrobial, and oxidative for organic pollutants (Koivisto et al., 2018; Haider et al., 2017). Coatings containing nanoparticles (TiO_2 and ZnO) exhibit antibacterial effect for Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa (Hochmannová et al., 2010).

Under wet and dry abrasion of walls protected by the coating containing nanoparticles of TiO_2, submicrometric and micrometric particles were released, but particles with the nanometric diameter (below 0.1 μm) were not detected.

No free or agglomerated TiO_2 nanoparticles were observed: TiO_2 nanoparticles (~ 30 nm) appear to be embedded in the paint matrix. Agglomerates of matrix particles of about 110 nm are observed. The sizes vary between 100 nm and 300 nm (Golanski et al., 2011).

It was performed determination of the number and mass distributions of dust particles before, during, and after paint because of lack of studies dealing with particles in indoor where paint was containing nano-TiO_2 component. The aim of this work is the determination of the number distribution and mass concentration of particles of the size from 0.006 to 10 µm during application of paint containing nano-TiO_2 and their influence on decreasing of total dust in an indoor environment.

Methods and sampling

Coat of paint containing nanoparticles TiO_2 Protectam FN (nanopaint), was applied on a ceiling in a meeting room with an area of 20 m². The paint consists of water suspension of photoactive titanium oxide with a mixture of inorganic binding materials. The function paint Protectam FN was developed for creating active photocatalytic layers on the wall surfaces. The coats of paint Protectam have nanoparticles of titanium oxide strongly bound in the pore structure of binder that ensures good cohesiveness and adhesiveness to the surface. Without a binding agent, nanoparticles of the photocatalyst are mutually bound solely electrostatically, which is not sufficient under real conditions (J. Heyrovský Institute of Physical Chemistry, Czech Academy of Science, Prague, online: https://fn-nano.com).

Measurements of the number and mass concentrations of PM were performed during selected days in December 2017 and January 2018 and lasted 24 hours or 48 hours (Table 1). During sampling, the meeting room was neither used by the staff of an organisation nor was cleaned, to prevent the resuspension of dust particles. The room was during sampling of dust particles visited only by operators of $ELPI^+$ instrument.

The sampling of dust particles was performed by electric low-pressure cascade impactor $ELPI^+$ manufactured by DEKATI (Dekati Ltd., Tampere, Finland) with air flow 9.88 l/min. $ELPI^+$ enables measurement of real-time particle size distribution (in the 14 different stages) in the size range of 6 nm (0.006 µm)–10 µm. Dust particles were caught on individual aluminium foils of 25 mm diameter, on which there was applied the Dekati® collection substrate to prevent particle bounce and blow-off from the impactor stages. The particle number distributions were measured for particles with aerodynamic diameters 0.006, 0.0175, 0.0307, 0.0539, 0.0945, 0.156, 0.258, 0.384, 0.606, 0.952, 1.64, 2.48, 3.67, 5.39, and 9.93 µm in 1 minute intervals using ELP^+. The gravimetric method was used for mass distribution of PM. Mass concentrations were determined for particles in the range from 0.0175 to 9.93 µm. Samples were repeatedly weighted using ultra-microbalances Mettler Toledo XP6U/M with the capacity of 6100 mg ± 0.1 µg.

Results and discussion

Mass distribution

The values of mass concentration of $PM_{2.5}$ or PM_{10} in any of the monitored samples did not exceed the permitted hourly limit of the $PM_{2.5}$ concentrations of 80 µg/m³ or PM_{10} 150 µg/m³ for the indoor environment as defined by the Decree of the Ministry of Health of the Czech Republic No. 6/2003 Coll. (which sets hygienic limits of chemical, physical and biological indicators for indoor living rooms of some buildings). The highest mass concentration of $\sum PM_{10}$ was detected the day before application of the nanopaint coating with the value of 117.11 µg/m³. The lowest weight concentration of $\sum PM_{10}$ was achieved during application of the nanopaint coating (44.13 µg/m³). In the next 2 days after application of the nanopaint coating, a 1.6-fold increase in $\sum PM_{10}$ concentrations occurred, and almost double the increase during the first control sampling compared to the nanopaint application day (Fig.1). The particles exhibit a unimodal distribution with a peak between 0.606–5.39 µm. Only during the nanopaint coating application, the particle distribution had a non-distinctive bimodal character with peaks in the range of 0.606–1.64 µm and 2.48–9.93 µm.

The highest weight concentrations were found for particles with an aerodynamic diameter of 1.64–2.48 µm (22–24% of $\sum PM_{10}$) and the lowest concentrations (0.03–0.5%) for 0.0175–0.0307 µm particles (Figure 2) before and after application of the nanopaint coating. During nanopaint application, the highest concentration for particles of 2.48–3.67 µm (22% of $\sum PM_{10}$) was found. The lowest concentration was found for particles 0.0175–0.0307 µm (0.012% of $\sum PM_{10}$) before and after coating application. The most extensive particle weight loss approximately one month (control sampling 2) after coating application can be observed in the grain-size class of 1–2.5 µm (about 50%), and in the grain-size class of 2.5–10 µm (about 60%). The smallest effect was observed for nanoparticles (up to 0.1 µm).

Number distribution

In the case of the particle number distribution in the individual grain-size classes in $\sum PM_{10}$, the opposite dependence applies to the mass concentrations (Figure 3). The highest number of particles in the grain-size class < 0.1 µm class is also confirmed by Kelly and Fussell (2012). Ultrafine particles (UFPs) dominate the number concentration of dust particles, but they represent only a negligible mass of total PM. The highest percentage of particle counts in $\sum PM_{10}$ (before application, during application of the nanopaint coating and control sampling I and II) was found for particles of 0.006–0.0175 µm (18 to 35% of $\sum PM_{10}$). An exception was the results obtained after application of the nanopaint coating, where the highest number of particles was found for 0.156–0.258 µm particles (17% of $\sum PM_{10}$). After the application of the coating, a temporary short-term (48 h) reduction of the 0.006–0.0175 µm dust particles occurred.

Before and during paint application, the highest number of particles in the grain-size class of 0.006–0.0175 µm was identified. The lowest number of particles was found for particles > 0.952 µm and above. The same tendency was also observed for the maximum particle count (Figure 4). After application of the nanopaint coating, the tendency of the number distribution of dust particles changed. The average number of particles decreased two to four times as compared to the nanopaint coating application. The mean particle count was the lowest at PM > 0.952 µm.

Fig 1. Scheme of sampling
Rys. 1 Schemat pobierania próbek

Date of sampling	Time interval of sampling	Process name	∑ PM_{10} (µg/m^3)	
30.11.-1.12.2017	24 h	Before application of nanopaint	117.11	working day
1.12.-2.12.2017	24 h	During application of nanopaint	44.13	working day/ non-working day
2.12.-4.12.2017	48 h	After application of nanopaint	87.64	non-working day
4.12.-6.12.2017	48 h	Control sampling I	69.38	working day
15.1.-17.1.2018	48 h	Control sampling II	60.81	working day

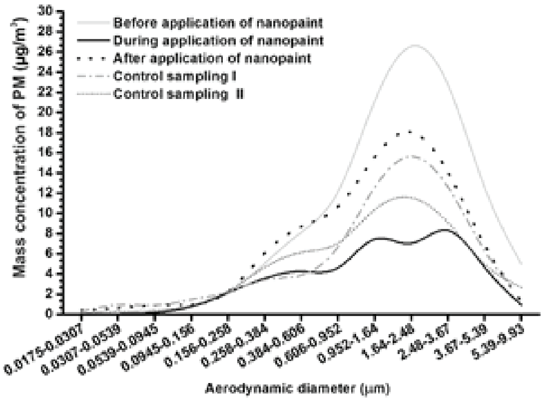

Fig. 2. Mass concentrations of particles before, during, and after application of paint including two control samplings
Rys. 2. Masowe stężenia cząstek przed, w trakcie i po nałożeniu farby, w tym dwie próbki kontrolne

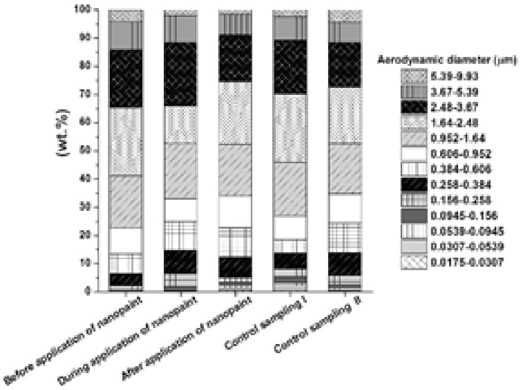

Fig. 3. Percentage of the mass concentration of individual grain size classes in ΣPM_{10}
Rys. 3. Procent stężenia masy poszczególnych klas wielkości ziarna w MPM10

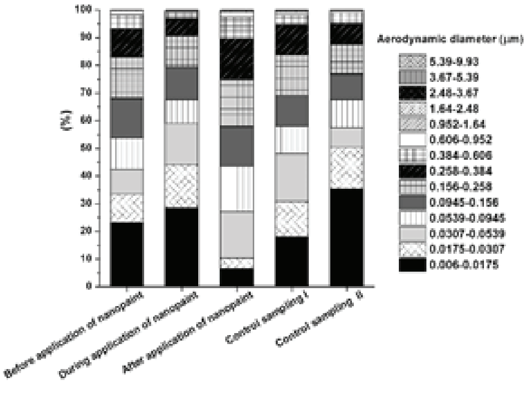

Fig. 4. The number of particles in individual grain size classes in ΣPM_{10} expressed in %
Rys. 4. Liczba cząstek w poszczególnych klasach wielkości ziarna w MPM10 wyrażona w%

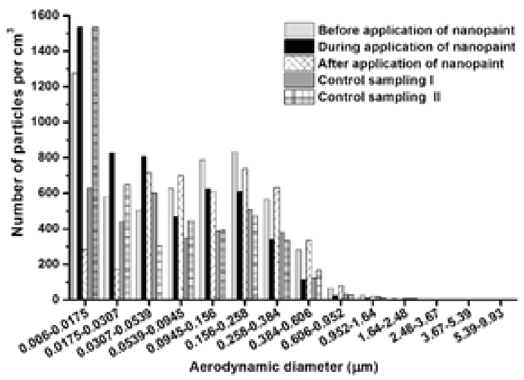

Fig. 5. Average number of particles in individual particle size classes of PM
Rys. 5. Średnia liczba cząstek w poszczególnych klasach wielkości cząstek PM

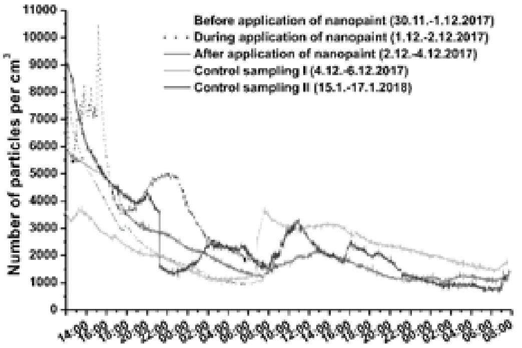

Fig. 6. Number of particles in dependence on the time interval of measurement
Rys. 6. Liczba cząstek w zależności od przedziału czasu pomiaru

With the application of the nanopaint coating, the highest number of particles was found in the grain-size class of 0.006–0.0175 μm, at the same time there was a significant increase in the number of particles in the grain-size classes of 0.0175–0.0307 μm and 0.0307–0.0539 μm. During coating application, nanoparticles release particles within the range of 0.0175–0.0539 μm.

The particle size distribution of the pooled classes from 0.006 to 0.0945 μm (< 0.1 μm) with minute intervals for individual sampling (before, during, after coating application and control sampling I and II) is shown in Figure 5. The highest particle counts were found during the first two hours of measurement between 10:00 and 12:00, followed by a decrease in the number of particles. This is due to the fact that at the beginning of the measurement, 2 or 3 persons were operating the ELPI$^+$ apparatus in the room. Figure 5 shows the values after achieving the equilibrium (after re-settling of the particulate matter 2 hours after the start of the measurement). After reaching the equilibrium state of the environment, the day before application of the nanopaint coating, a maximum value of 8,219 particles/cm3 was determined. Nanoparticles (with a maximum value of 10,500 particles/cm³) were temporarily increased during the application of the coating (on 1 December 2017), which was taking place from 12 a.m. to 2 p.m., but the number of particles was generally lower than the day before nanopaint application. During the day when the nanopaint coating was applied, there was a slight increase in nanoparticles (< 0.1 μm) between 5 p.m. and 12 p.m. The following days after coating application, nanoparticles decreased after application of the nanopaint coating (after equilibration of the environment) with a maximum value of 6,002 particles/cm³, and for the control sampling I of 3,785 particles/cm3. The control sampling II performed one month later showed that the number of nanoparticles in the room is the same as before the coating application with a maximum value of 9,264 particles/cm³.

The day before and during the application of the coating, the average number of $\sum PM_{10}$ particles was almost comparable and was (5,562 and 5,363 particles per cm³). The average number of $\sum PM_{10}$ particles (4,281 particles/cm³) was slightly reduced over the next two days after coating application. During the third and fourth day after application (control sampling I), the decrease in the average number of particles was even more pronounced (3,471 particles/cm³). By control sampling II in January 2018, it was found that the average number of $\sum PM_{10}$ particles (4,343 particles/cm³) was comparable to the results obtained after applying the nanopaint coating.

Conclusions

During all monitored sampling, the highest number of particles was identified in the grain-size class of 0.006–0.0175 μm. Particles had the lowest weight concentration. In all $\sum PM_{10}$ samples, the mass concentration of the 0.0175–0.0307 μm particles was less than 0.5%. During application of the nanopaint coating, particles are especially released in the range of 0.0175–0.0539 μm. On the day after coating application, the highest mass concentration was for the 0.0175–

0.0307 μm particles. At the same time, there was a total decrease in the number of particles. Although the total particle drop was detected immediately after application of nano-TiO_2 paints, one month after coating application, the number of particles was comparable to the conditions before application. During application of the nano-TiO_2 coating, nanoparticles (< 0.1 μm) are not released, and their number does not pose a risk to workers applying the coating. The importance of nanopaint application does not consist in the decrease in the particles, but especially in the effective removal of polycyclic aromatic hydrocarbon pollutants and the minimization of microbial activity (the antibacterial effect).

Acknowledgement

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Rozkład wielkości cząstek stałych w środowisku wewnętrznym podczas nakładania farby nanomateriałowej

W związku z rosnącą produkcją i rozwojem nanocząstek konieczne stało się kontrolowanie ekspozycji na ultradrobne cząstki (średnica aerodynamiczna <0,1 µm) gdy wykorzystuje się farby zawierające nanocząsteczki (nanopaint). Artykuł dotyczy liczby i rozkładu masowego cząstek stałych (PM) w środowisku wewnętrznym przed, w trakcie i po zastosowaniu farby Protectam FN zawierającej nanocząstki tytanu. Określenie rozkładu wielkości przeprowadzono za pomocą elektrycznego impaktora kaskadowego (ELPI +) w zakresie od 0,006 µm do 9,93 µm. Największą liczbę cząstek zaobserwowano w klasie ziarnowej od 0,006 do 0,0175 µm. Udział masowy cząstek w zakresie od 0,0175 do 0,0307 µm nie stanowił więcej niż 0,5% sumy PM10 podczas poszczególnych pomiarów. Stężenie cząstek wzrosło w zakresie od 0,0175 do 0,0307 µm, po nałożeniu powłoki nanopaint Protectam FN, ale zaobserwowano, że całkowita liczba cząstek zmniejszyła się. Z upływem czasu od nałożenia nanopaint, udział tej klasy ziarnowej spadał.

Słowa kluczowe: nanopaint, środowisko wewnętrzne, cząstki stałe, nanocząstki, ELPI +

Critical, Strategic and Deficit Raw Materials in the Waste of Electrical and Electronic Equipment and in Batteries and Accumulators

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Abstract

This article presents the waste electrical and electronic equipment and batteries and accumulators as a potential source of critical, strategic and deficit raw materials.

The dominant types of waste obtained after the disassembly of used electrical and electronic equipment are plastics: polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) and teflon and metals. These metals include: magnesium, cobalt, antimony and tantalum (critical raw materials), aluminum, nickel, iron and zinc (strategic raw materials) as well as copper and silver (deficit resources), as well as lead, tin, gold and cadmium. Batteries and accumulators are a source, among others metals such as: nickel and zinc (strategic raw materials), manganese and lithium (deficit resources), aluminum (strategic raw material), and cadmium, lead.

The article presents the results of analysis of the material composition of the waste electrical and electronic equipment conducted at the Institute of Mechanised Construction and Rock Mining. It also presents the level of imports and exports of waste and scrap-metal that are the subject of this article. In addition, the article presents a source of information about waste and recycled materials.

Keywords: waste electrical and electronic equipment, batteries and accumulators, recyclable materials, critical raw materials, strategic raw materials, deficit raw materials

Introduction

The concept of "critical raw materials" was created in the document entitled: „Critical raw materials for the EU – Report of the Ad-hoc Working Group on defining critical raw materials. EU Commission Enterprise and Industry", published in 2010. On 26 May 2014, a Communication from the European Commission to the European Parliament on the review of the list of critical raw materials for the EU was published. The Communication includes an updated list of critical raw materials for the European Union. A total of 54 raw materials were analysed. The following raw materials were listed as critical: beryllium, cobalt, tungsten, magnesium, antimony, germanium, gal, indium, niobium, chromium, metallic silicon, platinum, rare earth elements as well as fluorite, graphite, magnesite, borates, phosphate rock and coking coal. On the other hand, the following raw materials were listed as strategic: rhenium, tellurium, iron, aluminium, molybdenum, manganese, vanadium, zinc, nickel and bauxite, while the composition of the group of scarce raw materials has not changed and includes: barite, diatomite, perlite, talc, silver, copper, quartz sands, lithium, titanium and limestones. The following raw materials were listed as scarce: barite, diatomite, perlite, talc, ceramic clays (including kaolin), feldspar raw materials, boron raw materials, bentonite, silver, copper, quartz sands, lithium, titanium and limestones.

The list of raw materials critical for the EU is regularly updated at least every three years to take into account changes in production, market development and technology. On 13 September 2017, another Communication on the list of raw materials critical for the EU was published based on the previously conducted criticality assessment for 78 raw materials. This communication presents an updated list of 27 critical raw materials. Compared to the 2014 rating, the extended scope includes nine new raw materials: barite, bismuth, hafnium, helium, natural rubber, phosphorus, scandium, tantalum and vanadium. Two raw materials (chromium and magnesite) were not considered critical on the basis of the 2017 assessment.

The Branch Office of the Institute of Mechanized Construction and Rock Mining in Katowice conducted analyses regarding the problems of critical, strategic and scarce mineral resources, as shown in: (Baic et al., 2016; Biel et al., 2013, 2014a, 2014b, 2015; Blaschke et al., 2015a, 2015b, 2015c, 2016; Witkowska-Kita et al., 2016, 2014, 2015a, 2015b, 2016). Such studies were also carried out at the PAS Institute for Mineral Resources and Energy, which was presented, among others, in: (Blaschke, Ozga-Blaschke 2015, 2016; Galos 2011a, 2011b) and at the National Geological Institute, which was presented, among others in: (Radwanek-Bąk 2011; Smakowski 2011).

The subject of this article will be waste electrical and electronic equipment as a potential source of critical, strategic and scarce raw materials, i.e.: magnesium, cobalt and antimony (critical raw materials), aluminium, nickel, iron and zinc (strategic raw materials) as well as copper and silver (scarce raw materials), as well as lead, tin, gold, cadmium and tantalum. Batteries and accumulators are a source, among others, of metals such as: nickel, zinc and aluminium (strategic raw materials), manganese and lithium (scarce raw materials) and cadmium, lead, mercury.

The natural consequence of the constantly advancing technological development in the field of electrical and electronic equipment and the desire to have the new generation equipment is the increase in the amount of waste electrical and electronic equipment. An important element of waste prevention in the case of waste electrical and electronic equipment is extended producer responsibility for the electrical and electronic equipment placed on the market, because the entrepreneur is required to obtain an appropriate level of separate collection of waste electrical and electronic equipment from households with respect to the weight of the introduced equipment and levels of recovery and recycling for individual groups of electrical and electronic equipment. In accordance with the provisions of the Act of 11 September 2015 on waste electrical and electronic equipment, the management system of waste electrical and electronic equipment should ultimately include all users of this type of products, i.e. those introducing the equipment (i.e. producers and importers), as well as those collecting it, operators of processing plants, operators of installations for recycling and non-recycling recovery processes and finally end users. Waste electrical and electronic equipment from households should be collected by trade units on an exchange basis when the new equipment is bought (including wholesale and retailers), while municipalities should indicate places where residents can transfer this type of waste. In Poland there is a system of selective collection of waste electrical and electronic equipment based on a point located in each municipality. Unfortunately, not all such waste goes to these points - some of them are sent to scrap yards or to a stream of mixed municipal waste. In the case of used equipment from other sources than households, the equipment is picked up by specialized companies with appropriate permits, as shown in: (2016 Plan).

The amount of used electrical and electronic equipment put on the market was over 500,000. Mg/year. Whereas the mass of collected equipment amounted to over 170,000. Mg/year, of which almost 90% is equipment from households. The mass of selectively collected used equipment is gradually increasing and amounts to approx. 4 kg/inhabitant/year, as described in: (Krajowy 2014).

Batteries and accumulators, which supply small electrical and electronic equipment, should also be mentioned here (Krajowy 2014). Batteries and accumulators are also covered by the separate collection system. They come from both the municipal and the economic sector. Batteries and accumulators are a source, among others, of metals such as cadmium, lead, mercury, nickel, zinc, manganese and lithium. Aluminium can be recovered from used batteries and accumulators used to supply computers and mobile phones. The market for the production of lithium and lithium-ion batteries and accumulators (increases by 12–15%/year). In Poland, only approx. 4,000 Mg/year of used portable batteries and accumulators is collected. The level of collection of these wastes is systematically growing and reaches the level of approx. 40%. Every year, approx. 500 million pieces of batteries and accumulators are supplied to the market.

Metallic mineral raw materials are also necessary for the functioning and development of, among others automotive industry, metallurgy, as well as the computer industry, mobile telephony, electronics and electrical engineering, as well as the armaments industry or medical diagnostics.

Therefore, it is extremely important to ensure the security of raw materials supply and their effective management, which should lead to the creation of the "circular economy" system. This is particularly important if the country has limited own resources. Currently, in the European Union countries, including Poland, there are problems with ensuring a sufficient raw material base, mainly concerning metallic raw materials.

The possibilities of obtaining mineral resources in Poland are small, among others due to: lack of economic resources (e.g.: beryllium, magnesium, niobium, cobalt and antimony, tungsten and bauxite), lack of prospects for the discovery of new deposits, e.g. niobium ore, tellurium and fluorite, co-existence of raw materials with other metals (e.g. gallium, indium, germanium, manganese, molybdenum and nickel), depletion of mineral deposits or their low availability, and the mineralogical meaning of some deposits (e.g. rare earth elements).

In the last period of time, the importance of raw materials obtained from secondary and waste sources has increased. This is due to environmental, economic and technological reasons. Raw materials from these sources should be characterized by parameters similar to raw materials obtained from primary sources, being their full substitutes. Potential sources of obtaining raw materials are: mineral waste substances produced in industry, mineral secondary raw materials classified as waste, anthropogenic deposits, as discussed in: (Ney 2009).

Mineral secondary raw materials classified as waste are raw materials that can be used economically due to technological and economic reasons. Thus, despite their classification as waste, it should be treated as mineral waste raw materials, meaning mineral raw materials obtained from waste, i.e.: metal packaging, glass packaging, waste of electrical and electronic equipment, batteries and accumulators, spent catalysts, lining and refractory materials, waste of building materials, waste and scrap metal, as discussed in: (Ney 2009).

Strategic, critical and deficient raw materials in waste electrical and electronic equipment as well as in waste batteries and accumulators

The electrical and electronic equipment is mainly made of plastics (often with the content of flame retardants) and metals, and in a smaller amount of glass and paper. The percentage shares of particular types of materials obtained as a result of disassembly of waste electrical and electronic equipment are as follows:

- in the group of small household appliances, the basic material group consists of: metals (53.4%), plastics (24.7%) and combined materials (plastic + metal - 11.6%),
- in the group of electronic equipment, the prevailing types of materials are: metals (38.1%), plastics (29.5%), glass (12.4%), electronic components (12.5%) and combined materials, i.e. plastics + metals (6.9%).
- in the group of radio and TV equipment, the basic groups of materials are: glass (26.3%), metals (22.5%), plastics (20.2%), wood (11.8%), electronic components (7.6%), plastics + metals (6.6%) and other materials (5.1%),

Tab. 1. The turnover of waste and scrap-metals that can be recycled in the industry in 2010–2014 (wg: Bilans 2013, Bilans 2014, Bilans 2011, Rocznik 2014, Rocznik 2015)

Characteristic	Waste management and metal scrap in Poland in 2010-2014 [tys. Mg]									
	2010*	2011*	2012*	2013*	2014**	2010*	2011*	2012*	2013*	2014**
	import					export				
Magnesium waste and srap	0	0	0	0	no data available	0.889	0.961	1.044	0.98	no data available
Cobalt waste and srap	-	-	-	0	no data available	0,001	-	0	0.008	no data available
Aluminium waste and srap	84.9	106.4	111.8	176.5	130.2	124	150.6	156.1	154.8	8.4
Nickel waste and scrap and its alloys	0.9	0.6	0.3	0.4	no data available	1.2	0.7	0.7	0.3	no data available
Steel and iron scrap	382.3	408.8	383.4	509.4	0.8	1396.6	1889.3	1989.2	1972.4	92.6
Iron-bearing wastes	1.7	26.7	20.4	15.5	no data available	29.9	20.7	2.6	0.2	no data available
Copper waste and scrap	24.1	26.9	53.6	49.7	4.3	71.2	59.5	49.2	58.9	2.3

*wg Bilans gospodarki surowcami mineralnymi Polski i Swiata 2013, IGSMiE PAN, PIG PIB, Kraków-Warszawa 2015
** wg Rocznik Statystyczny Przemysłu, GUS Warszawa, 2015
Explanations:
– the phenomenon does not occur
0 – value less than 0.5 in the unit of measurement used

- in the group of power tools, the prevailing materials are: metals (73%), plastics (18.8%), plastics + metals (7.8%), and the remaining materials constitute 0.4%, according to: (Projekt 2013).

The dominant types of waste, according to (Projekt 2013, Witkowska-Kita et al. 2014, Witkowska-Kita 2015), obtained after the process of dismantling used electrical and electronic equipment are therefore plastics: polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) and teflon, as well as metals (mainly aluminium, copper, iron, cadmium and metal alloys, e.g. brass).

In (Projekt 2013, Stankiewicz et al. 2010), it was stated, among others, that:

- we can recover from a used computer set (computer + monitor) weighing 27 kg: 6.8 kg of glass, 6.2 kg of plastic, 5.6 kg of steel and metals in quantities: 3.8 kg of aluminium, 1.9 kg of copper and 1.7 kg of lead,
- we can recover from a used fridge weighing 51.3 kg, the following raw materials: iron scrap (23.7 kg), aluminium (approx.1 kg), copper (0.2 kg), glass (1 kg), polystyrene (26.8 kg), PUR foam (3.5 kg) and an aggregate weighing 0.9 kg, the rest being: pipes, gas and cotton wool,
- we can recover from the used kitchen stove primarily iron scrap, which accounts for as much as 92.2% of the stove's weigh. Other metals and alloys that can be recovered are: aluminium (1.7%), copper (0.1%) and brass (approx. 0.9%),
- a used washing machine may be the source of: 52.3% of ferrous scrap, 0.8% of aluminium, 0.1% of printed circuit boards. Other raw materials and elements are: concrete (27%), glass (1.1%), polystyrene (1.1%) and capacitors, motors, pumps, wires and rubber,
- the following waste materials can be recovered from a television set: printed circuit boards (8%), ferrous scrap (95%), aluminium (0.4%), kinescopes (35.1%), sodium and lead glass (in total: 28.5%), polystyrene (14.4%) of the device weight. Other raw materials and components are: coils, transformers and wires,
- from one million pieces of mobile phones you can recover the following amounts of metals: 34 kg of gold, 350 kg of silver, 15 kg of platinum and 18.85 Mg of copper,

and in: (Projekt 2013, Stankiewicz et al. 2010), it was found that: the share of gold-plated and silver-plated elements (based on copper alloys) in the TV set is around 0.8%, and gold and silver – 3.44 and 0.02 g respectively. Noble metals from electronic systems can be recovered in almost 100%. Printed boards account for almost 9% of the weight of such a set. Iron scrap is up to 32.5% of the used printer's weight, while printed circuit boards are 5.2%, plastics (as ABS) – 45.4%, and the remaining elements are: engine, power supplies and wires.

Whereas in: (Ney 2009) it was stated that the fans are constructed of plastic or aluminium. Silver was used for the production of various types of plugs. Silver has also been used as a component of solder. Some types of typewriters have a metal casing or a metal coating made of nickel, nickel-chromium or copper-nickel-chromium. On the other hand, among the materials used for the construction of computer speakers, the most common is copper in the form of a coil.

In: (Projekt 2013) it was found that printed circuit boards account for approx. 3% of the total mass of generated electronic scrap. Recycling of printed circuit boards involves the removal of metal (mainly copper and gold) and ceramic elements, as well as the separation of parts intended for re-use and toxic materials that need special treatment to reduce the harmful effects on the environment. For example, in the material composition of printed circuit boards (computers, mobile phones, TV sets and RTV equipment) the following metals can be distinguished: copper, iron, aluminium and beryllium, chrome, tin, zinc, gal, cadmium, nickel, lead, palladium, rhodium, mercury, tantalum, silver and gold. Copper is one of the basic materials included in printed circuit boards. From one ton of printed circuit boards we can recover up to 200 kg of copper. The standard computer set includes approx. 2 kg of this metal. The electronic sub-assemblies, coils and transformers of TV sets include approx. 400 g of copper (in total). Copper is also the basic material of power cords, plugs (cabling) and batteries. 1 Mg of printed circuit boards can also be source of 0.5–3 kg of silver.

In: (Projekt 2013) it was also found that the difficulty in determining the exact material structure of printed circuit boards is related to their complex construction and diversified material composition (metals, polymers, paper). Currently, there are two technologies for recycling printed circuit boards - thermal and non-thermal. The thermal technology includes pyrolysis, hydrometallurgy and metallurgy. The non-thermal technologies involve disassembly (manual or automatic), grinding, separation and chemical treatment. All elements recovered as a result of non-thermal methods require further transformation.

Available sources of information on the production and use of mineral waste materials

Referring to the fact that the importance of raw materials obtained from secondary and waste sources has recently increased, the available sources of information on the production and use of mineral waste materials can be found below. This knowledge is very dispersed.

Available sources of information include:

- „Bilans gospodarki surowcami mineralnymi Polski i świata” (IGSMiE, PAN, Kraków) (Bilans 2011),
- „Bilans zasobów złóż kopalin w Polsce” (PIG, Warszawa) (Bilans 2013, Bilans 2014),
- „Krajowy program zapobiegania powstawaniu odpadów” (National waste prevention program) (Krajowy 2014),
- Central Waste System maintained by the Ministry of the Environment, merging 16 Provincial Waste Systems,
- "Statistical Yearbook of Industry", publication by the Central Statistical Office (year 2014, year 2015).

In Poland, both imports and exports of waste and scrap of some of the discussed metals are carried out. On the basis of available sources, table 1 gives data on the trading of waste and scrap of some of the discussed metals and recyclable in industry in the sample years 2010–2014.

The export of metal waste and scrap in the sample years 2010–2013 remained at a similar level, while in 2014 the exports of aluminium waste and scrap, copper as well as steel and iron scrap slumped.

Data on exports concerning waste and scrap of other metals are unavailable for 2014.

Imports of magnesium and cobalt waste in the sample years 2010–2014 were not carried out.

The import of waste and scrap of aluminium, copper as well as steel and iron scrap in the analysed years increased, while the import of nickel waste and scrap as well as iron-bearing waste remains at a similar level. However, the level of imports of this waste and scrap can only slightly cover the demand for these metals, of course after the recycling operations. Nevertheless, the use of metal scrap and waste is a very important secondary source of these metals, that can have economic use.

Conclusion

1. The dominant types of waste obtained after the disassembly of used electrical and electronic equipment are plastics: polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), as well as teflon and metals. These metals include: magnesium, cobalt and antimony (critical raw materials), aluminium, nickel, iron and zinc (strategic raw materials), as well as copper, silver (scarce raw materials), lead, tin, gold, cadmium and tantalum.
2. Batteries and accumulators are a source of, among others, metals such as: nickel and zinc (strategic raw materials), manganese and lithium (deficient raw materials) aluminium (strategic raw material), cadmium, lead, mercury.
3. If the country has limited own resources of raw materials, ensuring security of raw materials supply and their effective management should lead to the creation of the "circular economy" system.
4. The export of metal waste and scrap in the sample years 2010-2013 remained at a similar level, while in 2014 the exports of aluminium waste and scrap, copper as well as steel and iron scrap slumped. Data on exports concerning waste and scrap of other metals are unavailable for 2014. Imports of magnesium and cobalt waste in the sample years 2010-2014 were not carried out.

The import of waste and scrap of aluminium, copper as well as steel and iron scrap in the analyzed years increased, while the import of nickel waste and scrap as well as iron-bearing waste remains at a similar level.

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Processing of Low-Demand Coal and Other Carbon-Containing Materials for Energy Production Purposes

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Abstract

The main area of coal application is energy production. During such stages as min-ing, transporting, treatment, storing and processing of coal, a large number of small products are formed, such as screenings, spills, sludges, etc. Such products are not used and significantly pollute the environment. Meanwhile, after agglomeration, they can eas-ily be used for the production of thermal energy. Of all the known agglomeration meth-ods, briquetting is most suitable. The technology of obtaining flammable briquettes based on coal is developed. A technology has also been developed to produce fuel bri-quettes from coal slurries and paper waste. The use of coal slurries and paper waste as binder materials makes it possible to obtain a fuel pellet that is simple in production and composition and at the same time allows to utilize coal and paper wastes. The technolo-gy of obtaining fuel extrudates (briquettes) from wood and shale wastes, as well as wood, shale waste and sludge was developed. Thus, technologies have been developed to produce fuel briquettes from various types of low-demand carbon-containing materi-als for domestic use.

Keywords: low-demand carbon-containing raw materials, briquetting, fuel briquettes, coal sludge, paper waste, waste woodworking, waste shale

Introduction

Despite the wide range of coal applications (cast iron, production of germanium, gal-lium and other elements, etc.), it has been and still remains the most important energy source. For example, from coal, it can get an effective type of fuel – coal gas [O.A. Dubovikov, V.N. Brichkin, D.A. Loginov, 2016; O.A. Dubovikov, V.N. Brichkin, 2016].

During such stages as mining, transporting, treatment, storing and processing of coal, a large number of small products are formed, such as screenings, spills, sludges, etc [V. Yu. Koptev, A.V. Kopteva, 2018; K. R. Argimbaev, H. A. Kholodjakov, 2016; M.N. Kruk, V.R. Alabyev, M.A. Korobitcyna, I.S. Stepanov, 2016]. Such products are not used and significantly pollute the environment due to accumulation of their vast re-serves. Meanwhile, in terms of their energy characteristics, they are usually not inferior to the coal being mined and with appropriate processing can be used to produce thermal energy.

Also for the production of thermal energy carbon-based materials such as paper, wood, slate waste and the like can be used.

Direct burning of the above-mentioned materials is difficult and ineffective because they are represented by small particles, which mean that they must be agglomerated first. Of all the known agglomeration methods, the most suitable is briquetting [A.T. Eleshevich, 1990].

Briquette production allows: to obtain high-quality and transportable fuel from mate-rials that are not used at present. Also that helps to partially solve the environmental problem at the same time.

Research work on briquetting

A technology was developed to produce household fuel briquettes with a low ignition temperature, ignited from low-energy heat sources (for example, matches) on the basis of coal. The production of such briquettes is possible, for example, by creating briquettes with a main part, a source of heat energy, and a special incendiary part. The ignition part can be ignited, for example, from the match, then ignites the main part. Briquettes were produced using various types of organic binders. To increase the completeness of com-bustion and reduce harmful emissions into the atmosphere, briquettes were produced with through perforation. The form of briquettes can vary within wide limits [V.B. Kus-kov, Y.V. Kuskova, D.V. Sukhomlinov, 2013].

A complex of studies was also carried out in which coal slurries and paper wastes were used as carbonaceous components of the charge. The use of coal slurries and paper waste as carbon-containing components makes it possible to obtain a simple fuel-briquette in the manufacture and composition and simultaneously utilize coal and paper waste. Coal slurries increase the calorific value of the fuel briquette. Paper waste is both a binder and a fuel component. The moisture content of the initial charge is 8–10%. Bri-quettes were formed by extrusion. The briquette has a longitudinal hole, the cross-sectional area of which is from 25 to 40% of the cross-sectional area of the briquette, which improves its combustion. The presence of a hole with a cross-sectional area of less than 25% of the cross-sectional area of the briquette reduces the completeness of com-bustion of the briquettes due to insufficient air flow. The presence of a hole with a cross-sectional area of more than 40% does not increase the completeness of combus-tion, excessively increases the volume of the briquette (without increasing the caloric content), lowers the strength of the briquette. The sizes of briquettes can vary within ra-ther wide limits. The optimal amount of coal slurries in the briquette is 30–60%, and of paper waste – 40–70%. If the content of coal slurries exceeds 60%, the strength of the briquette decreases, and they become more difficult to ignite. If the content of coal slur-ries is below 30% and paper waste is more than 70%, the calorific value of the fuel bri-quette is reduced. The mechanical strength of the briquettes was determined as the number of falls from a height of 1.5 m (this is twice the maximum overload height) that the briquettes withstood. The resulting briquettes showed sufficient mechanical strength. After ten drops from a height of 1.5 m, the amount of fines (a class smaller than 5 mm) did not exceed 3%.

There were also briquettes in which there was a special ignition layer (containing, for example, nitrates) which is easily ignited from low-energy sources of heat (for example, matches), then combustion is spread to the main part of the briquette. The briquettes were formed by an extruder having mixing and pressing zones. The nitrates were pressed into the base layer in a dry form, into the outer surface of the briquette due to the work of an additional screw of the bracer. In the pressing zone, the briquette is strengthened and leaves the extruder having a strength sufficient to transport it to the dryer. The briquettes after drying are easily ignited, burned steadily and did not actually emit smoke. Such a briquette is very convenient to use. It is also possible to use both types of briquettes with an incendiary layer and without it at an approximate ratio of 1:10. In this case, a highly inflammable briquette with an incendiary layer, ignites bri-quettes without an incendiary layer. At the same time, significant savings are achieved, because briquettes with an incendiary layer are more expensive than without it [V.B. Kuskov, Y.V. Kuskova, D.V. Sukhomlinov, 2013].

Relatively often coal slimes have an increased ash content. In this case, the sludge is concentrated, for example, on a concentration table, on a short-cone hydrocyclone, a spi-ral separator ets. In addition, these processes significantly reduce the sulfur content in the product [V.B. Kuskov, Y.V. Kuskova, 2015; A. Nad, 2010].

Many small products are formed (chips, sawdust, dust collection products, etc.) dur-ing the wood processing. This is very wasteful materials because they are practically not used which leads to environment pollution and create a fire hazard. A similar picture is observed in the processing of oil shale. Both wood and shale waste can be used to pro-duce energy. One of the ways of processing this kind of wastes is their briquetting [B. V. Yuryevich, K. V. Borisovich, 2016].

The use of fuel briquettes and pellets with inclusions of wood waste increases every year. Recycling is now no less important for the manufacturer than the production itself. On the other hand, there is the problem of recycling waste from the extraction of com-bustible shale. But research has shown that briquettes made from slate wastes only have insufficient mechanical strength, since shale does not have bonding properties. There-fore, it is of scientific and technical interest to study the possibility of briquetting shale waste with wood and paper waste and using briquettes as alternative sources of heat. Authors conducted researches regarding creation of briquettes out of residual wastes from wood and oil shale processing In the production of briquettes, wood waste, wood dust, shale dust in various proportions were used as a charge. Experimental studies have shown that the optimal ratio of wood waste, wood dust and shale dust is from 10:40:50 to 20:60:20 [B. V. Yuryevich, K. V. Borisovich, 2016].

Design of flowsheet for briquetting

It also developed technologies for the production of fuel briquettes from wood waste, wood dust, oil shale dust, paper waste and coal sludge. Experiments have shown that the ratio of these components close to the optimum is 20: 10: 20: 20: 30, 15: 10: 20: 30.The Equipment flowsheet of briquette productionis shown in Fig. 1.

The feedstock for briquettes production is loaded into storage bunkers 1-4.From the bunker 1 by the screw feeder 5 material is fed to the screen 6. Large particles are screened out on the screen, which can serve as fuel. Fine product screening, wood dust, shale dust, paper waste conveyor conveyed to the mixer 7. Also in the mixer 7 coal slur-ries are fed. After mixing, the mixture feds to the forming device 8 (extruder). Raw ex-trudates arrives at screener 9. Extrudates with conditioned particle size are fed to the drying 12, and sub-standard ones are fed to conveyor system are brought back to the mixer 7. Driedextrudatesare sent to screener 13 and are divided there into smaller sub-standard size, which are sent back to mixer 7 by conveyor system, and rightly sizedex-trudates, which are transported to the warehouse.

Briquettes were molded by both "conventional" pressing and extrusion. The specific dimensions and shape of briquettes or extrudates can vary within very wide limits in ac-cordance with the requirements of the consumer.

The mechanical strength of the product, which is its most important consumer proper-ty (since the product needs to be transported) was defined as the number of falls from a height of 1.5 m that the briquettes withstood. The results of the tests of both raw and dry briquettes showed their sufficient mechanical strength. For example, raw briquettes withstood 3–4 drops without noticeable damage. Dry briquettes kept more than 10 falls.

It should be noted that usually the products of wood and slate processing are dry and in the process of mixing it is necessary to add water until the optimum moisture is reached, which is 8–10%. Then this water must be removed during the drying process. Coal slurries, on the contrary, are watered (this is one of the reasons why they are diffi-cult to process). Therefore, the addition of coal sludge, as a component of charge, allows us to solve several problems at once: creating optimal moisture, increasing the caloric content of the product, and utilizing slurries.

This technology is versatile enough. The technology allows to use a variety of types of carbonaceous materials as components of the charge of briquettes.

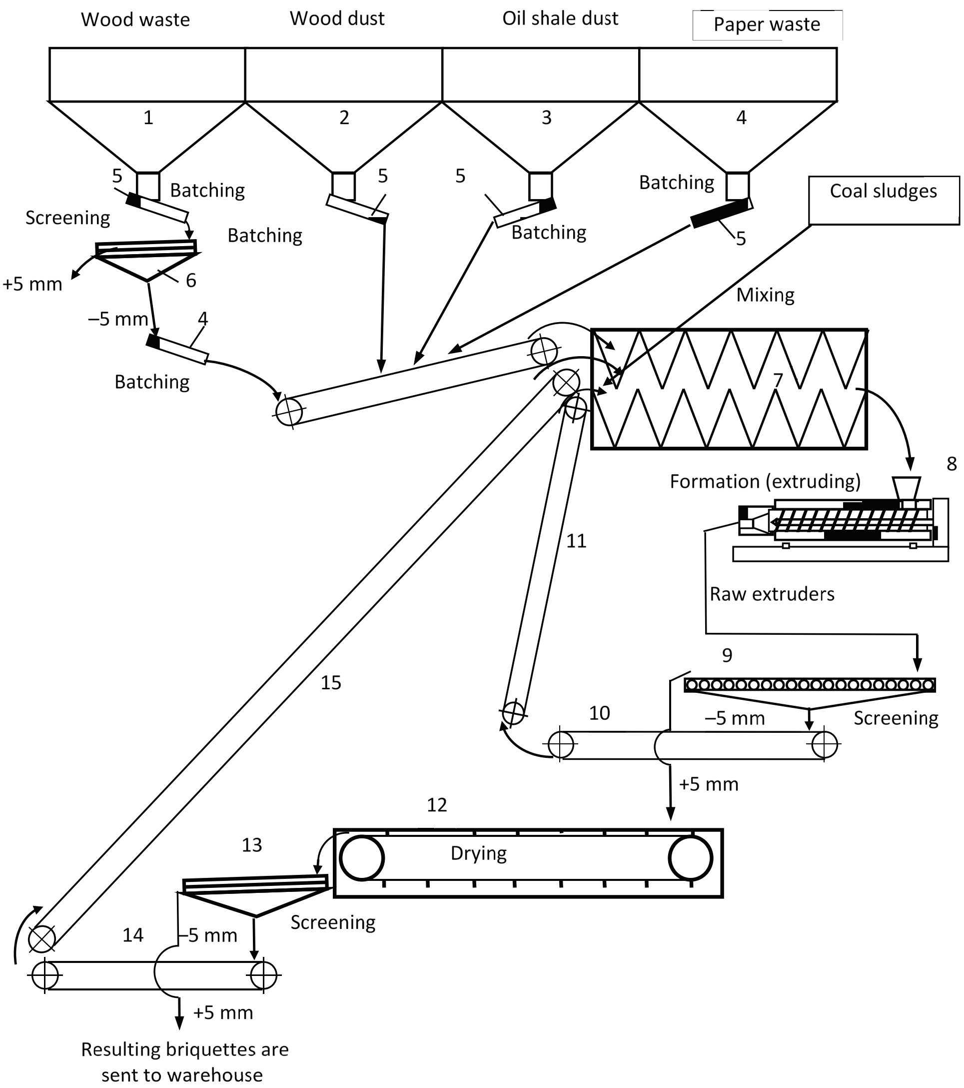

Fig. 1 Equipment flowsheet of briquette production
Rys. 1. Linia produkcyjna do produkcji brykietów

In such a flow sheet, the above-mentioned methods for removing ash from sludges are well suited. In this case, such equipment as hydrocyclone is compact and easily ac-commodated in any enclosure without increasing its dimensions.

The received briquettes are kindled like ordinary firewood. When burning, little smoke is emitted. They are more compact than conventional firewood, have a high spe-cific calorific value (calorie briquettes 4900–5940 kcal / kg), burn longer. Also, ash after burning briquettes may be an additional source of raw materials [R.Y. Feshchenko, O.O. Erokhina, V.L. Ugolkov, M.Y. Shabalov, V.V. Vasil'ev, 2017]. Thus, from products of wood processing, products of dust-catching processes of wood processing and shale processing and coal slurries, it is possible to obtain full-value energy products with their simultaneous utilization, which partially solves the environmental problem.

Conclusion

Developed technology for the production of fuel briquettes from of low-demand coal and other carbon-containing materials for energy production purposes. A technology has been developed for the production of household fuel briquettes with a low ignition tem-perature, ignited from low-energy heat sources (for example, matches). Also developed a technology for producing fuel briquettes from wood waste, wood dust, shale dust, pa-per waste and coal sludge. The production of such products allows to obtain additional amount of thermal energy and at the same time partially solves environmental problems.

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Przeróbka niskoenergetycznych węgli i innych materiałów zawierających węgiel do celów produkcji energii

Głównym obszarem zastosowania węgla jest produkcja energii. Podczas takich etapów, jak wydobycie, transport, przeróbka, magazynowanie i przetwarzanie węgla, powstaje duża ilość drobnouziarnionych produktów (szlamy, muł itp.). Takie produkty nie są wy-korzystywane i znacząco zanieczyszczają środowisko. Tymczasem po aglomeracji można je łatwo wykorzystać do produkcji energii cieplnej. Spośród wszystkich znanych metod aglomeracji, brykietowanie jest najbardziej odpowiednie. Opracowano technologię otrzymywania łatwopalnych brykietów na bazie węgla. Opracowano również technolo-gię produkcji brykietów paliwowych z zawiesin węglowych i odpadów papierniczych. Zastosowanie zawiesin węglowych i odpadów papierniczych jako materiałów wiążących umożliwia otrzymanie granulatu paliwa, który jest prosty w produkcji i składzie, a jed-nocześnie pozwala na wykorzystanie odpadów węglowych i papierniczych. Opracowa-no technologię pozyskiwania granulatów paliwowych (brykietów) z odpadów drzew-nych i łupkowych, a także drewna, odpadów łupkowych i mułu węglowego. Opracowa-no technologie wytwarzania brykietów paliwowych z różnych rodzajów materiałów wę-glowych o niskim uwęgleniu do użytku domowego.

Słowa kluczowe: surowce węglowe o niskiej zawartości węgla, brykietowanie, brykie-ty paliwowe, szlam węglowy, odpady papierowe, odpady drzewne, łupek odpadowy

Powody konieczności korekty pewnej części teorii wzbogacania grawitacyjnego

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Abstract

W pracy przedstawiono ogólny zarys wybranych problemów opisu procesu wzbogacania węgla w osadzarce, jakie rysują się na podstawie aktualnego stanu ważniejszych prac teoretycznych związanych z krzywymi rozdziału i rozpraszaniem się cząstek w procesie osadzania W dalszej części szczegółowej krytycznej analizie poddano fragmenty tych powszechnie akceptowanych bez zastrzeżeń prac, które w niewłaściwym świetle przedstawiają teoretyczne wyjaśnienie zachodzącego w osadzarce rozpraszania się cząstek wzbogacanego materiału. Szczególną uwagę zwrócono na pomijane do tej pory w pracach teoretycznych ograniczenia możliwości rozpraszania cząstek i tworzenia się gęstościowo zróżnicowanych warstw oraz skutki tego pominięcia dla opisu zjawisk zachodzących w procesie osadzania i oceny tego procesu.

Słowa kluczowe: wzbogacanie węgla, osadzarka, krzywa rozdziału, rozproszenie cząstek

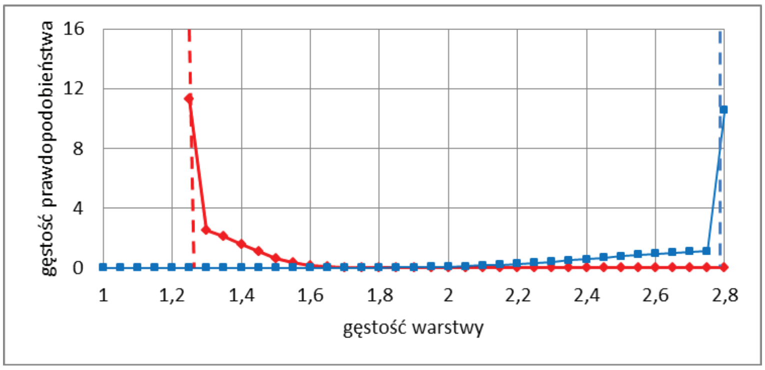
Wstęp

W ciągu ostatnich pięćdziesięciu lat nie pojawiła się żadna praca zmieniająca ugruntowany od dawna stan teorii wzbogacania grawitacyjnego kopalin. Na tej podstawie można sądzić, że ta teoria w swym podstawowym zarysie jest kompletna i jej dalszy rozwój nie jest potrzebny. Jednakże z całą pewnością istotne jest pytanie czy wszystko, co obecnie znamy z tej teorii jest poprawnie sformułowane. W opinii autora tej pracy pewnej i znacznej korekty wymaga część teorii opisującej krzywą rozdziału i interpretacja tej krzywej związana z oceną jakości wzbogacania w wodnych osadzarkach pulsacyjnych. Podstawą do takiej opinii jest zauważenie, że przedstawiane w pewnej części literatury opisy zjawisk zachodzących w osadzarce i ich uogólnienia zbyt daleko odbiegają od rzeczywistego działania osadzarki i do tej pory nie doczekały się odpowiedniej korekty. Sprostowanie tych nieprawidłowych opisów zachodzących w osadzarce zjawisk i ich teoretycznych uzasadnień jest ważne także dlatego, że większość z nich nadal istnieje w do dziś używanych podręcznikach grawitacyjnego wzbogacania kopalin. Znaczna część niepoprawnie sformułowanych teoretycznych zależności pochodzi z opracowań autorów powszechnie uznawanych jako niekwestionowane autorytety przeróbki kopalin. Z tego względu w związku z zakończoną niepowodzeniem próbą znalezienia w istniejącej literaturze jakichkolwiek śladów krytyki i chęci poprawienia tych błędów autor tego opracowania z konieczności czuje się zobowiązany do przedstawienia szczegółów niepoprawnych sformułowań uważając, że w tej sytuacji brak krytycznej reakcji przynosi tylko dalsze szkody. Niniejsza praca w swoim zamiarze jest zbiorową erratą do kilku istotnych dla teorii wzbogacania publikacji mającą zainteresowanym poznaniem tych zagadnień ułatwić przebicie się przez myślowe meandry twórców tych publikacji. W opinii autora krytyczne uwagi zamieszczone poniżej powinny były się znaleźć przed wielu laty w opiniach recenzentów lub w tych licznych pracach, których autorzy podali je jako literaturowe źródła swoich dokonań.

Ogólny zarys zagadnienia

Początek powstania teorii krzywych rozdziału wiąże się z opublikowaniem przez K.W. Trompa w lutym 1937 pracy (Tromp, 1937), w której wprowadzono pojęcia liczby i krzywej rozdziału. Oba te pojęcia mają zasadnicze znaczenie dla teorii wzbogacania grawitacyjnego. Znaczenie to wynika z możliwości oceny procesu wzbogacania bez odwoływania się do jakościowo-ilościowej oceny produktów wzbogacania. Tę możliwość stwarza wprowadzenie pośredniej oceny dotyczącej najistotniejszej części procesu, jaką jest rozdzielanie materiału surowego na dwa produkty wzbogacania według gęstości cząstek. Podobieństwo empirycznych krzywych rozdziału do dystrybuanty rozkładu normalnego zwróciło uwagę A. Terry (Terra,1938) na losowy charakter procesu wzbogacania, co zaowocowało wprowadzeniem wskaźnika oceny procesu określanego jako rozproszenie prawdopodobne Ep. Wskaźnik taki znany już był wcześniej w rachunku prawdopodobieństwa jako miara rozrzutu rozkładu pod nazwą odchylenia ćwiartkowego (Kubik, 1982). W połowie ubiegłego stulecia został wprowadzony, zupełnie niepotrzebnie zdaniem autora tej pracy, inny wskaźnik oceny procesu wzbogacania ściśle związany z rozproszeniem prawdopodobnym i nazwany imperfekcją (Belugou, 1950).

Widoczne podobieństwo empirycznych krzywych rozdziału dla odpadów do dystrybuanty rozkładu normalnego prawdopodobnie spowodowało powstanie niewłaściwej interpretacji losowego charakteru procesu wzbogacania powszechnie stosowanej także dzisiaj. Na tej interpretacji opierają się niemal wszystkie znane prace z tego zakresu z wyjątkiem pracy (Zapała 1988), której część zawierająca początki właściwej interpretacji nie została w całości opublikowana. Generalnie niewłaściwość interpretacji sprowadza się do nieuzasadnionego uogólnienia bez wątpliwości losowego charakteru zjawiska trafiania pojedynczych ziaren do danego produktu procesu wzbogacania na całościowe pojmowanie procesu wzbogacania grawitacyjnego jako procesu losowego. Objawem tej interpretacji jest rozumienie krzywej roz-



Rys. 1. Ograniczone rozpraszanie cząstek o skrajnych gęstościach
Fig. 1. Limited dispersion of grains of extreme densities

działu jako całkowej transformaty funkcji (krzywej) rozproszenia (Budryk, 1949), (Stępiński, 1964), (Nawrocki,1975), (Surowiak,2006), która jest podobna do funkcji gęstości prawdopodobieństwa tego rozkładu. Widocznym skutkiem tego błędu jest losowa interpretacja procesów o charakterze deterministycznym zawierających pewną składową losową, czego uzasadnieniem może być stwierdzenie zawarte w pracy (Tumidajski 1993), że statystyczną naturę procesów przeróbczych przyjmuje się bez zastrzeżeń. Poprawniejsze byłoby stwierdzenie, że statystyczną naturę mają właściwości wzbogacanych materiałów znacznie wpływające na przebieg tego procesu, podczas gdy sam proces wzbogacania jest ze swej istoty deterministyczny, pomimo że zawiera pewną, a w niektórych przypadkach znaczną składową losową związaną z jego techniczną realizacją. Krzywą rozdziału można także pojmować jako statyczną charakterystykę zdeterminowanego procesu wzbogacania. Użycie do jej matematycznego opisu innej funkcji o zbliżonym do dystrybuanty rozkładu normalnego kształcie jak np. tangens hiperboliczny nie sugerowałoby losowego charakteru procesu. Trzeba jednak zaznaczyć, że w pewnych szczególnych sytuacjach krzywa rozdziału i dystrybuanta rozkładu prawdopodobieństwa określającego rozproszenie cząstek wzbogacanego materiału w warstwach, jakie tworzy ten materiał w łożu osadzarki mogą mieć taki sam kształt i istnieje związek między tymi funkcjami. Ważną i zasadniczą różnicą jest natomiast to, że argumenty obu tych funkcji są różne. Podsumowaniem tych uwag może być stwierdzenie, że nachylenie krzywej rozdziału ma związek z losowym trafianiem poszczególnych cząstek do różnych warstw, spowodowanym nie losowym charakterem procesu, lecz głównie losowymi właściwościami wzbogacanego materiału. Te losowe właściwości są w znacznej części skutkiem niewłaściwego przygotowania materiału do wzbogacania zwykle spowodowanego zaniechaniem odpowiedniej klasyfikacji ziarnowej.

Trzeba jeszcze zauważyć, że osadzanie jako przemysłowy proces wzbogacania jest oceniane według nie do końca poprawnego dla tego rodzaju wzbogacania wzorca, jakim jest gęstościowe rozdzielenie wzbogacanego materiału. Dla wzbogacalników z cieczą ciężką jest to naturalny wzorzec, ponieważ wzbogacanie i jego ocena są jednolite pod względem zasady rozdziału. Osadzanie jako naturalnie zależne także od wielkość wzbogacanych ziaren i ich kształtu nie ma odpowiedniego wzorca, który pozwoliłby stwierdzić idealne rozdzielenie dla danego składu gęstościowego i ziarnowego. Dlatego ocena osadzarki według gęstościowego rozdziału produktów, pracującej często z przekroczeniem dopuszczalnego zakresu wielkości wzbogacanych ziaren, zawsze nie jest całkowicie obiektywna. Innym powodem, aby gęstościowej oceny rozdziału nie traktować jako ostatecznej jest to, że dla idealnego rozdziału gęstościowego ocena ilościowo-jakościowa produktów wzbogacania może być niekorzystna.

Podstawy poprawnego modelu rozwarstwiania się wzbogacanego materiału w łożu osadzarki

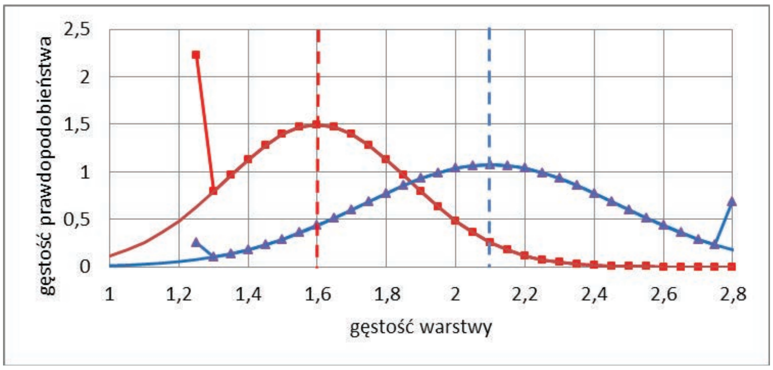
Podawany do koryta osadzarki materiał surowy w pulsującym w płaszczyźnie pionowej strumieniu wody rozdziela się na warstwy o zróżnicowanej gęstości i stopniowo przesuwa się w kierunku drugiego końca koryta. W tym końcu dolna część materiału opuszcza koryto jako produkt ciężki przez szczelinę wypustową, a pozostała część jako produkt górny wraz z wodą trafia do następnego przedziału lub opuszcza maszynę jako finalny lekki produkt wzbogacania (koncentrat węglowy). Materiał w końcowej części strefy rozwarstwiania można podzielić na pewną ilość warstw o rozróżnialnej pomiarowo gęstości. Z powodu nieidealnego rozwarstwiania każda z tych warstw składa się z ziaren o różnej gęstości i może być określona średnią gęstością ziaren tworzących tę warstwę. Poddawany wzbogacaniu materiał składa się z frakcji gęstościowych o różnym udziale w całości materiału. Zależność zawartości popiołu od udziału danej frakcji gęstościowej w nadawie jest nazywana charakterystyką częstościową nadawy (Stępiński 1964). Istnieje podobna charakterystyka nadawy, zazwyczaj nie używana w rozważaniach teoretycznych, podająca udział danej frakcji gęstościowej w funkcji jej gęstości. Charakterystyka ta w praktyce wzbogacania węgla zwykle jest wyznaczana pomiarowo w ograniczonym zakresie (dla trzech frakcji gęstościowych) dla określonej próbki nadawy i w praktyce przemysłowego wzbogacania przyjmuje się niesłusznie, że pozostaje ona stała w okresie przyjętym do kontroli jakości produktów. Wyniki pomiarów przedstawione w pracy Zapały (Zapała 1988) oraz rejestracje parametrów pracy przemysłowych osadzarek wykonane przez autora tej pracy jednoznacznie wskazują na ogromną zmienność charakterystyk nadawy i niesłuszność przedstawionego wyżej poglądu. Naturalnym skutkiem przyjmowania dużej zmienności nadawy powinno być traktowanie takiej pełnej charakterystyki częstości (dla co najmniej 8-12 frakcji gęstościowych) jako funkcję gęstości prawdopodobieństwa pewnego rozkładu. Taki rozkład jest charakterystyką wejściową wzbogacanego materiału dla przedstawianego modelu rozkładu gęstości ziaren w łożu osadzarki. Pojedyncze ziarna wzbogacanego w osadzarce materiału losowo trafiają do poszczególnych warstw łoża osadzarki. Prawdopodobieństwo trafienia ziarna frakcji gęstościowej nadawy o określonej gęstości do określonej warstwy zależy od ilości tej frakcji w nadawie, różnicy gęstości tej frakcji i średniej gęstości ziaren danej warstwy (Budryk, 1949) oraz przyjętego rodzaju rozkładu charakteryzującego rozpraszanie ziaren w warstwach łoża. Dla dalszych rozważań został przyjęty rozkład normalny. Przedstawione wyżej założenia mogą być podstawą do określenia dwuwymiarowego rozkładu podającego prawdopodobieństwo znalezienia się cząstki o określonej gęstości w warstwie, której gęstość określa średnia gęstość wszystkich cząstek tworzących tę warstwę. Postuluje się także, aby ten dwuwymiarowy rozkład uwzględniał skończony zakres gęstości cząstek i warstw oraz dowolny skład gęstościowy rozdzielanego materiału i pozwalał na pełną ocenę bilansu mas w procesie rozdzielania. Po uzupełnieniu o zależność zawartości popiołu od gęstości i prędkości warstw od ich gęstości powinien pozwalać także na ocenę produktów wzbogacania oraz obliczenie wysokości poszczególnych warstw łoża.

Zasadniczą trudnością w określeniu tego rozkładu jest spełnienie warunku, aby rozpraszanie cząstek wynikające z tego rozkładu miało miejsce tylko w tych warstwach, których istnienie jest uzasadnione składem gęstościowym wzbogacanego materiału. Ważny dla pokazania tej trudności jest fakt, że ograniczenie zakresu tworzących się warstw jest zależne także od przyjmowanego w modelu rozproszenia. Żaden z podawanych w literaturze teoretycznych modeli wzbogacania w osadzarce nie ma tego rodzaju właściwości. Dlatego w tym miejscu konieczne jest podanie krótkiego opisu poprawnego modelu niezbędnego dla pokazania błędów w istniejącej literaturze. Dokładny jego opis z podaniem matematycznych szczegółów zostanie przedstawiony w oddzielnym opracowaniu. Zasadniczym celem pokazania teoretycznego rozkładu cząstek w łożu osadzarki na tym etapie rozważań jest wyjaśnienie czym w swej istocie w losowej interpretacji procesu wzbogacania jest rozproszenie, liczba rozdziału, krzywa (funkcja) rozdziału oraz jakie relacje zachodzą między tymi pojęciami.

W rozważanym w tym miejscu zagadnieniu istotne znaczenie mają funkcje gęstości i dystrybuanty tylko niektórych rozkładów warunkowych rozkładu dwuwymiarowego, dla których warunkiem jest określona gęstość cząstki wzbogacanego materiału. Rozkłady te są dlatego szczególnie istotne, że odpowiadają rozumieniu rozproszenia podanego w dalszej części niniejszej pracy wzorem (1) oraz niektórym pojęciom używanym w teorii wzbogacania. Konieczne jest także zauważenie, że jeżeli istniejące w literaturze rozkłady opisujące rozpraszanie się cząstek przyjmują jakieś ograniczenia, to są one związane tylko z zakresem gęstości cząstek pomijając istniejące naturalne granice dla rozpraszania się tych cząstek. Tymi naturalnymi granicami są warstwy o najniższej i najwyższej gęstości średniej. Jest oczywiste, że cząstki wzbogacanego materiału nie mogą rozproszyć się w nie istniejących warstwach. Żaden z istniejących w literaturze wzorów określających możliwość rozproszenia się cząstek nie bierze pod uwagę tej oczywistości. Pierwszą i najistotniejszą uwagą dotycząca ograniczeń rozpraszania się cząstek jest zauważenie, że największe ograniczenia w możliwości rozpraszania dotyczą cząstek o najniższej i najwyższej gęstości wzbogacanego materiału. Cząstki o najmniejszej gęstości mogą z określonym prawdopodobieństwem trafić do każdej istniejącej warstwy. Najlżejsza warstwa dla wzbogacania rzeczywistego (nieidealnego) ma zawsze gęstość większą od gęstości najlżejszych cząstek, ponieważ trafiają do niej także cząstki wyższych gęstości i równocześnie nie mogą do niej trafić nie istniejące cząstki lżejsze. W tej najlżejszej warstwie muszą zatem gromadzić się wszystkie cząstki, które zgodnie z przyjętym rozkładem trafiłyby do nie istniejących warstw lżejszych. Funkcję gęstości prawdopodobieństwa takiego rozkładu, w rachunku prawdopodobieństwa określanego jako rozkład mieszany (Kubik, 1982), przestawia rys.1.

Na tym rysunku pokazano także analogiczną funkcję rozkładu dla cząstek o największej gęstości. Funkcje gęstości prawdopodobieństwa tego rozkładu dla cząstek ze środkowego zakresu gęstości i zróżnicowanym rozproszeniu pokazane są na rys.2. Na rysunku tym liniami bez znaczników pokazane są funkcje gęstości rozkładu przekraczające zakres ograniczeń. Na obu rysunkach gęstość cząstek rozpraszanej frakcji jest zaznaczona pionową przerwaną linią. Istotne jest zauważenie, że podane wykresy nie pokazują dodatkowych zmian funkcji gęstości rozkładu prawdopodobieństwa wynikających ze zmiany gęstości warstw. Zmian tych nie można pokazać na tym etapie rozważań, ponieważ w znacznym stopniu zależą one także od składu gęstościowego nadawy nieuwzględnionego w przykładach. Ponadto rozsądnie jest przyjmować, że gęstość tworzących się swobodnie warstw będzie inna niż gęstość poszczególnych frakcji nadawy. To założenie staje się szczególnie ważne dla modeli dyskretnych. W każdym z podanych przykładowych wykresów rozproszenia cząstek w warstwach to rozproszenie jest inne.

Liczba rozdziału dla produktu lekkiego określa jaka część masy cząstek o danej gęstości zawartej w nadawie trafia do tego produktu. Z drugiej strony funkcja gęstości prawdopodobieństwa rozkładu warunkowego dla stałej gęstości cząstki podaje jakie jest prawdopodobieństwo, że cząstki o tej gęstości znajdą się w warstwie o rozpatrywanej gęstości, a dystrybuanta tego rozkładu podaje prawdopodobieństwo trafienia tych cząstek do tej warstwy i warstw lżejszych od warstwy o rozpatrywanej gęstości. Na mocy twierdzenia Bernoulliego (Kubik, 1982) dla odpowiednio dużej próbki prawdopodobieństwo to może być rozumiane jako udział masy cząstek o danej gęstości odpowiednio w masie danej warstwy lub w masie warstw o gęstości równej i mniejszej od gęstości tej warstwy. Z powyższego wynika, że wartość dystrybuanty rozkładu warunkowego dla stałej gęstości cząstek w punkcie o gęstości warstwy ρ_w jest liczbą rozdziału dla cząstki o gęstości ρ_c. Jeżeli zatem dokonać idealnego podziału rozwarstwionego materiału na produkt lekki i ciężki obierając jako granicę konkretną warstwę to punkty dystrybuant rozkładów warunkowych o stałej gęstości cząstki są punktami krzywej rozdziału dla tak dokonanego podziału rozwarstwionego materiału na dwa produkty. Zatem można uważać, że krzywa rozdziału jest miejscem geometrycznym punktów różnych dystrybuant tych rozkładów warunkowych, dla których ustalona jest gęstość cząstki. Poprawny model rozwarstwiania się materiału w łożu osadzarki musi także uwzględniać w swej postaci naturalną zmienność średniej gęstości warstwy w wy-



Rys.2. Ograniczone rozproszenie cząstek o różnych gęstościach
Fig. 2. Limited dispersion of different density grains

niku zmian charakterystyki wzbogacanego materiału oraz zmian rozpraszania się cząstek w różnych warstwach dla cząstek różnych gęstości spowodowanych zmiennymi warunkami technicznymi prowadzonego procesu wzbogacania. Prowadzi to do sytuacji, w której postać modelu nie może ograniczać swobody kształtowania się gęstości poszczególnych warstw jak i ilości materiału gromadzącego się w tych warstwach. Brak tych ograniczeń powoduje, że mogą nie istnieć warstwy o niektórych zakresach gęstości. Takich założeń nie spełnia żaden z modeli przestawianych w istniejącej literaturze poza modelami klasy DEM (Mishra 1999), które na obecnym etapie rozwoju nie są dostatecznie precyzyjne i dlatego nie mogą być użyte w prowadzonych rozważaniach. Inne modele jak model Zapały (Zapała, 1988) lub model Kinga (Cierpisz, 2012) używane dla wyjaśniania rozproszenia w procesie osadzania opisują to rozproszenie stosując z góry ustalony liniowy rozkład gęstości warstw, który ma miejsce tylko dla wzbogacania idealnego, a w rzeczywistym wzbogacaniu jest on silnie nieliniowy. Uwzględnienie możliwości tworzenia się zróżnicowanych gęstości warstw prowadzi do modelu, w którym obliczanie gęstości warstw musi być iteracyjne, ponieważ każda zamiana gęstości warstw zmienia używany do obliczeń rozkład gęstości prawdopodobieństwa.

Krytyczna ocena niektórych podstawowych prac

Dostęp do niektórych z poniżej omawianych prac jest bardzo utrudniony głównie ze względu na upływ czasu od ich powstania. Dlatego w dodatku do tego artykułu przedstawiono wybrane cytaty z tych prac ułatwiające Czytelnikowi własną ocenę przedstawianych argumentów.

Praca K.F. Trompa

Podstawową pracą dającą początek tej gałęzi teorii wzbogacania grawitacyjnego jest praca K.F. Trompa opublikowana w lutym 1937 roku (Tromp, 1937). Jej ogromne znaczenie dla teorii polega głównie na wydzieleniu z całkowitej oceny procesu wzbogacania grawitacyjnego jego najistotniejszej części i poddanie tej części oddzielnej ocenie oraz na wprowadzeniu możliwości względnie prostej oceny poszczególnych urządzeń wzbogacających. Jednakże to bardzo istotne osiągnięcie Trompa zawiera pewne braki, które nie zostały skorygowane zarówno przez autora jak i kontynuatorów jego pracy.

Przed ich przedstawieniem trzeba zauważyć równoległe używanie w literaturze pojęć ciężaru właściwego i gęstości. Sens obu pojęć jest taki sam, pomimo różnych ich fizycznych definicji, a istniejąca w praktyce różnica wynika tylko z układu jednostek użytych do ich określenia. W dalszym ciągu pojęcia te będą używane zamiennie z zachowaniem zasady, że przy omawianiu danej pracy stosuje się pojęcie używane przez jej autora. W pracy Trompa oba te pojęcia są używane w równolegle.

Można wskazać trzy istotne niedostatki tej pracy. Pierwszy z nich to pominięcie pełnej oceny dokładności empirycznego wyznaczenia krzywej rozdziału. Problem ten pozostaje bez satysfakcjonującego rozwiązania do dnia dzisiejszego, pomimo licznych norm związanych z tym zagadnieniem (Głowiak,1996). Można sądzić, że Tromp był świadomy wagi tej sprawy pomijając w tabeli 1 i na podanym wykresie na rys. 5 (Tromp, 1937) ostatnią z możliwych do wyznaczenia liczb rozdziału. Liczba ta, obliczona z danych Trompa, całkowicie nie pasuje do trendu wyznaczonego przez liczby dla niższych ciężarów właściwych i ponadto zawiera sama w sobie problem przypisania konkretnego ciężaru właściwego dla pewnego, precyzyjnie nieokreślonego jego zakresu. Nie odniósł się także do różnych wychodów produktów wzbogacania uzyskiwanych dla frakcji o różnych ciężarach właściwych wzbogacanego materiału. Sytuacja ta jest obrazem braku pełnego bilansowania się masy tych frakcji w pomiarach procesu wzbogacania i ma duże znaczenie dla dokładności wyznaczania krzywej rozdziału. Brak zwrócenia uwagi na to zagadnienie jest zastanawiający, ponieważ Tromp znaczną cześć swojej pracy poświęcił dokładności dopasowania krzywej empirycznej do krzywej wynikającej z jego teoretycznych obliczeń. Warto jednak zauważyć, że dokładność eksperymentalnych badań Trompa znacznie przewyższa dokładność innych podobnych badań.

Drugi z zauważonych braków to nieudana próba zastosowania do teoretycznego opisu krzywej rozdziału bardzo specyficznie przekształconej funkcji gęstości prawdopodobieństwa rozkładu normalnego, podczas gdy można było do tego celu użyć dystrybuanty tego rozkładu. To specyficzne przekształcenie polega na przecięciu funkcji gęstości prawdopodobieństwa rozkładu normalnego w punkcie maksimum i zastąpienia części tej krzywej położonej na prawo od maksimum jej lustrzanym odbiciem względem poziomej prostej przechodzącej przez punkt maksimum (Tromp 1937, rys. 8). Trzecie niedociągnięcie to brak trafnej fizycznej interpretacji teoretycznej krzywej, co Tromp sam zauważa pisząc, że zależność, którą się posługuje nie ma sensu fizycznego. Gęstość rozdziału jest przyjęta jako gęstość tej frakcji, której liczba rozdziału wynosi 50. Problem powiązania ciężaru właściwego rozdziału z pojęciami znanymi wcześniej z teorii wzbogacania idealnego pojawia się w późniejszych pracach innych badaczy (Budryk 1949).

Praca A. Terry

A.Terra (Terra,1938) wykorzystał krzywe rozdziału do oceny pracy różnych wzbogacalników podając także definicję powszechnie i aktualnie używanego wskaźnika jakości procesu wzbogacania nazywanym rozproszeniem prawdopodobnym i oznaczanym zwykle symbolem Ep. W swoim opracowaniu do aproksymacji krzywej rozdziału zastosował całkową krzywą Gaussa dzisiaj częściej nazywaną dystrybuantą rozkładu normalnego, pozostawiając funkcję gęstości rozkładu normalnego do opisu rozproszenia cząstek materiału. Nie wszystkie spostrzeżenia Terry związane krzywymi rozdziału mają całkowicie pozytywny charakter. Pierwsze z jego niedociągnięć, bardzo ważne ze względu na jego dalekosiężne konsekwencje, to zasugerowanie nieistniejących w ogólności całkowo-różniczkowych związków między krzywą rozdziału i krzywą rozproszenia. Stało się tak z powodu nietrafnego przeniesienia na grunt teorii wzbogacania poprawnych związków zachodzących między, jak to Terra określa, "dzwonową i całkową krzywą Gaussa" znanych z rachunku prawdopodobieństwa. To spostrzeżenie potwierdza późniejsza jego praca, (Terra, 1954) chociaż według niego autorem tego przeniesienia pojęć jest Tromp. Terra nie podaje jednak literatury potwierdzającej ten fakt.

Drugie to nieprawidłowa interpretacja ograniczeń wynikających ze skończonego zakresu gęstości cząstek wzbogacanego materiału, co także zaowocowało skierowaniem dalszych badań w złym kierunku, a jest to szczególnie widoczne w niektórych późniejszych pracach [Budryk, 1949, Budryk, 1953, Stępiński, 1964). Poważnym błędem Terry jest wprowadzenia do teorii wzbogacania stwierdzenia o stałości Ep dla danego wzbogacalnika później także przeniesionego na związany z Ep inny wskaźnik zwany imperfekcją. Być może twierdzenie to zbytnio nie odbiega od prawdy dla innych niż osadzarka wzbogacalników, lecz z całą pewnością jest całkowicie nieprawdziwe w odniesieniu do osadzarki. Podstawową przyczyną takiego stanu rzeczy jest bardzo silna zależność prędkości wznoszenia i opadania cząstek w wodzie od rozmiaru i kształtu tych cząstek (Surowiak 2006).

Ponadto w końcowej części swej pracy dotyczącej łącznego lub oddzielnego wzbogacania węgli o różnych charakterystykach wzbogacalności Terra podaje nieprawidłowy matematycznie dowód prawdziwego twierdzenia. Poprawny dowód tego twierdzenia z wyjaśnieniem błędu Terry jest zawarty w końcowej części tego opracowania.

Warto zauważyć, że Terra podejmując badania Trompa związane z zależnością między zawartością popiołu i gęstością danej frakcji także nie podał szczegółów tej zależności dla najlżejszych frakcji gęstościowych węgla, co także zauważa Stępiński (Stępiński, 1964). Wyniki badań tej zależności podjęte przez innych badaczy pomijają tę szczególną kwestię, mającą duże znaczenie w praktyce wzbogacania dla dokładności stabilizacji zawartości popiołu w koncentracie węglowym (Bartoniek, 2008).

Prace W. Budryka

Wprowadzenie do polskiej literatury wyników prac wyżej wymienionych autorów zawdzięczamy przede wszystkim jednej z prac W. Budryka (Budryk, 1949).

Pracy tej poświęcone zostanie znacznie więcej uwagi niż pozostałym, ponieważ miała ona ogromny wpływ na utrwalenie się na polskim gruncie naukowym podstaw teorii krzywych rozdziału ze wszystkimi jej zaletami, ale także i nieprawidłowościami.

Budryk powołując się na badania Trompa i Terry dotyczących zjawiska układania się cząstek w poszczególnych warstwach powstających w trakcie wzbogacania w wodnej osadzarce pulsacyjnej podał poniższą zależność:

$$z(\delta) = \frac{h}{\sqrt{\pi}} e^{-h^2(\delta-\delta_i)^2} \qquad (1)$$

gdzie:
z – skupienie ziaren o ciężarze właściwym δ
h – parametr funkcji prawdopodobieństwa
e – zasada logarytmów naturalnych
δ_i – ciężar właściwy ziaren rozproszonej frakcji
δ – ciężar właściwy ziaren frakcji, do której trafiają ziarna o ciężarze właściwym δ_i

Oznaczenia i ich opis poszczególnych zmiennych podane są jak w pracy (Stępiński, 1964), ponieważ Budryk w swej pracy nie podał fizycznej interpretacji zmiennej z(δ) określając ją jako funkcję prawdopodobieństwa Gaussa. Zależność (1) mimo, że nie zostało podane jej formalne wyprowadzenie posiada wielka wagę, ponieważ jest historycznie pierwszym matematycznym zapisem relacji jakie zachodzą między ciężarem właściwym cząstki wzbogacanego materiału i gęstością warstwy jaką tworzy zbiór rozproszonych cząstek w trakcie procesu wzbogacania w osadzarce. Na wiele lat wytyczyła ona kierunek dalszego rozwoju teorii, mimo że jest tylko szczególnym, lecz ważnym przypadkiem. Zależność (1) podaje rozkład rozproszenia się cząstek o ciężarze właściwym δ_i w warstwach o ciężarze właściwym δ utworzonych przez wzbogacany w osadzarce materiał. Istotne w tym miejscu jest zauważenie, że podana zależność określa rozproszenie się cząstek tylko o jednym ciężarze właściwym równym δ_i. Tak więc, jeżeli zależność (1) potraktować jako funkcję gęstości jednowymiarowego rozkładu prawdopodobieństwa to zmienną losową tego rozkładu jest ciężar właściwy warstwy do której trafiają cząstki o różnej gęstości. Z tej uwagi wynika ważny wniosek, że dla oceny rozdziału wzbogacanego materiału między dwa produkty wzbogacania konieczna jest znajomość rozproszenia wszystkich frakcji gęstościowych nadawy.

Kierunek wytyczony przez tę pracę okazał się nie najlepszy z powodu kilku poważnych uchybień w dalszej jej części. Pierwszym z nich było niepoprawne wyprowadzenie z tej zależności wzoru określającego krzywą rozdziału, co w świetle przedostatniego z powyższych zdań nie jest możliwe. To wyprowadzenie zawiera dwa poważne błędy merytoryczne. Pierwszy z nich wyjaśnia fizyczna interpretacja wzoru (1) w połączeniu z uwagami zawartymi na stronach 879-881 (Budryk, 1949). Wzór (1) jest zapisem funkcji gęstości prawdopodobieństwa rozkładu podającego prawdopodobieństwo, że cząstka o ciężarze właściwym δ_i trafi do warstwy o ciężarze właściwym δ. Zmienną losową tego rozkładu jest ciężar właściwy warstwy δ, a ciężar właściwy rozpraszanych cząstek δ_i jest jego wartością oczekiwaną Takich rozkładów jest więc tyle, ile jest rozróżnialnych ciężarów właściwych δ_i. Całkowanie tej funkcji w całym zakresie istniejących warstw przyjętych jako trafiające do odpadów daje liczbę określającą jaka część wszystkich cząstek o ciężarze właściwym δ_i trafiła do odpadów, a tak definiowana jest liczba rozdziału dla frakcji cząstek nadawy o ciężarze właściwym δ_i. Zatem aby otrzymać krzywą rozdziału takie całkowanie trzeba oddzielnie przeprowadzić dla każdego ciężaru właściwego cząstki z rozważanego zakresu ciężarów właściwych δ_i, ponieważ dla każdego tych ciężarów właściwych funkcja podcałkowa jest inna. Dlatego wzór 11 ze str. 881 i jego dalsze przekształcenie nie przedstawia faktycznie krzywej rozdziału, lecz tylko jedna liczbę rozdziału z tej krzywej. Stąd także wzór 13 nie może być poprawny tym bardziej, że zmienione zostały granice całkowania wzoru 12 bez właściwego uzasadnienia. Możliwe jest jednak inne wyjaśnienie tej kwestii wynikające z rys.3 na str. 881 (Budryk. 1949). Na tym rysunku pokazana jest krzywa rozproszenia płuczki barytowej, w której fizycznie nie ma warstw materiału, zatem nie może istnieć rozproszenie w zrozumieniu podanym wzorem (1). W takiej sytuacji pojawia się pytanie o eksperymentalne podstawy krzywej rozproszenia dla płuczki barytowej. Jedyne takie eksperymentalne uzasadnienie pojawia się, gdy przyjąć że pod nazwą krzywej rozproszenia Budryk rozumie także pochodną krzywej rozdziału, czego potwierdzeniem może być wspomniana wyżej zmiana granic całkowania dla wzoru 13. Przypuszczenie to może uzasadniać nieprawdziwa i bardzo nie jasno sformułowana uwaga ze str. 881, że rozproszenie cząstek w poszczególnych warstwach jest takie samo jak zawartość cząstek o różnych ciężarach właściwych w danej warstwie. Niejasność wynika ze stwierdzenia "że krzywa rozproszenia z (ABC) jest jednocześnie krzywą z1 względnej (w stosunku do poszczególnych frakcji) zawartości ziarn o różnym ciężarze właściwym w danej elementarnej frakcji (δ_i)". Niejasność znika, gdy zamiast δ_i przyjąć δ lecz i tak nieprawdziwość tego stwierdzenia pozostaje. Jako błąd drukarski należy przyjąć nazwę rys. 4 ze str.881 bez wątpliwości przedstawiającego dwie krzywe rozproszenia. Z tego rysunku wynika, że ciężar właściwy rozdziału Δ jest ciężarem właściwym warstwy (a nie cząstki jak to wynika z definicji ciężaru właściwego rozdziału). Zatem formalnie ciężar właściwy Δ nie może być ciężarem właściwym rozdziału, tak jak to przyjmuje Budryk, nawet wtedy, gdy zgodnie z równaniem [9] ze str. 880 może także oznaczać ciężar właściwy Δ rozpraszanej frakcji.

Ponadto w omawianej pracy Budryk, prawdopodobnie zasugerowany błędem w pracy Terry, dokładnie analizuje ograniczenia zakresu gęstości cząstek wzbogacanego materiału, które to ograniczenie nie ma żadnego znaczenia dla rozpraszania się cząstek, ponieważ nie istniejące cząstki nie podlegają rozpraszaniu. Można przypuszczać, że źródłem tego błędu jest przyjęcie istnienia zależności między krzywą rozdziału i krzywą rozproszenia analogicznej jak w rachunku prawdopodobieństwa zależności między dystrybuantą rozkładu i funkcją gęstości prawdopodobieństwa czyli traktowania rozproszenia jako pochodnej krzywej rozdziału, czego początki są do zauważenia w pracy Terry. W związku z tym dalsze rozważania Budryka związane z położeniem ciężaru właściwego rozdziału w pobliżu skrajnych ciężarów właściwych cząstek występujących we wzbogacanym materiale są całkowicie nieprawidłowe. Te rozważania pociągnęły to za sobą dalsze skutki takie jak niewłaściwa interpretacja ograniczeń krzywej rozproszenia, która doprowadziła do wprowadzenia, nie mających uzasadnienia w tym rozumieniu zagadnienia, pojęć takich jak teoretyczna i rzeczywista krzywa rozdziału i niepoprawnych związków tych krzywych z ograniczeniami zakresu ciężarów właściwych cząstek wzbogacanego materiału. Przedstawione w pracy (Budryk, 1949) na rys. 7 krzywe rozdziału nie mogą być tymi krzywymi, ponieważ pokazane na tym rysunku wszystkie krzywe są funkcjami ciężaru właściwego warstwy. Dlatego wynikający z tego rysunku sposób wykreślania poprawionej krzywej rozdziału nie jest właściwy. W związku z tym także praca (Budryk, 1953), w której przedstawiono sposób znajdywania teoretycznej krzywej rozdziału na podstawie znajomości krzywej rzeczywistej nie może być poprawna. Najbardziej istotną nieprawidłowością w rozumowaniu Budryka jest przyjęcie, że ograniczeniem stosowalności krzywej rozproszenia jest ograniczenie zakresu ciężaru właściwego cząstek wzbogacanego materiału. Takie ograniczenie jest tylko przyczyną występowania innego istotniejszego ograniczeniem jakim jest zakres ciężarów właściwych warstw w łożu osadzarki zależny od zakresu ciężarów właściwych cząstek wzbogacanego materiału oraz rozproszenia cząstek w procesie wzbogacania. To ograniczenie nie ma także bezpośredniego związku z ciężarem właściwym rozdziału. Drugą nieprawidłowością jest przyjmowanie, że funkcję (krzywą) rozproszenia można poprzez jej całkowanie przekształcić w funkcję (krzywą) rozdziału, która jest funkcją innej zmiennej czyli gęstości cząstek wzbogacanego materiału. Doprowadziło to do rozpowszechnia w polskiej literaturze traktowania nie mającej fizycznej interpretacji pochodnej krzywej rozdziału jako funkcji rozproszenia. (Stępiński,1964), (Surowiak,2006).

Trzecim istotnym błędem w rozważaniach Budryka jest niezauważenie konieczności zmiany postaci rozkładu opisującego rozproszenie, gdy zakres rozproszenia cząstek przekracza granice zakresu istniejących warstw. Przedstawione w powyższych rozważaniach rys. 1 i 2 dają obraz zmian funkcji rozproszenia jakie należy przyjąć, aby zachować bilans masy rozpraszanych cząstek. Analizowane prace Budryka z tego zakresu zawierają także szereg pomniejszych innych nieścisłości, pozostających bez większego znaczenia dla dalszych rozważań. Aby nie tworzyć niewłaściwego wrażenia przypisania wszystkich tych niedociągnięć Budrykowi trzeba zauważyć, że w historii nauki znane są poważne błędy wielkich autorytetów (Galileusz, Newton, Laplace, Euler, Einstein) i popełnianie ich przy poznawaniu nieznanych zjawisk jest zawsze możliwe. Natomiast nie jest do zaakceptowania bezkrytyczne przyjmowanie tych błędów przez innych badaczy, a taka sytuacja dotyczy głównie kontynuatorów prac Budryka.

Praca B.S. Gottfrieda

Pojęcie uogólnionej krzywej rozdziału zostało wprowadzone przez Gottfrieda w jego pracy z 1978 roku (Gottfried, 1978). Ważność tego uogólnienia jest nie do zakwestionowania, jednakże warto przyjrzeć się bliżej ograniczeniom, jakie to uogólnienie powinno spełniać, a których próżno szukać w tej pracy. Jeżeli rozważać kilka takich samych krzywych rozdziału przesuniętych na osi odciętych, czyli krzywych różniących się tylko ciężarem właściwym rozdziału, to ich zastąpienie jedną krzywą wykreśloną dla argumentu, którym jest iloraz ciężaru właściwego cząstki i ciężaru właściwego rozdziału nie budzi żadnych wątpliwości. Z taką sytuacja mamy jednak do czynienia tylko dla pewnych szczególnych warunków. Według Gottfrieda te warunki ograniczają się do wzbogacanie takiej samej nadawy w jednym wzbogacalniku z różnymi ciężarami właściwymi rozdziału. Istotne jest jednak zauważenie, że sytuacja taka w praktyce może się zdarzać tylko dla wzbogacalników mogących pracować z wysoką skutecznością wzbogacania takich jak wzbogacalniki z cieczą ciężką, których skuteczność wzbogacania jest praktycznie niezależna od wybranego ciężaru właściwego rozdziału. Tego rodzaju sytuacja nie zachodzi dla osadzarek, których nachylenie krzywej rozdziału zwykle spada wraz ze zwiększaniem ciężaru właściwego cząstek wzbogacanego materiału dając efekt asymetrii tej krzywej rosnącej także wraz z ciężarem właściwym rozdziału. Dlatego uogólnione krzywe rozdziału nie powinny być stosowane do prognozowania wyników wzbogacania w osadzarkach. Krzywe uogólnione można stosować tylko wtedy, gdy wszystkie uzyskiwane empirycznie krzywe rozdziału mają takie samo nachylenie przy różnych ciężarach właściwych rozdziału.

Praca W. Zapały

W pracy (Zapała. 1988) podana jest jedyna w literaturze, znanej autorowi niniejszej pracy, poprawna interpretacja związków jakie zachodzą między krzywą rozdziału i krzywą rozproszenia. Najważniejszym efektem tej pracy jest pokazanie, że funkcja rozproszenia i funkcja (krzywa) rozdziału są opisane dla dwu różnych zmiennych. Krzywa rozdziału jest funkcją gęstości cząstek wzbogacanego materiału, podczas gdy funkcja (krzywa) rozproszenia jest funkcją gęstości warstw elementarnych, jakie wzbogacany materiał tworzy w łożu osadzarki. To wyraźne dla osadzarek rozgraniczenie obu zmiennych całkowicie burzy całkowo-różniczkową zależność obu tych funkcji podawaną w literaturze. Zwraca także uwagę na całkowicie niepoprawną interpretację krzywej rozproszenia jako pochodnej krzywej rozdziału.

Na stronach 46 i 47 pracy Zapały podana jest prawidłowa interpretacja związków, jakie zachodzą między krzywą rozdziału, a krzywą rozproszenia. Istotnym podsumowaniem tego jest stwierdzenie, że każdy punkt krzywej rozdziału jest także punktem dystrybuanty rozkładu określającego prawdopodobieństwo trafienia cząstki określonej gęstości do produktu lekkiego procesu wzbogacania. Z opisu tego jednoznacznie wynika, że zmienną losową rozważanego rozkładu jest gęstość warstwy, do której trafiają cząstki różnych gęstości. Krzywa rozdziału jest zbiorem punktów poszczególnych dystrybuant określonych dla różnych gęstości cząstek przy ustalonej gęstości warstwy, która jest graniczną warstwą dzielącą wzbogacony materiał na produkt lekki (górny) i produkt ciężki (dolny). Istotnym wnioskiem z przestawionego wywodu jest stwierdzenie, że liczba rozdziału określa także pewne prawdopodobieństwo, lecz zmienną losową przyjętą do określenia tego prawdopodobieństwa nie jest gęstość cząstek wzbogacanego materiału, lecz jest to gęstość warstw.

Jednakże Zapała nie zauważył bardzo istotnego dla poprawnego opisu tych zjawisk znaczenia ograniczenia zakresu gęstości możliwych warstw w łożu osadzarki oraz zależności tych ograniczeń od rozproszenia prawdopodobnego procesu wzbogacania. Ograniczenia te także powodują to, że jego dalsze rozważania związane z rozpatrywaniem wzbogacania ze stałym rozproszeniem lub ze stałą imperfekcją niezbyt precyzyjnie przedstawiają obraz rzeczywistego wzbogacania. Trzeba także zauważyć, że zastosowany w wyprowadzeniu jego modelu schemat losowania nie jest poprawny, ponieważ nie uwzględnia istotnej dla tego modelu zmiany gęstości cieczy ciężkiej imitującej gęstość warstwy w sytuacji, gdy trafi do niej cząstka o gęstości różnej od średniej gęstości warstwy, co musi spowodować zmianę gęstości warstwy (cieczy). Trzeba również dodać, że pojęcie imperfekcji przez niego używane jest pewnym uogólnieniem tego pojęcia dla opisu różnego rozpraszania się cząstek o różnych gęstościach. Rozważania Zapały dotyczące różnych teoretycznych sytuacji wynikających z wyprowadzonego przez niego modelu rozkładu warstw i cząstek doprowadzają do zauważenia istotnej sprawy jaką jest możliwość rozpraszania się cząstek o różnych gęstościach z różnym rozproszeniem. Z jego rozważań także wynika potwierdzenie dla obserwowanego empirycznie faktu, że wraz ze wzrostem gęstości cząstek rośnie także ich rozproszenie w warstwach łoża osadzarki

Ważnym osiągnięciem pracy Zapały jest pokazanie bardzo wysokiego udziału szumu białego w wynikach pomiarów składu densymetrycznego i zawartości popiołu węgla surowego oraz produktów wzbogacania w osadzarce, co może stanowić pewne usprawiedliwienie dla istnienia losowej interpretacji procesu wzbogacania w tej maszynie.

Poprawny dowód twierdzenia Terry

Dla mieszanki dwu różnych węgli wzbogacanych idealnie (Ep = 0) bilans mas i zawartości popiołu lekkich produktów wzbogacania można zapisać poniższymi równaniami:

$$\gamma = u\gamma_1 + (1-u)\gamma_2 \tag{2}$$

$$\gamma\vartheta = u\gamma_1\vartheta_1 + (1-u)\gamma_2\vartheta_2 \tag{3}$$

$$\vartheta_1 = \frac{\int_0^{\gamma_1} \alpha_1(\gamma_1)d\gamma_1}{\gamma_1} \tag{4}$$

$$\vartheta_2 = \frac{\int_0^{\gamma_2} \alpha_2(\gamma_2)d\gamma_2}{\gamma_2} \tag{5}$$

gdzie:

γ, γ_1, γ_2 – wychód mieszanki oraz odpowiednio wychody produktu lekkiego pierwszego i drugiego wzbogacalnika;

ϑ, ϑ_1, ϑ_2 – zawartość popiołu odpowiednio w mieszance oraz w produktach lekkich pierwszego i drugiego wzbogacalnika;

α_1 – zawartość popiołu we frakcji o gęstości γ_1 materiału surowego pierwszego wzbogacalnika

α_2 – zawartość popiołu we frakcji o gęstości γ_2 materiału surowego drugiego wzbogacalnika

u – udział składnika pierwszego w całości obu wzbogacanych węgli.

Tę samą, stałą zawartość popiołu mieszanki tworzonej z produktu lekkiego dwu wzbogacalników można osiągnąć na wiele sposobów, lecz tylko jeden z tych sposobów daje maksymalny wychód mieszanki.

Twierdzenie Terry:

Wzbogacając dwa różne węgle surowe i sporządzając mieszankę o stałej zawartości popiołu równej ϑ z produktów lekkich dwu wzbogacalników maksimum wychodu mieszanki uzyskamy, gdy granice separacji obu węgli będą tak dobrane, że zostanie spełniony warunek

$$\alpha_1(\gamma_1) = \alpha_2(\gamma_2)$$

Warunek ten według Terry ma wynikać z równania:

$$u\alpha_1 d\gamma_1 + (1\text{-}u)\alpha_2 d\gamma_2 = 0$$

(ostatnie z równań na str. 402 w pracy (Terra, 1938) które ma zachodzić, gdy $\alpha_2 = \alpha_1$

Wstawiając do tego równania $\alpha_2 = \alpha_1$ otrzymujemy $\alpha_1[ud\gamma_1 + (1\text{-}u)d\gamma_2] = 0$, co nigdy nie zachodzi ponieważ $\alpha_1 > 0$, $u > 0$ i $(1\text{-}u) > 0$ oraz $d\gamma_1$ i $d\gamma_2$ mają ten sam znak.

Poprawny dowód tego twierdzenia sprowadza się do znalezienia warunku koniecznego dla istnienia maksimum funkcji dwu zmiennych (równanie 2) przy ograniczeniu (równanie 3). Jednym ze sposobów rozwiązania tego zadania jest metoda Lagrange'a. Układ równań tej metody dla rozważanego przypadku jest następujący (Bronsztejn,1970):

$$\frac{u\gamma_1\vartheta_1 + (1-u)\gamma_2\vartheta_2}{u\gamma_1 + (1-u)\gamma_2} - \vartheta = 0 \tag{6}$$

$$\frac{\partial}{\partial\gamma_1}[u\gamma_1 + (1-u)\gamma_2 + \lambda(\frac{u\gamma_1\vartheta_1 + (1-u)\gamma_2\vartheta_2}{u\gamma_1 + (1-u)\gamma_2} - \vartheta)] = 0 \tag{7}$$

$$\frac{\partial}{\partial\gamma_2}[u\gamma_1 + (1-u)\gamma_2 + \lambda(\frac{u\gamma_1\vartheta_1 + (1-u)\gamma_2\vartheta_2}{u\gamma_1 + (1-u)\gamma_2} - \vartheta)] = 0 \tag{8}$$

gdzie λ - mnożnik Lagrange'a

Po wykonaniu różniczkowania i wykorzystaniu zależności (4) i (5) równania (7) i (8) przyjmują postać:

$$1 + \lambda(\frac{\alpha_1(\gamma_1)}{u\gamma_1 + (1-u)\gamma_2} - \vartheta) = 0$$

$$1 + \lambda(\frac{\alpha_2(\gamma_2)}{u\gamma_1 + (1-u)\gamma_2} - \vartheta) = 0$$

z których po porównaniu lewych stron powyższych równań natychmiast wynika zależność, którą należało udowodnić.

Można także zauważyć, że to twierdzenie pozostanie prawdziwe dla wzbogacania rzeczywistego ($Ep \neq 0$) jeżeli charakterystyki wzbogacalności zostaną zastąpione charakterystykami wzbogacania. Podane twierdzenie Terry jest szczególnym przypadkiem optymalizacji procesu mieszania koncentratów ze wzbogacania różnych węgli surowych. Ogólniejszy dowód tego twierdzenia wraz z fizyczną interpretacją wyników podany jest w pracy Cierpisza (Cierpisz,1980). Ponadto wypada zauważyć, że to bardzo interesujące z poznawczego i ważne z ekonomicznego punktu widzenia twierdzenie niestety nie ma aktualnie szerszego zastosowania w praktyce wzbogacania węgla. Jednym z istotnych tego powodów jest brak metod pomiarowych umożliwiających dostatecznie szybkie wyznaczenie charakterystyk wzbogacanych węgli surowych niezbędnych do obliczenia gęstości rozdziału dla oddzielnie wzbogacanych materiałów surowych, których produkty wzbogacania tworzą mieszankę.

Podsumowanie

1. Przedstawione uwagi do podstawowych i do dziś bez zastrzeżeń przyjmowanych prac są wystarczającym powodem do dokonania istotnych korekt w części teorii wzbogacania grawitacyjnego. Zmiany te zasadniczo sprowadzają się do skorygowania rozkładów prawdopodobieństwa związanych z opisem rozpraszanie się cząstek uwzględniających wszystkie istotne ograniczenia istniejące w procesie osadzania, usunięcia z rozkładów ograniczeń dla możliwości tworzenia się warstw o różnych gęstościach oraz pominięcia niepoprawnych związków między krzywą rozproszenia i krzywą rozdziału.

2. Wielokrotne cytowanie bez odpowiednich uwag błędnych prac pozwala zauważyć fakt powszechnego i trwającego wiele lat zjawiska bezkrytycznego przyjmowania niektórych z opublikowanych prac dotyczących wzbogacania grawitacyjnego.

3. Zamiarem autora jest przedstawienie w następnych publikacjach teoretycznego modelu procesu wzbogacania w osadzarce wolnego od zastrzeżeń do istniejących publikacji przedstawionych w tej pracy.

Dodatek

W dodatku zostały zamieszczone wybrane fragmenty ważniejszych i jednocześnie trudno dostępnych cytowanych prac, które mogą pozwolić Czytelnikowi na własną ocenę przedstawianych zagadnień.

Cytaty z pracy Trompa (Tromp 1937)

Cytaty z pracy Budryka (Budryk 1949)

1. str. 879–880

Z doświadczeń Trompa wynika, że im większa jest różnica ciężarów właściwych z różnych warstw, tym mniejsza jego ilość trafia z jednej warstwy do drugiej. Niezależnie od tego im większą mamy ilość ziarn o określonym ciężarze właściwym, tym większa ilość tych ziarn trafia do innych warstw, przy czym jak wykazało doświadczenie, udział węgla pewnej frakcji w różnych warstwach jest proporcjonalny do ilości tej frakcji występującej w nadawie. Jeżeli wobec tego będziemy operowali nie absolutną ilością rozproszonych ziarn frakcji, lecz ilościami względnymi do zawartości tej frakcji w nadawie, wówczas rozproszenie nie będzie zależało od udziału poszczególnych frakcji w materiale wejściowym, a więc od kształtu krzywej wzbogacalności. Rozproszenie to nie zależy poza tym od absolutnej wielkości ciężaru właściwego frakcji δi), lecz jedynie tylko od różnicy ciężarów właściwych $\delta-\delta_i$ gdzie δ_i jest ciężarem właściwym węgla rozproszonej frakcji, δ- ciężarem właściwym warstwy, do której on się dostaje. Prawo to, jak wykazały doświadczenia Terra, pokrywa się całkowicie z funkcją prawdopodobieństwa Gaussa:

$$z = z(\delta) = \frac{h}{\sqrt{\pi}} e^{-h^2(\delta-\delta_i)^2} \qquad [9]$$

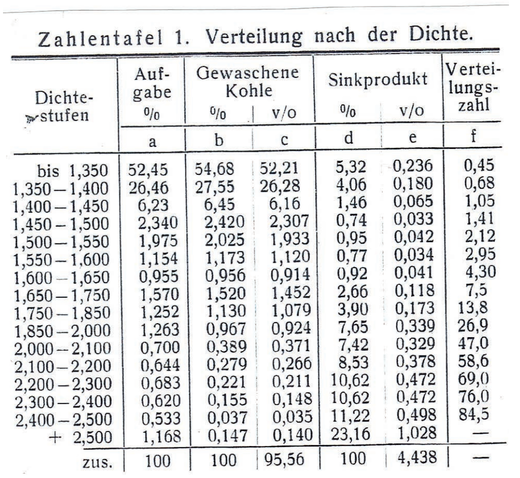
gdzie h jest parametrem funkcji prawdopodobieństwa.

2. str. 880–882

Na rys 3 przedstawione zostały krzywe rozproszenia z (wzór 9) dla wypadków przemysłowego wzbogacania w ośrodkach ciężkich (krzywa I) w płuczkach z automatyczną regulacją odprowadzania odpadów (II) oraz w wialniach. W pierwszym wypadku mamy największą dokładność wzbo-

Tab. 1. Rozdział według gęstości

Tab. 1. Distributin According to Density



Zahlentafel 1. Verteilung nach der Dichte.

Dichte-stufen	Auf-gabe %	Gewaschene Kohle %		Sinkprodukt %		Vertei-lungs-zahl
			v/o		v/o	
	a	b	c	d	e	f
bis 1,350	52,45	54,68	52,21	5,32	0,236	0,45
1,350—1,400	26,46	27,55	26,28	4,06	0,180	0,68
1,400—1,450	6,23	6,45	6,16	1,46	0,065	1,05
1,450—1,500	2,340	2,420	2,307	0,74	0,033	1,41
1,500—1,550	1,975	2,025	1,933	0,95	0,042	2,12
1,550—1,600	1,154	1,173	1,120	0,77	0,034	2,95
1,600—1,650	0,955	0,956	0,914	0,92	0,041	4,30
1,650—1,750	1,570	1,520	1,452	2,66	0,118	7,5
1,750—1,850	1,252	1,130	1,079	3,90	0,173	13,8
1,850—2,000	1,263	0,967	0,924	7,65	0,339	26,9
2,000—2,100	0,700	0,389	0,371	7,42	0,329	47,0
2,100—2,200	0,644	0,279	0,266	8,53	0,378	58,6
2,200—2,300	0,683	0,221	0,211	10,62	0,472	69,0
2,300—2,400	0,620	0,155	0,148	10,62	0,472	76,0
2,400—2,500	0,533	0,037	0,035	11,22	0,498	84,5
+ 2,500	1,168	0,147	0,140	23,16	1,028	—
zus.	100	100	95,56	100	4,438	—

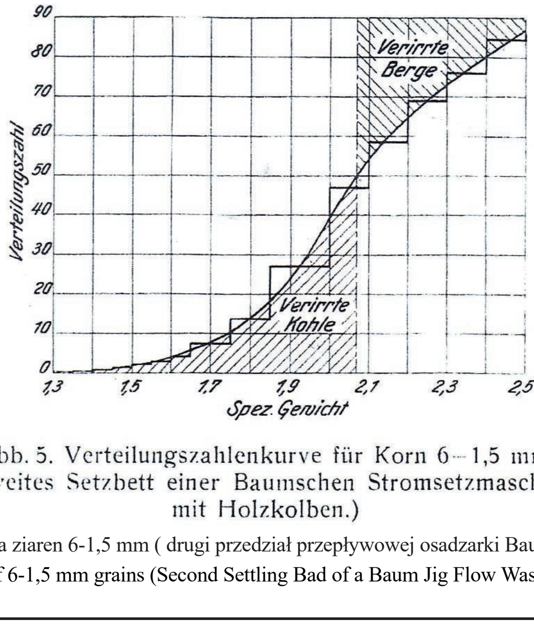


Abb. 5. Verteilungszahlenkurve für Korn 6—1,5 mm. (Zweites Setzbett einer Baumschen Stromsetzmaschine mit Holzkolben.)

Rys. 5. Krzywa rozdziału dla ziaren 6-1,5 mm (drugi przedział przepływowej osadzarki Bauma z drewnianymi tłokami)

Fig. 5. Partition curve of 6-1,5 mm grains (Second Settling Bad of a Baum Jig Flow Washer with Wood Plunger)

gacania, w wypadku natomiast wialni rozproszenie sięga daleko poza właściwą warstwę δ_i, a więc dokładność wzbogacania jest tu znacznie mniejsza.

Przyjmijmy, że rozproszenie elementarnej frakcji o c. wł. δ_i przedstawia się w postaci krzywej ABC (rys.4). Weźmy oprócz tego frakcję o c. wł. Δ, która w myśl powyższych wywodów zostaje rozproszona powyższych wywodów wg krzywej FGH, identycznej z krzywa ABC. Z wykresu tego widzimy, że wobec kompletnej symetrii obu krzywych rzędna DE jest równa rzędnej JK, a wskutek tego stosunkowa (nie absolutna) ilość węgla o c. wł. δ_i , jaka trafia do frakcji o c. wł. Δ, jest równa stosunkowej ilości węgla o c. wł. Δ trafiającej do frakcji o c. wł. δ_i. Okoliczność ta pozwala wyciągnąć wniosek. że krzywa rozproszenia z (ABC) jest jednocześnie krzywą z1 względnej (w stosunku do poszczególnych frakcji) zawartości ziarn o różnym ciężarze właściwym w danej elementarnej frakcji (δ_i).

3. str.881–882

Jeżeli ciężar właściwy Δ jest granicą rozdziału naszego materiału na koncentrat i odpady czyli ciężarem właściwym separacji, wówczas stosunek powierzchni zakreskowanej ADE (rys.4) do całkowitej powierzchni ograniczonej krzywa rozproszenia ABC określa nam względną ilość (x) węgla o ciężarze właściwym δ_i, która trafia do odpadów:

$$x = \frac{pow.ADE}{pow.ABC} = \frac{\int_{\Delta}^{\delta_{\max}} z d\delta}{\int_{\delta_{\min}}^{\delta_{\max}} z d\delta} \qquad [11]$$

Wartość ta będzie tym mniejsza, im bardziej c. wł. δ_i różnie się od c. wł. separacji Δ. W przypadku, gdy $\delta_i = \Delta$ względna ilość węgla o tym ciężarze właściwym trafiająca do odpadów, będzie taka sama, jak i ilość trafiająca do koncentratu, a wskutek tego wartość x będzie się równała 50%. Tak więc ziarna o ciężarze właściwym równym ciężarowi właściwemu separacji (Δ) trafiają w połowie do koncentratu, w połowie do odpadów.

Ciężar właściwy separacji (Δ) odpowiada również ciężarowi właściwemu tej frakcji, której krzywa rozproszenia (FGH-rys.4) posiada na granicy rozdziału swoje maksimum (punkt G).

W wypadku, gdy granice ciężarów właściwych frakcji węglowych ($\delta_{\min}$ i $\delta_{\max}$) są dostatecznie odlegle w obie strony od granicy separacji Δ, możemy bez popełnienia znacznego błędu przyjąć, że mianownik w równaniu [11] jest równy 1:

$$\int_{\delta\min}^{\delta maks} z d\delta = \int_{-\infty}^{+\infty} z d\delta = 1$$

Równanie [11] przedstawi się wówczas w postaci :

$$x = \int_{\Delta}^{\delta maks} z d\delta = \int_{\Delta}^{+\infty} z d\delta \qquad [12]$$

Przyjmując jako oś symetrii rzędną przechodzącą przez Δ, oraz wykreślając (rys.4) krzywą Gaussa FGH identyczną z krzywą ABC, widzimy, że powierzchnia zakreskowana ADE jest równa powierzchni KJH. Mając na względzie wzór [9],

$$x = \frac{h}{\sqrt{\pi}} \int_{-\infty}^{\delta} e^{-h^2(\delta-\Delta)^2} d\delta \qquad [13]$$

Jest to równanie całkowej funkcji Gaussa.

str. 884

Cytat z pracy Zapały (Zapała 1988)

str. 46 i 47

Podstawowe pojęcia takie jak: krzywa rozproszenia, liczba rozdziału, krzywa rozdziału są specyficznymi pojęciami i niezachowanie ostrości wyrażeń może doprowadzić do niejasności. W celu sprecyzowania określeń przyjmijmy, że gęstością prawdopodobieństwa zmiennej losowej Y będzie funkcja

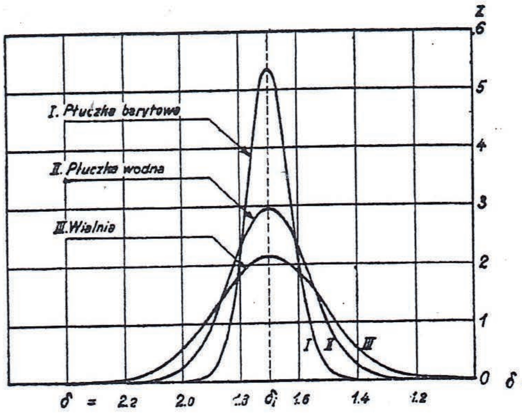
$$z(\frac{y-x}{\sigma})$$

gdzie: y- gęstość warstwy, do której trafiają ziarna frakcji elementarnej o gęstości x, σ -odchylenie standardowe rozkładu zmiennej losowej Y.

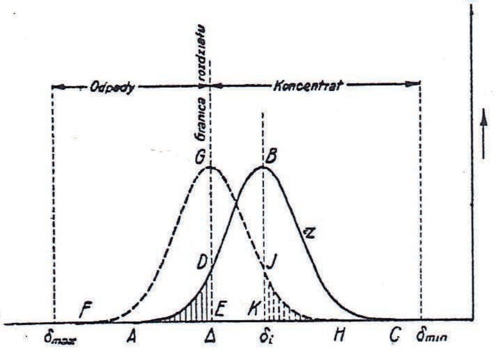
Dystrybuantą tego rozkładu jest funkcja

$$Z(y = \text{var.}, x = const) = \int_{-\infty}^{y} z(\frac{y-x}{\sigma}) dy$$

która przedstawia zależność funkcyjną liczby rozdziału dla

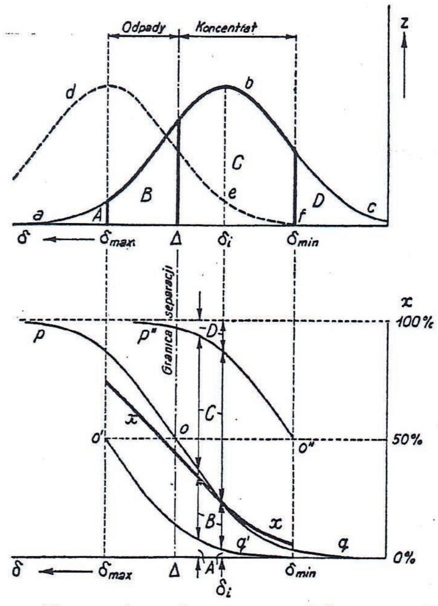


Krzywe rozproszenia z
Rys. 3



Krzywe rozdziału
Rys. 4

Fig. 3. Dispersion Curves z
Fig. 4. Partition Curves



Poprawiona krzywa rozdziału x
Rys. 6 i 7

Fig. 6 and 7. Corrected Partition Curve x

danej frakcji elementarnej od zmiennego położenia linii rozdzielającej wzbogacany materiał na produkt lekki i produkt ciężki. Pochodna funkcji Z(y = var., x = const.) względem zmiennej y (zmiennej gęstości warstw wzbogacanego materiału) jest krzywą rozproszenia, którą na wstępie przyjęliśmy. Liczba rozdziału dla frakcji elementarnej obliczana jest ze wzoru

liczba rozdziału = Z(y = yo= const., x = const.)

tzn. dla określonego położenia linii rozdzielającej wzbogacany materiał na dwa produkty i dla określonej gęstości frakcji, stanowi zatem określoną wartość. Przy określonym położeniu linii rozdzielającej wzbogacany materiał można obliczyć liczby rozdziału dla poszczególnych frakcji o gęstościach $x_1, x_2 \ldots x_n$. Na podstawie przyjętych wartości $x_1, x_2 \ldots x_n$ oraz obliczonych liczb rozdziału Z($y = y_o$, $x = x_1$), Z($y = y_o$, $x = x_2$),... Z($y = y_o$, $x = x_n$) można w układzie współrzędnych Z, x sporządzić wykres przedstawiający zależność liczb rozdziału od gęstości frakcji elementarnej. Podkreśla się, że krzywa rozdziału nie jest dystrybuantą zmiennej losowej Y. Przy wykreśleniu w przestrzeni trójwymiarowej, liczby rozdziału tworzą powierzchnię. Przecięcie tej powierzchni płaszczyzną $y = y_o$ utworzy linię, która jest krzywą rozdziału dla określonej gęstości rozdziału y_o. Natomiast przecięcie tej powierzchni płaszczyzną x = const. tworzy linię, która jest dystrybuantą zmiennej losowej Y i oznacza prawdopodobieństwo zdarzenia, że ziarna frakcji elementarnej o gęstości x = const. trafią do warstw wzbogacanego materiału o gęstościach mniejszych od y.

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The Reasons for the Necessity to Correct Some Part of Gravitional Enrichement Theory

The general outline of chosen problems concerning the theoretical presentation of the phenomena occurring in hard coal beneficiation in jigs on the basis up to date state of papers related to partition curve and grains disperion is presented. In the following part are presented the details of critical analysis of widely accepted without reservations papers, which in not correct manner theoreticly explaines the particle dispersion of material being beneficiated in the jig. Special attention was paid to omitted, up to now, limits of grain dissipation possibility, forming the density diversified layers and effects of skipping these details for appropriate theoretical explanation of the phenomena that occurs during the jig operation and in appraisal of this process.

Keywords: hard coal beneficiation, jig, partition curve, grains dispersion

Założenia probabilistycznego modelu rozkładu gęstości ziaren w warstwach łoża osadzarki

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Abstrakt

W pracy przedstawiono istotne ograniczenia rozpraszania cząstek w warstwach łoża osadzarki i skutki tych ograniczeń objawiające się w procesie osadzania. Ograniczenia te są wynikiem znacznego rozpraszania cząstek w stosunkowo wąskim zakresie gęstości warstw łoża. Do tej pory są one pomijane lub niewłaściwie przedstawiane w opisach zjawisk zachodzących w procesie osadzania. Przedstawiono założenia modelu łoża osadzarki uwzględniającego poprawnie te ograniczenia. Model ten jest także tak skonstruowany, że nie ogranicza gęstości tworzących się warstw jak i rozkładu mas w poszczególnych warstwach. Możliwe jest jego doświadczalne sprawdzenie w odpowiednio przygotowanych warunkach laboratoryjnych. Dodatkowo model pozwala wyjaśnić niektóre błędy istniejące w teorii wzbogacania grawitacyjnego.

Słowa kluczowe: wzbogacanie węgla kamiennego, osadzarka, modelowanie osadzania, krzywe rozdziału, rozpraszanie ziaren

Wstęp

W teorii wzbogacania grawitacyjnego do dziś istnieje poważny nie do końca rozwiązany problem. Jest to zagadnienie obliczenia wychodów i parametrów jakościowych produktów wzbogacania w osadzarce dla znanego składu densymetrycznego wzbogacanego materiału i parametru charakteryzującego efektywność pracy wzbogacalnika. Obecnie zagadnienie to jest rozwiązywane w dużym przybliżeniu przez przyjęcie funkcji aproksymującej krzywą rozdziału o założonym rozproszeniu charakteryzującym jakość wzbogacania. Przybliżenie rozwiązania wynika z przyjęcia wybranej idealizowanej aproksymanty krzywej rozdziału niezbyt dokładnie pasującej do rzeczywistego kształtu tej krzywej tym bardziej, że rzeczywisty jej kształt pochodzi z danych eksperymentalnych obciążonych znacznymi błędami pomiarowymi. Ponadto w literaturze daje się też zauważyć powątpiewanie w niezależność krzywej rozdziału od składu densymetrycznego wzbogacanego materiału (Hughes 1967). Jednym z możliwych rozwiązań przedstawianego zagadnienia może być odpowiednio precyzyjny model procesu wzbogacania.

Powszechnie nie jest zauważana w teoretycznych rozważaniach różnica między wzbogacaniem zachodzącym z wysoką skutecznością jak we wzbogacalnikach z cieczą ciężka, a pozostałymi wzbogacalnikami grawitacyjnymi, których efektywność jest znacznie niższa. Ta różnica powoduje, że zjawiska związane z procesem wzbogacania nieistotne dla niskich rozproszeń silnie zmieniają obraz tego procesu dla rozproszeń większych. Metody oceny pracy wzbogacalników, szczególnie metody związane z krzywą rozdziału nie pozwalają na zauważenie tych zjawisk. W przypadku osadzarek nie zauważanie tych różnic doprowadziło do pomijania zjawisk mających istotny wpływ na wzbogacanie takich jak ograniczenia dla fizycznych mechanizmów tworzenia się zróżnicowanych gęstościowo warstw w łożu osadzarki i istnienie naturalnych sprzężeń zwrotnych w procesie osadzania. Zjawiska te mogą być obiektem badań modeli, o ile te modele poprawnie przedstawiają stan łoża osadzarki. Taką możliwość stwarzają modele klasy DEM, lecz dla tego rodzaju modelowania konieczne jest znaczne zwiększenie liczby gęstościowych frakcji materiału surowego i liczby cząstek w modelu łoża osadzarki (Mishra 2001). Duże szanse na właściwe przedstawienie stanu łoża osadzarki mają modele probabilistyczne poprawnie przedstawiające ograniczenia rozpraszania się cząstek i nie ograniczające zakresu gęstości tworzących się warstw. Model, którego szczegóły założeń są przedstawiane w tym opracowaniu należy do tego rodzaju modeli.

Podstawy prezentowanego modelu

Poddawany wzbogacaniu w osadzarce materiał w wyniku działania pulsacyjnego ruchu wody przesuwa się po sicie i jednocześnie rozwarstwia się tak, że w końcowej części przedziału maszyny cięższe frakcje zajmują miejsce w dolnych warstwach łoża, a lżejsze w górnych. Takie usytuowanie cząstek odpowiada stanowi o minimalnej energii potencjalnej dla aktualnie zachodzącego w maszynie rozpraszania się cząstek o tej samej gęstości w różnych warstwach, z tym, że różnym rozproszeniom cząstek odpowiadają różne wartości minimalnej energii potencjalnej cząstek łoża.

Przedstawiany model ogranicza się do stanu ustalonego rozkładu cząstek w końcowej części przekroju podłużnego przedziału osadzarki przed strefą rozdzielania rozwarstwionego materiału na produkt górny i dolny. W związku z tym ten model nie pozwala śledzić czasowych przebiegów zmian rozproszenia cząstek w warstwach łoża osadzarki.

W osadzarce zachodzą jednocześnie dwa procesy: proces wzbogacania (klasyfikacji gęstościowej) i proces klasyfikacji ziarnowej. W rzeczywistym procesie wzbogacania różnice w wymiarach i kształcie poszczególnych ziaren można traktować jako podstawowe zakłócenie tego procesu. W dalszej części tej pracy losowa zmienność składu ziarnowego wzbogacanego materiału nie będzie rozważana. Przyjmuje się tylko, że ta zmienność wpływa na losowe rozpraszanie się cząstek tej samej gęstości w różnych warstwach. Nie będą także rozważane szczegółowo fizyczne zjawiska związane z procesem rozwarstwiania, a przyjmuje się, że zbiór wzbogacanych cząstek dąży do stanu o minimalnej energii potencjalnej, co wynika z zasady najmniejszego działania. Można przyjąć, że istnienie zjawiska rozpraszania się cząstek o tej samej gęstości w różnych warstwach może być interpretowane także jako skutek działania ograniczeń wynikających z tej zasady.

Przyjęcie powyższych założeń jest wyrazem dekompozycji zagadnienia rozpraszania się cząstek w łożu osadzarki na dwa oddzielne zagadnienia, z których pierwsze związane ze szczegółami fizycznych przyczyn powstawania tego rozproszenia zostanie pominięte. Pominięcie to jest wynikiem nieistnienia prac zawierających analizy sił działających na poszczególne cząstki w łożu osadzarki dostatecznie zbieżnych w danymi eksperymentalnymi. Istniejące prace (Innouhi 1978), (Srinivasan 1999), (Mishra 2001) można potraktować tylko jako wstęp do opracowania modelu wiążącego wszystkie zmienne procesu osadzania z istniejącym w tym procesie rozpraszaniem cząstek o stałej gęstości. Praca taka oparta na zasadach mechaniki stochastycznej z rozważeniem trójfazowego ośrodka, jakim jest przedział osadzarki, do tej chwili nie powstała i obecnie nie widać szans na jej powstanie. Znaczną trudność takiej analizy stanowi losowa zamienność istotnych cech wzbogacanego materiału, silnie nieliniowe zależności opisujące dynamikę ruchu wody i cząstek fazy stałej oraz nieliniowe sprzężenia zwrotne. Drugie z tych zagadnień obrazujące technologiczne i związane z tym także ekonomiczne skutki istnienia rozproszenia jest możliwe do rozpatrzenia dla z góry przyjętych postaci rozkładu opisującego rozpraszanie się cząstek i jest rozważane w tej pracy. Generalnie prezentowany model opiera się na podstawowym założeniu, że wszystko to, co nie jest dostatecznie wyjaśnione oraz to nad czym nie jesteśmy w stanie odpowiednio zapanować w trakcie technicznej realizacji procesu osadzania traktowane jest jako przyczyna rozpraszania się cząstek (ziaren) o stałej gęstości w warstwach o różnej gęstości.

Rozważany model może być uważany jako wynik takiego działania, kiedy losowo wybraną cząstkę nadawy wrzucamy do losowo wybranej warstwy przypisując jej z góry określone prawdopodobieństwo pozostania w tej warstwie zależne od różnicy gęstości cząstki i warstwy. Jest to założenie bardzo zbliżone do zastosowanego w pracy (Zapala 1988), lecz cele i stosowane metody obu tych prac są wyraźnie różne, a ponadto w tej pracy nie ma fizycznie niepoprawnych założeń istniejących w pracy Zapały.

Zasadniczym celem tworzenia tego modelu jest pokazanie znaczenia ograniczeń w możliwościach rozpraszania się cząstek do tej pory pomijanych w teoretycznych rozważaniach. Ograniczenie te stają się bardzo istotne dla rzeczywistej pracy osadzarek skazanych w wyniku zasady rozdziału i różnych zaniedbań w praktyce ich używania na działanie ze względnie niską efektywnością wzbogacania. Dodatkowym celem konstruowania tego modelu jest pokazanie poprawnych fizycznych interpretacji zjawisk losowych zachodzących w procesie osadzania i ich technologicznych skutków oraz przedstawienie modelu warstw łoża osadzarki pozwalającego obliczyć rozkład cząstek w poszczególnych warstwach i gęstości tworzących się warstw z dokładnością lepszą niż w modelach znanych do tej pory.

Wymagane cechy poprawnego modelu

Podstawowe wymaganie, które ten model musi spełniać to prawidłowe przedstawienie stanu łoża w trzech podstawowych sytuacjach teoretycznie możliwych w trakcie pracy osadzarki to jest wzbogacania idealnego, wzbogacania rzeczywistego i całkowitego braku wzbogacania. Tego wymagania nie spełnia w całości żaden z istniejących modeli (Budryk 1949), (Zapała 1988), (Cierpisz 2012). (Woolacott 2015). Brak spełnienia tych wymagań wynika przede wszystkim z nieistnienia w tych modelach właściwych ograniczeń dla rozpraszania się cząstek oraz z istnienia zbędnych ograniczeń dla gęstości warstw, co powoduje, że rozkład warstw łoża przedstawiany przez te modele nie jest podobny do jego rzeczywistego stanu. W przypadku modelu Kinga opisanego w dwu ostatnich z przywołanych pozycji literatury wątpliwości może budzić sposób modelowania wykorzystujący zjawisko dyfuzji nie istniejące w procesie osadzania w takim stopniu, aby istotnie wpływało na wynik modelowania.

Postuluje się także, aby rozważany model wyjaśniał działanie osadzarki dla dowolnego składu densymetrycznego nadawy, w tym także dla tak szczególnych idealizowanych przypadków jak istnienie w materiale surowym tylko dwu lub trzech gęstości cząstek. Po uzupełnieniu o zależność wiążącą zawartość popiołu z gęstością poszczególnych cząstek model powinien pozwalać na obliczenie wychodu i zawartości popiołu w produktach wzbogacania dla wybranej gęstości rozdziału. Przyjmuje się także możliwość rozszerzenia tego modelu dla opisania stanu łoża osadzarki jako funkcji położenia danej warstwy w stosunku do sita. Jest to możliwe, gdy znane są zależności określające związek między gęstością cząstek i ich rzeczywistą gęstością nasypową oraz gdy znany jest profil prędkości poziomej poszczególnych warstw dla ustalonej ich gęstości.

Wzbogacanie idealne zachodzi, gdy w każdej warstwie łoża znajdują się tylko cząstki wzbogacanego materiału o jednakowej gęstości i różnej od gęstości cząstek sąsiednich warstw. W przypadku wzbogacania rzeczywistego w każdej warstwie znajdują się cząstki różnych gęstości i zakres tych gęstości powinien być związany z zachodzącym w tym wzbogacaniu rozpraszaniem się cząstek o stałej gęstości w różnych warstwach oraz składem gęstościowym wzbogacanego materiału. Dla całkowitego braku wzbogacania każda warstwa składa się z cząstek wszystkich gęstości, co jest równoważne istnieniu tylko jednej warstwy zawierającej wszystkie cząstki o różnych gęstościach.

W tym miejscu konieczne jest zauważenie, że tylko stanowi idealnego wzbogacania odpowiada istnienie warstw o wszystkich gęstościach cząstek istniejących we wzbogacanym materiale. Zatem dla wzbogacania rzeczywistego powinno w modelu zachodzić zjawisko zanikania niektórych warstw w miarę pogarszania się jakości wzbogacania. Warto zwrócić uwagę na ten fakt, ponieważ żaden ze znanych z literatury modeli rozwarstwiania się materiału w łożu osadzarki nie zakłada istnienia takiej sytuacji, jak i to, że nie pojawia się ona jako wynik działania znanego modelu. Zanikanie warstw o różnych gęstościach w istotny sposób zmienia obraz działania osadzarki, co zostanie pokazane w dalszej części tej pracy.

Pojawia się pytanie czy zjawisko to ma istotne znaczenie dla efektywności działania osadzarki i czy brak opisu tego zjawiska w aktualnie istniejącej literaturze jest skutkiem jego marginalnego znaczenia. Prawidłowa odpowiedź na to pytanie z uwzględnieniem dostępnych aktualnie danych eksperymentalnych jest trudna, ponieważ te istniejące dane są dalece niewystarczające i ograniczają się do znajomości empirycznej krzywej rozdziału oraz rozproszenia prawdopodobnego Ep lub imperfekcji I jako wyników przeprowadzonych badań. Żadne z przeprowadzonych badań laboratoryjnych (Jonkers 1998), (Kowol 2010), (Woolacott 2015) nie opisuje wszystkich zależności pokazywanych przez przedstawiany model, a powodem tego jest zbyt niska dokładność przeprowadzonych analiz, aby można było te związki zauważyć eksperymentalnie.

W teorii wzbogacania grawitacyjnego zwykle rozważane są funkcje ciągłe odpowiadające istnieniu nieskończenie wielu frakcji gęstościowych wzbogacanego materiału. Funkcje te powstają w wyniku znacznej idealizacji dyskretnych wyników przeprowadzanych pomiarów. Zdaniem autora tej pracy opisywanie wielu zjawisk w teorii grawitacyjnego wzbogacania funkcjami ciągłymi nie ma pełnego uzasadnienia biorąc pod uwagę ograniczoną dokładność pomiarów charakterystyk wzbogacanego materiału. W tej pracy, dla zachowania jednak tradycyjnie stosowanych zasad, tylko bardzo ogólne idee będą przedstawiane także dla funkcji ciągłych, natomiast przedstawiany model zasadniczo opisuje stan warstw łoża tylko dla skończonej ilości frakcji gęstościowych wzbogacanego materiału i ilości warstw łoża.

Postać i parametry rozkładu prawdopodobieństwa rozpraszania cząstek

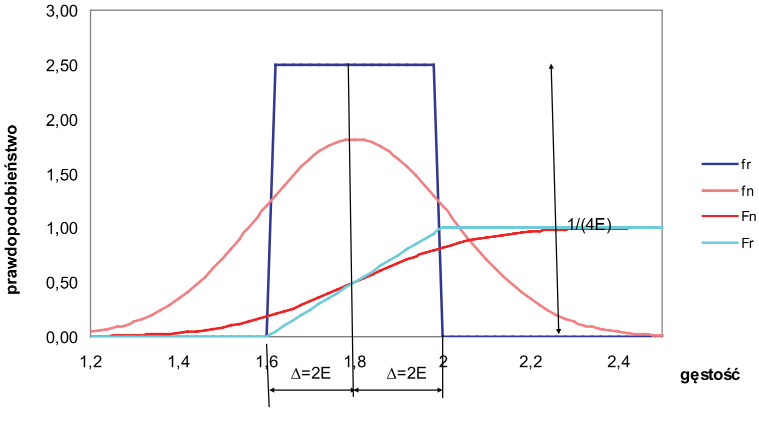
Naturalnym skutkiem przedstawionego powyżej podejścia do analizowanego zagadnienia musi być przyjęcie z góry określonego rozkładu prawdopodobieństwa opisującego rozproszenie się cząstek o znanej gęstości w warstwach łoża, jakie utworzą się w wyniku przyjęcia tego rozkładu. W tym miejscu pojawia się konieczność uzasadnienia dla postaci wybranego rozkładu, jaki i również jego parametrów.

Jako zmienną losową rozkładu przyjmuje się średnią gęstość warstwy ρ_w, do której mogą trafić cząstki o gęstości ρ_c, która to gęstość ρ_c jest także wartością oczekiwaną tego rozkładu. Przyjęcie założenia, że wartością oczekiwaną tego rozkładu jest gęstość rozpraszanych cząstek ρ_c wynika z konieczności spełnienia warunku, aby dla wzbogacania idealnego gęstość warstwy była równa gęstości tworzących ją cząstek. Parametrem rozkładu określającym rozproszenie zmiennej losowej jest jego odchylenie standardowe związane z innym parametrem najczęściej używanym w teorii wzbogacania do oceny skuteczności procesu wzbogacania nazywanym odchyleniem prawdopodobnym, a w rachunku prawdopodobieństwa określanym jako odchylenie ćwiartkowe (Kubik 1982). Jest to połowa różnicy górnego i dolnego kwartyla rozkładu. Parametr ten charakteryzujący rozpraszanie cząstek o danej gęstości w warstwach oznaczmy jako E z podkreśleniem podobieństwa, ale także różnicy dla innego parametru E_p charakteryzującego krzywą rozdziału. Oba te parametry mają wymiar gęstości, ale różni je materiał, z którego gęstością są z wiązane. Dla E jest to gęstość warstw, a dla E_p jest to gęstość cząstek nadawy. Zwraca się także uwagę na konieczność niejednoznacznego użycie słowa gęstość w dalszym tekście, wynikającą z nazwy rozpatrywanej zmiennej losowej, którą jest średnia gęstość warstwy łoża osadzarki. W dalszym ciągu rozważań gęstość może także oznaczać określenie funkcji opisującej rozkład prawdopodobieństwa np. funkcja rozkładu gęstości prawdopodobieństwa.

Początkowo dla łatwości wyjaśnienia przedstawianych dalej zjawisk i łatwości obliczeń przyjmiemy także, że proces rozdziału można w pierwszym przybliżeniu opisywać najprostszym ze znanych rozkładów ciągłej zmiennej losowej, to jest rozkładem jednostajnym czasem określanym także jako równomierny lub prostokątny. (Bobrowski 1980), (Kubik 1982). Szczególna przydatność tego rozkładu dla teoretycznych rozważań wynika z dokładnie sprecyzowanego zakresu rozpraszania cząstek. Taki zakres nie istnieje dla najczęściej używanego do opisu rozproszenia rozkładu normalnego, który będzie podstawowym rozkładem używanym w modelu.

Wyjaśnienie; fr i Fr to funkcja gęstości prawdopodobieństwa i dystrybuanta rozkładu równomiernego, a fn i Fn to funkcja gęstości prawdopodobieństwa i dystrybuanta rozkładu normalnego

Rys.1 przedstawia postać tego rozkładu oraz dla porównania rozkład normalny. Oba przedstawione rozkłady mają



Rys. 1. Gęstość prawdopodobieństwa i dystrybuanta rozkładu jednostajnego i normalnego
Fig. 1. Probability density funktion and cumulate distribution of uniform and normal distributions

identyczną wartość średnią i rozproszenie E. Dla rozkładu jednostajnego $E=\Delta/2$, a dla rozkładu normalnego $E= 0{,}6745\sigma n$, gdzie σn jest odchyleniem standardowym rozkładu. Teoretycznie jest możliwe, że ta miara rozproszenia zmiennej losowej może być jednakowa dla rozkładu prawdopodobieństwa jak i dla otrzymanej z takich rozkładów krzywej rozdziału, mimo że krzywa ta nie jest dystrybuantą żadnej zmiennej losowej. Użycie w modelu rozkładu normalnego jako rozkładu podstawowego wynika z powszechności stosowania w literaturze tego rozkładu dla opisu wzbogacania w osadzarce oraz braku dostatecznie uzasadnionych argumentów dla przyjęcia innego rozkładu. Być może istnieje postać rozkładu typu gamma lepiej modelująca rozpraszanie cząstek, lecz nie ma w literaturze wyników badań uzasadniających lepsze dopasowanie takiego rozkładu do danych empirycznych. Ponieważ funkcję gęstości prawdopodobieństwa i dystrybuantę rozkładu normalnego można z bardzo niewielkim błędem aproksymować funkcjami hiperbolicznymi możliwe jest wykorzystanie niektórych idei przedstawionych w pracy W. Zapały (Zapała 1988) jak i porównanie wyników obu prac.

Nie bez znaczenia pozostaje łatwość obliczeń dla tych rozkładów przy użyciu arkusza kalkulacyjnego jako podstawowego narzędzia używanego w następnej pracy przedstawiającej szczegóły obliczeń wykonywanych w modelu.

W dalszych rozważaniach kryterium rozróżniania poszczególnych warstw jest różnica gęstości tych warstw. Model nie definiuje zróżnicowania warstw wynikających z ich innego położenia względem sita osadzarki. To położenie w rozszerzonym modelu może być obliczane ze średniej gęstości i prędkości ruchu poszczególnych warstw.

Wszystkie stany pośrednie między już poprzednio przedstawionymi stanami krańcowymi opisują różne przypadki wzbogacania rzeczywistego. W dalszej części tych rozważań zostanie wykazane, że przyjęcia takiego samego rozkładu opisującego rozpraszanie dla wszystkich cząstek nie jest możliwe, ponieważ cząstki różnych gęstości muszą posiadać różne rozkłady opisujące rzeczywiste ich rozpraszanie, a przyczyną takiego stanu rzeczy jest istnienie skończonego zakresu gęstości cząstek wzbogacanych ziaren i gęstości warstw, w których zachodzi zjawisko przypadkowego rozpraszania cząstek. Warto także zauważyć, że przedstawione założenia są zgodne z poprawnymi fragmentami pracy Budryka (Budryk 1949), lecz wyniki dalszych rozważań są zdecydowanie różne od jego wyników.

Rozważany dalej model łoża osadzarki powinien także wyjaśniać przyczyny istnienia obserwowanych w praktyce wzbogacania węgla odkształceń krzywych rozdziału od ich zwykle przyjmowanych typowych postaci związanych nie tylko ze spektrum ziarnowym nadawy jak to zauważono w pracy (Jowett 1986), lecz także spowodowanych różnym rozproszeniem cząstek różnych gęstości.

Ograniczenia możliwości rozpraszania się cząstek w warstwach łoża osadzarki

Dla rozpraszania cząstek opisanego rozkładem jednostajnym istnieje dokładnie określony zakres gęstości warstw, w których możliwe jest rozproszenie cząstek o danej ich gęstości ściśle związany z wielkością rozproszenia E opisującego rozpraszanie się tych cząstek. Dla rozpraszania opisanego rozkładem normalnym taki zakres nie jest ściśle zdefiniowany, ponieważ funkcja gęstości prawdopodobieństwa i dystrybuanta tego rozkładu istnieją w zakresie od - ∞ do + ∞ i dla jego ścisłego określenia potrzebny jest wybór zakresu gęstości warstw, w którym zgodnie z przyjętą dokładnością obliczeń wartość funkcji gęstości prawdopodobieństwa jest różna od zera. Dokładność określenia zakresu rozpraszania cząstek przez rozkład jednostajny jest najistotniejszym powodem wybrania tego rozkładu do wyjaśnienia szczegółów ograniczeń rozpraszania się cząstek w warstwach łoża.

Zbliżenie się wartości oczekiwanej rozkładu jednostajnego do granicznej gęstości warstwy musi spowodować teoretyczne rozproszenie cząstek poza granicznymi warstwami. Ta sprawa wymaga bliższego wyjaśnienia, ponieważ w istniejącej literaturze jest pomijana lub niewłaściwie przedstawiana. Graniczna (najmniejsza lub największa) średnia gęstość warstwy w łożu osadzarki dla wzbogacania rzeczywistego (nieidealnego) będzie zawsze różna od granicznej gęstości cząstek wzbogacanego materiału. Jest tak dlatego, że do warstwy granicznej muszą trafić w wyniku rozpraszania cząstki o innych gęstościach powodując zmianę jej średniej gęstości. Ta zmiana gęstości zależy od istniejącego aktualnie rozproszenia i zwiększanie rozproszenia zawsze spowoduje zwiększenie gęstości najlżejszej warstwy w wyniku trafiania do niej coraz większej ilości ziaren o coraz większej ich gęstości. Istotne jest także to, że do tej warstwy nie mogą trafić nieistniejące we wzbogacanym materiale cząstki lżejsze od granicznej gęstości cząstek. Jednakże dla poprawności rozważanego rozkładu niezbędne jest określenie funkcji gęstości prawdopodobieństwa i dystrybuanty z uwzględnieniem braku możliwości rozpraszania się cząstek w tych nieistniejących warstwach, a to musi powodować konieczność odpowiedniego skorygowania przyjętego rozkładu prawdopodobieństwa. Idea takiej korekty dla rozkładu jednostajnego jest przedstawiona na rys.2, który przedstawia zmiany w rozkładzie prawdopodobieństwa dla warstw skrajnych gęstości w stosunku do przyjętego rozkładu dla gęstości warstw ze środka zakresu ich zmienności.

Dodatkowe objaśnienie do rys. 2,4,5
ρ_c i ρ_w - gęstość cząstki i warstwy, ρ_{cd} i ρ_{cg} – gęstość cząstki nadawy o najmniejszej i największej gęstości, ρ_d i ρ_g – gęstość warstwy do jakiej mogłaby trafić cząstka najmniejszej lub największej gęstości gdyby nie było ograniczenia, ρ_{wd} i ρ_{wg} – gęstość najlżejszej i najcięższej warstwy, E – odchyleniu ćwiartkowe rozkładu rozproszenia cząstek w warstwach

Funkcja δ Diraca dla przedstawianych na rys. 2 i 5 przypadków jest definiowana następująco (Niederliński 1983):

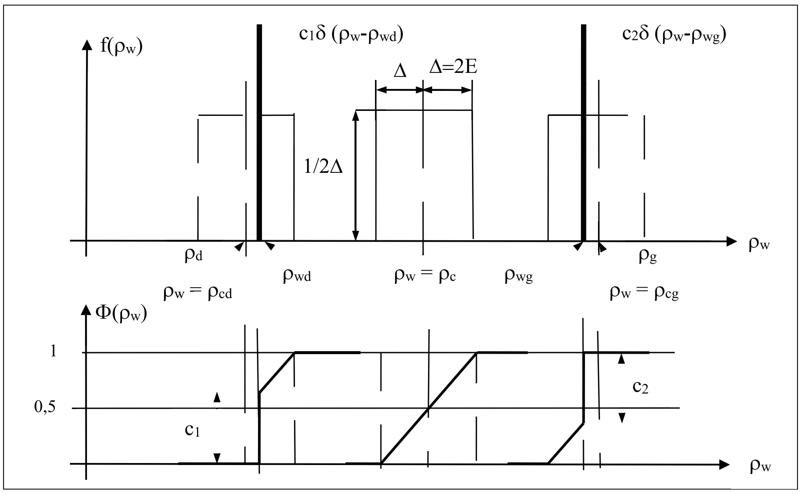
$$\delta\,(\rho_w - \rho_{wd}) = 0 \text{ dla } \rho_w \neq \rho_{wd}$$
$$\delta\,(\rho_w - \rho_{wd}) = \infty \text{ dla } \rho_w = \rho_{wd}$$

oraz

$$\int_{-\infty}^{+\infty} (\rho_w - \rho_{wd})\, d\rho_w = 1$$

Taką definicję funkcji δ Diraca przyjmuje się w zastosowaniach technicznych mimo braku jej matematycznej poprawności.

Wartość stałych c_1 i c_2 podają poniższe zależności:
$c_1 = 0{,}5+(\rho_{wd} - \rho_{cd})/4E$ $\qquad$ $c2= 0{,}5+(\rho_{cg} - \rho_{wg})/4E$



Rys. 2. Gęstości prawdopodobieństwa i dystrybuanty rozkładów dla frakcji skrajnych i jednej frakcji środkowej
Fig. 2. Probability density funktions and cumulative distributions of extreme and midle range particles densities

Wartość stałych c_3 i c_4 (dla rys.5) wynoszą:
$c_3= (\rho_{wd} - \rho_{cd})/4E$ $c_4= (\rho_{cg} - \rho_{wg})/4E$

Gdyby nie było ograniczeń dla istnienia warstw cząstki o najmniejszej gęstości ρ_{cd} rozproszyłyby się równomiernie w warstwach o gęstości od $\rho_w = \rho_{cd}-\Delta$ do $\rho_w = \rho_{cd}+\Delta$, a ponieważ nie istnieją warstwy z zakresu $\rho_{cd}-\Delta$ do ρ_{wd} to cząstki o gęstości ρ_{cd} nie mogą do nich trafić. Przyjmuje się, że cząstki te z takim samym prawdopodobieństwem, z jakim trafiłyby do nieistniejących warstw trafią do najlżejszej warstwy, do jakiej mogą trafić. Jest to warstwa o minimalnej gęstości ρ_{wd}. Przyjmuje się także, że możliwość trafienia cząstek o gęstości ρ_{cd} do warstw cięższych od ρ_{wd} pozostaje taka sama jak sytuacji, gdyby istniały warstwy o gęstości mniejszej od ρ_{wd}. Dla cząstek nadawy o największej gęstości ρ_{cg} i warstwy ρ_{wg} o największej gęstości zachodzi zmiana rozkładu podobna jak dla najmniejszych gęstości cząstek i warstw. Taka sytuacja przedstawiona na rys.2 prowadzi do konieczności zastosowania rozkładu w rachunku prawdopodobieństwa określanego rozkładem zmiennej losowej mieszanej (Bobrowski 1980) lub rozkładem skokowo-ciągłym (Kubik 1982). Funkcja gęstości prawdopodobieństwa takiego rozkładu składa się z funkcji ciągłej dla $\rho_w>\rho_{wd}$ oraz iloczynu pewnej stałej c1 i funkcji osobliwej, jaką jest funkcja δ Diraca dla $\rho_w = \rho_{wd}$. Dystrybuanta tego rozkładu jest funkcją skokową dla $\rho_w = \rho_{wd}$ i funkcją ciągłą poza tym punktem.

Ogólny przebieg zmian w rozkładzie normalnym wynikających z przedstawionej wyżej korekty jest przedstawiony w pracy (Glowiak 2019).

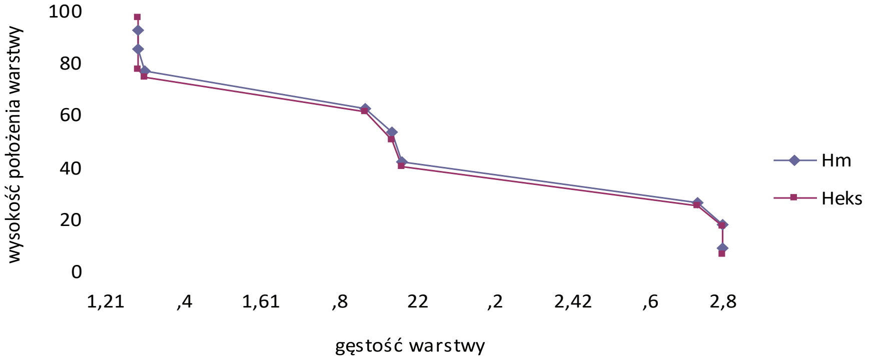
W tym miejscu konieczne jest zauważenie, że rozkład mieszany zdecydowanie różni się od rozkładu uciętego szczególnie w punktach ρ_{wd} lub ρ_{wg}, co pokazują rys. 4 i 5. Ta różnica jest wyraźnie widoczna dla wartości dystrybuanty w tych punktach. Powodem podkreślenia różnicy między tymi rozkładami jest praktyka częstego stosowania w przeróbce surowców mineralnych rozkładów uciętych.(Tumidajski 1993). Taki rozkład jest alternatywnym możliwym rozwiązaniem dla rozpatrywanego zagadnienia. Dlatego w tym miejscu konieczne jest szczegółowe uzasadnienie dla wyboru rozkładu mieszanego.

Istotna różnica między rozkładami polega na tym, że użycie rozkładów uciętych usuwa warstwy, do których z powodu ograniczenia zakresu gęstości warstw cząstki nie mogą trafić zmieniając odpowiednio prawdopodobieństwo trafienia do wszystkich pozostałych warstw, a rozkład mieszany zmienia tylko prawdopodobieństwo trafienia cząstek do warstw o najmniejszej i największej gęstości. Wybór właściwego rozkładu dla dalszych rozważań powinien być dokonany na podstawie badań empirycznych. Takie badania o minimalnym potrzebnym zakresie zostały wykonanie w osadzarce laboratoryjnej i ich wyniki są uzasadnieniem dla stosowania rozkładu mieszanego. Bez wnikania w zbędne na tym etapie rozważań szczegóły eksperyment potwierdził bardzo dobrą zbieżność doświadczalnego rozkładu gęstości warstw w łożu osadzarki oznaczonego na rys.3 jako Heks i rozkładu teoretycznego Hm obliczonego z zastosowaniem rozkładu mieszanego.

Za odrzuceniem zastosowania rozkładów uciętych przemawiają także poniższe względy:

– rozkład ucięty jest modelem zjawiska, w którym populacja o znanym rozkładzie w wyniku zastosowania dodatkowych kryteriów (np. odrzucenie części wyprodukowanych elementów przez kontrolę jakości) zostaje ograniczona do określonej jej części (Bobrowski 1980). W rozważanym przypadku zachodzi odrzucenie niektórych warstw, lecz nie następuje żadne ograniczenie populacji czyli ilości rozpraszanej w warstwach frakcji gęstościowej cząstek nadawy.

– z fizycznej interpretacji rozkładu uciętego dla rozważanego zagadnienia wynika, że cząstki nie mogące trafić do warstw, których nie ma, muszą odpowiednio zmienić swoje rozproszenie w warstwach istniejących. Trudno jest wskazać fizyczne przyczyny, które miałyby spowodować, że cząstki nie mogące trafić do nie istniejących warstw rozproszą się zgodnie z rozkładem uciętym. Ponadto oznacza to, że ograniczenie w rozkładzie uciętym zmienia rozkład także dla cząstek, które nie podlegają ograniczeniom. Skutkiem tej zmiany jest także fizycznie nieuzasadniona zmiana wartości oczekiwanej rozkładu o Δ_o (Rys. 4). Z przyjętych założeń wynika, że wartością oczekiwaną rozkładu powinna być niezależna od postaci przyjętego rozkładu gęstość cząstek rozpraszanej frakcji nadawy. Alternatywny rozkład mieszany nie zmienia rozproszenia cząstek wewnątrz przyjętych ograniczeń, kieru-



Rys. 3. Teoretyczny i doświadczalny rozkład gęstości warstw w łożu osadzarki
Fig. 3. Theoretical and empirical distribution of density layers in jig bed

jąc cząstki podlegające ograniczeniu do warstw o skrajnych gęstościach.

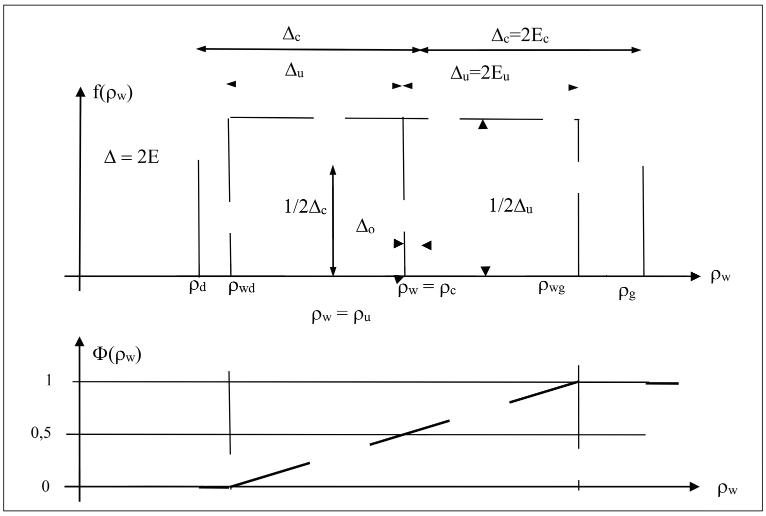
– stosowany do modelowania zjawiska fizycznego rozkład prawdopodobieństwa powinien prawidłowo oddawać cechy tego zjawiska oraz mieć odpowiednią i w miarę możliwości prostą interpretację fizyczną. To kryterium jest zdecydowanie lepiej jest spełnione przez rozkład mieszany niż przez rozkład ucięty.

Na rys. 4 przedstawiono zamiany jakie zachodzą dla asymetrycznego ucięcia rozkładu jednostajnego. W tym przypadku szczególnie wyraźnie widoczna jest zmiana wartości oczekiwanej rozkładu o wartość Δ_o w wyniku jego ucięcia. Indeksy c i u oznaczają te same parametry rozkładu pełnego i po ucięciu. Porównanie rys. 4 i 5 pozwala zauważyć, że dla rozkładu mieszanego nie ma zmiany jego wartości oczekiwanej. Przedstawiana na obu tych rysunkach sytuacja dotyczy dużego rozpraszania cząstek jednej frakcji nadawy poza granice istniejących warstw.

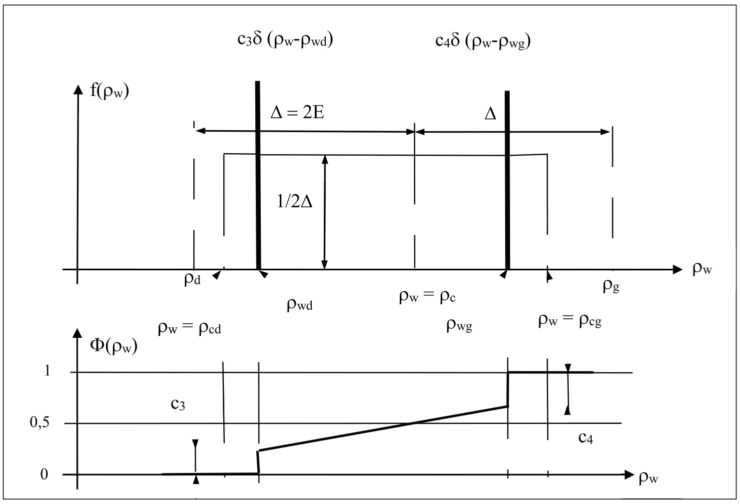
Rys. 5 przedstawia funkcję gęstości prawdopodobieństwa i dystrybuantę rozkładu jednostajnego dla bardzo dużego rozproszenia przekraczającego zakres gęstości cząstek występujących w nadawie. Jest to sytuacja często spotykana w praktyce wzbogacania węgla w osadzarkach. Gęstość warstwy jest wtedy głównie kształtowana przez rozproszenie cząstek materiału o różnych gęstościach trafiających do tej warstwy, co powoduje, że teoretycznie jest możliwa sytuacja, kiedy w warstwie nie istnieją cząstki niektórych gęstości, ponieważ nie ma ich we wzbogacanym materiale. W przypadku ich istnienia stanowiłyby one wyraźnie widoczną liczbę cząstek danej warstwy. Tej sytuacji nie można pominąć, ponieważ konstruowany model powinien także poprawnie opisywać wzbogacanie materiału składającego się w krańcowej sytuacji tylko z dwu różnych frakcji gęstościowych. Podane skutki działania ograniczeń rozpraszania cząstek dla rozkładu równomiernego są takie same dla rozkładu normalnego z tym, że dla tego rozkładu konieczne jest przyjęcie ściśle określonej granicy rozpraszania dla prowadzonych obliczeń ustalonej jako wartość średnia rozkładu ± kσ, gdzie k jest tak dobrane, aby przyjęty zakres rozpraszania dla cząstek objął wszystkie warstwy do których mogą trafić cząstki zgodnie z przyjętym rozkładem, w tym także te, których istnienie wykluczają przyjęte ograniczenia. Dobranie odpowiednio dużego k jest szczególnie istotne dla bilansu masy rozpraszanych cząstek, który musi być bezwzględnie zachowany, aby wyniki obliczeń w modelu odpowiadały wynikom w rzeczywistym wzbogacaniu. Z przedstawionych założeń wynika pewien teoretyczny paradoks polegający na tym, że dla dwu krańcowo odmiennych stanów działania osadzarki to jest wzbogacania idealnego i całkowitym ustaniem wzbogacania mamy do czynienia z rzeczywistym zerowym rozproszeniem cząstek. Wyjaśnienie tego paradoksu staje się możliwe, gdy rozróżnia się rozproszenie potencjalne wynikające tylko z postaci zastosowanego dla jego opisu rozkładu prawdopodobieństwa i rozproszenie rzeczywiste obejmujące także wszystkie ograniczenia możliwości rozpraszania się poszczególnych cząstek. Dla wzbogacania idealnego rzeczywiste i potencjalne rozproszenia jest zerowe. Dla braku wzbogacania mamy nieskończenie wielkie rozproszenie potencjalne i równocześnie zerowe rozproszenie rzeczywiste wynikające z braku możliwości rozproszenia się cząstek w nieistniejących warstwach. W tej pracy poza powyższym akapitem rozproszenie rozumiane jest jako rozproszenie potencjalne. Ogólnie można przyjąć, że dla niskich rozproszeń o rzeczywistym rozproszeniu decyduje tylko rozproszenie potencjalne, a dla dużych rozproszeń potencjalnych o faktycznie małym rzeczywistym rozproszeniu decydują ograniczenia zakresu powstałych warstw. Sprawa ta nie została do tej pory zauważona, ponieważ teoretycznie nie rozważano rozpraszania się cząstek i gęstości istniejących warstw dla dużych rozproszeń najczęściej będących skutkiem bardzo małego rozluzowania łoża osadzarki. Z powyższego wyraźnie widoczne jest znaczenie ograniczenia zakresu gęstości istniejących warstw.

Wybór gęstości warstwy przyjętej jako współrzędna modelu i skutki tego wyboru

W istniejącej literaturze używane jest pojęcie gęstość warstwy lecz często bez dokładnego wyjaśnienia, co ono oznacza. Najczęściej jest ono rozumiane jako średnia gęstość warstwy, lecz może także oznaczać średnią gęstość cząstek tworzących daną warstwę. Na użytek tych rozważań średnia gęstość warstwy nie może być brana pod uwagę, ponieważ ta gęstość zależy także od porowatość fazy stałej pomijanej w tym modelu. Pozostaje zatem przyjęcie jako współrzędnej modelu średniej gęstości cząstek tworzących daną warstwę. Trafienie do warstwy o ustalonej średniej gęstości cząstki o takiej samej gęstości, lecz do tej chwili nieistniejącej w warstwie nie zmieni średniej gęstości cząstek tej warstwy. Trafienie do tej warstwy cząstki o każdej innej gęstości musi



Rys. 4. Gęstość prawdopodobieństwa i dystrybuanta rozkładu jednostajnego pełnego i uciętego
Fig. 4. Probability density funktions and cumulative distributions of full and truncate uniform distributions



Rys. 5. Gęstość prawdopodobieństwa i dystrybuanta rozkładu mieszanego przy dużym rozproszeniu
Fig. 5. Probability density funktions and cumulative distributions of mixed distribution probability for large grains dispersion

spowodować zmianę średniej gęstości cząstek warstwy. Jest tak dlatego, że średnia gęstość cząstek każdej warstwy jest funkcją zawartości poszczególnych frakcji gęstościowych nadawy i prawdopodobieństwa trafienia poszczególnych cząstek do ustalonych warstw. Aby ta średnia była równa z góry ustalonej wartości to wartości oczekiwane wszystkich rozkładów prawdopodobieństwa muszą być odpowiednio dobrane, a to jest sprzeczne z przyjętym założeniem o wartości oczekiwanej rozkładu równej gęstości rozpraszanych cząstek. Zatem dla dowolnego składu gęstościowego nadawy dla opisu składu tworzących się warstw o zróżnicowanej gęstości konieczny jest wybór między przyjętym rozkładem prawdopodobieństwa i a priori ustaloną średnią gęstością cząstek warstwy. Dla potrzeb prezentowanego modelu jedynie możliwe jest przyjęcie ustalonego rozkładu prawdopodobieństwa, co oznacza, że mogą nie istnieć warstwy o z góry ustalonej gęstości, lecz tylko warstwy o takich gęstościach jakie wynikają ze składu wzbogacanego materiału i przyjętego rozkładu prawdopodobieństwa. W takiej sytuacji model pozwala na przedstawienie wszystkich wynikających z niego zależności w funkcji obliczonych średnich gęstości tych warstw. Aby to obliczenie było możliwe konieczne jest przyjęcie początkowych średnich gęstości poszczególnych warstw. Przyjmuje się, że te początkowe gęstości warstw są takie jakie istniałyby przy idealnym wzbogacaniu, a to jest równoważne przyjęciu jako gęstości warstw gęstości poszczególnych klas gęstościowych wzbogacanego materiału. Dlatego w rozważanym modelu na każdym etapie obliczeń muszą istnieć dwie różne średnie gęstości każdej warstwy; gęstość początkowa i gęstość obliczona w danym kroku obliczeń. Ta właściwość modelu będzie wykorzystywana do iteracyjnego obliczania gęstości tworzących się warstw. Konieczność stosowania obliczeń iteracyjnych wynika ze zmiany średniej gęstości wszystkich warstw łoża osadzarki w kolejnych krokach, co powoduje, że prawdopodobieństwo trafienia cząstek do danej warstwy ulega zmianie w każdym kroku obliczeń. Stosując takie obliczanie zauważyć można, że kolejne różnice między wektorem gęstością początkowych i wektorem gęstości obliczonych najczęściej maleją w kolejnych krokach obliczeń aż do pewnego kroku, od którego zaczynają rosnąć. Kryterium zatrzymania iteracji jest wzrost sumy ważonych kwadratów różnic gęstości poprzedniej i obliczonej lub pomijalnie małe wartości obliczanej różnicy lub pojawienie się w obliczeniach niemożliwych (np. ujemnych) gęstości warstw. Wagami kwadratów różnic są masy cząstek zgromadzonych w poszczególnych warstwach. Taki wybór wag zapewnia odpowiednio duży wpływ na wynik obliczeń warstw gromadzących znaczne ilości wzbogacanego materiału

Graniczne gęstości warstw

Dla dyskretnego modelu warstw łoża osadzarki zapewniającego swobodne tworzenie się gęstościowo zróżnicowanych warstw niezbędne jest przyjęcie granicznych gęstości poszczególnych warstw. Konieczność precyzyjnego określenia tych granic wynika z idei tworzonego modelu oraz z przyjętego sposobu obliczania średniej gęstości poszczególnych warstw i dlatego w tym miejscu jedynie zaznacza się istnienie tego zagadnienia, a jego szczegóły zostaną przedstawione w następnym opracowaniu podającym dokładnie realizację wszystkich obliczeń w przedstawianym modelu.

Zależność rozpraszania cząstek od ich gęstości

W teorii i praktyce wzbogacania węgla zauważana jest zależność rozpraszania cząstek o stałej gęstości od wielkości tych cząstek i ich kształtu (Surowiak 2006), natomiast prawie pomijana lub marginalizowana jest zależność tegoż rozproszenia od gęstości cząstek. Jedyną pracą w literaturze znanej autorowi niniejszego opracowania, oprócz znacznie późniejszych prac związanych z modelowanie DEM i wyżej wymienioną pracą, zwracającą uwagę na to zagadnienie jest praca Zapały (Zapała1988). Pomijanie zależności rozproszenia od gęstości cząstki zostało w praktyce niechcący ugruntowane przez teorię krzywych rozdziału. Zauważa się w niej różne odchylenia empirycznej krzywej rozdziału od przyjmowanej krzywej modelowej, lecz nie łączy się tego zagadnienia z gęstością rozpraszanej cząstki, lecz z gęstością rozdziału. Jednocześnie wszystkie znane prace związane z analizą ruchu pojedynczych cząstek w łożu osadzarki od Rittingera (Stępiński 1964) począwszy bezpośrednio wiążą prędkość lub przyspieszenie cząstki z jej masą, co jest nieuchronną konsekwencją istnienia praw dynamiki. Dla stałej objętości cząstki oznacza to jako dalszy skutek zależność rozproszenia od gęstości tej cząstki. Jest tak dlatego, że stały pod względem wielkości strumień wody przepływającej przez łoże osadzarki ziarna musi powodować istnienie zależności rozluzowania łoża od gęstości cząstek, wynikającej bezpośrednio z amplitudy ruchu cząstek o zróżnicowanej gęstości. Rezultatem takiego działania strumienia wody jest mniejsze rozluzowanie cząstek o dużej gęstości ulokowanych w dolnych warstwach i wyraźnie większe rozluzowanie lekkich cząstek w warstwach górnych. Zatem w modelu, którego założenia są rozpatrywane w niniejszej pracy konieczne jest uwzględnienie takiej sytuacji, gdy poszczególne frakcje gęstościowe wzbogacanego materiału nie rozpraszają się jednakowo. Dlatego przyjmuje się jako ważne założenie modelu możliwość wybrania rozproszenia indywidualnie dla każdej frakcji gęstościowej nadawy lub przyjęcia z góry ustalonej funkcyjnej zależności rozproszenia od gęstości frakcji gęstościowych nadawy.

Dwuwymiarowy rozkład cząstek w łożu osadzarki

Łoże osadzarki można traktować jako losowy ciągły lub dyskretny zbiór cząstek i warstw, do których te cząstki trafiają. Zasadniczym celem tworzenia modelu, którego założenia są rozważane w tej pracy jest obliczenie średnich gęstości warstw, jakie utworzą się w łożu i ich składu densymetrycznego. Do tego konieczna jest znajomość charakterystyki gęstościowej wzbogacanego materiału oraz przyjęcie z góry określonego rozkładu opisującego rozpraszanie się tych cząstek w poszczególnych warstwach. Dla realizacji takich obliczeń naturalne będzie przyjęcie dwuwymiarowego rozkładu, którego zmiennymi losowymi są gęstość cząstki i gęstość warstwy dla rozkładu ciągłego lub odpowiednio średnie gęstości ziaren danej klasy gęstościowej nadawy i średnie gęstości warstwy łoża dla rozkładu dyskretnego. Rzeczywista objętość właściwa danej warstwy jest średnią ważoną objętości właściwych tworzących ją cząstek, a wagami w obliczaniu tej średniej są masowe udziały cząstek danych gęstości w warstwie. W takiej sytuacji rzeczywista gęstość warstwy musi być funkcją rozproszenia cząstek o znanych gęstościach w poszczególnych warstwach łoża osadzarki i także funkcją masy cząstek danej frakcji gęstościowej nadawy, która została rozproszona w warstwach czyli funkcją składu densymetrycznego wzbogacanego materiału.

Rozkłady związane z rozkładem dwuwymiarowym

Dla dwuwymiarowego rozkładu losowego oprócz dwuwymiarowej funkcji gęstości prawdopodobieństwa i dwuwymiarowej dystrybuanty określone są jeszcze jednowymiarowe rozkłady brzegowe i rozkłady warunkowe (Goldberger 1972). Dla rozkładu opisanego ciągłymi funkcjami ilość rozkładów warunkowych jest nieskończona, a w przypadku opisu dyskretnego ich ilość jest określona ilością różniących się gęstością frakcji gęstościowych nadawy i ilością rozpatrywanych warstw łoża. Rozkłady te powinny być istotną częścią modelu, ponieważ właśnie w nich jest zawarta interesująca fizyczna interpretacja zjawisk losowych istniejących w procesie osadzania.

Uzasadnienie braku możliwości dokładnego empirycznego sprawdzenia modelu

Dokładne empiryczne sprawdzenie modelu wymaga podziału rozwarstwionego w osadzarce laboratoryjnej łoża na względnie dużą liczbę (16-48) warstw przy ustalonej wysokości sumy wszystkich warstw. Zasadniczą trudnością tego sprawdzenia są ziarna, które z powodu swoich rozmiarów mieszczą się w większej liczbie warstw. Zatem, aby z dostateczną dokładnością określić zawartość frakcji gęstościowych w poszczególnych warstwach z zachowaniem warunków odpowiadających rzeczywistemu wzbogacaniu rozmiar ziaren musiałby być dostatecznie mały. Dla utrzymania podobieństwa wzbogacania w osadzarce laboratoryjnej i w osadzarce przemysłowej powinno być utrzymane geometryczne podobieństwo wymiarów otworów sita i wymiarów cząstek. Wymaga to bardzo małych otworów w sicie osadzarki laboratoryjnej , a to z powodów konstrukcyjnych prowadzi do konieczności stosowaniu w niej sita o bardzo małym współczynniku prześwitu. Mały prześwit jest istotnym powodem braku podobieństwa wzbogacania w osadzarce laboratoryjnej i rzeczywistym procesie. Brak podobieństwa wynika z ograniczenia przepływu wody przez sito i wzbogacany materiał prowadzącego do zbyt małego rozluzowania spowodowanego dużym spadkiem ciśnienia wody na samym sicie. Empiryczne określenie rozkładu cząstek o stałej gęstości w poszczególnych warstwach jest konieczne, ponieważ porównanie krzywych rozdziału generowanych przez model z krzywymi empirycznymi nie może jednoznacznie określić przyczyny istnienia różnic między tymi krzywymi. Wynika to z możliwości istnienia różnic spowodowanych zależnością rozproszenia od gęstości cząstek lub zmianą asymetrii rzeczywistego rozkładu. Z wstępnego porównania krzywych rozdziału generowanych przez modele z użyciem rozkładu równomiernego i rozkładu normalnego wynika, że kształt krzywej rozdziału jest związany z rodzajem rozkładu opisującego rozpraszanie się cząstek w warstwach. W przypadku, gdy rozkłady nie są jednakowe dla gęstości wszystkich cząstek nadawy i ich rozproszenie rośnie wraz z gęstością cząstek powstają zjawiska podobne jak w rzeczywistym wzbogacaniu polegające na zmniejszaniu się nachylenia krzywej rozdziału dla większych gęstości dające efekt asymetrii krzywej rozdziału. Jeżeli rozkłady są asymetryczne to krzywe rozdziału także muszą być asymetryczne. Rodzi to istotną trudność rozróżnienia przyczyn asymetrii krzywych rozdziału, bowiem dla eksperymentalnej asymetrycznej krzywej nie można jednoznacznie określić przyczyny jej asymetrii. Może to być rzeczywista asymetria rozkładów opisujących rozpraszanie się cząstek lub sytuacja, gdy poszczególne rozkłady są symetryczne, lecz każdy z nich o innym rozproszeniu. Możliwe jest jednak mniej dokładne pośrednie sprawdzenie modelu przez porównanie eksperymentalnego pomiaru rozkładu gęstości warstw w pionowym przekroju łoża z takimi rozkładami generowanym przez model dla takiego samego składu gęstościowego wzbogacanego materiału i różnych modelowanych rozproszeń. Taka metoda wspomniana już przy rozważaniach dotyczących rozkładów uciętych i pokazana na rys. 3 zostanie zastosowana do weryfikacji poprawności działania przedstawianego modelu. Sposób weryfikacji modelu i jej wyniki będą przedmiotem odrębnego opracowania.

Realizacja obliczeń w modelu

Dla realizowanego przez model iteracyjnego algorytmu obliczeń konieczne jest by model ten opierał się na obliczeniach możliwie najdokładniejszych, a to wymaga zastosowania w obliczeniach dystrybuant poszczególnych rozkładów. Obliczenia realizowane na podstawie przyjętych funkcji gęstości prawdopodobieństwa poszczególnych rozkładów są zbyt niedokładne ze względu na kumulowania się błędów aproksymacji tej funkcji w obliczeniach iteracyjnych. Aproksymacja taka jest konieczna dla rozkładu normalnego ponieważ w obliczeniach niezbędne jest całkowanie, którego wynik nie jest funkcją elementarną.

Rozważany model wykorzystuje do obliczeń rozkłady związane z dwuwymiarowym rozkładem gęstości prawdopodobieństwa znalezienia cząstki o gęstości ρ_{ci} w warstwie o gęstości ρ_{wj} i dodatkowo rozkłady gęstości poszczególnych warstw i zawartości popiołu w cząstkach ulokowanych w warstwach. Jest on z założenia modelem dyskretnym, lecz ilość frakcji gęstościowych w tym modelu wynosząca 32 dla większości obliczeń jest wystarczająco duża, aby mógł być on praktycznie traktowany jako model ciągły. Dla zbadania wpływu ilości dyskretnych warstw i frakcji gęstościowych nadawy na wynik obliczeń przewiduje się zbadanie działania modeli także dla ilości frakcji gęstościowych równych 16 i 48. Porównanie wyników wykonanych wstępnych obliczeń pozwala zauważyć, że zmiana ilości fakcji gęstościowych cząstek i warstw nie zmienia zasadniczo obrazu wzbogacania w osadzarce wynikającego z tego modelu.

Podsumowanie

Przedstawione powyżej szczegóły założeń probabilistycznego modelu rozkładu gęstości warstw łoza osadzarki nie pozwalają na wyciąganie szczegółowych wniosków o działaniu tego modelu. Wynika z nich jeden podstawowy fakt, że na etapie formułowania założeń zrobiono wszystko, co jest aktualnie możliwe, aby zapewnić istnienie w modelu tylko tych mechanizmów działania osadzarki i ich ograniczeń zgodnych z rzeczywistym jej działaniem. W następnej pracy zostaną podane wszystkie szczegóły obliczeń niezbędne dla jego poprawnego działania. Pozwoli to zauważyć istotne różnice działania tego modelu i już istniejących modeli teoretycznych oraz istnienie zjawisk w procesie osadzania, których wykrycie eksperymentalne jest bardzo trudne ze względu na niezadowalający stan techniki pomiarowej stosowanej w przeszłości i także aktualnie w badaniach procesu osadzania.

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Assumptions of Probabilistic Model of Grains Density Distribution in Jig Bed Layers

Significant limits of grain disperion in layers of the jig bed and the consequences of these limits are shown in the presented paper.They are the results of large grains dispersion in relatively small range of jig bed density layers. These limits are omitted or incorrectly presented in the descriptions of the phenomena occuring in the jig operation in most of existing papers. Correct conditions and assumptions of probabilistic model of these phenomena are presented. The construction of this probabilistic model does not have any restrictions for proper creation of the density layers of jig bed and amount of mass distributed in these layers. The experimental validation of this model in the laboratory conditions is possible in particular situation. Additionally this model explains some errors existing in gravitional benefication theory.

Keywords: hard coal beneficiation, jig, modeling of the jig operation, partition curve, grains dispersion

Water Pollution Assessment of an Abandoned Copper Mine in Lasail, Sultanate of Oman

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Abstract

Abandoned mining sites are largely responsible for the release of heavy metals into water systems. This study assessed heavy metals in the water collected from the mine sumps and bore-wells of an abandoned copper mine in Lasail, northern Oman. Other physiochemical parameters of the water were also evaluated. The waters were extremely acidic with very high electrical conductivity. Aluminium (Al), boron (B), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn) and zinc (Zn) were in very high concentrations, well above the limits recommended by Oman and World Health Organisation (WHO) standards. The principal component analysis (PCA) explained 93% of the variability. The impact of mining on the water quality of Lasail area is presented and remediation measures are recommended.

Keywords: water pollution, abandoned copper mine, heavy metals, multivariate data analysis, Omans

Introduction

Industrial activities such as mineral exploitation is highly responsible for the input of toxic elements into water systems. The toxic elements are released not only at the big mining sites, but also in places of artisanal mineral exploitation (Atibu et al., 2013) and abandoned mining sites (Neiva et al.,2014). The adverse effects of abandoned mines were known to persist for decades, even after the decommissioning of mines, most often till the sulphides were completely weathered (Carvalho et al., 2009; Lopes et al.,2016). Water is one of the vital compounds for all forms of life (Valoon and Duffy, 2005). Hence, water pollution receives considerably more attention when compared to soil and air. When the concentration of the metals exceeds the retention capacity of soils, they leach into groundwater and soil solution (Zamani et al., 2012). Metals can be distinguished from other toxic pollutants, since they are non-biodegradable, and can be concentrated and accumulated throughout the food chain (Dubey et al., 2014).

Acid Mine Drainage (AMD) is one of the major environmental impacts of sulphide mines. AMD is produced mostly when pyrite ore is left exposed on the surface and thus oxidized by a combination of water, oxygen, and existing bacteria (Johnson and Hallberg., 2003). It is characterized by extremely low pH values and high concentrations of heavy metal ions, which pollute large areas and surface/groundwater systems (Foucher et al., 2001; Stylianou et al., 2014). Numerous studies have been undertaken on trace element contamination derived from mining activities in soils, plants, waters and sediments in various countries (Lee et al., 2001). However, no previous study has been carried out in Oman on water pollution due to mining activities. So, the main objective of this study was to determine the water quality of the abandoned Lasail copper mine area by evaluating the composition and concentrations of heavy metals.

Materials and methods

Study area

Lasail copper mine is located in Northern Oman (Lat. 24°16´44.1″N; Long. 56°25´43.0″E). The Lasail copper mine was one of the largest single ore deposits that operated from 1983 to 1994. The mine was abandoned in 1994, but large amounts of waste piles were left behind. The mine area includes two mine sumps and two open bore-wells. The area is arid with long summers and short winters (Months) (Ahmed and Choudri, 2012).

Sampling

Water samples were collected in the months of July 2016 and January 2017 representing summer and winter seasons. Three samples were taken in each season randomly from two mine sumps (referred to as red and yellow sump) and two open bore-wells (referred to as well 1 and well 2) situated in the study area. The coordinates for red, yellow sump, well 1 and well 2 are 24°16´25.00″ N 56°26´3.88″E, 24°16´29.44″N 56°26´3.30″E, 24°16´25.33″N 56°25´58.44″E, 24°16´31.82″N 56°25´59.53″E respectively. The water samples were collected in a pre-cleaned PVC containers. The pH and Eh were measured in the field itself (Hand-held Mettler Toledo SG2). Electrical conductivity (EC) and Total dissolved solids were measured in the laboratory (Aquaread 800, Aquaread Ltd.). Heavy metals were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the samples were filtered with 0.45 μm filter paper prior to the analysis. In the ICP- OES, the measurements were repeated thrice for every sample. Control samples were collected in nearby wadis and from a well in a nearby village.

Statistical analysis

SPSS (Version 21.0 IBM, USA) was used for the data analysis. ANOVA for two samples was performed to evaluate the differences in the means between the summer and winter samples. Principal component analysis (PCA) was used as a dimension reduction tool to reduce a large set of variables to a small set that still do not affect the integrity of the in-

Tab. 1. Water physiochemical analysis (Units of measurement: EC µS/cm, Eh mV, TDS mg/l, Metals mg/l)
Tab. 1. Analiza fizykochemiczna wody (Jednostki pomiaru: EC µS/cm, Eh mV, TDS mg/l, Metals mg/l)

Parameters	Sample locations							
	Red sump		Yellow sump		Well 1		Well 2	
	Jul-16	Jan-17	Jul-16	Jan-17	Jul-16	Jan-17	Jul-16	Jan-17
pH	3.11	2.80	3.78	3.10	4.28	4.09	4.40	4.27
EC	21360	27640	26230	18730	11220	7033	7733	2256
Eh	685.30	423.00	595.90	375.00	650.00	236.00	390.00	230.00
TDS	14830	18240	19580	11450	9097	4040	5202	1491
Al	89.95	100.15	31.39	80.36	8.56	9.52	1.32	0.56
B	4.44	6.33	4.82	5.54	2.48	3.57	1.02	1.69
Ca	74.99	47.04	70.28	47.35	84.43	53.54	79.34	51.61
Cu	57.91	48.17	40.27	78.65	5.69	5.34	1.07	0.27
Fe	514.08	395.11	518.67	367.00	409.92	403.22	256.68	253.53
Hg	12.01	60.77	21.93	36.89	6.45	34.95	3.02	12.29
K	5.93	2.93	8.62	11.58	5.28	6.34	3.19	3.50
Mg	44.67	34.58	39.91	36.36	48.51	35.50	45.93	33.01
Mn	66.58	83.03	68.46	89.72	24.12	25.02	9.37	9.67
Na	81.56	166.95	77.29	184.38	63.03	128.34	58.99	95.30
Si	91.96	79.58	58.75	79.22	35.37	36.60	16.67	16.49
Zn	19.37	19.17	21.99	18.39	6.35	6.29	0.50	0.29

formation content in the large data set. PCA was used here to find a more meaningful basis for the data collected using variance –covariance matrix (Tabachnick and Fidell, 2007). Hierarchical cluster analysis (HCA) was performed to group the identified metals.

Results and discussion

The water samples in the mine sumps were yellow and red. The colour of water in the mine site significantly depended on the mineralogical composition of the iron oxides and oxide phases and varied between reddish (hematite) and yellow (jarosite). The water pH, Eh, EC, TDS and mean concentration of heavy metals are presented in Table 1. The results revealed that the pH was extremely acidic in the red and yellow sump water samples in the range of 2.80-3.78. The pH varied from 4.10 - 4.27 in the well water (WHO limit 6.50-8.50). The lowest values of pH can be attributed to the influence of underground water leaching the mine waste and tailings, which contain sulphides (Lopes et al., 2016). The EC values varied between 2256 µS/cm (well 2) and 27640 µS/cm (red sump). The pH and EC values exceeded the WHO permissible limit (400-600 µS/cm) in all samples, thus indicating the high quantities of total dissolved solids. Oman standards: Al 0.02, B 0.50, Cu 2, Fe 1, Hg 0.001, Mn 0.40, Zn 3. WHO standards Ca 75, Cu 1, Fe 0.10, Hg 0.001, Mg 50, Mn 0.5, Zn 5.

The mean concentration of Cu was very high in two mine sump water samples when compared to the Oman and WHO water standards. Similarly, the Cu concentration was high in well 1 samples, where the water was at an approximate depth of 150 m. The Cu mean concentration reached as high as 5.69 mg/l and 5.34 mg/l during summer and winter (Table 1). It appears that the chemical composition of the groundwater was affected by the tailings water. On the other hand, water in well 2 contained comparatively lesser heavy metals concentration. This could be due to dilution of metal concentrations by rain water surface runoff, since the well head is about 1m below ground surface level. However, similar to mine sumps and well 1, the heavy metals such as Al, B, Fe, Hg and Mn exceeded the WHO and Oman standards in all the water samples of well 2. Particularly, the Fe concentration was very high. The primary and secondary minerals likely to be found in the massive sulphide ore are pyrite (FeS2), chalcopyrite (CuFeS2) and sphalerite (ZnS). The primary metals which tend to leach are iron (Fe), copper (Cu), and zinc (Zn) (Stylianou et al., 2014). This could be the reason for getting high concentrations of Cu, Fe and Zn in this study. Lasail deposits that belong to Volcanogenic Massive Sulphide (VMS) are very rich in these metals. Further, Al, B, Ca, Hg, Mg and Mn concentrations were very high in the mine sumps, well1 and 2 water samples.

When comparing the means of these metals between summer and winter, the metals such as Al, B, Cu, Fe, K, Mn, Si and Zn are not significantly different, indicating no seasonal variation. Ca, Hg, Mg and Na are significantly different (ANOVA for two samples; $P < 0.05$). The difference could be due to the temperature variation and monsoonal precipitation. No significant contamination observed in the control water samples taken from the nearby areas

Principal Component Analysis (PCA)

In this study, variance - co-variance matrix was applied as all the variables have the same unit of measurement. The rotation of the principal components was performed by the Varimax orthogonal rotation option. Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were applied to assess suitabil-

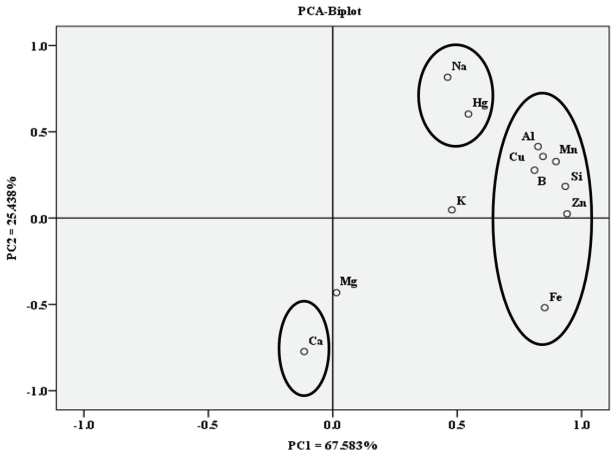

Fig. 1. PCA biplot showing the grouping of 12 heavy metals. PC1 and PC2 show 93.021% of variability.
Rys. 1. Analiza PCA dla 12 metali ciężkich. PC1i PC2 wykazują 93,021% zmienności

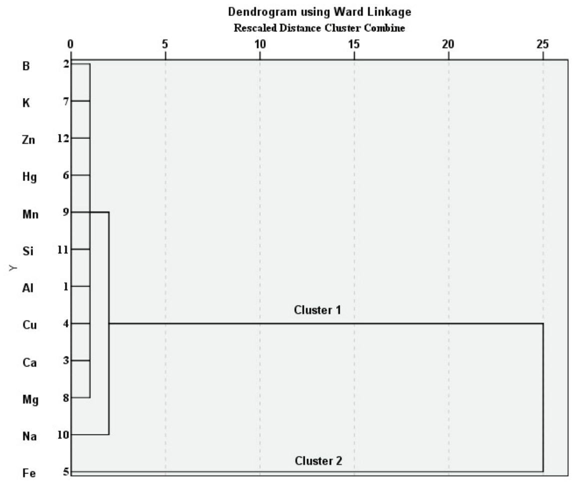

Fig. 2. Hierarchical dendrogram of the potential toxic elements obtained by the Ward-distance clustering method
Rys. 2 Hierarchiczny dendrogram potencjału pierwiastków toksycznych uzyskany metodą grupowania na odległość Warda

ity of data for PCA (PCA – Principal Component Analysis).

The PCA shows two principal components for the heavy metals which explain 93.021% of the total variance. Zn, Si, Mn, Fe, Cu, Al and B were closely associated with the first component (PC1), explaining 67.583% of total variance (Figure 1), and PC1 was the most important component. PC1 confirmed that these elements were from anthropogenic sources such as mining activities, since these metals are closely associated with Cu. However, PC2 comprised of Na, Ca and Hg explained 25.438% and Ca is negatively related to Na and Hg. Thus, it can be concluded that these metals are influencing the overall water quality in Lasail mining area.

Hierarchical Cluster Analysis (HCA)

HCA was performed to group the identified metals into clusters. Two clusters were identified based on the concentration of metals. Al, B, Ca, Cu, Hg, K, Mg, Mn, Na, Si and Zn were in the first cluster. Fe alone in the second cluster (Figure 2). The metals in the same cluster have close similarities in concentration. Metals in the first cluster were from anthropogenic sources. Whereas, Fe was from both anthropogenic and lithologic sources.

Conclusion

The water in the mine sumps and wells were characterised as extremely acidic with very high electrical conductivity and high heavy metal concentrations. The very high concentration of iron and acidity are typical features of acid mine drainage and there is a possibility of metal transportation and formation of acidic ponds. The greatest concern is about the Hg contamination level, as it was approximately 60,000 times higher than those of the Oman and WHO limits. Cu and Fe concentrations were approximately 39, 500 times higher than those of the standard limits. Therefore, proper remediation measures should be taken to cleanse the area to avoid further ground water contamination. PCA results revealed Zn, Si, Mn, Fe, Cu, Al B, Na and Hg are responsible for the poor and unacceptable quality of water in the Lasail area.

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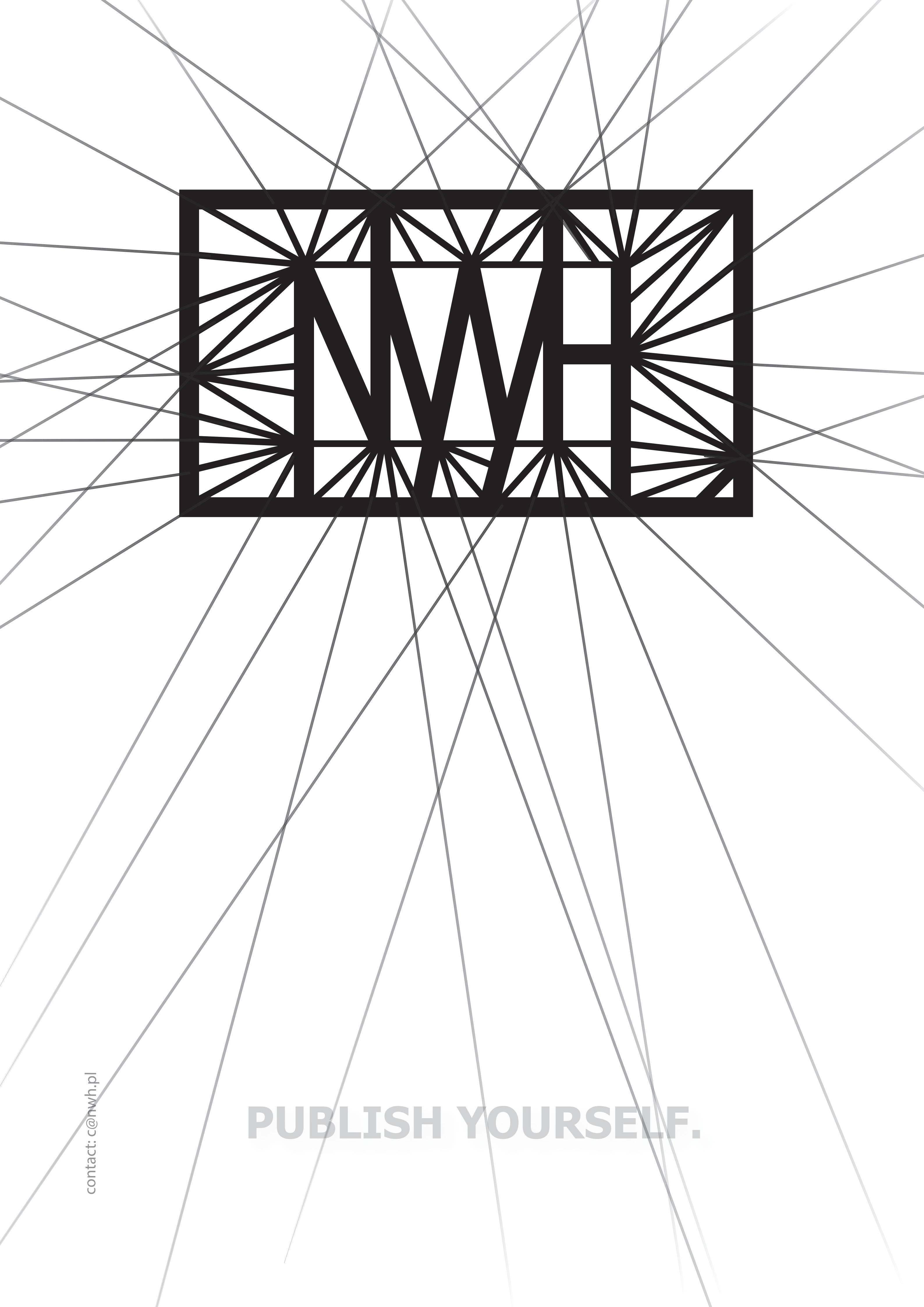
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The Contemporary Employee in the Creation of Organisational Culture in the Polish Mining Industry

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Abstract

This paper describes the relationship between the employee and the organisational culture in a company. It places particular focus on the characteristics of today's employees, resulting from the typology of current working generations and highlights the characteristic features of baby boomers, Generation X, and Generation Y. The practical part of this paper characterises employees and HR policies of two groups operating in the mining industry – Jastrzębska Spółka Węglowa SA and Lubelski Węgiel Bogdanka SA.

Keywords: Employee, organisational culture, Generation Y, mining industry

Introduction

Organisational culture is a corporate element which allows defining the company from a different perspective than the organisational perspective or one measured by economic values. This is such an extensive subject covering a broad range of aspects of a company's operations that it is difficult to clearly define the concept at hand, especially within the mining industry. The authors of this article have already discussed this topic in publications [1], [2], [3], [5], [6], [13], [14], [15], [16], [17], [18], [19]. Nevertheless, it is without any doubt that the organisational culture of a company is related to its employees. Holland defines culture as the beliefs and views which are spreading in the company, on how to do business, and desirable employee conduct and their treatment [7], [8], [12], [24]. Therefore, the role of the employee is crucial in the shaping of organisational culture. Furthermore, companies, especially those operating in the mining industry, should take particular care of their employees and create good HR policies, so that their organisational culture is profiled appropriately.

An employee's functioning within an organisation is strongly determined by the level, type, and form of the organisational culture in the company. On the other hand, this functioning can also influence the form and level of this culture. Figure 1 presents the interactions involved in shaping organisational culture.

One can assume that employees come to organisations "equipped" with their own system of values, temperament, their own beliefs and views. They begin to function in an organisation with a defined system of standards, values, and procedures for action in place, and all the other elements which define and constitute its organisational culture. At some point, these "cultures" begin to intertwine. This is where appropriate human resources management comes into play. Its role should be to ensure that an employee "adopts" the culture of a given organisationand observes and applies its principles and guidelines. As a result, this can and should enhance the organisation's culture. Without appropriate management, the culture of an organisation can be weakened by its employees' individualism.

The characteristics of contemporary working generations

The workforce of Polish industry, including the mining industry, currently includes several generations. Representatives of the generation which sociologists refer to as Generation Y make up the predominant group. 1980 is the bottom limit for the classification of this group and its oldest representatives are in their late thirties, so they are vocationally active.

The general characteristics of this generation are presented in Figure 2.

After analysing these characteristics, it can be noted that this generation has many traits which predispose it to work in the mining industry, but also exceptionally unfavourable features when seen in the context of the present state of the profession.

One of the roles of the management is to streamline cooperation between this generation and other people. Several suggestions can be made on how to reorganise human resources management, i.e. how to change the organisational culture in this respect, to facilitate effective cooperation [4]:

- increase expenditures on training in basic skills, especially soft skills (ability to conduct correspondence, use book sources and magazines, and not only the Internet),
- explain cause-and-effect relationships; representatives of Generation Y are not very good at solving non-standard problems in the workplace, are more effective in solving typical, routine problems, but are unable to improvise,
- streamlining communication channels using the electronic media (instant messengers, mobile messaging, etc.)
- developing the culture of communication, especially of communication with customers, since Generation Y tends to communicate with other people as if they were their peers, which can be detrimental to the image of the organisation,
- introduce more frequent evaluations, as this generation grew up with video games, where the player can

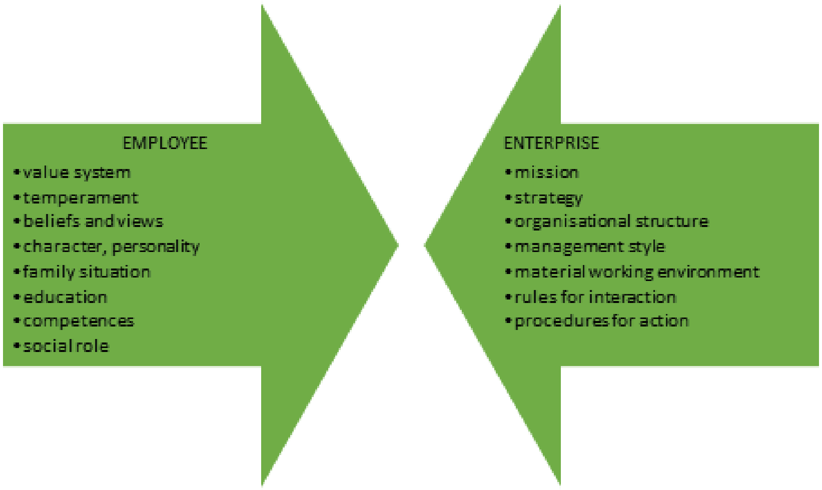


Fig. 1. The employee-enterprise interactions involved in shaping organisational culture. Source: own work
Rys. 1. Interakcje pracownik-przedsiębiorstwo w procesie kształtowania kultury organizacyjnej. Źródło: opracowanie własne

- see his/her score on screen, so in the workplace young people also expect quick feedback;
- focus on the results, which is associated with granting them greater freedom in the workplace, e.g. allowing to make private phone calls. Generation Y works differently from older generations, more impulsively, and should be assessed based on the results.
- stimulate people to work, as Generation Y needs constant stimulation,
- take care of contact, young people can be loyal, but to other employees, not the organisation itself, if it provides them with opportunities for development, it will gain their loyalty, otherwise they will not hesitate to leave and join the competition,
- ensure a balance between professional and personal life; Generation Y values highly flexible working hours; spare time is very important for this generation.

The general profile of Generation Y in terms of views on work and professional life can be based on the most important theses and elements determining this generation [11]. These are:

- a high level of attained education and capacity for learning
- team working skills
- ability to carry out several tasks at the same time
- country-wide and global mobility
- a short-term outlook on career (in terms of the workplace as well as profession)
- expecting quick responses to their actions (e.g. evaluation, answers and advice)
- expecting a friendly atmosphere in the workplace and opportunities for self-development
- lower expectations for promotion in the organisational hierarchy
- unwillingness to be loyal to the employer
- appreciation of one's own values and life goals
- creating communities in the virtual world and communicating within these communities
- interpersonal difficulties in the real world, including the lack of ability to solve everyday conflicts

The current generation of workforce has, therefore, evident potential. Nevertheless, in terms of their employment in the mining industry, it is important to take into account the wide range of employees working in mining companies. There are senior as well as junior workers. Therefore, one should take good care of their good relations, so that the work culture and culture of the organisation are developed in a positive way. In order to do this, knowledge of the basic characteristics of all the working generations is necessary. These include baby boomers, i.e. those born between 1946 and 1964, Generation X (1965–1977) and the aforementioned Generation Y (1978–1994).

Figure 3 presents the characteristic features of the vocationally active generations.

One objective of corporate culture is also to integrate employees. This integration does not apply to interpersonal relations of the staff, but it should be understood as the mental integration of employees with the company. Employees should feel that the mission, vision, and values of the company are also their own.

Culture should also facilitate the understanding of the mission, by identifying those elements which employees should prioritise. This is not only in the case of official duties, but also in creating the external image, brand, and value of the company.

However, the most fundamental task of corporate culture is to indicate algorithms, models and procedures recommended by the company. This builds in employees a sense of belonging to the company [20], [21] and, at the same time, it is an indicator of corporate culture.

The generational structure may, thus, strongly influence the processes, but it also significantly contributes to the shaping of the organisational culture.

The characteristics of the workforce and HR policy at JSW SA.

Jastrzębska Spółka Węglowa SA declares that its "greatest asset are its people. The most valuable employees for us are those who identify with our company and its mission." [24]. This declaration is largely in line with the basic premises of creating a good, strong organisational culture.

The HR policy of JSW provides for the employment of new, educated individuals and investing in their education. Mining schools also serve this purpose. They attract young

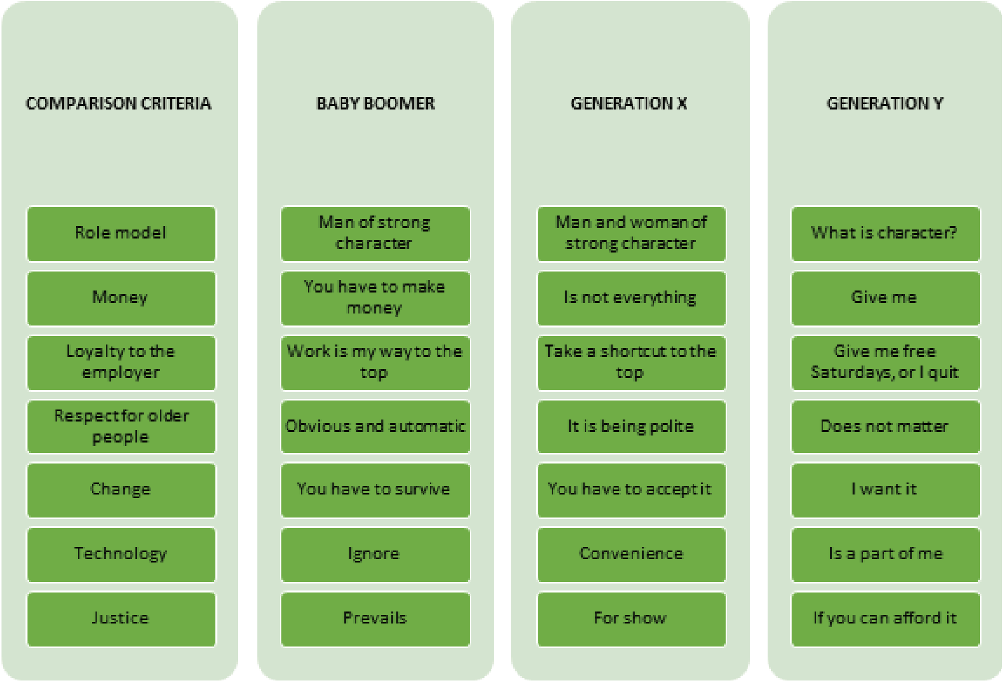
Positive characteristics

- no major differences between Generation Y in Poland and other Western countries
- they have many skills which employers find useful, e.g. are computer-literate and can find various information but often have no idea what to do with it
- they are very well prepared to navigate areas related to the global economy and cultural diversity
- they are good team players
- they assess themselves through comparison with their peers
- they create communities and often communicate with one another
- they can multitask

Negative characteristics

- no ability to make decisions independently
- unrealistic expectations
- impatience
- they become bored relatively quickly
- they require a constant flow of stimuli (e.g. by means of music or image)
- they lack the ability to make decisions independently

Fig. 2. The characteristics of Generation Y. Source: own work on the basis of [4]
Rys. 2. Cechy pokolenia Y. Źródło: opracowanie własne na podstawie [4]



COMPARISON CRITERIA	BABY BOOMER	GENERATION X	GENERATION Y
Role model	Man of strong character	Man and woman of strong character	What is character?
Money	You have to make money	Is not everything	Give me
Loyalty to the employer	Work is my way to the top	Take a shortcut to the top	Give me free Saturdays, or I quit
Respect for older people	Obvious and automatic	It is being polite	Does not matter
Change	You have to survive	You have to accept it	I want it
Technology	Ignore	Convenience	Is a part of me
Justice	Prevails	For show	If you can afford it

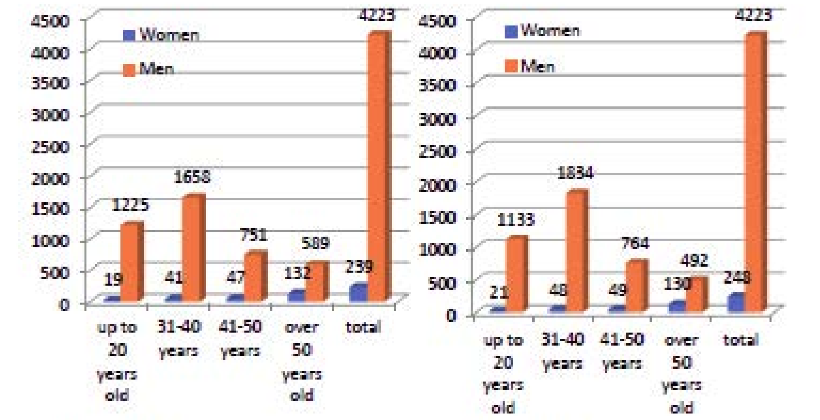
Fig. 3. A comparison of the features of baby boomers and Generations X and Y. Source: own work on the basis of [10]
Rys. 3. Porównanie cech pokolenia baby boomer, X i Y. Źródło: opracowanie własne na podstawie[10]

people, often from traditional mining families, complementing the implementation of production plans with one crucial element - the human factor as affecting local communities. Today, JSW employs approximately 21,500 people, of whom about 17,000 work underground. The specificity of underground operations necessitates mutual respect and observance of OHS procedures. Occupational health and safety rules and culture are among the basic elements of organisational culture. In mining companies, these are especially important in terms of its shaping and improvement.

As declared by the management of JSW, the main objectives of its HR policy include the provision of appropriately qualified specialists; the effective and rational use of human resources, and encouraging the professional development of employees through a career system, professional education and training. In order to meet these objectives, JSW utilises a number of HR policy tools, including subsidised holidays, support for sick employees, non-repayable financial support, and special gifts for employees' children.

The pursued HR policy results in a fully shaped and continuously improved organisational culture. The company's es, shirts, and sports T-shirts.

In respect of improving the qualifications and education of the workforce, JSW has entered into agreements with AGH University of Science and Technology and Silesian University of Technology on student placements at JSW facilities. The best alumni of these universities are usually employed by JSW. The company is engaged in ongoing cooperation with AGH University of Science and Technology, Silesian University of Technology, and the University of Silesia.



Data for 2016

Data for 2017

Fig. 4. The employment structure at GK LW Bogdanka SA by gender and age. Source: own work on the basis of [23]
Rys. 4. Struktura zatrudniania wg płci i wieku w GK LW Bogdanka SA. Źródło: opracowanie własne na podstawie [23]

The characteristics of the workforce and HR policy at LW Bogdanka SA

The Lubelski Węgiel Bogdanka SA group offers its potential employees, as part of its HR policy, such benefit as:

- introductory and refresher training
- obtaining experience allowing further growth
- opportunities for developing professional skills
- the necessary working tools to carry out the entrusted tasks
- organisational culture focused on ensuring a friendly working atmosphere
- extensive social packages.

Therefore, the organisational culture is strongly highlighted already at the initial stage of the company-employee relationship. According to the company itself [8], human capital is defined as the most valuable kind, which influences the most the achievement of business and social objectives, building a market position, and, as a result, the development of all spheres of the Group's activity.

Employees of GK LW Bogdanka mostly have higher and upper-secondary education, who systematically improve their professional qualifications and who are active also “out of work”. The Company supports both areas of employee engagement; on the one hand, by co-funding vocational courses and training or postgraduate studies, and on the other hand, by offering a wide range of cultural, sports and tourist events financed from the social benefits fund for employees and their families. The group declares that, being a responsible employer, it understands the work-life balance idea. The specificity of the mining industry does not support gender parity in employment; however, the company makes sure to offer employment for both genders. Nevertheless, a low female representation is evident, with the majority of them being over 50 years old (Fig. 4).

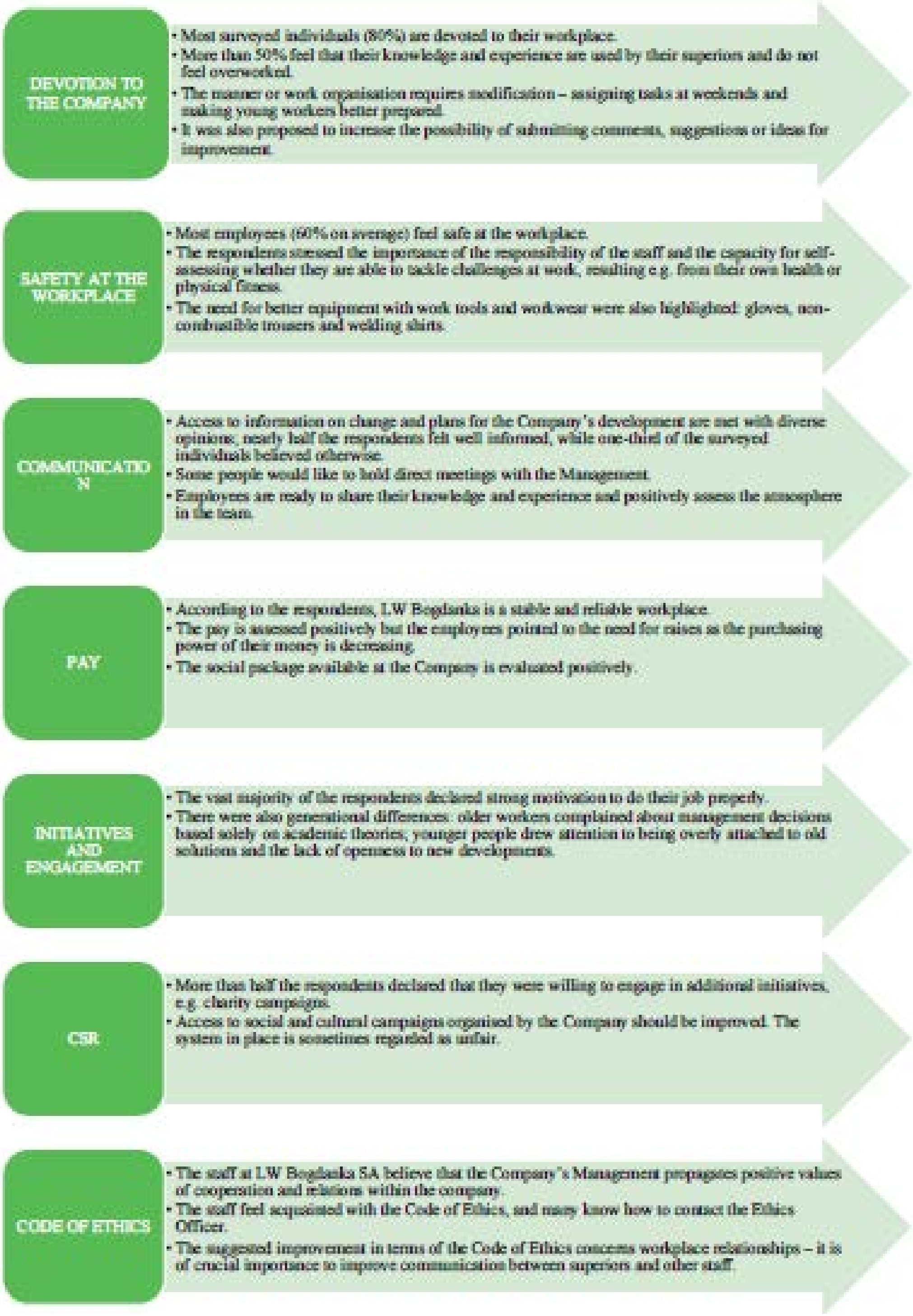
Lubelski Węgiel Bogdanka is a special company in its being the largest local employer. Local employees constitute a large group. This results in a strong bond between the company and the region and its residents. The employees come mainly from the Łęczna District and surrounding areas, located within a distance of about 50 km. There is also a large group of employees who moved to the region to work for this company. They usually hold managerial and executive positions. This proves their determination to work there, but also the strong reputation of the company as a good employer. In order to maintain this image, the company places great emphasis on the development of human capital through continuous improvement of their professional and interpersonal skills and effectively motivating them.

LW Bogdanka, similarly to the other company operating in the mining industry, faces the typical problems observed in this sector. These are in particular the generation gap and generational change in the employment structure. LW Bogdanka SA has implemented the Programme for Generational Change to secure its staffing needs. Its first stage was the Voluntary Leave Programme facilitating rational, coordinated, and spread-in-time closing of the generation gap, while maintaining business continuity. The programme provided younger mining staff with employment opportunities and ensured the stable onboarding of a new generation of employees. Its objective was to reduce employment levels and introduce organisational change, as well as to prevent uncontrolled competence drain. Preventing generation gap also involves close cooperation with industry-specific schools and higher-education institutions. The company is a signatory of letters of intent in this respect with AGH University of Science and Technology, the Mining School Complex in Łęczna, and the School Complex in Ostrów Lubelski.

The results of the cyclical employee survey provide a relatively faithful image of the organisational culture at LW Bogdanka in terms of human resources. The survey was made one of the principles of the Social Responsibility Strategy for 2014-2017 as leading to improvement in staff safety. Its results were collected and are presented in Figure 5. They point to the organisational culture at LW Bogdanka requiring improvement in terms of the employee's role; however, in general, the staff are satisfied with their jobs and assess the company positively.

Conclusion

This article evaluates the human resources policies of two enterprises operating on the mining market. Both companies strongly identify themselves with the shaping of organisational



DEVOTION TO THE COMPANY

- Most surveyed individuals (80%) are devoted to their workplace.
- More than 50% feel that their knowledge and experience are used by their superiors and do not feel overworked.
- The manner or work organisation requires modification – assigning tasks at weekends and making young workers better prepared.
- It was also proposed to increase the possibility of submitting comments, suggestions or ideas for improvement.

SAFETY AT THE WORKPLACE

- Most employees (60% on average) feel safe at the workplace.
- The respondents stressed the importance of the responsibility of the staff and the capacity for self-assessing whether they are able to tackle challenges at work, resulting e.g. from their own health or physical fitness.
- The need for better equipment with work tools and workwear were also highlighted: gloves, non-combustible trousers and welding shirts.

COMMUNICATION

- Access to information on change and plans for the Company's development are met with diverse opinions; nearly half the respondents felt well informed, while one-third of the surveyed individuals believed otherwise.
- Some people would like to hold direct meetings with the Management.
- Employees are ready to share their knowledge and experience and positively assess the atmosphere in the team.

PAY

- According to the respondents, LW Bogdanka is a stable and reliable workplace.
- The pay is assessed positively but the employees pointed to the need for raises as the purchasing power of their money is decreasing.
- The social package available at the Company is evaluated positively.

INITIATIVES AND ENGAGEMENT

- The vast majority of the respondents declared strong motivation to do their job properly.
- There were also generational differences: older workers complained about management decisions based solely on academic theories; younger people drew attention to being overly attached to old solutions and the lack of openness to new developments.

CSR

- More than half the respondents declared that they were willing to engage in additional initiatives, e.g. charity campaigns.
- Access to social and cultural campaigns organised by the Company should be improved. The system in place is sometimes regarded as unfair.

CODE OF ETHICS

- The staff at LW Bogdanka SA believe that the Company's Management propagates positive values of cooperation and relations within the company.
- The staff feel acquainted with the Code of Ethics, and many know how to contact the Ethics Officer.
- The suggested improvement in terms of the Code of Ethics concerns workplace relationships – it is of crucial importance to improve communication between superiors and other staff.

Fig. 5. Display of organizational culture GK LW Bogdanka SA. Source: own work on the basis of [23]
Rys. 5. Obraz kultury organizacyjnej GK LW Bogdanka SA. Source: opracowanie własne na podstawie [23]

culture in their structures. After analysing the undertaken actions and initiatives, it is clear that they want to secure a good organisational culture. Both these entities employ appropriate measures related to HR policy. The companies are aware of the need to diversify their tools for the various generations which will use them. Presenting the characteristics of the baby boomers, Generation X, and Generation Y, and the awareness of these, allows one to intentionally and deliberately shape an HR policy contributing to an improvement in the entity's organisational culture.

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Współczesny pracownik w kreowaniu poziomu kultury organizacyjnej w polskim przemyśle wydobywczym

W artykule opisano zależność występującą pomiędzy pracownikiem a kulturą organizacyjną firmy, w której on pracuje. W szczególności skupiono się na cechach dzisiejszych pracowników, wynikających z typologii pokoleń obecnie pracujących. Wskazano cechy charakterystyczne dla pokoleń baby boomer, pokolenia X i pokolenia Y. W praktycznej część pracy dokonano charakterystyki pracowników i polityki pracowniczej realizowanej w dwóch grupach działających w branży wydobywczej, Jastrzębskiej Spółce Węglowej SA oraz Lubelskim Węglu Bogdanka SA.

Słowa kluczowe: pracownik, kultura organizacyjna, pokolenie Y, przemysł wydobywczy

Analysing Data with the R Programming Language to Control Machine Operation

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Abstract

This article describes the benefits offered by the analysis of data from production processes. With the correct processing, such data allows issues to be identified both within the analysed process and in the ways machines are used. The paper presents an initial analysis of data from the fragmentation process in a hard coal mine using longwall shearers. The analysis is described using R programming language functions.

Keywords: data analysis, R language, analysing machine operation

Introduction

For many years now, effective management of any company has relied more and more extensively on quantitative methods. Analyses of large amounts of data, modelling, and simulations are becoming the basis for informed decision-making like in [3,4,5,6]. Such calculations have become widespread and easy to make as a result of the tremendous advancement of computer technologies.

By identifying issues in their production processes, companies can reduce production costs through avoiding long downtimes, reducing repair costs, enforcing and maintaining discipline among employees, and optimising machine uptime to ultimately enhance production processes. Appropriate lessons learned from the analysis of production-process data can also be the basis for the adjustment of machine operation procedures and troubleshooting.

IT personnel, who usually are well-versed in the details of individual processes, can develop software to control and analyse machines' and people' work. With contemporary programming languages, it is possible to quickly create applications that offer such functionalities, and if they use server databases which store information also from outside the controlled area, this facilitates a more general analysis of correlations between issues identified in production processes. In-depth analysis of production processes and the knowledge it offers can provide a company with competitive advantage, which is why businesses should employ advanced computing technologies to optimise their processes. [7]

The R programming language, which has been designed to support statistical computations, has recently been upgraded to handle data exploration. Examples of such computations were presented by [9].

Below you will see how the operation of a longwall shearer can be analysed using the R programming language by examining the electrical current drawn by its motors. This analysis is part of a larger system developed to support decision-making on the basis of an expert system. For more information on the system, see [1,2].

R programming language

R is an R software environment programming language and is designed mainly for the purposes of statistical computations. It is available under the GNU General Public Licence, so it is completely free of charge. Furthermore, as an open-source project, it is continuously expanded to include libraries of new functions available on the Internet as packages. Many users of this language claim that it can be used to develop any program, but what is of greatest benefit for analysts is that it supports modelling, testing, classification, clustering, time-series analysis, etc. What is also important to note are its capabilities related to the production of a wide range of high-quality graphs.

Another asset of the R software environment is its open-source package repository (Comprehensive R Archive Network, CRAN). It is a collection of libraries created by users from all around the world and includes relevant documentation. Commercial equivalents of such packages can be worth at least tens of thousands of zlotys. Anyone can upload their library to that repository to make it available to other people. With interfaces to many other programming languages, code for such additional libraries can be written not only in R, but also in Java, C or Fortran. [10]

R can be used to organise data in various structures, the simplest of which is a vector, i.e. a series of numbers arranged in a specific order. There are no simpler structures in R, so a single number is a vector with a length of 1. [11]

An analysis example

The example provided below shows the basic analysis of the operation of a longwall shearer on the basis of the current drawn by its four motors. A similar analysis, carried out on the basis of a spreadsheet and the VBA language, was provided by [8]. Shearer motors are responsible for its movement, coal-cutting action, and power-cable handling. Their symbols are presented in Table 1 below.

The electronic system on board of the shearer measures the current drawn at each of the four sensors every second. Then these data are immediately communicated to the database, from which it can be analysed with a negligible delay.

Tab. 1. Shearer motor symbols. Source: Author
Tab 1. Oznaczenia silników kombajnu

Motor	description	No.
M1	Coal-cutting component	2992
M2	Cable-carrier tensioner	2919
M3	Main drive	2871
M4	Auxiliary drive	2895

The data are communicated as three key-value pairs, including motor number, reading date and time, and current. In order to avoid unnecessary data recording during shearer downtime, a solution was adopted to communicate data only if the current changed between 1-second intervals. This helped reduce the number of recorded data. When a motor is turned off, its current is zero and is recorded as such in the database with its timestamp. The next piece of data will be recorded for a time when the measurement is greater than zero, so that no data is recorded for motor downtime. Any downtime can be computed on the basis of the difference between consecutive timestamps. To analyse machine operation, an additional algorithm has to be used to identify and parse any gaps in changes to current values.

Importing data to the R programming language

Originally, measurement data is stored as csv (comma separated values) files, in which, as its name suggests, the data has the form of rows with values separated by commas.

In the R programming language, such data can be imported using the function read.csv:

```
data <- read.csv(file=”prady1.csv”,sep=”;”, header=TRUE, dec=”.”)
```

This imports the data from the csv file into computer’s operating memory as a data frame named “data”.

Data decompression

Data can only be analysed after they are converted back into their original form. This is achieved through a function designed to read each row from the data array and complete it with subsequent rows containing timestamps (at one-second intervals) and the last recorded current. This action is performed as many times as indicated by the time between the consecutive rows of compressed data. This cycle is repeated for the time interval specified in the function parameters. The other parameters of the function, in addition to the start and end times, include data frame name and the name of the motor for which the data is to be decompressed. The signature of this function is presented below with comments.

```
decPrady <- function(dt, motor, st, en){
   ‘dt – compressed data frame
   ‘motor – motor number
   ‘st – start time
   ‘en - end time
  ‘filtering data that meet the time and motor number
criteria
      dx <- filter(dt,time>=as.double(strptime(st,format=”%Y-%m-%d %H:%M:%S”)),
       time<=as.double(strptime(en,format=”%Y-%m-%d
%H:%M:%S”)),motor_no==motor)
  ‘reading the number of data that meet the criteria
  cx <- as.integer(count(dx))
  ‘preparing a vector for the loop
  x <- c(2:cx)
  ‘reading the first time value
  k <- dx[1,2]
  ‘preparing a current vector
  nt <- dx[1,3]
  ‘preparing an empty data frame
  d <- filter(dx,time==0)
  ‘looping through filtered data
  for(i in x){
    ‘preparing a vector with missing timestamps
    c1 <- (k:dx[i,2])
   ‘eliminating the first element in vectors with more than
1 element
    if (length(c1)>1) c1 <- head(c1,-1)
    ‘timestamp loop
    for(j in c1) {
      ‘inserting parsed time and current values into the
prepared data frame
        d <- rbind(d, data.frame(motor_no=motor,time=-
j,electr_curr=nt))
    }
  }
‘returning decompressed data frame
return(d)
}
```

Data is decompressed when the function is called with accurate arguments:

```
d <- decPrady(data, 2992, “2013-04-02 10:30:00”,
“2013-04-02 11:21:00”)
```

The resulting data frame d contains data about the current drawn by motor 2992 every second.

Analysis of electrical current

The R programming language makes it possible to create box plots, which can be used to identify the basic characteristics of data. The lower side of the rectangle corresponds to the first data quartile (Q1), the line inside the rectangle corresponds to the median (Q2), and the upper side of the rectangle is the third quartile (Q3). Below and above the rectangle there are whiskers, which indicate the limits beyond which outliers can be identified. The ends of the whiskers are determined as

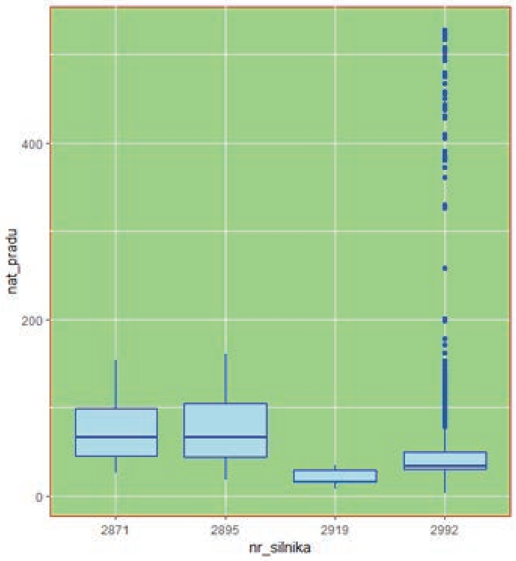

Fig. 1 Current distribution. Source: Author [x – motor¬¬_no., y – electr_curr]
Rys. 1. Aktualny rozkład

follows on the basis of the interquartile range (IQR):

start of the upper whisker:

$W1 = Q1 - 1.5 * IQR$,

end of the upper whisker:

$W2=Q3 + 1.5 * IQR$,

where $IQR = Q3 - Q1$

If the data contains values lower than W1, or greater than W2, these are treated as outliers and should not be taken into account during the development of the model, but, on the other hand, should be analysed to explain them.

Fig. 3 shows a box plot for the distribution of recorded current drawn by machine’s motors. This data visualisation accounts only for values greater than zero.

The graph was created in the R programming language, using the ggplot function.

```
ggplot(data=filter(data2,electr_curr>0))+geom_boxplot(mapping=aes(y=electr_curr,
x=motor_no., group=motor_no))
```

Electrical current outliers can be observed (as individual points above the upper whisker) for the motor that powers the coal-cutting component (2992). Since such large current can cause damage, it is important to analyse what situations caused these surges to occur.

To identify outliers, the global dataset (exclusive of zeroes) needs to be processed to identify any data with current greater than W2. In the R programming language, this can be done as follows:

```
‘filtering the data to identify current values greater than zero
data2992gz <- filter(data2992,electr_curr>0)
‘calculating W2
W2 <- quantile(data2992gz$electr_curr,0.75)+1.5*IQR(data2992gz$electr_curr)
‘filtering the data to identify current values greater than W2
data2992ggw <- filter(data2992,electr_curr>W2)
```

As you can see in the graph (Fig. 1), the continuity of current values is disrupted as values reach around 200A. Therefore, for the purposes of further analysis, time data for values greater than 200A was identified.

```
t <- select(filter(data2992,electr_curr>200), time)
```

The identified times are the basis for finding in the primary data the currents at times immediately (by a second) preceding values greater than 200A.

```
filter(data2992,time %in% (t[,1]-1), electr_curr>0)
```

The resulting dataset contains only the data where current is equal to zero. This means that the data which were identified during the previous analysis as outliers are recorded when motor starts.

As a result, the electrical current during motor start was examined. This allowed the identification of the times when current at time t was equal to zero, but at time t+1 was greater than zero:

```
k <- select(filter(data2992,electr_curr==0, data2992[data2992$X+1,4]>0),time)
```

and then to identify current at times t+1

```
starts <- filter(data2992,time %in% (k[,1]+1), electr_curr>0)
```

The resulting dataset was the basis for the creation of a histogram (Fig. 2) which presents the distribution of current

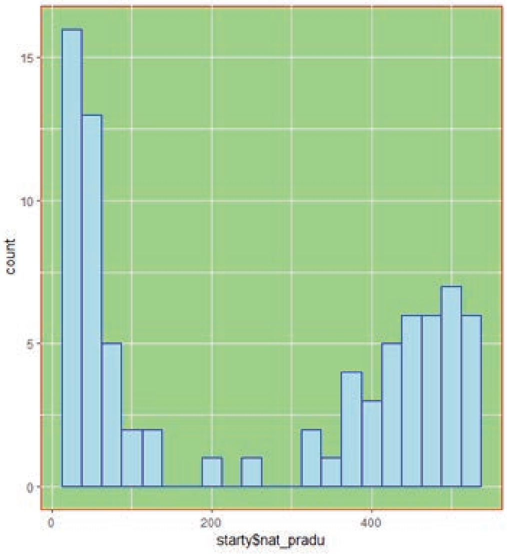

Fig. 2. Current distribution as motor starts. Source: Author [electr_curr starts]
Rys. 2. Aktualny rozkład w momencie startu

values during the first second after the motor starts.

```
ggplot(data=starts)+geom_histogram(mapping=aes(x=starts$electr_curr), binwidth=25)
```

The histogram presented in Fig. 2 shows two groups of data. The current values observed during motor start can be grouped into two ranges – up to around 150A and above 300A. There are also single data items between these two ranges, but these are marginal cases. Such distribution of data suggests two types of motor starts – with and without a load.

- softstart – without a load, is characterised by low motor current values,
- hardstart – with a load, characterised by high motor current values, which makes them undesirable, as they cause a significant increase in machine wear and failure rate. [Kesek, Zagórska, 2015]

Summary

Under current economic conditions, the accurate assessment of production processes is vital. It can help maximise machine use, reduce downtime, bring down repair costs, and, consequently, lower production costs and increase revenue by boosting production over time. With the right computer tools to analyse database input and process such data, production processes can deliver valuable knowledge.

While initially perhaps incomprehensible, the ways to use R programming language functions described in the article quickly become clear and useful, and the opportunities for automating such computations prove instrumental. What is also great about this language is its graph-generating capability, which can be tailored to one's needs with additional commands. Another important functionality of R is its communication with databases through the ODBC interface, which makes it useful for analytical purposes in complex database systems.

The performed analysis produced a dataset with critical cases where electrical current during motor start was high. These findings can be used to individually examine each case identified during the analysed time period.

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Analiza danych z wykorzystaniem języka R w kontroli pracy maszyn

W artykule przybliżono korzyści płynące z analizy danych pochodzących z procesu produkcyjnego. Odpowiednia ich analiza pozwala na wykrywanie nieprawidłowości zarówno w realizowanym procesie, jak i w sposobie użycia maszyn. Zaprezentowano wstępną analizę danych pochodzących z procesu urabiania w kopalni węgla kamiennego za pomocą kombajnu ścianowego. Przedstawiono sposób prowadzenia analizy z wykorzystaniem funkcji języka R.

Słowa kluczowe: data analysis, R language, analysing machine operation

Volatility in the Raw Materials Market and Risk Mitigation Methods

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Abstract

Companies in the raw materials market operate in a volatile and unstable market. Business downturns exert a particular effect on the level of cash flows and generate insolvency risk among companies, all the more so when crises are driven by objective circumstances beyond human control. Being well-versed with these risks, a company should take steps to mitigate the risk of raw materials price volatility affecting the planned results in at least the medium term. The subject of this analysis is to point out the interdependencies between the basic economic categories when it comes to how the steel market functions and the risks stemming from the volatility of the raw materials market. Moreover, it portrays the main financial instruments that can be used to mitigate the consequences of the risk of movement of raw materials prices.

Keywords: financial risk, hedging, risk mitigation

Introduction

The stable operation of a company and its development are driven by macroeconomic factors and the ability to secure sources of funding business on the debt market as well as using financial instruments to hedge risk. This analysis assumes that growth is driven by the consumption of goods manufactured by the company and the resultant development of other industries. Therefore, one may venture to assert that three key elements should be analyzed whether during business cycle upturns or during a crisis, i.e.:

- to what extent GDP, population and the production of steel and coking coal are related,
- to what extent random events affect price volatility in raw materials markets, thereby contributing to corporate performance,
- how can the risks of random events be mitigated through the selection of optimal hedging instruments.

During business downturns the prices of raw materials bottom out. Sharp price decreases affect the profitability of companies operating in the raw materials sector: in recent years these companies have experienced greater turbulence than companies in other sectors. These circumstances are also unpredictable due to objective conditions beyond a company's control. Hence these companies need financial instruments to be able to hedge effectively the risk of prices falling and efficiently manage the volatility of raw materials prices.

This article endeavors to illustrate the nature of the relations between economic categories such as the population, GDP, coking coal consumption and steel production. The relevance of factors beyond a company's control is referenced and selected instruments to hedge price risk related to raw materials are presented.

Volatility of the raw materials market

As G.A. Holton points out, risk entails two indispensable factors: exposure and uncertainty. Precisely this risk weighs heavily on raw materials markets and related markets. The steel market and coking coal consumption play a major role in the global economy, generating GDP linked to consumption levels. The financial statements of major companies in the mining industry have been analyzed. On this basis one may claim that the raw materials industry heavily hinges on the business cycle phase and on related markets such as the steel market.

M. Krzak and A. Paulo also note that global steel production and consumption have risen over a century very unevenly, outpacing population growth. Four periods were observed: slow growth before 1945, post-war acceleration in 1945–1980, slowdown in 1980–2000 and rapid acceleration driven by China after 2000. The disruptions to economic growth precipitated by financial and economic crises in 1929–1932 and 2008–2009 were reflected in steel production levels and proved to be of short duration. Moreover, the authors note that urbanization is a global economic phenomenon. It extends to the construction industry as it employs reinforced concrete on a great scale, travel and transport infrastructure, mechanical vehicles, household appliances, sewage systems, etc. This is particularly visible in developing countries. The authors stress that urbanization is likely to trigger higher demand and thereby elevated steel production. They write that an important premise for forecasts concerning iron raw materials market is the assessment of demographic growth, while this growth is a factor stimulating consumption and production, as confirmed in the analysis presented in this article in the context of coking coal consumption in steel production.

The analyzed financial statements of companies in the raw materials industry indicate that the steel market is dominated by global smelting conglomerates, with steel manufacturing being increasingly concentrated in Asia. In 2015 the global production of raw steel recorded its first downswing since 2009. The greatest decrease in terms of tonnage was recorded in Asia where steel production slumped 26m tons (2.3% y/y). China, which accounts for 49.5% of global output recorded a drop of 19m tons (2.3% y/y). Lower steel production was also recorded in Japan, Korea and Taiwan. The region with the steepest decline in 2015 was North America where production decreased by almost 9% from 2014. That was caused by steel production in the US falling by as much as 10.5%. Raw steel production in South America dipped 2.5%. Total steel production in Europe in 2015 was 304m tons, which was 3.2% lower than 2014. Steel production in the European Union dropped by over 3m tons, while in the CIS it fell by 4.5m tons.

Price drops and the coal glut on global markets triggered significant deterioration of the financial standing of numerous companies in the mining industry, leading many of them to bankruptcy or business suspension or curtailment. Many coking coal producers pursued profound restructuring plans to align their operations to the soft market. Some producers sold selected mining assets and the entire industry implemented comprehensive cost cutting plans. US producers, including Alpha Natural Resources, Arch Coal, Mechel, Patriot Coal, Walter Energy, James River and Suncoke announced they would limit their coal mining operations. Australian mining companies, including BHP, Peabody, Glencore and Yancoal also announced their attention to cut back on coal mining. The implementation of restructuring plans entailed planned or actual downsizing in the largest coal mining companies across the world. The total reduction in coking coal production worldwide at approx. 50m tons was announced. Due to the coking coal glut on the market, in 2015 coal prices posted their lowest levels since 2009.

To determine the interdependencies among the key indicators of the raw material market and related markets, their performance in 2006-2015 was examined. In that period the global economy underwent a full economic cycle, i.e. its business trough in 2008-2009, economic expansion in 2011-2013 and another deep downturn in 2015 with a rebound at the turn of 2016 and 2017.

The purpose of the analysis was to determine the nature of the relation between the independent variable (steel production, population and GDP) and the dependent variable (coking coal consumption) with coking coal being a strategic raw material in the production of steel needed in the process of manufacturing environmentally-friendly goods such as electrical cars, wind farms, etc.).

Linear models were employed to conduct this analysis. The period of 2006-2015 was studied. The analysis drew on information from standalone and consolidated quarterly financial statements of companies in the raw materials sector as well as data from the website World Development Indicators.

The analysis consisted in selecting the data and building an appropriate model. In order to examine the interdependencies between the variables and estimate the parameter for a given value of the independent variable, the least squares method was used. For example, the impact of coal consumption on steel production, population and GDP was to be determined. Simple linear regression was adjusted to determine the population, steel production and GDP for a given value of coal production. To make the linear regression analysis applicable, the following requirements were assumed to be met:

- observations must be independent.
- The dependent variable Y must be random.

The use of linear regression analysis allowed us to determine whether two variables are related without having to draw any conclusions on a cause and effect relationship.

Stepwise regression was used for the analysis. Stepwise regression is an automated tool used to build the best model for selected variables. The process automatically returns the most relevant variable or removes the least relevant variable with each step. The results below show the regression models after the tool's use. To examine whether there is a relation between coking coal consumption and population, steel production and GDP on individual continents, separate linear regression analyses were made for each continent.

Africa

The data in table 1 below show that the estimator value for population in millions is 1.33×10^{-5}. The coefficient indicates that as the population grows by one million, coking coal consumption may be expected to grow on average by 1.33×10^{-5} Mt.

Based on the analysis, we note that only population is statistically significant as a predictor ($p<0.01$).

The model explains 58% of the variability of the dependent variable around the mean.

Asia

The regression result indicates that the "steel production" variable is statistically significant ($p<0.001$). The value of this estimator in Mt is 0.52933. With steel production growth of 1 Mt, coal consumption rises 0.52933 Mt.

The model explains 97% of the variability of the dependent variable around the mean.

Australia

Population is statistically significant as a predictor ($p<0.01$). The value of this estimator in millions is 1.262×10^{-2}. The coefficient indicates that each additional million inhabitants in population leads coking coal consumption to grow on average by 1.262×10^{-2} Mt.

The model explains 81% of the variability of the dependent variable around the mean.

Europe

Population, steel production and GDP are statistically significant predictors. The p-value for steel production is lower than 0.001, for population it is lower than 0.01, and for GDP it is lower than 0.05. The value of the estimator for steel production is 8.813×10^{-2}, for population it is -3.431×10^{-4}, and for GDP it is -4.876×10^{-13}.

The model shows that as steel production grows by 1 Mt, coal consumption rises 8.813×10^{-2} Mt. When population or GDP increases by a million, coking coal consumption falls 3.431×10^{-4} and 4.876×10^{-13} Mt, respectively. All predictors explained 97% of the variability of the dependent variable.

Tab. 1. Coking coal consumption and population
Tab. 1. Zużycie węgla koksowego a liczba ludności

	Estimator value	Standard error	t-value	alue
Intercept	-9.653×10	3.740×10	-2.581	2738
Population	1.33×10^{-5}	3.599×10^{-6}	3.696	0414
Determination coefficient	0.5774			
P-value of the model	0.004135			

Tab. 2. Increase in steel production and coking coal consumption in Asia
Tab. 2. Wzrost produkcji stali a zużycie węgla koksowego w Azji

	Estimator value	Standard error	t-value	alue
Intercept	43.80486	26.77427	1.636	
Steel production	0.52933	0.02917	18.144	
Determination coefficient				
P-value of the model				

Tab. 3. Population and increase in steel production in Australia
Tab. 3. Liczba ludności a wzrost produkcji stali w Australii

	Estimator value	Standard error	t-value	
Intercept	2.633×10^{2}	9.102×10	2.892	
Steel production	8.813×10^{-2}	1.556×10^{-2}	5.663	
Population	-3.431×10^{-4}	1.246×10^{-4}	-2.753	
GDP	-4.876×10^{-13}	1.532×10^{-13}	-3.183	
Determination coefficient				
P-value of the model				

Tab. 4. Steel production and coking coal consumption in Europe
Tab. 4. Produkcja stali a zużycie węgla koksowego w Europie

	Estimator value	Standard error	t-value	p-value
Intercept	-2.821×10^{2}	8.990×10	-3.138	0.01197
Population	1.262×10^{-2}	3.052×10^{-3}	4.134	0.00254
GDP	-3.849×10^{-11}	1.757×10^{-11}	-2.190	0.05624
Determination coefficient	0.8097			
P-value of the model	0.0005722			

Tab. 5. Steel production and coal consumption in North America
Tab. 5. Produkcja stali a zużycie węgla w Ameryce Północnej

	Estimator value	**Standard error**	**t-value**	**p-value**
Intercept	-1.242×10^{3}	5.688×10^{2}	-2.191	0.0598
Steel production	7.316×10^{-1}	3.414×10^{-1}	2.143	0.0645
GDP	-1.636×10^{-11}	1.104×10^{-11}	-1.482	0.1767
Population	4.424×10^{-3}	2.098×10^{-3}	2.109	0.0680
Determination coefficient	0.7322			
P-value of the model	0.01122			

Tab. 6. Increase in steel production and coking coal consumption
Tab. 6. Wzrost produkcji stali a zużycie węgla koksowego

	Estimator value	**Standard error**	**t-value**	**p-value**
Intercept	-3.522×10	9.348×10	-3.800	0.00524
Steel production	1.778×10^{-1}	6.219×10^{-2}	2.860	0.02116
GDP	-2.727×10^{-13}	1.694×10^{-13}	-1.610	0.14607
Population	5.599×10^{-5}	1.518×10^{-5}	3.689	0.00614
Determination coefficient	0.8149			
P-value of the model	0.01122			

North America

The table above shows that steel production and population are statistically significant predictors ($p<0.1$). GDP is not a statistically significant predictor; its value is higher than the significance level 0.1.

Based on the estimated parameters it may be noted that as steel production grows by 1 Mt, coal consumption growth of 7.316×10^{-1} may be expected. If the population grows by a million, coal consumption will increase by 4.424×10^{-3} Mt.

The model explains 73% of the variability of the dependent variable.

North and Central America

Steel production and population are statistically significant predictors.

Based on the regression analysis, as steel production rises by 1 Mt, coking coal consumption may be expected to grow by 1.778×10^{-1} Mt. With a population increase of a million, coal production will grow by 5.599×10^{-5} Mt.

The model explains 81% of the variability of the dependent variable around the mean.

Various dependencies between coking coal consumption and other variables result from the above regression analysis. The dependence between coal consumption and population was observed in Africa, Australia, Europe, North America, South and Central America. The analysis showed significant correlation between coking coal consumption and steel production in Asia, Europe, North America, South and Central America. The dependence between coal production and GDP was observed only in Europe.

One may venture to claim that companies operating in the raw materials sector are largely exposed to objective stimuli fundamentally beyond their control. Likewise, a crisis in consumption may contribute to the emergence of crisis foci, which are also significantly enhanced by natural factors. Information published by a leading company in the mining industry concerning relevant factors contributing to coking coal price levels (TSI HCC Premium $/t FOB Australia) is presented below:

- 2Q2017 – cyclone Debbie (constraints in extraction and transport) – price growth to approximately $314/t;
- 2Q2017 – opening of a railway line in Queensland and greater export opportunities – price decline to $140/t,
- 3Q2017 – force majeure in South, strike in Oaky North, Hunter Valley, extraction problems in China, high margins on steel – price above $200/t,
- 4Q2017 – pressure to cut spot prices – availability of spot loads and announced cuts in steel and coke production in China – price at approximately $180/t,
- 4Q2017 – shortages in the supply of HCC premium coal, logistic problems in Australia and USA – over $263/t,
- turn of 2017/2018 – gridlock in an Australian port, ships wait over 3 weeks to be loaded compared with the average of 10 days, supply problems of producers in Australia – price at approximately $260/t,
- 1Q2018 – clearing of the bottleneck in an Australian port, higher coal supply, downward trend in steel and coke market - price at approximately $214/t,

- 2Q2018 – dispute concerning the Australian Aurizon railways, steel market in China exhibits upward trend – price at approximately $180/t,
- 3Q2018 – rebuilding of coking coal inventories after the monsoon season in India and replenishing of stock before winter in China – price at $180/t,
- 3Q2018 – fire and announcement of a force majeure event in the North Goonyella mine in Australia – price growth to approximately $200/t,
- 4Q2018 – fear of cyclone Owen in the Queensland region contributed to elevated coking coal purchases to secure volume before the cyclone – price growth to approximately $220/t.

After the soft period of 2014-2016, the coal price rebounded in 2017. The demand for steel is generated above all by investments: in the construction industry (this sector accounts for almost half of domestic steel consumption), roads, energy and railways. Also, the construction and machinery industry, ship building, household appliances sector and automotive industry are major consumers of steel. However, as presented above, economic growth is supported not only by attempted reconstruction after a downturn, but also by relevant random factors beyond a company's control.

Selected methods of managing raw materials price risk

As noted by R. Węgrzyn , the role of risk management in a company increases in particular in turbulent times in financial markets. From the vantage point of risk mitigation it is important to curtail the risk of lower future financial results exposed to fluctuations in the prices of products and the costs of materials, energy and services, in particular cash flows; determine the maximum level of cash in the company to secure continuity of the core business and secure continuity of investment, that is the business targets defined in the strategy and ensure stability during business downturns.

Throughout the business cycle a company is affected by a series of risks influencing its financial condition and cash position. The risks include:

- currency risk related to the index quotations for main products,
- counterparty risk related mainly to the assessment of creditworthiness (credit risk) of the financial institution with which hedging transactions and derivatives are concluded, and the assessment of a counterparty's creditworthiness,
- liquidity risk related to the loss or curtailment of the ability to pay current payables and unplanned expenditures under a given trade,
- operating risk resulting from the structure and implementation of risk management processes in a company's on-going operations (e.g. IT risk, legal risk, etc.).

Apart from these risks, A. Węgrzyn also enumerates business risk, legal risk and event risk. Therefore, it is not difficult to observe that throughout the business cycle a company – regardless of the sector in which it operates – uses hedging instruments suitable for the type of operations without the possibility of affecting macroeconomic factors. Mining sector companies are particularly susceptible to fluctuations in the prices of raw materials.

Steps taken to hedge the risk of raw materials prices focus on crafting a risk management strategy. Hedging is an effective tool to overcome the adverse effects of price movement to stabilize cash flow. As stated by M. Baxter , each market practitioner selling derivative instruments for its own account will say that hedging is the key to valuation.

Hedging is the basic function of every commodity market. The basic philosophy that underlies hedging is its use as a form of protection against sudden changes in market prices. Additionally, it is a mechanism for price discovery on organized exchanges and contains no speculative elements, hence it should not be treated as an instrument to generate income but merely as a tool to stabilize cash flow.

Other goals pursued as part of raw materials price risk management are to reduce financial market volatility, increase the likelihood of achieving the owner's strategic assumptions, increase the likelihood of maintaining financial liquidity and optimum financial results and secure funds in the future proceeds for investment activities. Equally important tasks include the reduction of revenue sensitivity to lower prices of raw materials and currency exchange rates.

The choice of the nature of the transaction should take into account the cost of implementing a given hedging strategy (e.g. the premium to buy an option) and depends on the flexibility of this strategy (e.g. the possibility of using price increases in raw materials markets) as well as on the expected financial situation of the company. As part of hedging strategies and hedging transactions companies use the following instruments:

- futures / forward contracts,
- commodity swap contracts,
- sell options for acquired commodities.

In the futures / forward contracts the core group comprises forward contracts. A forward contract is a contract concluded at present, obliging the party unconditionally (regardless of any future circumstances) to buy or sell a quantity of foreign currency or another underlying instrument at a set term in the future at the exchange rate agreed by the parties at the time of concluding the contract. A forward contract is an over-the-counter contract with one of its parties usually being a bank. Both parties to the contract agree the contract terms and conditions such as the quantity of the underlying instrument, term of fulfilment. The bank specifies (quotes) the price of the contract and the price may be negotiable. At the moment of concluding the contract neither party makes a payment, while contract settlement occurs at the term. The futures contract is a contract on the stock exchange in which the parties thereto take appropriate positions by placing their buy and sell orders. The terms and conditions of the contract such as the quantity of the underlying instrument and term of fulfilment (that is expiry term) are determined by the stock exchange. In turn, the parties to the contract determine the contract price by placing their orders.

A swap contract is a derivative instrument in which two parties to the contract undertake to make payments to each other at determined moments in the future. Swap contracts consist in simultaneous both parties buying and selling series of financial streams characterized by a fixed or floating interest rate, in the same or difference currencies whose value is considered to be equal by the parties to the transaction at the moment of concluding the contract.

An option is the other fundamental derivative. It differs from other derivatives by being an asymmetrical instrument. There are two basic types of options: a call option (also called a call) and a put option (also called a put). A call option is the right to buy a determined quantity of the underlying instrument at a determined price at a specific term. A put option is the right to sell a determined quantity of the underlying instrument at a determined price at a specific term. A call option (a call) is the right to receive at a specific term an amount of money depending on the difference between the value of the underlying instrument and the strike price. A put option (a put) is the right to receive at a specific term an amount of money depending on the difference between the value of the underlying instrument and the strike price .

The optimum hedging strategy, including the choice of instruments, should begin with understanding the changing market and determining the main market variables. Apart from developing a risk map, the key activities include:

- analysis of exposure to price risk,
- analysis of the market situation of raw materials and hedging instruments,
- determining the volume to be hedged,
- time horizon of hedging and selection of optimum hedging instruments,
- preparation and analysis of hedging scenarios,
- preparing an analysis of potential effects of hedging strategy implementation,
- assessment,
- concluding of a hedging transaction and its monitoring.

As the raw materials market is extremely unstable, the hedging strategy should first of all use natural hedging by transferring the risk of changes in raw materials prices to offtakers, e.g. by agreeing a fixed contractual price.

After exhausting the possibilities offered by natural hedges, hedging activities that rely on derivative transactions in operational hedging and strategic hedging are used. Derivative transactions should have the following characteristics:

- liquidity in the derivative instrument market should be aligned to the scale of hedging followed by a company,
- have an opposite risk profile to offset the risk profile resulting from exposure,
- their quotations are based on the same future price curve as the curve constituting the base for determining changes in the reference index value in contracts positing physical delivery,
- the company has the ability to conduct independent valuation of these trades.

As I. Šperanda and Z. Tršinski write, in the contemporary political and economic world the level of uncertainty is extremely high. Numerous political, social and other factors may affect the prices of various instruments and commodities in global markets. Effective and broadly used hedging instruments offer protection against these price fluctuations. Hedging methods were developed by contemporary brokers and managers in response to the high risk of loss potential. Global trade, liberalization of nearly all world economies and ever broader opportunities of trade in futures markets gave rise to hedging. That is why the primary role of hedging as a futures contract is to protect a business against risk, i.e. against rapid and significant increase / decrease in commodity prices or international service market.

The authors write further that risk refers to the possibility and, to a certain degree, the probability of the occurrence of an event with adverse effects. Therefore, risk and business results are negatively correlated. The fact that business in a highly globalized world is risky is beyond doubt. This trend will become more pronounced in the future.

An important issue raised in the publication of S. Lleo and W. T. Ziemba entitled: How to Lose Money in Derivatives: Examples From Hedge Funds and Bank Trading Departments is the choice of institution with whose participation a company conducts its hedging transactions as well as the risk appetite a company has taking into account opportunities and threats.

Conclusion

The practices pursued by companies in the raw materials sector worldwide indicate that raw materials risk is one of the actively managed risks. Derivatives are commonly used to manage this risk. They are a response to the current, changing economic situation as well as an attempt to offset the effects of objective random events. However, the most important purpose of these practices is to stabilize cash flows and financial results in the medium term. The price level of raw materials is also affected by global events beyond a company's control (e.g. weather events, competitors' logistic problems). They may significantly undermine financial liquidity. A company's identification of its key tasks in raw materials price risk management, division of responsibilities, analysis of risk exposure and market situation, as well as sensitivity and scenario analysis constitute a pillar in the correct completion of the process. One pillar of success will be to articulate a correct hedging strategy based on which a company enters into transactions and subsequently monitors their performance in the form of duly posted records in financial accounts, settlements and management accounting.

As C.J. Hull and E. Dziawgo write, the skillful use of derivative instruments is one of the most efficient ways to manage financial risk. The financial leverage effect that can be obtained by using derivative instruments in financial transactions professionally enhances the attractiveness of these instruments, since significant transaction values may be obtained with low capital exposure. .

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Zmienność rynku surowców i wybrane instrumenty finansowe ograniczenia tego ryzyka

Przedsiębiorstwa branży surowcowej funkcjonują na zmiennym i niestabilnym rynku. Okresy dekoniunktury w szczególny sposób wpływają na poziom przepływów pieniężnych i generują ryzyko niewypłacalności spółek, tym bardziej że kryzysy wspierane są przez obiektywne okoliczności, na które człowiek nie ma wpływu. Mając wiedzę o tych ryzykach, przedsiębiorstwo powinno podjąć działania ograniczenia wpływu ryzyka zmienności cen surowców na planowane wyniki w okresie co najmniej średnioterminowym. Przedmiotem analizy jest wskazanie zależności pomiędzy podstawowymi kategoriami ekonomicznymi w aspekcie funkcjonowania rynku stalowego oraz ryzyk wynikających ze zmienności rynku surowcowego. Zaprezentowane zostały ponadto podstawowe instrumenty finansowe, które mogą złagodzić skutki ryzyka zmiany cen surowców.

Słowa kluczowe: ryzyko finansowe, hedging, mitygowanie ryzyka

The Impact of the Management System on Developing Occupational Safety Awareness Among Employees

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Abstract

This paper discusses the subject of occupational safety using the example of a leading hard coal mining company in Poland. It presents some examples of occupational safety management systems implemented and functioning in enterprises. It also characterises the role of awareness in developing the appropriate attitudes and conduct among employees in the workplace. The paper presents the selected results of surveys conducted among the executive employees of JSW S.A. The obtained results served as the basis for preparing preliminary conclusions and identifying potential areas for further studies in this field.

Keywords: occupational safety, mining enterprise, management systems, employee awareness

Introduction

Contemporary enterprises are interested in adopting consistent actions to improve the occupational safety of their employees. To this end, they implement health and safety management systems, and adopt innovative methods. The efficacy and effectiveness of these actions requires conducting them as part of a structured management system in place at these organisations. The OHS management system itself is also part of an enterprise or institution management system, the objective of which is to ensure the implementation of tasks connected with the management of occupational risk in the workplace environment [2]. The idea behind such a system involves the full involvement of the executives and each employee in activities aimed at occupational safety improvement [6]. The correct deployment of such a system is desirable both as a response to public expectations and as an opportunity to obtain positive company-wide and countrywide economic effects.

The concept of safety is not directly used in this paper, but it is difficult to discuss the risk or threats connected with performing a job without referring to this general concept. The employees' individual features, and especially their needs, may be a very important source of motivation promoting healthy and safe behaviour. According to the best-known classification of human needs by A.H. Maslow, they can be divided into basic needs and motivational needs. The most important basic needs are physiological needs, and safety needs are just behind them [3]. Psychologists understand safety more as a person's mental, emotional and material stability than as the lack of physical injuries and occupational diseases. This interpretation is closer to the understanding of safety in the context of performing professional work.

Poland's accession to the European Union has led to the publication of Polish ISO standards (18000) containing a definition of occupational health and safety, which is as follows: "The status of the work conditions and organisation and employee behaviour ensuring the required level of health and life protection against the threats present in the work environment" [10].

This paper contains a review of the occupational health and safety management systems implemented and operating at Polish mining enterprises. Anonymous surveys filled in by managers at one of the Polish coal mining enterprises were used for this purpose. Identifying weaknesses is a key element in implementing remedial action and improving safety [5]. This allows the process of continuous improvement, which is essential for the organisation's correct functioning, as it enables it to gain a competitive advantage [8].

The occupational health and safety management system in an enterprise

Enterprises which introduce occupational health and safety management systems (OHSMS) are looking to obtain measurable benefits connected with employee safety, as well as measurable economic benefits. The functioning of every occupational health and safety management system is based on legal documents, particularly the Constitution of the Republic of Poland and the Labour Code [13,14].One of the most important provisions of the Labour Code is Article 207, which clearly states that it is the Employer who "is responsible for the state of occupational health and safety in the workplace." This obliges the Employer to protect the health and life of employees by ensuring the safe and healthy conditions of work with appropriate use of scientific and technological achievements.

There are a number of safety management systems, and it is up to the enterprise's executives to make the decision about which system will be the best suited to a given company's capabilities and needs. Polish enterprises usually have systems in place based on the following standards:

- PN-N-18001:2004,
- OHSAS 18001:2007,
- ISRS: 2007,
- SCC,
- SEVESO II.

Tab. 1. Milestones in OHS management. Source: authors' work based on "Zarządzanie bezpieczeństwem pracy" (Occupational safety management) Karczewski, 2012 [7]

Tab. 1. Kamienie milowe w zarządzaniu BHP

Period	Event
Early 19th century	Recognising accidents
1930s	Personal protective equipment and covers
1940s÷50s	Ergonomics
1960s	Technical safety
1970s	Risk analysis – the human factor
1980s	Organisation and safety
1990s	Occupational safety management systems
21st century	A culture of occupational safety

The choice and implementation of the OHS management system is often connected with the size and economic capabilities of the enterprise. Safety Health Environment Checklist Contractors (SCC) systems are meant for small companies and are developed on the basis of formulated mandatory and additional questions. For large enterprises, it is much more common to use extended OHS management systems, i.e. PN-N-18001 or ISRS, which distinguish several monitoring and audit areas. Additional systems are often integrated with other systems functioning in enterprises, such as:

- ISO 9001 – requirements for the quality management system,
- ISO 14001 – requirements for environmental management,
- ISO 22000 – requirements for the food safety management system,
- ISO 27001 – requirements for information security management,
- ISO 50001 – requirements for energy management.

The benefits from implementing an OHS management system in an enterprise include primarily:

- reducing the level of occupational risk,
- regulating the formal and legal status,
- increasing the personnel's awareness of the nature of OHS issues,
- an actual improvement in the working conditions,
- quick detection and elimination of potential non-compliances by prevention, not correction,
- a smaller number of employees exposed to harmful factors as a result of identifying threats and implementing specific actions,
- reducing the number of accidents (supervision over near misses),
- a lower number of employees suffering from occupational diseases,
- reducing the number of sick leaves,
- boosting the company's credibility,
- building the company's image as a Safe Enterprise,
- meeting the expectations of employees and customers,
- improving work efficiency,
- improving the relationship between the employer and supervisory bodies in the field of working conditions.

Running an enterprise under the conditions of a free market and competition requires the introduction of innovative management methods to facilitate better functioning in a changing environment. Effective tools assisting the activities of an enterprise include occupational safety management systems based on Polish and international standards. Occupational safety management has a relatively short history, as it dates back to the 1990s. It is assumed that the first comprehensive occupational safety management system based on occupational risk assessment was created by W.G. Johnson. In his book, MORT Safety Assurance Systems, he described a concept of formal risk acceptance by a company's management, acceptable risk and the reason for an accident as a consequence of the adopted risk level [4]. The MORT system introduced in the U.S. energy sector largely contributed to the appreciation of a safety management system consisting of the product of the probability of an incident and the extent of the related result. Replacing danger with risk was a milestone in the progress towards rationalising occupational safety management. Through this, occupational safety management has become an integral part of managing an enterprise, which is profitable in terms of improving economic status. Table 1 presents the decades and events that marked the milestones in the development of occupational safety.

It should also be noted that the concept of the occupational safety management systems being developed differed between Europe and overseas countries (USA, Japan). In Europe, safe work was largely understood as aspects aimed at preventing threats to employees or people present in the workplace (enterprise). By comparison, in the USA the concept of occupational safety was extended to include issues connected with protecting the company's property, production and service safety, and safe products. Such a different approach to occupational safety management is a factor that determines effectiveness and profitability. It can be stated that the more extensive the risk assessment and analysis, the greater the chance to develop an effective occupational safety management system. Furthermore, emphasising the significance of the human factor is currently an important element of the culture of occupational safety. The level of safety in an enterprise is shaped by the daily behaviour of all employees, which results from their beliefs and values. For this reason, many contemporary companies implement employee conduct improvement programmes as some of the most important elements of their occupational safety management

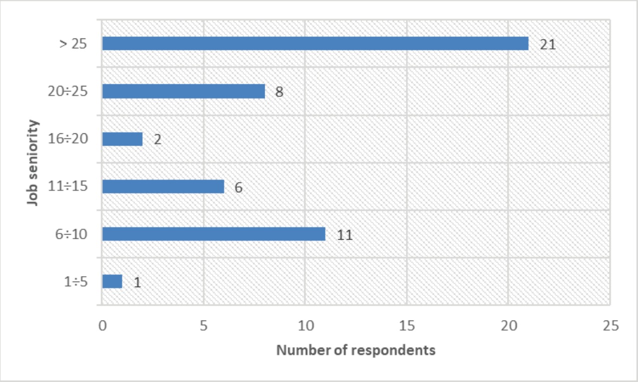

Fig. 1 The job seniorities of employees covered by the survey. Source: prepared by the author, 2019
Rys. 1. Staż pracy pracowników objętych ankietą

systems [1]. The requirement to have such a programme in place is mandatory under the SCC.

Employee awareness in developing safe attitudes and conduct

Awareness, or consciousness, is a vast concept used within many social sciences. These include philosophy, psychology, sociology, history, law and education studies. Philosophy and psychology provide us with the most complete knowledge about awareness. In philosophy, being aware initially referred to the sense of experiencing the world, directly feeling something, feeling present within the inner perception – the area of consciousness. Psychology offers a similar definition, describing it as being conscious, awake or able to receive environmental stimuli. In a narrower, stricter and more human-specific sense , it is the highest level of mental development in which it is important to be aware of your own representation of reality and your activity within it. The representation of reality depends on the structure and functioning of the senses through which the human being receives information about what is going on in the external world, and within himself or herself, and on the structure and operation of the brain, which applies complex analysis and synthesis processes to the data received by the senses. In education studies, awareness means:

- the ability to perceive one's own conduct, its circumstances and consequences, which is characteristic of human beings,
- the human psyche, as a specific function of the central nervous system and the highest form of regulating the behaviour of humans, setting them apart from animals,
- the processes of receiving information and controlling human behaviour,
- the state of being aware, or conscious, in contrast to dreaming or loss of consciousness; psychoanalysis also distinguishes between the unconscious and the subconscious, and the ability to experience emotional states, i.e. the self.

Employee awareness in terms of occupational safety has an impact on the way of thinking and working of employees in a working environment [11]. The principal role in shaping awareness is played by all kinds of educational activities, starting from knowledge obtained at school, through workplace training and all forms of media education (television, radio, press), to promotional projects [9]. By developing awareness combined with appropriate knowledge, we prepare employees to behave and act in a desirable way. These actions will be effective if we achieve a state in which the employee is aware of the purpose and meaning of his or her actions, and the potential consequences for the public. Legal regulations oblige supervisory bodies and employers to provide occupational health and safety training to their personnel [13]. An organisation should adopt and maintain specific procedures to make its employees aware of:

- the types of threats present across the organisation and at individual workstations, and the occupational risk associated with them,
- the benefits for employees and organisations from eliminating hazards and reducing occupational risk,
- their tasks and responsibility in making their actions compliant with the occupational health and safety management policy, and the procedures and requirements of the occupational health and safety management system, along with the requirements concerning readiness for and responding to accidents and major accidents at work,
- the potential consequences of non-compliance with the specified procedures.

Actively engaging employees in occupational health and safety management processes facilitates achieving both general and specific objectives [12].

Surveys among JSW S.A.'s executive employees

An important element in an implemented occupational safety management system is the knowledge and awareness of the enterprise's employees. A survey was conducted in November 2018 to obtain answers to the question regarding the awareness of JSW S.A.'s executive employees and their impact on improving OHS conditions. The questions were formulated in such a way to obtain information on a wide range of subjects within occupational safety. Furthermore, the survey part was supplemented with information obtained during conversations and face-to-face interviews with the respondents. Closed-ended questions with yes/no answers or grade scales from 1 to 5 could be supplemented with comments and opinions. This survey methodology affords a higher precision in identifying

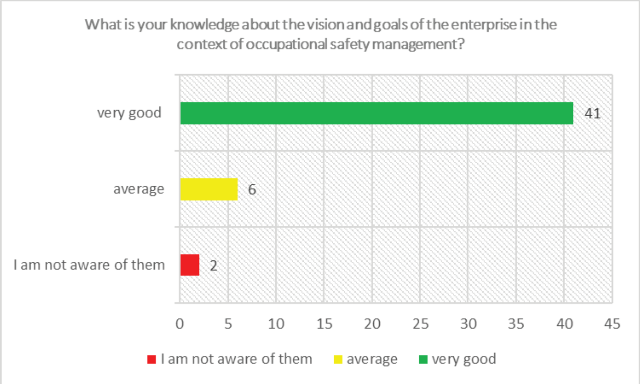

Fig. 2 The enterprise's vision and goals. Source: prepared by the author, 2019
Rys. 2. Wizja i cele przedsiębiorstwa

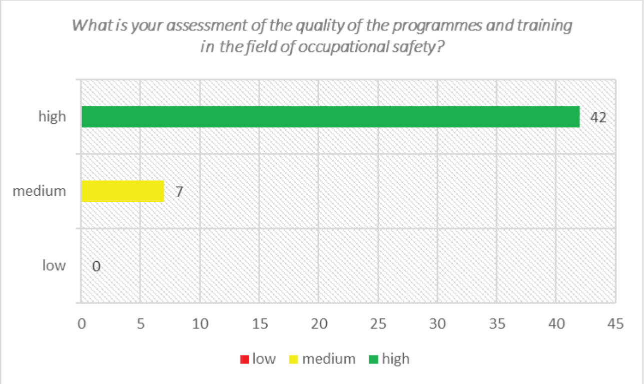

Fig. 3 Programme and training quality. Source: prepared by the author, 2019
Rys. 3. Jakość programu i szkoleni

hazards by taking into account the remarks and comments of the respondents. The first part of the survey concerned the age and job seniority of the respondents. The survey was conducted during post-graduate classes for JSW S.A.'s executive employees and involved 49 respondents. Fig. 1 presents the job seniorities of employees who took part in the survey.

Fig. 1 shows that 29 executive employees, representing 60% of the surveyed sample, have a job seniority of over 20 years. The respondents clearly have a long-standing work experience and can objectively assess the enterprises activities in terms of developing an occupational safety policy. Furthermore, the mean respondent age was approximately 44 years.

Figs. 2÷6 show the responses to selected questionnaire questions. Using the 1÷5 grade scale was meant to elicit more accurate answers to individual questions. However, certain assumptions were adopted to facilitate further analysis. Values 4÷5 were considered positive and 1÷2 were seen as negative. Answers with a value of 3 were classified as neutral.

The answers provided by executive employees demonstrate that a majority assign relatively high scores to the activities conducted by the enterprise in terms of improving OHS conditions. Particularly high scores were provided for the vision and objectives set by the company, and the programmes and quality of occupational safety training. 41 and 42 respondents gave positive answers, respectively, which accounted for 84% and 86% of the surveyed employees. Only two respondents declared that they did not know the objective and vision of the enterprise's occupational safety policy. An important management area is the full involvement of executive employees in activities promoting safe conduct among employees. Two respondents from the analysed sample said that the managers were not engaged in any activities and 38 respondents said that they were fully engaged.

The most important element in an occupational safety system is the compliance of employees with the OHS regulations. The question: "What is your assessment of OHS compliance by employees at workstations" yielded positive answers from only 24 respondents, which accounted for 49% of the surveyed population. At the same time, as many as 29% of the respondents gave a negative response, and the remaining 22% did not provide a clear answer. This area is essential for any occupational safety system in an enterprise. Identifying the system's weaknesses makes it possible to introduce comprehensive solutions and a restructuring plan. One method involves further certification and refinement of safety procedures. The respondents are aware that the company updates and implements new procedures in the field of accident prevention and working conditions improvement. Nearly 84% of the executive employees surveyed were aware of the implemented and functioning safety certificates at their enterprise.

Conclusions

Implementing an occupational health and safety management system in an enterprise may bring both tangible and intangible benefits to the organisation. Without question, the presence of a management system should improve the company's reputation on the market and in relation to its stake-

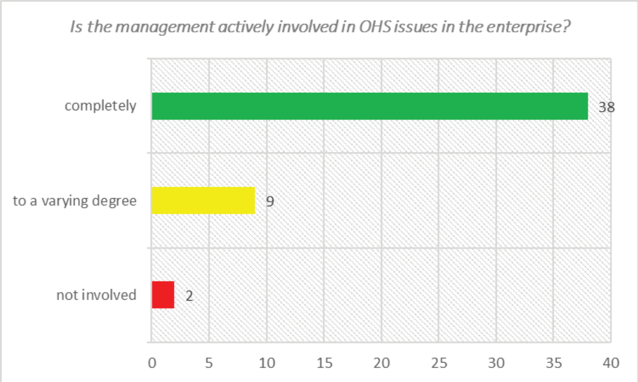

Fig. 4 The management's involvement in occupational safety. Source: prepared by the author, 2019
Rys. 4. Struktura zatrudniania wg płci i wieku w GK LW Bogdanka SA. Źródło: opracowanie własne na podstawie [23]

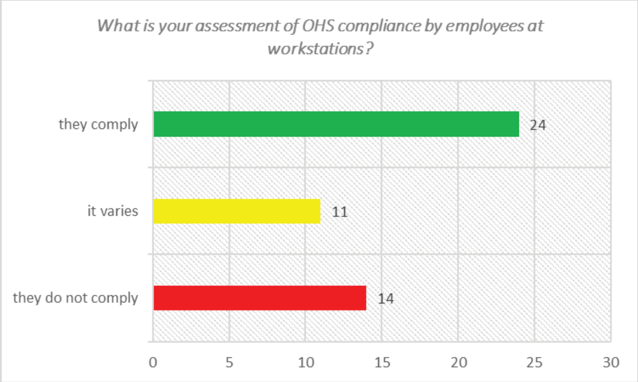

Fig. 5 Employee compliance with regulations. Source: prepared by the author, 2019
Rys. 4. Struktura zatrudniania wg płci i wieku w GK LW Bogdanka SA. Źródło: opracowanie własne na podstawie [23]

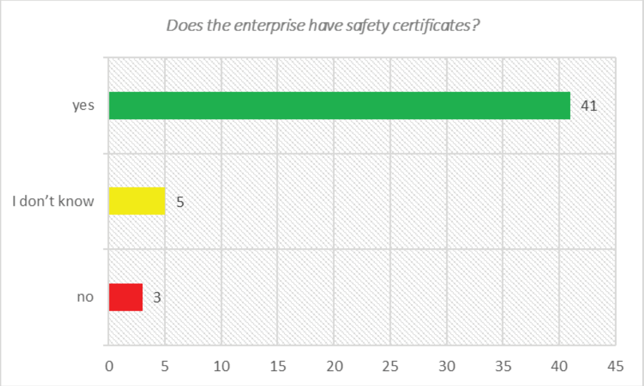

Fig. 6 Safety certificates in an enterprise. Source: prepared by the author, 2019
Rys. 4. Struktura zatrudniania wg płci i wieku w GK LW Bogdanka SA. Źródło: opracowanie własne na podstawie [23]

holders, such as customers, subcontractors, the local community and state authorities supervising working conditions. The increased awareness and gained experience among employees may be used in other fields of enterprise management, such as finance and human resources. By developing awareness and providing appropriate knowledge, we prepare employees to behave and act in a desirable way. These actions will be effective if we achieve a state in which the employee is aware of the purpose and meaning of his or her actions, and the potential consequences for the public.

The survey demonstrates that there is still room for improvement in terms of improving the OHS conditions by enterprises. Achieving a high level of occupational safety requires the activity and effort of executives, but also the full involvement and participation of regular employees. The survey, which was conducted in November 2019, involved 49 executive employees of JSW S.A. The surveyed individuals assigned high scores to the preventive actions conducted by the employer in terms of developing safe working conditions. However, they are aware that the weak link in the system is employee compliance. The identification of strengths and weaknesses allows defining the directions of action, which should significantly improve occupational safety.

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Wpływ systemu zarządzania na kształtowanie świadomości pracownika w zakresie bezpieczeństwa pracy

Artkuł przedstawia problematykę dotyczącą bezpieczeństwa pracy na przykładzie wiodącej spółki wydobywającej węgiel kamienny w Polsce. Przedstawiono przykłady wdrożonych i funkcjonujących systemów zarządzania bezpieczeństwem pracy w przedsiębiorstwach. Ponadto scharakteryzowano rolę świadomości w kształtowaniu właściwych postaw i zachowań pracowników w miejscu pracy. W formie graficznej zaprezentowano wybrane wyniki z ankiet przeprowadzonych wśród pracowników zatrudnionych na stanowiskach kierowniczych JSW S.A. Na podstawie otrzymanych wyników sformułowano wstępne wnioski oraz kierunki dalszych badań w prezentowanym obszarze.

Słowa kluczowe: bezpieczeństwo pracy, przedsiębiorstwo górnicze, systemy zarządzania, świadomość pracownika

Selected Aspects of Building and Developing a Modern High-Performing Team

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Abstract

The publication presents selected issues related to the creation, development and retention of staff teams. It discusses team building stages and the characteristics of modern teams. Another discussedaspect is the identification of team characteristics according to Belbin's concept and their relevance for the selection of team members. Outdoor training is presented as a form of team development.The publication also presents conflicts in a team, their causes and conflict-solving methods as well as the characteristics of a good leader.

Keywords: management, teams, personality traits, conflict

Introduction

In contemporary times human resourcesmanagement has become an essential but difficult task. On the one hand, civilisational progress and increased worker mobility facilitates labour force acquisition from other regions of the country. On the other hand, the said mobility creates a risk of losing the current employees to other business entities. Another player on the Polish job market is made up by anumerous group of employees from neighbouring countries, especially from Ukraine and Belarus. It is estimated that in 2018 the Polish job market included approx. 2 million legal workers from Ukraine alone. A considerable number of incoming workers has had a substantial impact on the Polish job market. A vast majority of them are blue-collar workers, but they are also found in sectors requiring specialised education, such as the medical or IT sector. The high worker supply forces Polish employees to undertake extensive measures to protect their job positions and employers to retain their best employees, who are looking for better jobs, also in other cities or towns or even in other countries.

The mentioned factors should also motivate human resources managers in companies to ensure stable employment and to take steps to retain the most valuable employees. This can be achieved in a number of ways, including formal and legal, economic and motivational mechanisms. A mining company differs in work characteristics from other companies, especially as far as underground work is concerned. However,it resembles other sector in terms of staff rotation, which is present in this industry as well. More and more often the hired individuals do not have a mining education background. This is partially a result of a considerable limitation of the number of occupational schools in Poland. In mining it is often the case that underground works are outsourced to external companies whose employees sometimes lack a mining-related education background. While in many branches of industry employees can be provided with supplementary training suitable for a given job position fairly quickly and safely, the process is much more complex and associated with greater risk in the mining industry.

With the above circumstances in mind, it seems sensible to build effective teams capable of long-term cooperation. The fulfilment of tasks set before a group of employees (a team) often determines the success of the whole project in which the team is involved. However, one could ask about the difference between a group of people who perform tasks together and a team. How to build an effective team and manage it efficiently? This study focusses on aspects of this process.

Stages of building a high-performing team

The objective of human resources management is for the company to achieve success thanks to the people hired by it. The main objectives of this process include: [1]

- to provide a number of services supporting the company's objectives and constituting an element of the organisation governance process,
- to acquire and retain qualified employees,
- to improve and develop people's inborn capabilities – their input, potential and the ability to find employment through providing training and continuous development opportunities,
- to create an atmosphere contributing to harmonious relations between the managerial staff and employees facilitating mutual trust,
- procedural justice – dealing with all issues related to how – people are treated,
- transparency – openness and explaining to employees the proposals, decisions and procedures established by the managerial staff.

At present one of the key factors impacting the selection of candidates in a recruitment process involves their predispositions for team work (one of the pillars of recruitment at Toyota).In turn, the employee selection philosophy at Phil-

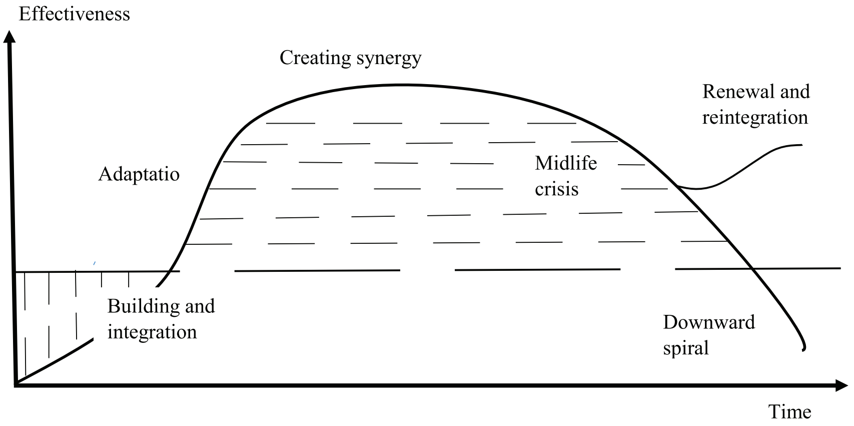

Fig. 1. Life cycle of a team. Source: [7]
Rys 1. Fazy życia zespołu. Źródło: [7]

lip Morris is based on the assumption that candidates should have communication and cooperation skills.

When embarking on the task to manage a group of people with common goals, cooperation should begin with transforming the groupinto an effective team. This requires some effort and does not always bring the expected results. However, team building should take advantage of the synergy effect (the result of the work of closely cooperating people is greater than the sum of results achieved by each of them individually).In addition, team work increases the effectiveness of communication and is more motivating.

Teams are not created automatically and good cooperation does not arise spontaneously – team building is a process which requires considerable effort. The first step towards effective team building is to realise what a group is, how it functions and what its characteristics are. Teams usually have basic and supplementary characteristics.

1. Basic characteristics:
- A common goal,
- A good leader,
- Willingness to cooperate,
- Good communication,
- Division of tasks in a team,
- Good team relations.

2. Supplementary characteristics:
- Intrinsic motivation of the members,
- Trust towards other people,
- Mutually established operation rules,
- Building on differences,
- Flexibility and openness to change,
- Continuous improvement.

Each team goes through a life cycle. Fig. 1 presents the typical life cycle of a team.

In the “Building and integration” phase, the team’s effectiveness is lower than the cost of maintaining it. This is a typical phenomenon resulting from the incomplete integration between its members, which reduces team effectiveness. Attempts should be made to reduce the duration of this phase to the maximum possible extent. Usually high emphasis is placed on training (such as outdoor training sessions). This is a time for identifying team members’ skills and predispositions and for verifying the selection of group members, inter alia through shifting human resources between teams, promoting leaders and building positive relations between team members. It is important for team members to accept the fact that their personal goals are less important than those of the entire team.

In the second phase, i.e. “Adaptation”, group members become more and more familiar to each other, and personality differences become evident. Rules of team work are developed. Disputes and clashes between team members may be observed, which is a natural phenomenon in this phase of a team’s life cycle. The first arguments and crises take place.

The key stage in the life cycle is the third phase, in which team synergy is used to achieve the set objectives and tasks. This phase should last as long as possible. Attempts should be made to maintain the highest possible effectiveness. The basic tasks of a team manager include setting goals, avoiding unnecessary interventions, delegating authorisations, motivating, individual coaching and monitoring the team’s work.

Even a well-performing team can go through a “Midlife crisis”. There are visible first symptoms of the crisis, which should draw the manager’s attention. These include fatigue and boredom, low motivation, the lack of a sense of development, falling into a routine, team members’ burnout or attempts to find something new (if they don’t find it in the team, they often start looking elsewhere). This is a very important moment in a team’s life cycle. When it is overlooked, the team may move on to the “Downwardspiral” phase. If leaders respond early enough to the crisis symptoms, there is a chance for the group to renew and reintegrate. The leaders’ role is to take measures to rebuild motivation in the group. This may involve a change in the range of duties, assigning new tasks to the team, introducing a new person, promoting selected team members, increasing the degree of delegating authorities and responsibilities, involving the team in planning, consulting ideas, training and team building trips.

However, if the management does not respond effectively at the right time, it may seem necessary to accept the fact of the team’s disintegration and the necessity to rebuild it.

A key element in the team building process is the selection of its members. Diversity in a team is crucial – according

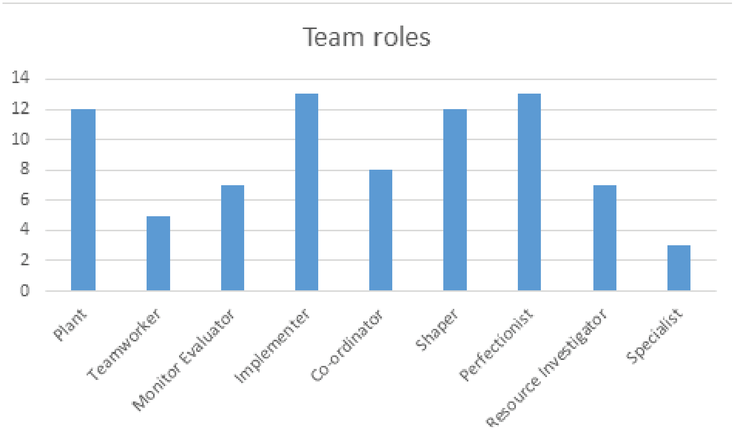

Fig. 6 Safety certificates in an enterprise. Source: prepared by the author, 2019
Rys. 4. Struktura zatrudniania wg płci i wieku w GK LW Bogdanka SA. Źródło: opracowanie własne na podstawie [23]

to the author only a proper level of diversity makes it possible to achieve the set outcomes. Errors are often made in the team building process, consisting in assigning similar roles to all team members and imposing roles on team members by using a top-down approach.

One of the methods used in the selection of employees is Belbin's concept. It is based on identifying (analysing) the predisposition of a given team member to perform one of the team roles mentioned in Belbin's test. The test can be carried out even before the formal assignment of members to the team. Belbin's test provides information on the possibility for specific individuals to function in a team. Team role diagnosis can be used for building a new team, adding a new person to a team and increasing the effectiveness of team operations. Belbin identified 9 typical team roles; through analysing the test results, it can be determined with a fairly good accuracy which role a given person is suited to play in the group.

Belbin provided a list of the following roles: [2]

- Plant

Plant's role is mainly providing new ideas and solutions to problems. Typically the most creative and intelligent person in the team. Often involved in the process of initiating new stages of the project or adjusting the existing assumptions during its implementation. Too many Plants in a team can lead to conflicts. Plant's strengths include innovativeness, imagination and seriousness. Possible weakness are changing moods, from euphoria to discouragement, a tendency to be chaotic.

- Monitor Evaluator

The Monitor Evaluator is great at analysing problems, developing concepts and suggestions. Good at analytical tasks. Can be viewed as a slow and boring person who lacks enthusiasm. Performs well in difficult moments for the team. Monitor Evaluator's strengths include being practical and composed.

- Co-ordinator

Good at leading and co-ordinating work in a highly diversified team. Able to effectively cooperate in the team, organise discussion in the group, usually able to solve problems in a practical way. Good at utilisinghuman resources and potential. Strong points: goal-oriented, enthusiastic, trusting and composed.

- Implementer

Very useful in a group due to reliability and ability to adapt. Effective and intuitive. The Implementer sees to the completion of tasks which should be fulfilled. Often involved in passing information on team's tasks and operations. Implementer's strengths include discipline, practicality and being able to provide support. The weak points are submissiveness and the lack of flexibility in action.

- Completer Finisher

The Completer Finisher is particularly valuable for tasks which require concentration and a high level of precision. Typically best at paying attention to details in the team's work. Sees to the keeping of deadlines, monitors the performance of tasks as per the schedule. Precise, able to execute ideas and tasks. Aware of the tasks and goals set for the team. Completer Finisher's strengths include being disciplined, composed and striving for perfection in his/her actions.

- Shaper

Typically a good leader. Thrives on pressure, demonstrates a proactive approach. Able to motivate the team to action. Capable of taking action when complications arise. Takes action quickly and usually effectively. Action is his/her priority. Good at introducing changes. Typically the most effective member of the team, responsible for its actions. Strong points: resistance to stress, efficiency. Thrives in a team. Shaper's weakness is impatience.

- Teamworker

Teamworker's main tasks is keeping a good atmosphere in the group and preventing interpersonal issues. Avoids conflicts, is able to include the team to limit their occurrence and good at mitigating those that have already arisen. A sensitive person. Perfect at sensing and improving moods in the team. Teamworker's strong points are enthusiasm, being articulate, trusting and able to compromise. His/her weakness include submissiveness and often excessive faith in people.

- Resource Investigator

Highly valuable in developing and implementing ideas from outside the team. Good at acquiring and maintaining external contacts and at negotiating. Has an ability to obtain information and analyse data. A very crucial role at the beginning of team formation and throughout its existence. Enjoys a good opinion in the team. Resource Investigator strengths include resourcefulness, ability to search for information, being articulate and enthusiastic. His/her weaknesses are changing moods and sometimes being overoptimistic.

- Specialist

The Specialist is a very important team member. Without his/her skills, the team would not be able to carry out its tasks. Able to implement tasks efficiently, but usually not very creative. Able to calmly analyse group's ideas. His/her strong points are an analytical mind, practical skills, impartiality and prudence. The weaknesses include the lack of creativity, weaker interpersonal contacts and an excessively critical approach.

According to Belbin, well-functioning teams include members with highly diversified roles. When building a team, attention should be paid to selecting people with the essential qualifications (with proper education, knowledge, skills and experience).However, it is also crucial to select the right people for the respective roles in a team.

Belbin's research also shows that in order to create an effective team it is important to compose it in such a way to fill all the roles and, when necessary, for other team members to be able to replace a given person.

During team building classes, the author carried out Belbin's test on a group of 80 students. The studied group comprised full-time students,with a majority having no previous job experience. Part of the group was active on the labour market, but these were usually temporary jobs not related to their field of studies. Thus, it can be assumed that these people did not have experience in the profession which they intended to practise in the future. [9]

Having analysed the obtained results, it can be concluded that in the group of students of a technical higher education institution most people saw themselves in creative roles or those which required perfectionism. A smaller group showed predispositions for being teamworkers or specialists. However, the studied group was not highly diversified. It is recommended to carry out research on a less homogeneous group.

To recapitulate the discussion of team roles, it can be stated that when building a team it is important to choose people with diverse team characteristics.

Team development

Staff teams require continuous improvement and development; otherwise they may experience situations of crisis and decline in performance. Currently there are many methods available to motivate employees and enhance team development. These are particularly popular in corporations, especially in the trade and IT sector. Team formation and development, however, are also crucial in production enterprises, such as those operating in the mining industry. [8]

Team building may involve the following initial situations:

- Building a team out of people who are just getting to know each other
- Streamlining the work of the existing team
- Integrating the team formed out of two (or more) teams
- Maintaining the team's energy in moments of changes or crisis
- Building formal relations between departments
- Building informal cooperation between departments

Regardless of the team's phase and status, its evolution should be supported.[4]

HR departments should manage team development on an ongoing basis. This is often achieved through such methods as cooperation between teams, company events or the creation of active leisure zones. Outdoor training sessions are an interesting option for employees and become increasingly popular among them.

They have a unique character, differing completely from those organised at the workplace.

The main objective of these measures, in addition to the content-related aspects, is building atmosphere in the team, which usually translates into an improved quality of its future work.

As the name suggests, outdoor training sessions are organised outside the workplace, often outside of the workers' place of residence. The main reason for choosing such location is to completely isolate training participants from the outside world, their families, friends, professional and personal problems. The basic task of the organiser in their choice of the location is to meet the following assumptions: [7]

- a place distant from civilisation
- lack of Internet access
- minimal contact of the participants with family or friends
- maximum integration of the participants
- extensive space to use for field games
- comfortable lodging contributing to participants' integration

The fulfilment of the above assumptions should be based on a prior inspection of the potential training location. A place distant from civilisation, preferably without Internet access, is difficult but possible to achieve.In order to ensure complete independence of external factors, it can be suggested to put mobile phones in a deposit (at least for a while), which, of course, requires the participants' consent. This way they would be able to completely focus on the activities and would not be distracted by the nearby attractions or virtual reality.

It is a good idea to start the event by asking the participants to reach the location individually as a form of a car orienteering exercise – the participants would receive instructions on how to reach the lodging place with a description of the successive sections of the road, number of kilometres, direction, road number, etc.

When planning the training trip, its main goal should be clearly specified. Usually the priorities are participant integration and soft skills development. This means that the content-related aspects of the training are important, but they are not the ultimate goal. Therefore,in planning this type of training emphasis is placed on group work, frequent interactions between participants, multidimensional tasks which require creative solutions to complex and interdisciplinary problems.

People in charge of the specific modules/panels should be to a greater extent moderators than trainers. Independently solving a problem by the participants is much more valuable and conducive to development than receiving a ready-made solution by the trainer.

The key aspects related to designing and executing training trips that are worth considering include: [7]

- Determining the details of risks
- Building the atmosphere of the training
- The manner of conducting the respective modules
- Feedback
- Subcontracting costs
- Analysis of training needs and participants' limitations
- Constructing the content of the training
- Selecting and testing the activities
- A list of questions – a starting point for discussion
- Finding subcontractors
- Organisational and insurance arrangements
- Carrying out the training
- Assessing the effects – conclusions for the future
- Positive energy

In the training execution process, the so-called "ice breakers" are very crucial, i.e. people who take care of the atmosphere of the training, solve any possible interpersonal problems and initiate group's actions if its members do not know how to start. These persons' task is also to make the participants aware of their role in the team and to coordinate activities, especially those which are interdisciplinary in nature.

Another important role during training is that of a Facilitator. Their tasks are as follows:

- not being an expert, but a moderator
- not providing ready-made solutions, but leading participants towards their own solutions
- must have training skills, be able to ask questions and transform information into concrete outcomes for the company.

Training trips have a huge potential. When well-planned and executed, they provide extensive opportunities for team integration and leadership development. After such training employees often find it much easier to cooperate with each other. The time spent together, on both team work and recreation and integration in the positive sense), usually has a great impact on the group's future endeavours. Despite the fact that arranging training trips is time-consuming and usually expensive, companies should consider this form of training. In many enterprises training trips have become a tradition, and are organised regularly, often more than once a year.

Team malfunctions and how to eliminate them

In the work of each team there may be failures resulting from the team's malfunctioning.The typical stages associated with team's malfunctioning are:

- The group makes an error during task implementation
- Error – goal not achieved – FAILURE
- Analysis of the causes of failure – discussion
- Redoing the task (IMPROVEMENT)
- Analysis results – identification of SUCCESS factors
- Discussion and conclusions for the future

The most frequent team malfunctions:

- Analysis of the company's situation from the perspective of one's own interest and not of the company as a whole
- Following an initially established strategy even when the internal or external situation suggests that change is needed
- Considering the current productivity, work organisation or cost indicators, etc. optimal, with no room for improvement
- A failure to adjust operations to strategic goals, especially after changing the company's strategy
- Poor information flow between teams
- Unintentionally generating gossip through gaps in communication and its being unadjusted to the co-workers
- Overlong, poorly organised meetings, arrangements only on paper
- A failure to utilise well-known and simple methods supporting manager's work (e.g. SWOT, Gantt chart, brainstorming)

The knowledge of the above sources of errors facilitatesthe early detection and prevention of at least some of them.

A team needs a leader to function properly. The major characteristics of a good leader include:[6]

- Charisma
- Being able to provide solutions
- Being a recognised authority
- Listening, giving advice, motivating
- Effective division of tasks
- Introducing enhancements
- Being trustworthy
- Being empathic
- Effective conflict solving
- Taking care of staff development
- Developing a superior strategy
- Facing challenges
- Integrating a group
- Negotiating effectively

In addition, a leader should have the following personality traits:

- Self-esteem
- Being proactive
- Independence
- Positive thinking
- Interdependence
- Internal cohesion
- Sense of abundance
- Ability to create a vision
- Ability and willingness to continuously learn
- Intuition

Conflicts in a team and methods of solving them

Conflict is a natural phenomenon even in healthy, well-functioning organisations. It usually occurs where two or more parties strive for opposite or different goals. However, actual problems are not necessary for a conflict to arise. It is enough for the involved parties to be convinced of the opposite side's hostility.[5]

The causes of conflicts can also be sought in human emotions. This issue is an area of interest for work and business psychologists. Leaders should be aware that often people under the influence of strong emotions can behave completely irrationally. The nature of emotions and their impact on human activity was the subject of publication [3]

In terms of the subject of the conflict, the following can be specified:

- subject-matter conflicts – are non-personal in nature and refer to specific matters, specifically to the difference in opinions as to their solution. The subject of the conflict is quite easy to define, and the solution lies in the appropriate adjustments in the division of assets or changes introduced in an organisation;
- emotional conflicts – refer to states of frustration and the related emotional tension caused by a negative attitude (i.e. hostility) in human interactions. The actual subject of the conflict is often difficult to capture, and the best solution is to prevent this type of conflicts.

In terms of their range, the following conflicts are identified:

- between groupsof employees – resulting from different interests of particular groups, different temporal and spatial horizons, goals and ways of solving problems;
- between individuals – often ascribed to personality differences, but generally caused by disrupted relations between individuals resulting from differing roles or the personalisation of antagonisms between groups;
- interpersonal – occur when an individual does not have clearly defined workplace duties, some tasks are mutually exclusive or expectations exceed the level of perception of an individual's own capabilities

A list of the types of conflict and their basic causes is presented below.

- Conflict of interest:
  – procedures
  – subject-matter issues
  – psychological needs

- Structural conflict:
  – varying range of power
  – poor spatial organisation
  – time constraints
  – unclear division of tasks, authorisations and responsibilities

- Conflict of values
  – central values
  – peripheral values

- Conflict of relations
  – strong emotions
  – stereotypes and prejudice
  – poor communication
  – negative experiences

- Data conflict
  – lack of information
  – misunderstanding
  – varying interpretations of the same information
  – different data collection and analysis procedures

If a conflict arises in a team, it should be solved so as not to lead to a complete disbanding of the team. Solving a conflict requires an accurate diagnosis and remedial measures.

Stages of conflict solving:

- the diagnosis stage
  – recognising the type of the conflict
  – determining causes
  – dispelling negative emotions

- the solution stage
  – choosing the conflict solving style
  – removing actual causes of the conflict
  – reducing emotional tensions.

The most frequent conflict solving styles are as follows:

- avoiding – ignoring or omitting the issue
- adjusting – restructuring one's position not because of accepting the other party's views but for the sake of cooperation
- competing – adopting the winner/loser attitude and striving for winning at all costs
- compromising – finding a solution by giving up some of one's needs in return for adequate concessions on the partner's side
- solving the problem – seeking mutual benefits of a common resolution of the conflict treated as a problem-solving task

Problem-solving strategy – basic stages

- defining the problem – the source of the problem and its essence should be specified, the causes should be named, without blaming others or the environment
- generating alternative solutions – a list of possible solutions should be developed. It is important not to assess the alternatives before the list is closed.
- choosing the best solution – benefits and costs related to adopting a given solution. Through a thorough analysis of each of the possibilities, a mutual decision on choosing the best proposal should be made.
- putting the solution into action and controlling the results – the time needed for the completion of a given solution should be specified and its progress should be monitored. When needed, if the selected option does not lead to the expected results, a different solution should be selected. It is important not to adhere to only one solution.

Summary

Nowadays, managing a team requires the application of suitable methods for its creation and development as well as mitigating the effects of their malfunctioning. However, even the best team management does not guarantee the lack of conflicts or problems. Fast and effective response to the changing circumstances is key in such situations. A good leader is able to respond early enough, which may often safeguard the team from failure.

Teams operatingwithin mining companies are governed by the same principles as other teams. Regardless of the specific characteristics of working underground, these teams may also face problems or conflicts. Mining supervision bodies should detect such threats early enough. What makes it even more important is that the nature of work performed by these teams requires their members to maintain good relations, as their life and health often depends on it.

In addition to the right selection of employees, it is a very important problem to look after the appropriate organizational culture in mining companies. The human factor in the production process, in particular in the mining process, is an extremely important link. This issue has been presented in publication [10].

Mid-level managers should also be guided by interpersonal criteria when selecting employees for a team. The information presented in the publication systematizes knowledge in the field of team building theory. It is particularly important to identify the role that a potential employee can play in a team.

The second important issue for the team leader in the mining industry is the ability to solve problems and conflicts. The publication presents the reasons for their formation and a set of methods for solving them. This is not an easy task, often requires personal experience of the leader or cooperation with professionals in this field.

In addition to professional skills, a modern manager should possess good teamwork skills, such as being able to choose the team members accurately, promote its development, and notice any potential problems to deal with them directly or with the assistance of experts. The ability to identify problems at an early stage is a crucial trait.

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Wybrane zagadnienia budowy i rozwoju współczesnego zespołu wysokiej wydajności

W publikacji przedstawiono wybrane zagadnienia związane z budową, rozwojem oraz utrzymaniem zespołów pracowniczych. Omówiono etapy budowy zespołu, cechy współczesnych zespołów. Kolejnym poruszanym zagadnieniem była identyfikacja cech zespołowych według koncepcji Belbina i znaczenie tych cech przy doborze członków zespołu. Przedstawiono szkolenia typu outdoor jako jedną z form rozwoju zespołu. W publikacji przedstawiono również konflikty w zespole, przyczyny ich powstawania oraz metody rozwiązywania, a także cechy dobrego lidera.

Słowa kluczowe: zarządzanie, zespoły ludzkie, cechy osobowości, konflikt

Comparison Analysis of Muck Pile Fragmentation Obtained Through the Photogrammetry Method and Based on the Kuz-Ram Empirical Model

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Abstract

This paper presents an evaluation of muck pile fragmentation based on the Kuz-Ram empirical model. Furthermore, a comparison of the cumulative size distribution curves obtained from the photogrammetry analysis and based on the Kuz-Ram model was made. Size distribution was performed based on the Kuz-Ram model and further validated in the O-Pitblast software. It was established that the algorithm applied in O-Pitblast software was not modified. The difference between empirical results and in-situ analysis could be explained by, inter alia, the subjective assumption of the RMD index value.

Keywords: blasting works, muck pile fragmentation, Split Desktop 2.0, Kuz-Ram, O-Pitblast

Introduction

Muck pile fragmentation by blasting is the subject of numerous studies. This is due to the impact of defragmentation on the costs of drilling works, the process of loading and hauling of the rock material and the selection of equipment for processing (Mackenzie 1966), (Bozic 1998), (Morin and Ficarazzo 2006), (Sanchidrian et al. 2007), (Bahrami and Monjezi 2011), (Faramarzi et al. 2013). In addition, Morin and Ficarazzo (2006) stated that in the case of opencast mining, mechanical processing of the rock mass is more costly than similar works performed with explosives. As reported by Cunningham (2005), determining the optimum fragmentation not only streamlines the extraction process but also leads to minimising losses resulting, inter alia, from the possibility of limiting the percentage of the finest fraction (below 4 mm).

Muck pile fragmentation is determined through the use empirical modelling (to better estimate the fraction with a low grain diameter) and mechanical modelling (applying the basics of detonation physics and passing the energy generated through the explosive transformation through the rock mass on the basis of the well-established strength parameters of the rocky matrix) (Cunningham 2005). As stated by Jahani and Taji (2015), the major empirical models include: the Dnis and Gam (1970), Larson, Kuznetsov (1973), SveDeFo (1974), Kuz-Ram (1983), modifications of the Kuz-Ram model (1987), Kou and Rustan (1993), CZM, TCM (1999), CK (2003), KCO (2005) and Gheibi et al. model (2009).

However, it should be noted that the attempts at estimating muck pile fragmentation are carried out mainly on the basis of the Kuz-Ram model or the modified Kuz-Ram model (Badroddin et al. 2012), (Ghaeini et al. 2017), (Mohammadi and Barati 2018). The theoretical basis of the Kuz-Ram model was discussed in detail in studies by Cunningham (1983 and 1987). Morin and Ficarazzo (2006) applied the Monte Carlo analysis on the basis of the Kuz-Ram model in order to estimate output, and Mohammadi and Barati (2018) modified the Kuz-Ram model to use it in the blasting works carried out during tunnelling.

It should be noted that the development of IT systems has made it possible to apply state-of-the-art statistical modelling (Bahrami et. al. 2011), (Shams et al. 2015). Monjezi et al. (2010) used muck pile fragmentation modelling on the basis of artificial neural networks for the Sarcheshmeh copper mine. Using the CAM (Cosine Amplitude Method) sensitivity analysis they concluded that the time delay, the number of series in the blasting pattern, charge weight per delay, the powder factor and the ratio between the burden and the spacing have the greatest impact on the degree of fragmentation. Research carried out by Monjezi et al. (2010) was continued by Shams et al. (2015), who in their fragmentation modelling made use of the FIS (Fuzzy Inference System) and the MRA (Multiple Regression Analysis). On the basis of the obtained coefficients of determination, RMSE and VAF and data from the Sarcheshmeh copper mine they concluded that the FIS model provides a better compliance of the modelled fragmentation with the data from in-situ measurement. Bahrami et. al. (2011) applied a four-level neural network in their modelling. Through the sensitivity analysis they determined the main parameters, partially consistent with the results (Monjezi et al. 2010). Hasanipanah et al. (2018) and Mojtahedi et al. (2018) suggested the use of the hybrid method employing respectively the ANFIS (Adaptive Neuro-Fuzzy Inference System) in combination with the PSO (Particle Swarm Optimization) algorithm and the ANFIS with the FA (Firefly Algorithm), while Enayatollahi et al. (2014) compared the potentials of the results obtained through neural networks with various regression models.

The assessment of fragmentation, i.e. the possibility of verifying the modelled results, can be made for in-situ measurements with the use of, inter alia, the indirect method based on the photogrammetric analysis. The very use of the photogrammetric method in underground and opencast mines was discussed by Biessikirski et al. (2016a), Biessikirski et al. (2016b), Biessikirski et al. (2017) and Mustafin et al. (2017).

The objective of the article is to present the Kuz-Ram model and to verify it by comparing it with the results obtained on the basis of the photogrammetric method.

The theoretical basis of empirical models

The possibility of estimating muck pile fragmentation can be established on the basis of empirical correlations. The general form of the equation for the average grain size (D_{50}) is presented in equation 1.

$$x_{50}=C\cdot D\cdot E\cdot F \qquad (1)$$

where:
x_{50} – average grain size, cm,
C – statistical constant,
D – coefficient for the strength parameters of the rock mass,
E – coefficient specifying the geometrical parameters of the designed series,
F – coefficient specifying the properties of the explosive.

Ghaeini et al. (2017) state that the empirical correlation, regardless of the model, consists of two parts: first determining the average grain size (D50) or (D80) and second responsible for the statistical distribution.

One of the first broadly applied models among the developed solutions was Larsson's model – equation 2 (Jimeno et al. 1995), (Bakhtavar et al. 2015).

$$x_{50}=s'\cdot e^{(0,58\cdot \ln B-0,145\cdot \ln\left(\frac{a}{z}\right)-1,18\cdot \ln(\frac{q}{c})^{-0,82})} \tag{2}$$

where:
s' – blastability index (coefficient specifying the impact of the rock mass structure on the result of blasting works) (Chatziangelou and Christaras 2013),
Z − burden, m,
a − spacing, m,
q – powder factor, kg/m^3 ,
c – constant arising from the rock mass properties.

In the SveDeFo model (equation 3) rock mass properties and geometrical parameters of blast holes (inter alia, the length of the blast hole)

$$x_{50}=s'\cdot(1+4,67\cdot(\frac{T}{L})^{2,5})\cdot e^{(0,29\cdot \ln Z^2\cdot\sqrt{\frac{a}{1,25}}-1,18\cdot \ln(\frac{q}{c})^{-0,82})} \tag{3}$$

where:
T – stemming length, m.
L – length of the borehole, m,
a – spacing, m,
q – powder factor, kg/m^3 ,
c – constant arising from the rock mass properties,
Z − burden, m.

Kou and Rustan (1993) used in-situ measurements to develop correlation 4, on the basis of which it is possible to estimate muck pile fragmentation for a specific type of material with an accuracy of up to ±0.15% (Bakhtavar et al. 2015). However, as Monjezi (2009) stated, models developed for data obtained from in-situ measurements in specific mining and geological conditions have local applications, as results obtained for other mines are subject to statistical error.

$$x_{50}=0,01\frac{({}_r\cdot C_p)^{0,6}\cdot(\frac{S}{B})^{0,5}\cdot B^{0,2}}{(\frac{L}{H})^{0,7}\cdot D^{0,4}\cdot q_t} \tag{4}$$

where:
γ_r – specific density of the rock, kg/m^3 ,
C_p – longitudinal wave propagation velocity (P), m/s,
D − explosive material's detonation velocity, m/s,
L − total length of the explosive charge in the blast hole, m
q_t – powder factor including charge weight in the subdrill, kg/m^3 .

The Kuz-Ram model

One of the models most frequently used for estimating muck pile fragmentation is the Kuz-Ram model developed by Cunningham (Shams et al. 2015), (Adebola et al. 2016). The Kuz-Ram model was conceived from three equations: the Kuznetsov (equation 5), Rosin-Rammler (equation 6), and uniformity equation (equation 7) (Cunningham 2005). The Kuznetsov equation was revised by Cunningham with the so-called blastability index. The use of the Rosin-Rammler equation enabled the statistical distribution of grain size.

$$x_m=A\cdot q^{-0,8}\cdot Q^{1/6}\cdot\left(\frac{115}{RWS}\right)^{19/20} \tag{5}$$

where:
A – rock factor (depending on the hardness and structure, from 0.8 to 22), derived from equation 8,
q – powder factor, kg/m^3 ,
Q – total charge weight per hole, kg,
RWS – weight strength relative to ANFO.

$$R_x=\exp\cdot\left(-0,693\cdot\left(\frac{x}{x_m}\right)^N\right) \tag{6}$$

where:
x – grain size, mm,
x_m – characteristic grain size, mm,
N – uniformity index (usually within the range between 0.7 and 2.0).

The impact of blasting works parameters on the degree of fragmentation was accounted for in the form of a uniformity index (N), as in equation 7 (Adebola et al. 2016), (Bakhtavar et al. 2015), (Cunningham 2005).

$$N=\left(2,2-\frac{14\cdot B}{d}\right)\cdot\sqrt{\left(\frac{1+\frac{a}{Z}}{2}\right)}\cdot(1-\frac{W}{Z})\cdot\left(\frac{|BCL-CCL|}{L}\right)+0,1)^{0,1}\cdot\frac{L}{H} \tag{7}$$

where:
Z – burden, m,
a – spacing, m,
d – hole diameter, mm,
W – standard deviation of drilling precision, m,
L – charge length,
BCL – bottom charge length, m,
CCL – column charge length, m,
H – bench height, m.

Tab. 1. Joint Condition Factor (Cunningham 2005)
Tab. 1.Wartość wskaźnika spękań JCF (Cunningham 2005)

Parameter	Coefficient value
Tight joints	1
Relaxed joints	1.5
Gouge-filled joints	2

Tab. 2. Joint Plane Spacing (Cunningham 2005)
Tab. 2. Wartość wskaźnika JPS (Cunningham 2005)

Distance between cracks (JF)	Coefficient value
JF <0,1	10
JF =0.1÷0.3	20
JF =0.3÷0.95·P	80
JF > P	80

Tab. 3. Joint Plane Angle (Zou 2017)
Tab. 3. Wartość wskaźnika JPA (Zou 2017)

Joint Rock Factor	Coefficient value
Dip out of face	40
Strike out of face	30
Dip into face	20

The impact of geology on muck pile fragmentation is defined by the following coefficients: A (equation 8), RMD , RDI (equation 9), HF (equation 10).

$$A = 0,06 \cdot (RMD + RDI + HF) \tag{8}$$

where:
RMD is Rock Mass Description, indicating the geological structure of the rock mass
RDI is Rock Density Influence, as in equation 9,
HF is Hardness Factor, see equation 10.

The influence of the RMD coefficient is assigned on the basis of rock mass fragmentation. A highly fragmented, powdery/ friable rock mass is assigned a score of 10, while a rock mass with few cracks (distance between boreholes lower than the distance between the joints) the RMD coefficient value is 50 (Cunningham, 2005).

The rock mass density coefficient is determined with equation 9, into which the specific density of the rock mass, γ_r in $t \cdot m^{-3}$, is substituted.

$$RDI = 25 \cdot \gamma_r - 50 \tag{9}$$

The hardness factor (HF) is derived from equation 10 or equation 11 depending on the value of Young's modulus (Y).

$$HF = \frac{Y}{3} when\ Y < 50 \tag{10}$$

$$HF = \frac{UCS}{5} when\ Y < 50 \tag{11}$$

where:
Y – Young's modulus, GPa,
UCS – Unconfined Compressive Strength, MPa.

In the case of vertical joints at the working level (Cunningham, 2005) the JF (Joint Rock Factor) is recommended, as in equation 12:

$$JF = (JCF \cdot JPS) + JPA \tag{12}$$

where:
JF – Joint Rock Factor,
JCF – Joint Condition Factor – Table 1,
JPS – Joint Plane Spacing, Table 2,
JPA - Joint Plane Angle, Table 3.

The JPS value is determined as a reduced pattern (P), defined according to the equation 13.

$$P = (Z \cdot a)^{0,5} \tag{13}$$

where:
P – reduce pattern index,
Z – burden, m,
a – spacing, m,

As provided by Spathis (2004) and Cunningham (2005), the Kuz-Ram model is one of the most frequently used models for estimating muck pile fragmentation. Only recently, depending on the blasting technology (opencast and underground mines, tunnelling) and on the level of adjustment of changing geological conditions, some coefficients have been modified (Faramarzi et al. 2013), (Mohammadi and Barati 2018).

Cunningham (2005) claimed that in the case of empirical models an increase in energy generated by the detonation of the explosive material impacts on the degree of fragmentation (lower grain size) for the entire pile. As stated by Cunningham (2005), the assumption is accurate, but not necessarily applicable to in situ conditions. Cunningham (2005), Faramarzi et al, (2013), and Mohammadi and Barati (2018) pointed to such factors as the properties of the rock mass (strength parameters and degree of cracking), blasting parameters (the number of

Tab. 4. Blasting parameters and calculated rock mass parameters
Tab. 4. Rzeczywiste parametry robót strzałowych oraz wyznaczone parametry masywu skalnego

Parameter	**Value**
Number of blast holes, n	6
a	3 m
Z	3 m
H	10 m
d	105 mm
q	0.43 kg/m^3
Max. charge in the borehole, Q_c	41 kg
Max. charge per delay Q_z	24 kg
Subdrill, L_p	1 m
γ_r	2850 kg/dm^3
RMD	50
Y	110 GPa

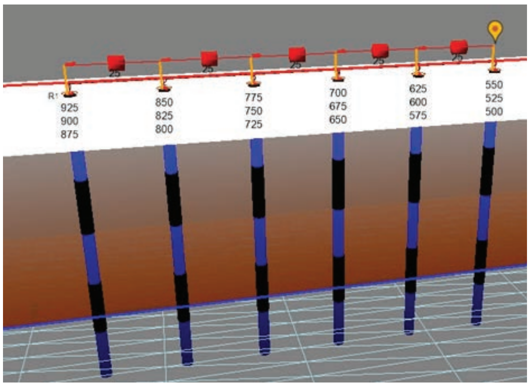

Fig. 1. The blasting series designed in the O-Pitblast software
Rys. 1. Zaprojektowana w programie O-Pitblast seria strzałowa

Tab. 5. Output size distribution based on the Kuz-Ram model and Split Desktop 2.0
Tab. 5. Procentowy udział frakcji na podstawie modelu Kuz-Ram i Split Desktop 2.0

Grain size; mm	**Output size distribution, %**	**Output size distribution, %**
	The Kuz-Ram model	**Split Desktop 2.0**
4.0	0.79	13.78
5.5	1.09	15.47
7.8	1.54	17.28
11.0	2.17	17.24
16.0	3.15	22.09
22.0	4.32	25.18
31.0	6.08	29.14
44.0	8.60	33.98
63.0	12.25	39.44
88.0	17.00	44.60
125.0	23.92	48.70
250.0	46.28	61.98
500.0	86.30	77.24
750.0	95.48	85.39
1000.0	96.38	89.83
2000.0	99.98	95.69
4000.0	100.00	100.00

Fig. 1. The blasting series designed in the O-Pitblast software
Rys. 1. Zaprojektowana w programie O-Pitblast seria strzałowa

Grain size; mm	**Output's size distribution, %**
	O-Pitblast
0	0.0
93	10.0
142	20.0
185	30.0
226	40.0
269	50.0
315	60.0
368	70.0
433	80.0
475	85.0
530	90.0
615	95.0
2000	100.0

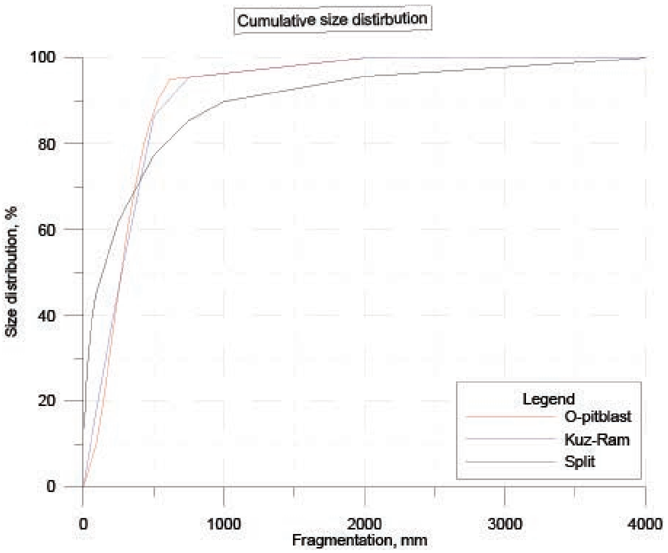

Fig. 2. Cumulative size distribution curves depending on the type of analysis
Rys. 2. Krzywe składu ziarnowego w zależności od rodzaju analizy

series, the number of holes in a series, time delay, precision which depends on the initiation system, stemming type and the ratio between the height of the bench to the length of the stemming and subdrill) as well as the properties of the explosive material (detonation velocity) must be known in order to precisely determine fragmentation.

Measurement methodology

Output size distribution was calculated with the use of the theoretical Kuz-Ram model; see equation 5÷7. The results were verified with the dedicated computer software O-Pitblast and with the photogrammetric analysis. O-Pitblast was used to design a blasting series (Fig. 1) and muck pile fragmentation was estimated with the analytical module. A comparison of the obtained cumulative grain size distribution curve (based on the theoretical model and correlations applied in the O-Pitblast software module) enabled a verification of the algorithm used in the software (checking for possible additional modifications of the formula). Table 4 presents the actual parameters on which the blasting works were based and the rock mass parameters were determined.

The photogrammetric analysis was performed on the basis of data from blasting works carried out in an opencast dolomite mine. The mine is located in the Małopolskie Province. The measurement methodology and the detailed results of the photogrammetric analysis are presented in the studies by Biessikirski et al. (2016a and 2016b). The photogrammetric analysis was performed for the output directly after the blasting works and for a partially extracted output in the Split Desktop 2.0 software. The obtained results were averaged and formulated in Table 5, Table 6, and Fig. 2. Output size distribution was specified on the basis of the Kuz-Ram model and presented in Table 4, Table 5, and Fig. 2.

Results

Based on the comparison of the shape of the cumulative size distribution curves determined with the use of the Kuz-Ram model (Fig. 2, the blue line) and with O-Pitblast (Fig. 2, the red line) it was found to be almost identical. For the Kuz-Ram model, the highest calculated size range was 2000-4000 mm, and for the O-Pitblast software the range was 650-2000 mm, see Table 6. This difference could be due to the inclusion of the charge structure by the software (a three-part charge), which is not the case for the theoretical Kuz-Ram model (a division into an upper and lower charge only). The shape of the curves obtained for the Kuz-Ram model and on derived from the same model in the O-Pitblast software shows that no additional modifications of the algorithm were carried out. A common practice in the algorithm's modification is their application only to specific mining and geological conditions. Comparing the obtained values for the theoretical models with photogrammetric analysis data (Fig. 2, the black line) a substantial difference was recorded, especially for the size ranges 4-125 mm and 750-1000 mm. The difference reached around 28.0%. This could have resulted from the calculated rock mass coefficient, for which RMD is defined on the basis of inspecting the rock mass and experience.

Conclusions

The article discusses the methodology for predicting muck pile fragmentation using the Kuz-Ram model and compares the determined theoretical values (equations 5÷7, the O-Pitblast software) with the data obtained from the performed photogrammetric analyses.

The achieved shape of the cumulative size distribution curve calculated with the theoretical model (the Kuz-Ram equation) and with the analytical module of the computer software shows that the Kuz-Ram algorithm was not subjected to additional modifications. Minor differences result from a better reflection of the charge structure in the software as compared to the Kuz-Ram equation. In addition, as stated by the software's producer, a higher precision can be obtained for modelling the blasting grid on the basis of a scan of the wall. Due to the lack of an actual scan, the model was designed for a perfectly even sidewall, which further facilitated a comparison of the results from the software with those from the Kuz-Ram equation. It could be expected that the impact of sidewall shape and the actual geometric parameters of the blast holes could contribute to a greater similarity between the output size distribution calculated in the software module and the results determined on the basis of photogrammetric analysis. For verification purposes, further analyses could be performed in the future.

Differences in size distributions for theoretical values and those derived from photogrammetric analyses can result not only from not taking into consideration the actual mining conditions but also from the adopted RMD parameter. This parameter is determined subjectively, solely based on experience and site inspection.

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Analiza porównawcza fragmentacji urobku wyznaczonej na podstawie metody fotogrametryczną oraz modelu Kuz-Ram

artykule przedstawiono teoretyczne podstawy wyznaczania przewidywanej fragmentacji urobku oparciu model Kuz-Ram. Dodatkowo, wykonano porównanie krzywych składu ziarnowego uzyskanych na podstawie metody fotogrametrycznej oraz modelu Kuz-Ram. Procentowy udział frakcji dla charakterystycznych wielkości ziarna wyznaczono na podstawie równania Kuz-Ram, zaś dodatkową weryfikację przeprowadzono programie O-Pitblast, przy użyciu modułu analitycznego bazującego na analizowanym modelu fragmentacji. Na podstawie przeprowadzonych badań stwierdzono brak wprowadzenia modyfikacji do algorytmu programu O-Pitblast. Uzyskane różnice procentowego udziału frakcji wyznaczonej na podstawie obliczeń teoretycznych, oraz badań in-situ, można tłumaczyć m.in. subiektywnym przyjęciem współczynnika RMD.

Słowa klucze: roboty strzałowe, fragmentacja urobku, Split Desktop 2.0, Kuz-Ram, O-Pitblast

IoT platforms for the Mining Industry: An Overview

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Abstract

Industry 4.0 and the Internet of Things are now very common concepts as solutions that can revolutionize the industry. Constant technological progress increases the possibilities of using computer tools and solutions to support processes in industry and production optimization. The use of the Internet of Things is particularly important in complex processes in mining, enabling the extraction of valuable information from data. The integration of physical facilities in the enterprise enables the digitization of production processes and the increase of efficiency and security.

This article presents an overview of the selected internet of things platforms and analytical tools that can be used in industry, with particular emphasis on the mining sector. It is pointed out, that the number of suppliers of IoT technologies and analytical tools offering advanced data analytics services for industry is significant and constantly evolving. The aim of the article is to evaluate selected IoT solutions based on the following criteria: offering predictive analytics, implemented artificial intelligence (AI) or machine learning (ML) algorithms, a mining-oriented process approach, advanced data visualization, interoperability, real-time data capture, remote device management and cloud-based technology. The review was prepared to provide knowledge about IoT vendors operating on the market, as well as to indicate the functionalities that are the most popular among solutions.

Keywords: Industrial Internet of Things, analytics platforms, mining, data analysis

Introduction

In the world of fast-growing technologies, enterprises are forced to constantly improve their processes to keep their market position or confirm competitive advantage. A response to a growing demand can be developing technology, especially the Internet and information technologies, which provide new solutions for the industry. The various components of the process are a valuable source of information, that properly interpreted and used, enable the overall management of a company. Hence, the integration of physical objects and infrastructure equipped with sensors enables them to communicate with computers (Krupanek, Bogacz, 2018; Boyes et al., 2018). This combination makes it possible to computerize and digitalize manufacturing processes. Transformation of the industry allows traditional machines to become self-learning and self-aware devices, which interact with the manufacturing environment. In this context, we often hear about the term Industry 4.0, what means the fourth industrial revolution (Vaidya et al., 2018).

Industry 4.0 is closely connected with a conception of the Internet of Things (IoT). The term Internet of Things was first used in 1999 by Kevin Aszton in the presentation for the company Procter&Gamble (Ogórek, Zaskórski, 2018). IoT is a broad concept with numerous definitions. One of them, introduced in (Gubbi et al., 2013) defines the Internet of Things as “an interconnection of sensing and actuating devices providing the ability to share information across platforms through a unified framework, developing a common operating picture for enabling innovative applications. This is achieved by seamless ubiquitous sensing, data analytics and information representation with cloud computing as the unifying framework”. Connecting IoT technologies with the manufacturing process to create smart enterprise led to the formulation the concept of The Industrial Internet of Things (IIoT). A definition presented in (Boyes et al., 2018) states that: “The IIoT vision of the world is one where smart connected assets (the things) operate as part of a larger system or systems of systems that make up the smart manufacturing enterprise”.

The operation of an IoT platform enables data processing and storage, remote monitoring and support of the decision-making process. Various devices connected to a network provide data exchange between machines without human participation.

The increasing capability of collecting and processing information allows individual companies to independently store and process data to better understand their own processes and improve them. Production companies can reach for new solutions, which are much better adjusted to their requirements and the scale of operation. An enormous number of connected devices and the necessity of measuring different process parameters, puts a very high demand on providers regarding functionality, security and application’s functionality. In addition, a key role in choosing the IoT platform has the selection of tools for data visualization and analytics as an essential component of the solution.

Mining is considered to be a very complex and difficult process to predict, where not only human error or the unreliability of equipment, but also nature plays a significant risk factor. Mining companies decide to use IoT solutions to enhance process effectiveness, and as a result achieve better economic and technical outcomes. Industrial IoT platforms connect industrial machinery and specially designed devic-

Tab. 1. Functionalities of IoT platforms and analytical tools, [Source: own elaboration]
Tab. 1. Funkcjonalności platform IoT i narzędzi analitycznych, [Źródło: opracowanie własne]

Name of IoT platform	**Predictive analytics**	**AI/ML**	**Mining oriented**	**Visualization**	**Interoperability**	**Real time data capture**	**Device management**	**Cloud-based**	**Support and service**
ABB Ability	+	+	++	+	+	+	+	+	+
Buddy's IoT Data Graph	N/A	N/A	+	+	N/A	+	N/A	+	N/A
C3 IoT	+	+	N/A	+	+	+	N/A	+	+
Connected Mine	+	+	++	+	N/A	+	N/A	+	N/A
Cumulocity	+	+	N/A	+	+	+	+	+	○
DeviceHive IoT	+	+	N/A	+	+	+	N/A	+	N/A
Dingo Trakka	+	N/A	+	N/A	N/A	+	N/A	+	+
Hexagon Mining	N/A	N/A	+	N/A	N/A	+	N/A	+	+
IBM Watson	+	+	+	+	+	+	+	+	+
IntelliSense	+	+	+	N/A	N/A	+	N/A	+	N/A
IoT.nxt	+	N/A	+	N/A	+	+	N/A	N/A	N/A
Kaa IoT	+	+	N/A	+	N/A	N/A	+	+	N/A
Loop IoT Cloud	N/A	N/A	N/A	+	N/A	+	+	N/A	N/A
Losant	+	+	+	+	N/A	+	+	N/A	N/A
Hitachi's Lumad	+	+	○	+	+	+	N/A	+	+
Microsoft Azure+Power BI	+	+	N/A	+	+	+	+	+	+
Modular Mining	N/A	N/A	+	+	N/A	+	N/A	+	+
Predix GE	+	+	○	+	N/A	+	+	+	+
PTC Thingworx	+	+	N/A	+	N/A	+	N/A	+	+
SAP Leonardo	+	+	○	N/A	+	+	+	+	+
Siemens Mindsphere	+	+	○	+	N/A	+	N/A	+	+
Thinger.io	N/A	N/A	N/A	+	+	+	N/A	+	N/A
Uptake	+	+	+	N/A	+	+	N/A	+	+

Explanations of markings: ++advanced, + well-developed, ○ satisfactory, N/A - not available

es to ensure comprehensive insight into operational data. At present, especially in industry, IoT platforms are heading towards predictive maintenance to provide exactly planned processes without undesirable events and defined future states of the manufacturing environment.

The main purpose of this paper is to provide an overview of selected industrial IoT platforms. A significant number of IoT platforms and their constant development among new technology providers indicate the scale of this phenomenon and the growing popularity of analytical solutions used in production processes to provide reliability. Taking into consideration contemporary trends, an analysis of the industrial internet of things (IIoT) platforms and analytical tools will be performed. To identify solutions available on the market, main vendors websites and white papers will be searched.

Overview of IoT platforms

The number of platforms and analytical solutions that offer comprehensive services for advanced data analysis is significant. The range of services is also extensive and wide. Platforms include artificial intelligence algorithms and machine learning applications. Moreover, remote monitoring and management are used to provide alerts in real time. Visualization ensures a better understanding of enormous and diversified data sets, visual exploration and visual analytics. Storing data in the cloud offers their security without expensive infrastructure. By means of predictive analytics, companies use data to predict equipment failures and future trends.

The following section presents an overview of 23 IoT platforms and analytical tools which could be applicable in the mining industry. Some solutions are developed by companies from the mining domain or are prepared as platforms dedicated typically for mining enterprises. Examples of such solutions that were chosen for analysis are as follows: the ABB Ability IMS (Intelligent Mining Solution), Uptake, Hexagon Mining, IntelliSense, Modular Mining and Connected Mine.

The overview includes also platforms with significant market presence, often offered by well recognized producers such as: the IBM Watson IoT Platform, Siemens Mindsphere IoT, Hitachi's Lumada, Cumulocity IoT, SAP Leonardo IoT, The C3 IoT Platform, PTC ThingWorx IoT and Microsoft Azure IoT with analytical tool Power BI.

In the analyzed solutions only a small percentage are open-source platforms. Examples of platforms offered in such a business model are: the Kaa IoT Platform, the GE Digital Predix Platform, DeviceHive IoT, Thinger.io IoT according to the information on the vendor's websites.

In the prepared survey also were considered IoT platforms and analytics solutions such as: Dingo Trakka, Loop IoT Could, Losant Enterprise, Buddy's IoT Data Graph and IoT.nxt to point out some lesser known solutions and evaluate the possibility to adapt them in the mining industry.

Based on available materials from producers, the IoT platforms and analytical tools were evaluated taking into account the main functions and criteria as: predictive analytics, implemented artificial intelligence or machine learning algorithms, the mining oriented approach to the process, data visualization, interoperability - as a possibility to integrate different tools, products or systems, real time data capturing, device management and cloud-based technology. Furthermore, support, consultations and services from providers were taken into account. The category of support and service includes a wide range of professional services such as: trainings, deployment, engineering support, guidance in the technological as well as in the analytical fields and support from provider's partners, not only remotely, but also on site.

The evaluation was based on the grounds of available information and descriptions, with paying attention to the mentioned, essential points. The characteristic of the selected platforms is presented in Table 1.

Crucial, in choosing the appropriate platform, is to have access to a complete and accurate offer. The majority of the vendors provided precise products' descriptions, which are the basis in the preselection during market research. The features, chosen for the analysis, were collected to compose general outlook for the issue. The summarisation could be advantageous for the potentially interested users in comparing IoT solutions for industry. In some cases, there is a lack of information about certain properties or functionalities of platform in the provider's offer. Such cases are marked in the mentioned table.

The key aspect for a customer is also the safety of data and technical functionalities of the presented platforms, such as: device management, interoperability and well-developed analytical and visualization tools. Important is also the provider's size as a company and reputability, which often entails market stability, service and guidelines in the future. From an industrial point of view, maintenance and reliability, early detection of defects and machinery failures are essential to effective processing. By knowing past and current states, enterprises are able to make predictions and support decision making processes through real time data capturing. Furthermore, this knowledge enables the enhancement of processes and the entire company.

Selected platforms differ to some extent, depending on the level of adaptation of their functionalities to the industry, in particular to the mining sector. Some technologies are widely adopted and implemented in most of the considered platforms or tools. Nevertheless, some functionalities are not equivalent to each other. Depending on the industry and the specifics of the process, certain features will be considered as more valuable to implement in the company. A compilation of selected features' frequency was developed to indicate the most popular properties of platforms. The frequency of reported features in the IoT solutions is shown in Figure 1.

The most frequent functionalities among the analyzed platforms and tools are: real time data capturing, cloud based servicing and predictive analytics. The results of the evaluation indicate that the vast majority of vendors offer not elementary analytics but diversified and highly advanced techniques and algorithms for analyzing data and making predictions based on it. The mining oriented approach is distinguished for 15 platforms, similarly the ML and AI implementation are found in 16 offers. Highly evolved visualization abilities are provided by 17 platform providers from the analyzed group. It can be seen, that the least commonly provided properties are: device management, interoperability with another tools and equipment, besides vendor's support and service.

The above resume constitutes about the distinguishing features of the evaluated platforms and point out some technological fields in which providers might develop their offers to compete on the rapidly growing market.

The majority of the analyzed IoT platforms are addressed to the industrial sector. These solutions can operate with various processes and are able to connect industrial devices. However, an industrial profile is not always equivalent to working effectively in mines. A mining-oriented solution means that a platform should be accustomed to complex processes, carried out in different areas of operation, with specialized equipment, numerous of hazards and the necessity of interoperability.

It is difficult to conclude on the usefulness of the majority of the listed and analyzed platforms for the mining industry solely based on the solution description. Taking into consideration the specificity of mining and data from this sector, it can be deduced that conventional platforms are not adapted to the analysis of specific and unstructured data sets without the process-oriented approach. Partly, analytical tools and IoT platforms specialized for the mining industry are usually characterized by lower analytical sophistication, whereas highly advanced platforms are not typically targeted at the mining industry. The process-oriented approach is particular-

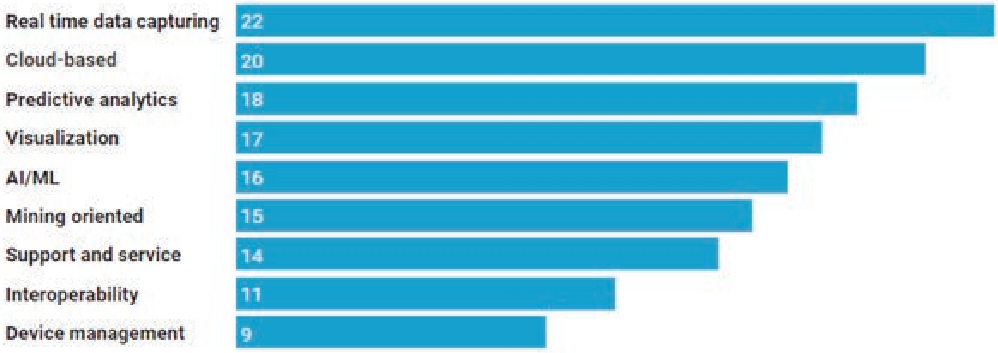

Fig. 1. The number of IoT platforms regarding to the offered functions, [Source: own elaboration]
Fig. 1. Liczba platform IoT oferujących poszczególne funkcjonalności, [Źródło: opracowanie własne]

ly important for underground mining, where the specifics and requirements are substantial.

Summary

Mining processes are complicated, unpredictable and require a special and tailored approach. The necessity of process improvement and the possibility of accurate data based prediction, require production automation and new technologies utilization. These technologies should include IoT as a comprehensive solution for overall process management.

Currently, the number of data is growing constantly, and hence the percentage of useless data increases as well. The point is to extract from produced data only valuable and important information. Due to this fact, data need to be captured, recorded and processed with the appropriate tools and algorithms to transform them into valuable knowledge. Having regard to the mentioned trends, in the article, survey of IoT platforms and analytical tools applicable in industry was drawn.

The collected information according to the IoT platforms for industry and analytical tools was analyzed in terms of selected aspects. Afterwards, a summary of the frequency of using selected functionalities and technologies was presented in the bar chart. An evaluation is based on platforms providers website and published white papers.

With technological progress, IoT platforms and solutions are gaining a very high level of sophistication. Development is visible in many fields to meet the requirements of customers. For the selected group of platforms, offered by various suppliers, from large technology companies, through open source solutions to the mining industry enterprises suppliers, the analyzed solutions offer a wide range of functionalities and services to ensure full control, support as well process optimization in the industry, productivity improvement, cost reduction and interaction with technology.

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Przegląd platform Internetu rzeczy dla przemysłu górniczego

Koncepcje Przemysłu 4.0 i Internetu rzeczy są obecnie bardzo powszechne, jako rozwiązania, które mogą zrewolucjonizować przemysł. Nieustanny postęp technologiczny zwiększa możliwości wykorzystania narzędzi i rozwiązań komputerowych do wspomagania procesów w przemyśle i optymalizacji produkcji. Zastosowanie Internetu rzeczy ma również istotne znaczenie w skomplikowanych i złożonych procesach w górnictwie, umożliwiając pozyskanie wartościowych informacji z danych. Ponadto, integracja obiektów fizycznych w przedsiębiorstwie umożliwia digitalizację procesów produkcyjnych oraz zwiększenie wydajności i bezpieczeństwa prowadzonych prac.

W artykule przedstawiono przegląd wybranych platform internetu rzeczy i narzędzi analitycznych, które mogą być wykorzystywane w przemyśle, w szczególności z uwzględnieniem branży górniczej. Zwrócono uwagę na fakt, że liczba dostawców technologii IoT i narzędzi analitycznych, oferujących usługi zaawansowanej analityki danych dla przemysłu jest znacząca i ciągle się rozwija. Celem artykułu była ocena wybranych rozwiązań IoT na podstawie następujących kryteriów: zastosowanie predykcyjnej analityki, wdrożone algorytmy sztucznej inteligencji lub uczenia maszynowego, podejście procesowe zorientowane na górnictwo, zaawansowana wizualizacja danych, interoperacyjność, przechwytywanie danych w czasie rzeczywistym, zdalne zarządzanie urządzeniami oraz technologia oparta na chmurze. Przegląd został przygotowany, aby zestawić wiedzę na temat dostawców rozwiązań IoT działających na rynku, a także wskazać funkcjonalności wyróżniające poszczególne rozwiązania.

Słowa kluczowe: przemysłowy Internet rzeczy, platformy analityczne, górnictwo, analiza danych

Contract Prices for Road Construction as a Function of Landform

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Abstract

In the context of the terrain conditionings, the volatility of unit prices of road construction in Europe and Poland was analyzed. On the basis of the price volatility index of twelve contracts concluded in 2016 by the Directorate of National Roads and Motorways (DDKiA), there was little variation in the average construction prices of 1 km of technical class S expressways on flat and undulating terrain, over a large area of Poland, above Wrocław and Lublin towards the north. However, also for the expressway, but in mountainous terrain in Małopolska, between Lubień and Chabówka, on three sections of S7, together with a length of 15.8 km, the coefficient of variation in unit prices was very large (5.7 times greater than in the flat and corrugated areas mentioned above). Among the reasons for this high price volatility, it was pointed out that it was necessary to adapt to difficult mountain conditions - through the use of specialized technical solutions, costly in implementation and other on almost every of these sections. Necessary were, among others over a 2-kilometer tunnel (many times more expensive than the other sections of the route), intensive reinforcement of escarpments with ground nails (with a total length of over 350 km) and foundation of embankments on gravel columns, as well as construction of numerous flyovers, viaducts and bridges with a total length of 5,752 km. Attention was also paid to the necessity of taking into account the proportion of the tunnel's length to the length of the remaining road section, as this is a condition of correct expenditure analysis.

Keywords: express roads, landform, road costs

Components of road construction costs

Roads besides absorbing a wide strip of land, even several dozen meters, eg under the motorway, contribute to pollution by exhaust fumes and noise of space within a radius of up to several kilometers. In addition, the area is artificially separated into separate parts. There is a need to move habitats and build passages for animals and other pro-environmental objects. As a result, according to [2] the value of elements of environmental protection, it constitutes about 18%, and sometimes it reaches even 35% of motorway construction costs, Figure 1.

The costs of population resettlement and land purchase account for about 15%, and in urban areas they can reach up to 30% of the total investment value (eg in the construction of M74 in Glasgow, in 2009). While the design costs range from 3% to 5%, currently expert opinions and consultancy usually amount to about 7%, and sometimes they reach 15% of the investment value. The construction itself usually costs about ¼ of the motorway value, while the administrative costs of such projects amount to around 30%.

Implementation conditions

Routes of roads depend on the conditions resulting from international agreements and performed functions in the general road network, as well as must be compliant with spatial development plans. However, the road design itself should meet the requirements of applicable law [4] and technical standards [3].

Roads, in particular, fulfill the basic requirements in terms of: safety of use, load-bearing capacity and stability, fire safety and other local hazards, environmental protection and protection against excessive noise, vibrations, air, water and soil pollution and provide conditions for using the road in accordance with its intended purpose, also by people with disabilities [3]. The route of the road should be properly inscribed in the surrounding area, with the most convenient crossing of obstacles, i.e. existing rivers and habitats and the existing development, as well as meet the conditions related to its maintenance and economics of the solution.

Among these many conditions, as a result, the road as an engineering object must be built in the existing terrain. Depending on the natural shape of the surface and the local conditions of foundation, the size of embankments and excavations, the need to reinforce slopes, the construction of bridges and viaducts and possibly the construction of tunnels are directly dependent. Naturally, the scope of these construction works directly affect the construction costs of individual roads.

Variability of road construction costs in europe

Analyzing, the costs of road construction in Europe, according to [16], Figure 2, in 1998 the lowest expenditures for completing the 1st kilometer of the motorway were in Spain. In flat and corrugated areas, they amounted to 1.9 million €, with a double the average cost of constructing motorways across the country of 3.8 million €. Much greater price differentiation was in Italy. In wavy areas, the lowest cost amounted to 7.5 million € for 1 km, and the average for the whole, including roads in the mountains and the need to build tunnels was 25 million €, ie 3.3 times higher. At the same time, in Switzerland, the cheapest section, at more affordable execution conditions, cost EUR 12.5 million per km. The cost was 5.4 times lower than the average price of motorways amounting to 67.5 million €. In Switzerland, due to extremely

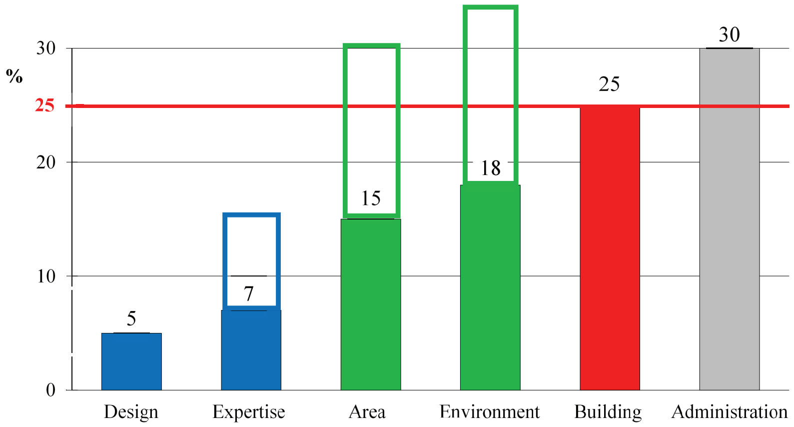

Fig. 1. Average share of components in the motorway construction costs [own elaboration based on 2]
Rys. 1. Średni udział składowych w kosztach budowy autostrad [opracowanie własne na podstawie 2]

complicated, high-altitude terrain conditions, it is necessary to drive roads in numerous, even multi-kilometer-long tunnels (eg in 2017, the network of road tunnels in Switzerland was the largest in Europe and was 421 kilometers long).

Therefore, even this brief comparison allows to notice that in difficult mountainous conditions the costs of road construction are even many times higher than in flat and undulating terrains.

Analyzed contracts for construction of roads in Poland

The total length of public roads in Poland in 2016 was about 420,000 km and there were over 35,000 bridge structures and tunnels with a total length of over 1,05 thousand km. According to plans (2016), the length of motorways in Poland, in 2020 will be about 7,800 km, including 2,000 km of highways and 5,800 km of expressways. There are currently 1991 km of highways and 5,813 km of expressways [9]. The progress of road construction on 13/04/2019, according to the data of the Directorate of National Roads and Motorways (DDKiA) [13], is shown in Figure 3.

The analysis covered 15 contracts for the construction of S-class express routes in Poland, which concluded DDKiA [13] in the first half of 2016. To assess the differences in road construction costs, the volatility coefficients of V were examined below.

Coefficient of variation

The assessment of the variation in the distribution of the examined feature, in this case the unitary costs of constructing S-class roads, can easily be carried out using the classic measure, ie the coefficient of variation. The coefficient of variation V, as a relative measure, is determined by the dependence:

$$V = s / x,\ x \neq 0, \tag{1}$$

where:
s – standard deviation from the sample,
x – the arithmetic mean of the sample.

According to Wawrzynek [7], if the value of the variation coefficient V expressed in% is in the range <0%, 20%> then the diversity of the population is small. At the V values belonging to the next interval (20%, 40%> is said about the average population differentiation, and the large variation is at the rate in the range (40%, 60%> and very large at V> 60%.

Contractual prices for technical class s roads

The surveyed contract prices of 15 contracts, which the Directorate of National Roads and Motorways [13] concluded in 2016 for the construction of S-class express routes (with two separate, two-lane roadways, load capacity 115 kN/axle, with emergency lanes, with viaducts and footbridges), passenger service areas, culverts and animal passes) are summarized in Table 1. One should notice a very large spread of average values of unit prices, from 14.27 million PLN to 322.93 million PLN for 1 km of the route.

The average price for all 15 analyzed contracts was x15 = 51.05 million PLN/km, and the standard deviation s15 = 75.91. Hence, the value of the coefficient of variation V15 = 149% was much higher than 60% - this means that the price differentiation was very large.

However, when analyzing 12 contracts for the construction of S-class roads in flat and wavy areas, i.e. in Poland, above Wrocław and Lublin towards to the north, the average cost of these routes was x12 = 22.8 million PLN/km, with the standard deviation s12 = 3.4, Figure 4. Due to the coefficient of variation V12 = 14.8%, smaller than 20%, as above it can be assumed that the price differential between these contracts was small.

Prices for the construction of S7 sections road in mountainous terrain

In Małopolska, on the fragment of the S7 Kraków-Zakopane route between Lubień and Chabówka, 15.8 km long, Table 2, in difficult mountain terrain, with indispensable reinforcement of embankment and excavation slopes with retaining walls and anchors, and with the need to build many long overpasses, as well as a two-chamber tunnel, the execution of works is much more expensive than in the roads of the S class, but in flat areas.

For example, section I, 7.6 km long, Lubień - Naprawa will be built, on average, 68.6 million PLN/km, Figure 5. The most difficult, approximately 3-kilometer stretch II road, the Naprawa-Skomielna Biała will be completed at 322.9 million PLN/km, Figure 6. Episode III of this route, 5.2 km long,

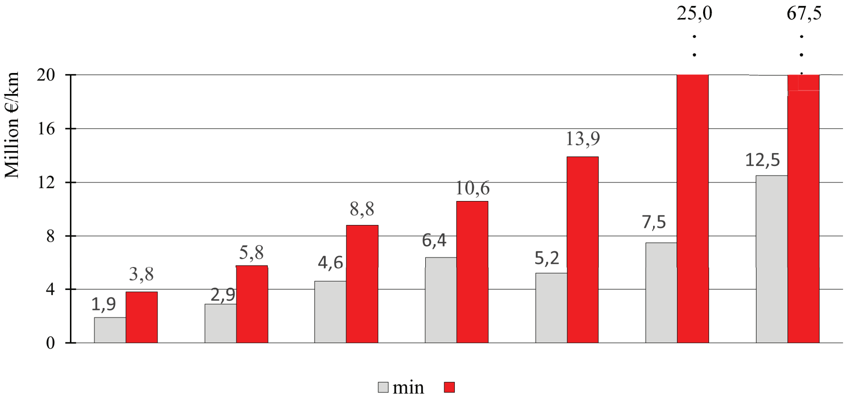

Fig. 2. Volatility of unit costs of motorway construction in selected European countries, in 1998 [own elaboration based on 16]

Rys. 2. Zmienność jednostkowych kosztów budowy autostrad w wybranych krajach Europy, w 1998 r. [opracowanie własne na podstawie 16]

Fig. 3. Road construction progress in Poland, 04/2019; roads are marked with colors:
green – existing, red – under construction, gray – planned [source: 9]

Rys. 3. Postęp budowy dróg w Polsce, 04/2019; drogi są oznaczone kolorami:
zielonym – istniejące, czerwonym – w budowie, szarym – planowane [źródło: 9]

Tab. 1. S-class expressway sections, for which in the first half of 2016, the Directorate for National Roads and Motorways concluded contracts for performance [own development based on 13]

Tab. 1. Odcinki dróg ekspresowych klasy S, dla których w pierwszej połowie 2016 r. Dyrekcja Dróg Krajowych i Autostrad zawarła umowy na wykonanie [opracowanie własne na podstawie 13]

Section of the road	**Road**	**Length km**	**Price million PLN**	**Average million PLN/km**
Radziejowice - Paszków	S8	21,5	306,9	14,27
Kościan Południe – Radomicko	S5	16	303,0	18,94
Wronczyn - Kościan	S5	19	360,0	18,95
Kołbiela - Garwolin	S17	13	290,0	22,31
Radomicko - Leszno	S5	19	440,0	23,16
Poznań – Wrocław	S5	19	443,0	23,32
Lubelska - Kołbiela	S17	15,2	370,5	24,38
Leszno - Kaczkowa	S5	9,5	232,6	24,48
Wyszków - Białystok	S8	16	404,5	25,28
Wyszków – Poręba	S8	13	334,7	25,75
Lubelska - Kołbiela cd.	S17	8,7	225,5	25,92
Ostrowia M. – prov. border podlaskie	S8	9,4	250,0	26,60
Lubień - Naprawa	S7	7,6	521,4	68,60
Naprawa – Skomielna Biała	S7	3	968,8	322,93
Skomielna Biała – Rabka Zdrój	S7	6,1	615,0	100,82

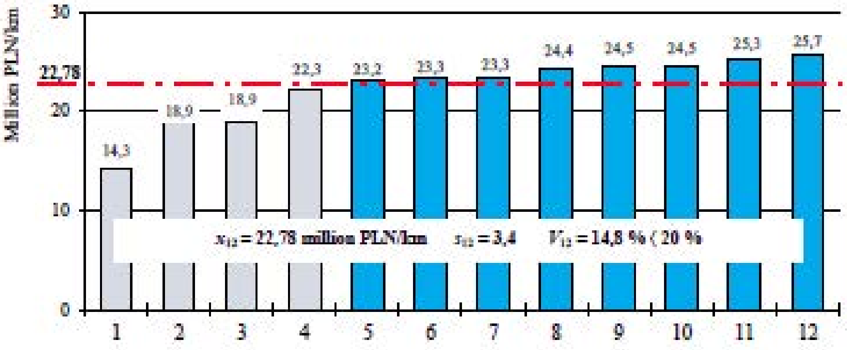

Fig. 4. Unit prices for S-class road construction contracts in Poland, on flat and undulating areas, contained in the first half of 2016 [own elaboration, based on 13]
Rys. 4. Ceny jednostkowe kontraktów na budowę dróg klasy technicznej S w Polsce, na terenach płaskich i falistych, zawarte w pierwszej połowie 2016 r. [opracowanie własne, na podstawie 13]

Skomielna Biała - Chabówka together with the GP dk47 route Rabka Zdrój - Chabówka length of 0.9 km will be on average, after 100.8 million PLN/km, Figure 7. The average price of these sections of the S7 road was x3 = 164.1 million PLN/km, and the standard deviation s3 = 3 4, Figure 8. Thus, the coefficient of price variation for these road sections was V3 = 84.4% and was significantly higher than 60%, which means that the volatility of contract values is very large, Figure 8, [7, 8].

The main reasons for these large unit price divergences were the different technical solutions necessary to apply in individual local conditions of each of these sections. These implementation restrictions can be divided into three groups:

- great diversity of the landform,
- variability of foundation conditions,
- uneven intensity of occurrence of accompanying road facilities.

Variables landform of the mountain terrain, among others caused the necessity of building a two-chamber tunnel under the Luboń Mały mountain, 2,06 km long, with a unit cost of about 3.8 times higher than the rest of the road Naprawa - Skomielna Biała [9]. At the same time, the tunnel was not implemented either on the first episode of Lubień-Naprawa or on the third Skomielna - Chabówka. Also, the landform has required the construction of numerous flyovers constituting 24%, 33% and more than 40% of the lengths of sections I, II and III, respectively. The construction of 12 bridge structures and 6 small ones with a total length of 2045 m is planned for section 1. On the second section (as above, beyond the tunnel) there was one viaduct with a length of 311 m, and on the third section of 17 viaducts and flyovers, and 4 small bridges with a total length of 3396 m (including ~ 2.3 km of the road on the viaducts, the largest 999 m long, with a 140 m span and the height of the support with load bearing structure 49.4 m and 4 smaller for the road link with lengths of 356.00 m to 446.00 m).

In addition to the varied terrain, there was a large variability of foundation conditions resulting from the various properties of the Carpathian flysch. For example, in section I, there was strong reinforcement of slopes using the total, up more than 350 km ground nails, while in the third section there was a need to make embankments on gravel columns closed with a aggregate mattress, [6].

In addition, the uneven intensity of occurrence of associated road objects on individual parts of the route was the result of both the location of such facilities and the route of roads in the existing communication network, as well as the very diversified mountain terrain and relatively smalls lengths of the analyzed routes. As a result, road junctions were located only on the Skomielna - Chabówka section. The first one in Skomielna Biała for the connection of roads S7 and dk28 (for the direction Wadowice - Nowy Sącz) and the second one in Zabornia for the fork S7 on dk47 (towards the direction of Chyżne and Zakopane). Also in this episode was the most favorable location of the express road maintenance base. Similar objects did not appear on sections I and II. In addition, the construction of passenger service areas (ILO) was unevenly planned: two in the I section in Lubień and Krzeczów and one in Zbójecka Góra on the III section (there was no ILO at the second section).

Commentary on the costs of road construction with tunnels

Unit costs for the construction of a section of road in the tunnel are usually many times greater than the construction of road sections in the open area, [1]. In the case of such relatively difficult to compare road construction costs of various sizes of tunnel sections, attention should be paid to the proportions of p - length of tunnels in relation to the entire analyzed routes. When checking the average construction costs of roads with different proportions p, calculations can be made in accordance with the proposed relationship:

$$k_p = k_t p + k_d (1-p)$$

where:
k_p – average cost of 1 km of the route for the assumed proportions p, million PLN/km (million €/km),
p – the value a proportions of the tunnel's length – l_t km, relative to the length of the analyzed road section – l_d km, $p = l_t / l_d$,
k_t, k_d – construction costs of 1 km, respectively, of the tunnel and the remaining part of the section of the road outside the tunnel, million PLN/km (million €/km).

Tab. 2. Characteristics of the S7 expressway on the Lubień-Chabówka section [own elaboration, based on 13]
Tab. 2. Charakterystyka drogi ekspresowej S7 na odcinku Lubień – Chabówka [opracowanie własne, na podstawie 13]

	Expressway S7, section Lubień - Chabówka,		
	length 15.830 km, value of contracts PLN 2105 million		
Sections	I. Lubień - Naprawa	II. Naprawa – Skomielna Biała	III. Skomielna Biała – Chabówka (Rabka Zdrój– Chabówka)
Contractors	IDS-BUD S.A.	**Astaldi S.p.A.**	Salini Impregilo S.p.A.
	ul. Grzybowska	**Via Giulio Vincenzo Bona 65,**	Via dei Missaglia 97,
	87, 00-844 Warsaw	**00156** Rome, Italy	20142 Milan, Italy
	ALTIS-HOLDING Corporation,		
	ul. Kaczałowa 5w, 03146 Kiev, Ukraine		
Contract dates	29.06.2016 r.	29.02.2016 r.	31.03.2016 r.
Cycles, months	22	54	22
Lengths, km	7,59	3,05	5,19
		(including the tunnel)	(and 0.877 km GP dk47)
Gross values, PLN	521 519 095,35	**968 835 650, 11**	615 068 976,27
Tunnel, km	-	• 2,058 (near the Luboń Mały mountain)	-
Road junctions and facilities	-	-	• Skomielna Biała S7-dk28 (directions: Wadowice i Nowy Sącz, • Zabornia S7-dk47(directions: Nowy Targ i Chyżne) • Place of service for travelers
Place of service for travelers	• Lubień, • Krzeczów	-	• Zbójecka Góra
Viaducts and flyovers	• 24% of the road length,	• 33% of the length of the road (outside the tunnel)	• 40.3% of the road length,
	• total length 2045 m,	• length 311 m,	
			• total length of 3396 m (~ 2.3 km of road on overpasses)
	• 12 objects and 6 small ones	• 1 object (box construction, traditional method, stationary scaffolding)	• 17 objects and 4 small ones (reinforced concrete, beam and box construction, one and two-chamber, compressed, largest: 999 m long, including 140 m span, height of the support together with the supporting structure 49.4 m; 4 smaller for ramps, lengths 356.00 m to 446.00
Placing	• large diameter foundation piles	• large diameter foundation piles	• large diameter foundation piles, caissons, gravel columns with a mattress of broken aggregate, directly with the exchange of ground

For example, in Slovenia (where, according to [17] in 2012, the average cost of building motorways amounted to 7.3 million €/km and was 22% lower than the average price in Europe) implementation of the route with length l_{dS} = 4.5 km, with the długości l_{dS} = 1.5 km tunnel it amounted to 59 million €/km, i.e. it was 6.3 times higher than the European average and at the same time 8-times higher than the average motorway cost in this country.

The section of the S7 expressway - Skomielna Biała (dual carriageway with a two-chamber tunnel, [1, 14]) length l_{dP} = 3.05 km, with a tunnel l_{tP} = 2.057 km, according to the tender result will cost an average of 79.4 million €/km (34.6% more expensive than the average section of the route with a tunnel in Slovenia).

After considering the same proportion of tunnel length to the remaining road section pS = 0.3333, as on the road route

Fig. 5. The viaduct on the I section Lubień-Naprawa (402 m long) [source: 10]
Rys. 5. Wiadukt na odcinku I Lubień-Naprawa (402 m długości) [źródło: 10]

Fig. 5. Loading and transportation of excavated material from the tunnel [surce: 11]
Rys. 5. Załadunek i wywóz urobku z tunelu [źródło: 11]

Fig. 6. A fragment of the longest flyover on the Skomielna Biała–Chabówka section III (992 m long; largest: span the span 140 m, height of the support together with the supporting structure 49.4 m) [source: 12]
Rys. 6. Fragment najdłuższego wiaduktu na III odcinku Skomielna Biała – Chabówka (992 m długości; największe: rozpiętość przęsła 140 m, wysokość podpory wraz z konstrukcją nośną 49,4 m) [źródło: 12]

in Slovenia and with S7 costs on average, k_{tP} = 104.5 million €/km tunnel and k_{dP} = 27.5 million €/km for the remaining section of the road, calculated in accordance with the relation (2), the average cost of 1 km of this route S7 would be k_{pP} = 53.1 million €/km, ie it is 9.9% less than at the motorway in Slovenia, figure 3.

In the case of a 4.7 km section of the S69 Szare-Laliki road (single-station, with a one-chamber tunnel, [5, 15]), the construction cost was on average € 20.9 million €/km. After conversion according to the same proportion of tunnel length, to the remaining road section, for pS = 1/3, as in Slovenia, the average cost is k_{pL} = 27.5 million €/km.

Therefore, in order to better reflect the actual high expenditure on tunnels in the unit cost analysis, attention should be paid to the proportions of p – length of tunnels in relation to the entire test sections.

Summation

Road construction interferes very much with the natural environment

A large area of land is taken and divided into separate parts. There is pollution of the surrounding area with fumes and noise. As a result, in Europe the value of environmental protection elements constitutes about 18% (sometimes even 35%) of the construction costs of motorways. Purchase land and resettlement costs account for approximately 15% (in cities, up to 30%). The construction costs are usually around 25% and administrative costs about 30% of the value of highways. Design costs representing about 3% to 5% of the total costs of projects are unfavorably low.

The level of unit costs of road construction remains in direct dependence on the terrain conditions occurring on their routes

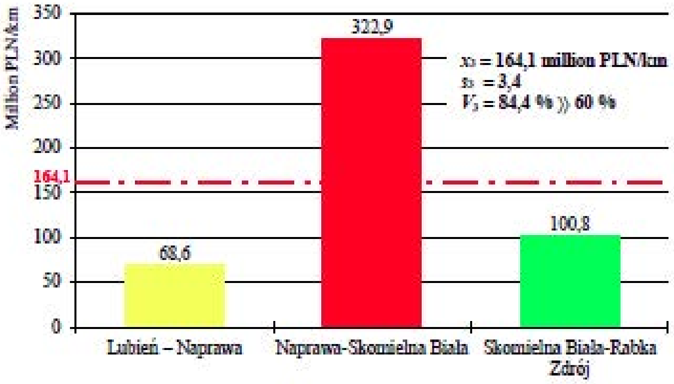

Fig. 7. Unit prices of contracts for the construction of S7 road sections between Lubień and Skomielna Biała [own elaboration, based on 14]
Rys. 7. Ceny jednostkowe kontraktów na budowę odcinków dróg S7 między Lubniem a Skomielną Białą [opracowanie własne, na podstawie 14]

In Europe, for example in 1998, the lowest expenditures for making the one kilometer of highways were in Spain. In the whole country, in large part on flat and undulating terrain, road construction costs amounted to an average of € 3.8 million per 1 km. In Italy, in the majority of wavy areas, the lowest cost was 7.5 million €/km. With the average cost for the whole country, with a higher share of roads in the mountains and the need for tunnels construction was costs were 3.3 times higher and amounted to 25 million € per km. In Switzerland however, the cheapest section cost more than 5.4 times less (in more accessible field conditions) than the average cost of motorways there, which amounted to as much as 67.5 million €/km. There, too, due to the extremely difficult alpine implementation conditions, it was necessary to drive roads on numerous overpasses and in multi-kilometer tunnels.

In Poland, similarly, on the basis of the analysis of contracts for the construction of S-class express routes, which concluded DDKiA [13] in the first half of 2016, it was found that found that, in areas of flat and corrugated have 12 sections of such S-class roads (with two separate, two-lane roadways, with emergency lanes, with viaducts, overpasses and footbridges, passenger service areas, culverts and passageways for animals) in the part of Poland, above Wroclaw and Lublin towards the north, they are they are characterized by low prices and low volatility. They the average price was x_{12} = 22.8 million PLN/km, with the standard deviation s_{12} = 3.4, and the coefficient of variation V_{12} = 14.8%, was less than 20% (which means that the coefficient of variation V of these contracts was small).

In Malopolska, the three contracts, for the sections of the S7 Kraków-Zakopane road, between Lubień and Chabówka, 15.8 km long (in difficult mountainous terrain, with the necessary strengthening of slopes with retaining walls and with anchoring and with the need to build many long overpasses, as well as a two-chamber tunnel) the performance of works was 7.2 times more expensive than in the previously analyzed 12 roads, also technical class S, but in flat and corrugated areas. The average price of these three sections of S7 was x_3 = 164.1 million PLN/km, standard deviation s_3 = 3.4, and the coefficient of variation V_3 = 84.4% (it was much larger than 60%, which means that the differentiation of the value of contracts was very big).

The main reasons for these several times higher contract prices were difficult conditions for road construction in mountainous terrain. In particular, large variations in the shape of the surface of the mountain terrain and the variability of foundation conditions (on the Carpathian flysch) and indirectly also related to the landform an uneven intensity of occurrence of road objects almost every time required individual technical solutions and consequently completely diferents construction costs.

The landform on the first section of the S7 Repair - Skomielna Biała required the most expensive construction of a two-chamber tunnel with a length of 2.06 km, under the Luboń Mały mountain, with a unit cost of about 3.8 times higher than the rest of the section (one kilometer long, with a 311-meter long overpass). On the other sections, 1st Lubień-Naprawa (7.59 km long) and Skomielna III - Chabówka (5.19 km plus 0.877 km) there were several overpasses and viaducts.They accounted for 24% and over 40%, respectively, in relation to the length of all these sections. On the third section, these objects together were 3,396 km long, including the road on the flyovers – 2.3 km long, In the III section, these objects together were 3,396 km long, with the longest section: of 0.999 km, with a span of 140 m and a total height of 49.4 m).

Variable conditions of the Carpathian flysch were the cause that when performing drill hole on the part of the tunnel there was a need to pre-support the ceiling of ancestor with a steel pipes jacket and strengthen the forehead ancestor using workable anchors, made of fiberglass rods. On the first section of the road, there was a need to strong reinforcement of slopes where was using together, up more than 350 km ground nails, while in the third section there was a need to make embankments on gravel columns closed with aggregate mattress.

An uneven intensity of occurrence of accompanying road facilities on particular parts of the route resulted from both the principles of the location of such facilities and the course of existing roads, as well as from the very diversified terrain. Therefore, it was necessary to build two road interchanges in Skomielna Biała and Zabornia.

An uneven intensity of occurrence of accompanying road facilities on particular parts of the route resulted from both the principles of the location of such facilities and the course

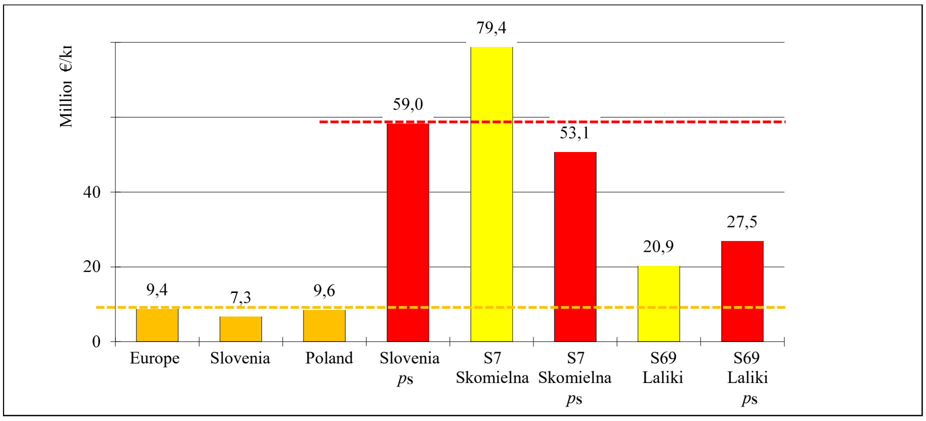

Fig. 3. Unit average costs of the analyzed roads and after considering the proportion pS = 1:3 (of the tunnel's length in relation to the total length of the road section) [own elaboration]

Rys. 3. Średnie jednostkowe koszty analizowanych dróg oraz po uwzględnieniu proporcji pS = 1:3 (długości tunelu w stosunku do całkowitej długości odcinka drogi) [opracowanie własne]

of existing roads, as well as from the very diversified terrain. Therefore, it was necessary to build two road interchanges in Skomielna Biała and Zabornia and the of the express road maintenance base in the III section as well as constructions of passenger service areas (ILO): two in the I section in Lubień and Krzeczów and one in Zbójecka Góra on the III section.

Unit costs of roads with tunnels, due to the many times higher expenditure on tunnels, than the other sections of routes should take into account the proportions p of their mutual lengths. For example, the average cost of building motorways in Slovenia amounted to 7.3 million €/km, 22% lower than the European average, while a 4.5 km section of the route with 1.5 km tunnel cost 59 million €/km, i.e. it was 8 times more expensive. At the same time, the section of the S7 Naprawa - Skomielna Biała express road, 3.05 km long with a 2.057 km tunnel, will cost an average of 79.4 million €/km according to the result of the tender. However, when comparing unit costs, in order to express the actual expenditures for execution of works, the same proportion of *p* - lengths of tunnels to the analyzed road sections should be taken into account. Then, after taking into account considering the same proportion of $p = 0.33$ (the length of the tunnel to the length of the route, as in Slovenia), the unit price of this section of the S7 is much lower, being lower by 9.9% than in Slovenia and amounts to 53.1 million €/km.

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Ceny kontraktowe na budowę dróg jako funkcja ukształtowania terenu

W kontekście uwarunkowań ukształtowania terenu przeanalizowano zmienność cen jednostkowych budowy dróg w Europie i w Polsce. Na podstawie badań wartości współczynnika zmienności cen dwunastu kontraktów zawartych w 2016 roku przez Dyrekcję Dróg Krajowych i Autostrad (DDKiA) stwierdzono małe zróżnicowanie jednostkowych wartości budów dróg ekspresowych klasy technicznej S na terenach płaskich i falistych, na dużym obszarze Polski, powyżej Wrocławia i Lublina w kierunku północy. Natomiast, również dla drogi ekspresowej, lecz w terenie górzystym w Małopolsce, między Lubniem i Chabówką, na trzech odcinkach S7, razem długości 15,8 km, współczynnik zmienności cen jednostkowych był bardzo duży (5,7 razy większy, niż jw. na terenach płaskich i falistych). Pośród przyczyn tej dużej zmienności cen wskazano konieczność dostosowania do trudnych warunków górskich – specjalistycznych rozwiązań technicznych, kosztownych w realizacji, odmiennych na każdym z tych odcinków. Niezbędne były, m.in. ponad 2-kilometrowy tunel (wielokrotnie droższy od pozostałych odcinków trasy), intensywne wzmocnienia skarp gwoździami gruntowymi (o łącznej długości ponad 350 km) lub posadowienia nasypów na kolumnach żwirowych, jak też budowy licznych estakad, wiaduktów i mostów o sumarycznej długości 5,752 km. Zwrócono również uwagę na konieczność uwzględniania proporcji długości tunelu do długości pozostałego odcinka drogi, bowiem jest to warunek prawidłowej analizy nakładów.

Słowa kluczowe: drogi ekspresowe, ukształtowanie terenu, koszty dróg

Financial and Non-Financial Reporting – an Attempt to Correlation Between Selected Chosen Variables

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Abstract

This paper describes a study designed to find correlations between intellectual capital efficiency, measured using the Value Added Intellectual Coefficient (VAIC), and selected components of reports submitted by KGHM Polska Miedź S.A., a Polish mining company. The study examined such components as the company's intangible assets, number of jobs/FTEs (Full-time equivalent) and the net financial result. The timeframe explored here is the period between 2004 and 2018 (the last 14 years). We assumed that intellectual capital efficiency should be correlated with intangible assets, which are part of fixed assets, but the results of our study proved otherwise. Our analysis demonstrated that intellectual capital efficiency was correlated the strongest with the company's financial performance.

Keywords: intellectual capital, financial reporting, correlation

Introduction

In the era of knowledge society in which we currently live, one of the basic premises underlying decisions that people make in order to manage their lives or run a company is information. People undertake specific activities based on the information that they possess and the knowledge that is built on such information. Every company is aware of the fact that a broad group of stakeholders, both external (shareholders, contractors, suppliers, local environment, etc.) or internal (employees), make specific decisions pertaining to relations with the company, its operation and its products on the basis of information that reaches them. Thus, access to the most comprehensive information is in the interest of both of the above-mentioned groups. This does not involve onlythe financial standing and the condition of the company with respect to material aspects, but also the forecasts of such condition in the future and the non-financial aspects of the company's operations.

Currently, it is crucial for stakeholders to be provided with status reports on the situation of their business. The reported data is not only financial or quantitative, but also qualitative. Reporting requirements for non-financial data are expanding to cover more and more companies.

In order to meet such reporting requirements for non-financial data, it is also important to consider intangible assets, also known as intellectual capital. Due to its non-quantifiable nature, this intangible asset does not lend itself easily to reporting. But it plays a major role and its value translates into the market value of traded companies. This is why this paper addresses the question of whether there is a correlation between selected financial data and intellectual capital. If there was one, it could be the basis for managing the value of intellectual capital and exploring its relationships with the financial items reported in the profit and loss account.

Non-financial reporting of (publicly) traded companies

Integrated reporting is now a standard for companies to present an account of their performance. If a business is also a traded company, these requirements are very important, and they cover not only financial reporting but also corporate social responsibility reports on intangible operations of the company.

Financial reporting standards include such guidelines as those developed by the International Standards Organization, Sustainability Accounting Standards Board, Social Accountability International and UL Environment. But the most commonly used guidelines are those by the Global Reporting Initiative (GRI) and the International Integrated Reporting Commitee (IIRC) (Kowal, Kustra, 2016). GRI guidelines provide a consistent framework for reporting business performance in relation to economic, social, and environmental activities. And they provide measures to compare the performance of companies operating in the same industry, as well as to collate single-company data submitted over several years (Lorenc, Kustra, 2016). In 2013, GRI published G4, additional guidelines for social reporting. With the advent of this standard, the scope of reporting is extended to cover social matters related to the involvement of stakeholders in the reporting process. This suggests that they play a crucial role by providing valuable advice on the relevance of the content to be included in the report.

IRC framework, on the other hand, includes guidance on the relationships between financial reporting and sustainable development reporting. The information to be reported includes the external environment impacting the company, any resources and relationships used and created by the company, and the interaction between the company's external environment and its resources in the short, medium and long terms of value creation (IIRC, 2013, p. 10).

In addition to integrated reporting based on the most common guidelines, as mentioned above, since 2017, under the

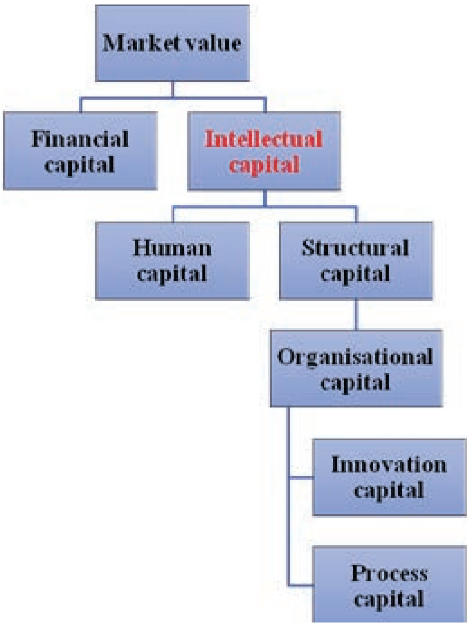


Fig. 1 Classification of intellectual capital, as proposed by Edvinsson L. and M. Malone M. Source: Jemielniak D., Koźmiński A. K. Scientific Editor Zarządzanie wiedzą [Knowledge management], Warsaw 2012

Rys. 1. Klasyfikacja kapitału intelektualnego, jak zaproponowali Edvinsson L. i M. Malone M.

Act of 15 December 2016 [DzU,, 2017], traded companies are required to publicly disclose their Corporate Social Responsibility (CSR) reports. This concept approaches strategy-creation by taking into consideration social needs and environment protection, as well as relationships with company's stakeholders, (Podobińska-Staniec, 2018), (Kowal, Kowal, 2011).

But all of the above-mentioned guidelines for integrated reporting are still lacking in information about methods for creating and using intellectual capital to build corporate value. There is no clear indication that businesses know where such capital is generated and what are its outcomes. Therefore, it seems important to consider if the reported data on intangible assets, employees, training and R&D outlays, or, by extension, profits at various levels of operations, is linked in some way to intellectual capital. This is to check whether with more adequate research funding, better-qualified personnel and greater balance-sheet value of intangible assets, the value of intellectual capital, i.e. its efficiency, is significantly greater.

Attempt to correlate tangible assets with intellectual capital

This study proposes and examines a hypothesis suggesting that there is a correlation between tangible assets, as presented in financial statements, and non-tangible assets, here considered to be equivalent to intellectual capital. Based on selected tangible variables, we sought correlations with intellectual capital measured as a difference between market and book values, and one computed using the Value Added Intellectual Coefficient (VAIC).

The choice of variables for this model from tangible data is not accidental, and it relies on individual capital types, such as human capital and structural capital, and in particular investments and R&D, which are parts of intellectual capital. Divided into two main groups, human capital and structural capital, these capital types are presented as follows:

Ø Human capital – included in the model asemployee benefit expenses, taken from natural cost accounts, employment figures – annual average employment level in the capital group expressed as the number of jobs, salary level – annual average salary in the group.

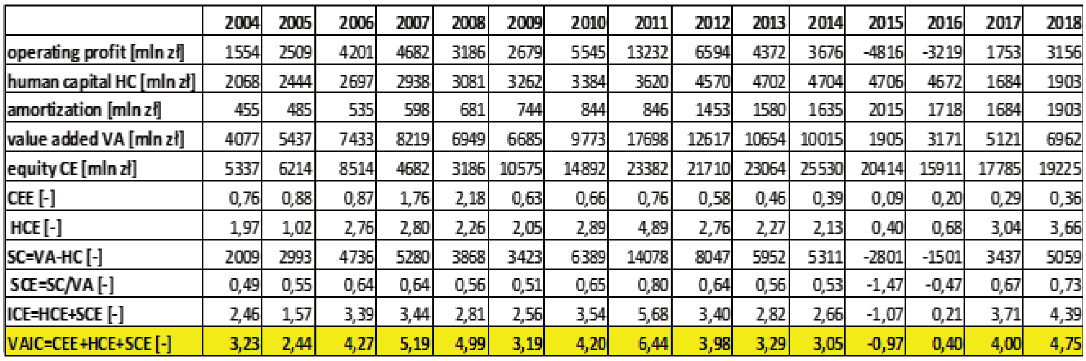
In addition, it is important to note that there are data that could directly represent the efficiency of intellectual capital, but these are not unambiguously recorded. A selected capital group monitors information on R&D costs and scope, but such information is not presented in each executive report, hence it cannot be compared or included in the model. Similar is true for data on the number of training hours, number of training participants, or number of improvement requests. Moreover, it is also recommended to monitor the number of employees who have raised their professional qualifications, e.g. through university education, specialist courses, coaching, or placements, during any specific year. With continuous and unambiguous monitoring, these data could constitute additional information about the efficiency of intellectual capital and its generation by human capital.

Ø Structural capital is included in the model through the book value of:

- equity,
- net result,
- operating profit,
- net cash flows from investment activities
- intangible assets,
- advertising costs,
- ROA and ROE.

No significant correlations were found between these tangible assets and the difference between market and book values for the examined capital group. Thus, the first model was abandoned. In order to represent intellectual capital, we selected VAIC, a method that describes how efficiently intellectual capital is used to generate value added. Based on this approach, the

Tab. 1. VAIC for the selected capital group. Source: own work on the basis of financial reports by the selected capital group
Tab. 1. VAIC dla wybranej grupy kapitałowej



	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
operating profit [mln zł]	1554	2509	4201	4682	3186	2679	5545	13232	6594	4372	3676	-4816	-3219	1753	3156
human capital HC [mln zł]	2068	2444	2697	2938	3081	3262	3384	3620	4570	4702	4704	4706	4672	1684	1903
amortization [mln zł]	455	485	535	598	681	744	844	846	1453	1580	1635	2015	1718	1684	1903
value added VA [mln zł]	4077	5437	7433	8219	6949	6685	9773	17698	12617	10654	10015	1905	3171	5121	6962
equity CE [mln zł]	5337	6214	8514	4682	3186	10575	14892	23382	21710	23064	25530	20414	15911	17785	19225
CEE [-]	0,76	0,88	0,87	1,76	2,18	0,63	0,66	0,76	0,58	0,46	0,39	0,09	0,20	0,29	0,36
HCE [-]	1,97	1,02	2,76	2,80	2,26	2,05	2,89	4,89	2,76	2,27	2,13	0,40	0,68	3,04	3,66
SC=VA-HC [-]	2009	2993	4736	5280	3868	3423	6389	14078	8047	5952	5311	-2801	-1501	3437	5059
SCE=SC/VA [-]	0,49	0,55	0,64	0,64	0,56	0,51	0,65	0,80	0,64	0,56	0,53	-1,47	-0,47	0,67	0,73
ICE=HCE+SCE [-]	2,46	1,57	3,39	3,44	2,81	2,56	3,54	5,68	3,40	2,82	2,66	-1,07	0,21	3,71	4,39
VAIC=CEE+HCE+SCE [-]	3,23	2,44	4,27	5,19	4,99	3,19	4,20	6,44	3,98	3,29	3,05	-0,97	0,40	4,00	4,75

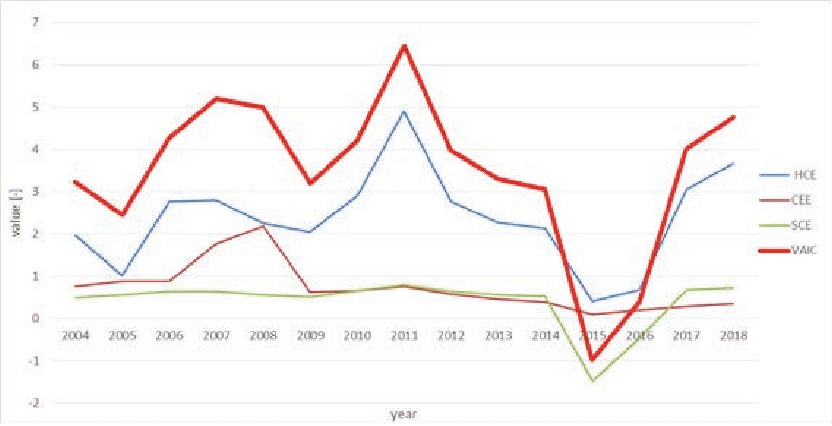
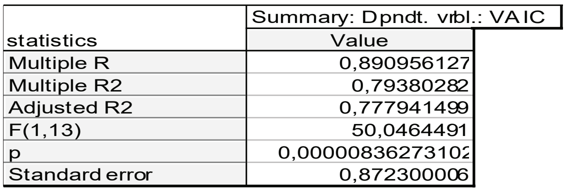


Fig. 2. VAIC and its components HCE, CEE, and SCE. Source: own work on the basis of financial reports by the selected capital group
Rys. 2. VAIC i jego komponenty HCE, CEE i SCE

Tab. 2. Statistics of VAIC. Source: own work
Tab. 2. Statystyki VAIC



statistics	Summary: Dpndt. vrbl.: VAIC Value
Multiple R	0,890956127
Multiple R2	0,79380282
Adjusted R2	0,777941499
F(1,13)	50,0464491
p	0,0000083627310
Standard error	0,872300006

model showed significant correlations and good data fit, which constituted the basis for further econometric analysis.

For the examined capital group, traded at the Warsaw Stock Exchange (WGPW) in the extractive industry, VAIC was calculated for the period between 2004 and 2018. The obtained results are presented in Table 1.

These were also calculated as part of VAIC (Pulic, 2000):

- human capital efficiency (HCE) in creating value added;
- capital employed efficiency (CEE) in creating value added;
- structural capital efficiency (CEE) in creating value added;
- intellectual capital efficiency (intellectual power) of the company (ICE= HCE + SCE).

This study focuses on the value of VAIC, which describes the efficiency of intellectual value added, which, in turn, shows how physical, human, and structural capitals are used to create intellectual capital.

VAIC values were compared to selected tangible data for 2004-2017, as found in the profit and loss accounts of the examined capital group.

The first comparison (Analysis Part 1 – Tables 2, 3, and 4) showed VAIC to have the highest correlation with net result, operating profit, and ROA and ROE. But due to the correlations between these variables, what had the largest impact on VAIC values was net result. Net result was then broken down by accounts which made up its value. This level of detail was necessary to assess how the individual variables from the set of selected tangible assets affected VAIC. The second part of the analysis (Analysis Part 2 – Tables 5, 6, and 7) showed VAIC to have the strongest correlation with Other operating income.

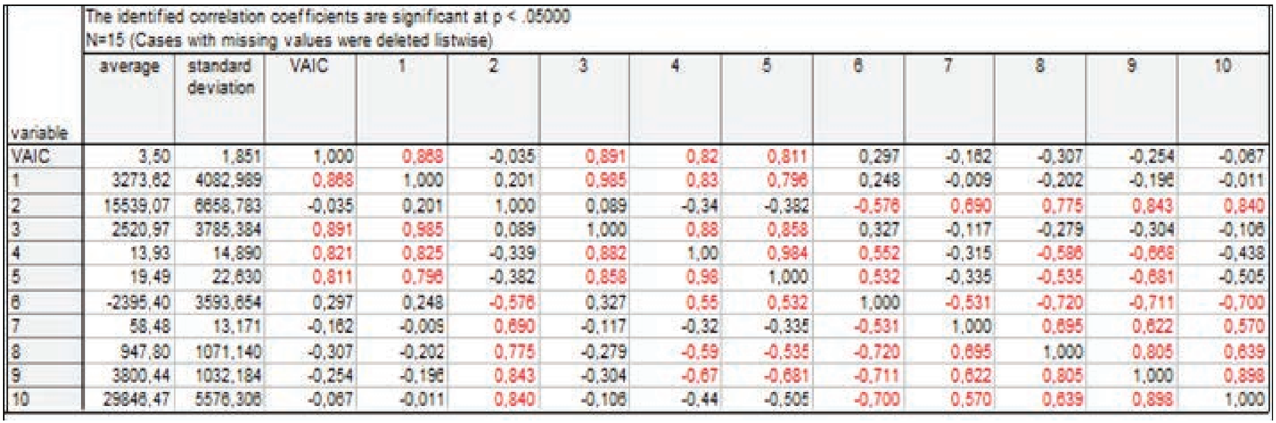
Summary

The purpose of this paper was to examine the impact of

Tab. 3. Summary of dependent variable regression of VAIC. VAIC=0,0043x+2,39874,   x-net results. Source: own work.
Tab. 3. Podsumowanie regresji zmiennej zależnej VAIC

N=15	Summary of dependent variable regression: VAIC R= ,89095613 R^2= ,79380282 Popraw. R2= ,77794150 F(1,13)=50,046 p<.00001 Standard error: .87230					
	b*	st. error from b	b	st.error z b	t(13)	p
b			2,398746	0,273556	8,768764	0,000001
net result	0,890956	0,125942	0,000436	0,000062	7,074351	0,000008

T ab. 4. Correlations between variables 1-10. Source: own work
Tab. 4. Korelacje między zmiennymi 1-10



variable	The identified correlation coefficients are significant at p < .05000 N=15 (Cases with missing values were deleted listwise) average	standard deviation	VAIC	1	2	3	4	5	6	7	8	9	10
VAIC	3,50	1,851	1,000	0,868	-0,035	0,891	0,82	0,811	0,297	-0,162	-0,307	-0,254	-0,067
1	3273,62	4082,989	0,868	1,000	0,201	0,985	0,83	0,796	0,248	-0,009	-0,202	-0,196	-0,011
2	15539,07	6658,783	-0,035	0,201	1,000	0,089	-0,34	-0,382	-0,576	0,690	0,775	0,843	0,840
3	2520,97	3785,384	0,891	0,985	0,089	1,000	0,88	0,858	0,327	-0,117	-0,279	-0,304	-0,106
4	13,93	14,890	0,821	0,825	-0,339	0,882	1,00	0,984	0,552	-0,315	-0,586	-0,668	-0,438
5	19,49	22,630	0,811	0,796	-0,382	0,858	0,98	1,000	0,532	-0,335	-0,535	-0,681	-0,505
6	-2395,40	3593,654	0,297	0,248	-0,576	0,327	0,55	0,532	1,000	-0,531	-0,720	-0,711	-0,700
7	58,48	13,171	-0,162	-0,009	0,690	-0,117	-0,32	-0,335	-0,531	1,000	0,695	0,622	0,570
8	947,80	1071,140	-0,307	-0,202	0,775	-0,279	-0,59	-0,535	-0,720	0,695	1,000	0,805	0,639
9	3800,44	1032,184	-0,254	-0,196	0,843	-0,304	-0,67	-0,681	-0,711	0,622	0,805	1,000	0,898
10	29846,47	5576,306	-0,067	-0,011	0,840	-0,106	-0,44	-0,505	-0,700	0,570	0,639	0,898	1,000

Legend:
1 – operating profit
2- equity
3- net result
4- ROA
5- ROE
6- net cash flows from investment activities
7- advertising costs
8- intangible assets
9- human capital
10-regular post

Tab. 5. Statistics of VAIC. Source: own work
Tab. 5. Statystyki VAIC

statistics	Summary.: Dpndt. vrbl.:VAIC Value
Multiple R	0.93885517
Multiple R2	0.881449029
Adjusted R2	0.859894308
F(2,11)	40.8935468
p	0.00000806265598
Standard error	0.706378895

Tab. 7. Summary of dependent variable regression of VAIC – information about other operating income. VAIC=10-6x+10-6z+3,2924, x-other operating income, z-financial result. Source: own work
Tab. 7. Zmienna regresja VAIC - informacje o innych przychodach operacyjnych

N=14	Summary of dependent variable regression: VAIC (Sheet 143) R= .93885517 R^2= .88144903 Adjusted R2= .85989431 F(2.11)=40.894 p<.00001 Standard error: .70638 b*	st. error from b	b	st.error z b	t(11)	p
Absolute term			3,292395	0,192110	17,13805	0,000000
Other operating income	0,850657	0,115687	0,000001	0,000000	7,35310	0,000014
Financial result	0,171195	0,115687	0,000001	0,000001	1,47982	0,166983

Tab. 6. Correlations between variables 1-8. Source: own work

Tab. 6. Korelacje między zmiennymi 1-8

	Correlations (Sheet 143) The identified correlation coefficients are significant at p < .05000 N=14 (Cases with missing values were deleted listwise)																
	1	2	a)	b)	c)	d)	e)	f)	f1)	f2)	3.	4.	5.	6.	7.	8.	**VAIC**
1	1,00	0,93	-0,72	0,78	-0,15	0,39	-0,58	0,26	0,41	-0,49	0,53	0,64	-0,05	0,52	-0,76	0,47	0,32
a)	0,93	1,00	-0,92	0,55	-0,45	0,67	-0,83	-0,11	0,04	-0,46	0,19	0,32	-0,24	0,17	-0,52	0,11	-0,04
b)	-0,72	-0,92	1,00	-0,18	0,69	-0,85	0,97	0,41	0,30	0,31	0,18	0,06	0,36	0,21	0,16	0,26	0,38
2.	0,78	0,55	-0,18	1,00	0,33	-0,13	-0,02	0,58	0,73	-0,48	0,87	0,91	0,16	0,86	-0,96	0,83	0,70
c)	-0,15	-0,45	0,69	0,33	1,00	-0,93	0,81	0,68	0,68	-0,00	0,61	0,52	0,25	0,61	-0,35	0,64	0,63
d)	0,39	0,67	-0,85	-0,13	-0,93	1,00	-0,93	-0,63	-0,57	-0,15	-0,47	-0,37	-0,30	-0,49	0,16	-0,52	-0,58
e)	-0,58	-0,83	0,97	-0,02	0,81	-0,93	1,00	0,56	0,46	0,26	0,36	0,23	0,37	0,38	-0,01	0,43	0,52
f)	0,26	-0,11	0,41	0,58	0,68	-0,63	0,56	1,00	0,95	0,13	0,90	0,86	0,29	0,90	-0,64	0,92	0,84
f1)	0,41	0,04	0,30	0,73	0,68	-0,57	0,46	0,95	1,00	-0,20	0,95	0,93	0,44	0,96	-0,75	0,97	**0,93**
f2)	-0,49	-0,46	0,31	-0,48	-0,00	-0,15	0,26	0,13	-0,20	1,00	-0,18	-0,22	-0,48	-0,21	0,36	-0,19	-0,30
3.	0,53	0,19	0,18	0,87	0,61	-0,47	0,36	0,90	0,95	-0,18	1,00	0,99	0,27	1,00	-0,88	0,99	0,88
4.	0,64	0,32	0,06	0,91	0,52	-0,37	0,23	0,86	0,93	-0,22	0,99	1,00	0,23	0,99	-0,92	0,97	0,84
5.	-0,05	-0,24	0,36	0,16	0,25	-0,30	0,37	0,29	0,44	-0,48	0,27	0,23	1,00	0,35	-0,11	0,38	0,55
6.	0,52	0,17	0,21	0,86	0,61	-0,49	0,38	0,90	0,96	-0,21	1,00	0,99	0,35	1,00	-0,87	1,00	0,90
7.	-0,76	-0,52	0,16	-0,96	-0,35	0,16	-0,01	-0,64	-0,75	0,36	-0,88	-0,92	-0,11	-0,87	1,00	-0,83	-0,68
8.	0,47	0,11	0,26	0,83	0,64	-0,52	0,43	0,92	0,97	-0,19	0,99	0,97	0,38	1,00	-0,83	1,00	0,91
VAIC	0,32	-0,04	0,38	0,70	0,63	-0,58	0,52	0,84	0,93	-0,30	0,88	0,84	0,55	0,90	-0,68	0,91	1,00

Legend:

1. Total operating revenue
   - a)Net sales revenue
   - b) Cost of goods sold
2. Gross profit
   - c)Selling and distribution expenses
   - d) Administrative expenses
   - e) Depreciation, amortization and impairment charges
   - f) Net other operating result
     - f1)Other operating income
     - f2) Other operating expenses
3. Operating profit (EBIT)
4. EBITDA
5. Financial result
6. Profit before income tax
7. Income tax
8. Net Profit (Loss) for the Period

selected components of financial reports by KGHM Polska Miedź S.A., a publicly traded company, on VAIC. We selected the variables for the analysis by choosing those elements that, in our opinion, should be correlated with VAIC. Hence, these included such variables as employment level and intangible assets. The study found that intellectual capital efficiency is not dependent on the above-mentioned factors, i.e., the number of personnel members hired or the value of intangible assets (insignificant correlation between these variables and VAIC). The main component that affected the coefficient was net result (correlation with VAIC at 0.89). Therefore, what is considered by the coefficient as efficiency is not the number of patents held or improvements made, but the impact of these on the company's financial performance. The second part of the study focused on the individual components of a profit and loss account with classification of expenses by function. This part explored the fact that corporate profit depended on generated income and costs. Consequently, intellectual capital could help reduce costs or increase profit. Based on the adopted methodology, the study found that, for the analysed company, intellectual capital was generally concentrated around the revenue part in the form of other operating income (correlation at 0.93). There are many factors that can influence this item in the profit and loss account, but these were not analysed in more detail due to the inaccessibility of relevant data.

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Raportowanie finansowe i niefinansowe – próba korelacji wybranych zmiennych

Niniejszy artykuł został poświęcony badaniu polegającemu na znalezieniu zależności pomiędzy efektywnością wartości kapitału intelektualnego mierzonego za pomocą metody VAIC – (Value Added Intellectual Coefficient) a wybranymi składnikami raportów przedkładanymi przez polskie przedsiębiorstwo górnicze KGHM Polska Miedź S.A. Składniki, które wzięto pod uwagę w badaniu to między innymi: wartości niematerialne i prawne, liczba etatów czy też poziom wyniku finansowego netto spółki. Horyzont czasowy jaki był wzięty pod uwagę w ramach artykułu to okres od roku 2004 do roku 2018 (ostatnie 14 lat).

Autorzy artykułu założyli, iż efektywność wartości kapitału intelektualnego powinna być skorelowana ze składnikiem aktywów trwałych w postaci wartości niematerialnych i prawnych, wyniki badań dały jednak rezultaty niezgodne ze wstępnymi założeniami Autorów niniejszego artykułu. Po przeprowadzeniu analizy stwierdzono, iż najwyższy poziom korelacji z efektywnością wartości kapitału intelektualnego mają wyniki finansowe spółki.

Słowa kluczowe: kapitał intelektualny, sprawozdawczość finansowa, korelacja

An Assessment of Selected Work Organisation Variants in an Underground Hard Coal Mine with Consideration to Unit Mining Costs

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Abstract

The aim of the paper is to compare two forms of work organisation, the first of which assumes extending the mine's operation from five to six days a week, and the other – implementing a continuous work organisation system. To illustrate this in terms of unit mining costs, a model hard coal mine was used. In addition to the current organisational solution, which serves as the starting point for comparative analysis, solutions were proposed to increase the degree of utilisation of the existing production potential, mainly with regard to technical means of production and human resources. The proposed solutions assume increasing the intensity of use of technical means of production on an annual basis by extending the annual working time of selected mining crews. For the comparative analysis, three variants of the mine's operation in terms of the production organisation system were adopted. Under Variant I, treated as the baseline option, the current organisation of production is to be continued (5 days a week, Monday to Friday, excluding public holidays). Variant II provides for extending the working time of some mining crews to 6 days a week (from Monday to Saturday, excluding public holidays). Variant III assumes continuous operation for 7 days a week (excluding public holidays and several days for shaft inspections). Having adopted appropriate baseline assumptions for simulation calculations and a set of input data reflecting the characteristics of a specific mine, simulation calculations were performed and their results were used to carry out a comparative analysis of selected organisational solutions.

Keywords: hard coal mining, mine management, economics of mining production, unit production costs

Introduction

The favourable situation on the hard coal market, characterised by the prevalence of a relatively high price level, justifies undertaking study and research work on the possibilities of increasing production volumes in hard coal mines which currently operate on the market. Accordingly, two basic options can be identified in this respect: first – investing in new production potential, and second – increasing the utilisation of the production potential available at the moment. If the first option is followed, one must account for a relatively long waiting period before the production volume increases and for the need to allocate significant funds for that purpose. In the second option, the waiting period will be definitely shorter and the spending lower, allowing a more flexible adaptation of the production volume to fluctuations on the hard coal market.

The current production potential can be used to a broader extent through the application of suitable forms of work organisation, entailing, e.g. an increase to the production days over a specific period (week, month, year), which should result in a boost to the mining volume in that period.

The aim of this paper is to compare two forms of work organisation, the first of which assumes extending the mine's operation from five to six days a week, and the second one – implementing a continuous work organisation system. A model hard coal mine was used as an example. Unit mining costs were adopted as the criterion for comparative analysis.

In order to achieve the assumed research objective, the modelling of the account of costs by type was used for the three separate calculation variants, taking into account division into fixed and variable costs. Variant I (the baseline variant of the comparative analysis) assumes the current state of work organisation (five mining days per week, from Monday to Friday, excluding public holidays). The other two variants account for the above-mentioned work organisation forms, under which the mine's operation time is to be extended. Based on the data specific to Variant I, cost account models were developed for the other variants which take into account the forms of work organisation adopted for the analysis, i.e. extension of working time from five to six days per week (Variant II) or continuous work organisation (Variant III).

Comparative analysis of the adopted calculation variants

For the purposes of analytical research, three variants of systemic organisational solutions were adopted, as described below.

Variant I, considered a baseline for comparative analysis, concerns the standard four-shift work organisation on working days (Monday to Friday), excluding public holidays; the length of the working shift is 8 hours and the length of work at the coal face is 6 hours. The working conditions and terms for the payment of wages and other work-related benefits are governed by the provisions of the Labour Code, the collective labour agreement in force at the company, and the company's work regulations. The work is performed on working days from Monday to Friday, with an average of 40 hours of work performed by employees underground during a five-day working week. For work on Sundays, public holidays and other days off work (resulting from the work schedule), in addition to the daily wage, an employee receives a day off which may but does not have to be taken. If an employee reports for work on a day which would otherwise be a day off, in addition to the daily wage, he or she is entitled to an allowance in the form of a grade pay for the work performed. The work regulations provide for the organisation of work on days off on a voluntary basis and allow overtime of no more than 416 hours annually.

Under Variant II, the mine's working time is to be extended from five to six days a week (Monday to Saturday), excluding public holidays; the length of the working shift is 8 hours and the length of work at the coal face is 6 hours. It differs from Variant I in terms of the mining volume (through the addition of Saturday output) and an increase in those items of the cost-by-type division, which result from the extension of the mine's operating time and an increase in the volume of annual coal production. The extension of the mine's operating time from five to six days a week, and including Saturdays in the working time balance, results primarily in a significant increase in personnel costs, as work on Saturdays should be treated as work on a day off, with all the consequences for personnel costs, as provided for in the above-mentioned provisions [6].

Variant III concerns an organisation system involving a continuous operation of the mine. In this system, mining continues on all days of the week (not only working days, but also Saturdays and Sundays), with the exception of public holidays and days for necessary service breaks to the production process in order to perform shaft inspections [7]. Under an organisational system in which a mining plant operates continuously, the majority of employees are directly involved in securing uninterrupted production, while the rest of the staff, who do not have to work under the continuous system, are employed on working days (Monday to Friday).

The continuous work system in a mine has been addressed by a number of papers [2,3,4,5] which followed in the wake of the concept for work organisation advocating the deployment of shift- and brigade-based systems. The crew working in the continuous work system is divided into equal teams (brigades), several of which work during the day on different shifts (each on a different one), while the rest of the crew rests. Work and rest day arrangements in a shift- and brigade-based system can be developed in a multi-variant way depending on mutual combinations of the frequency of breakdowns, the accumulation or splitting of days off, the length of the recurring cycle of days on and off work, and the rhythm of days off [2].

The shift-altering frequency specifies the interval between when a brigade moves from one shift to another and the length (expressed as the number of man-days) of work of a brigade on a specific (first, second, third or fourth) shift.

Assuming that each brigade works for several days on the same shift and then has one, two or several days off work, it is possible, by combining the number of shifts and the number of brigades, to distinguish a number of variants of work and rest day arrangements, while observing the rule that the number of working teams (brigades) is at least one more than the number of shifts.

For a 4-shift system (where the length of a shift is 8 hours and the length of work at the coal face is 6 hours), the following work-rest patterns can be developed, as presented in Fig. 1:

- the 4s-5b-1 variant (four shifts–five brigades–variety 1) – four days of work on shift 1, one day off, four days of work on shift 2, one day off, four days of work on shift 3, one day off, four days of work on shift 4, one day off, and so forth. On each day, four teams work, one team has a day off, and the cycle continues for 20 days;
- the 4s-5b-2 variant (four shifts–five brigades–variety 2) – five days of work on shift 1, one day off, five days of work on shift 2, one day off, five days of work on shift 3, one day off, five days of work on shift 4, two days off, and so forth. On each day, four teams work, one team has a day off, and the cycle continues for 25 days;
- the 4s-5b-3 variant (four shifts–five brigades–variety 3) – six days of work on shift 1, one day off, six days of work on shift 2, two days off, six days of work on shift 3, one day off, six days of work on shift 4, two days off, and so forth. On each day, four teams work, one team has a day off, and the cycle continues for 30 days.

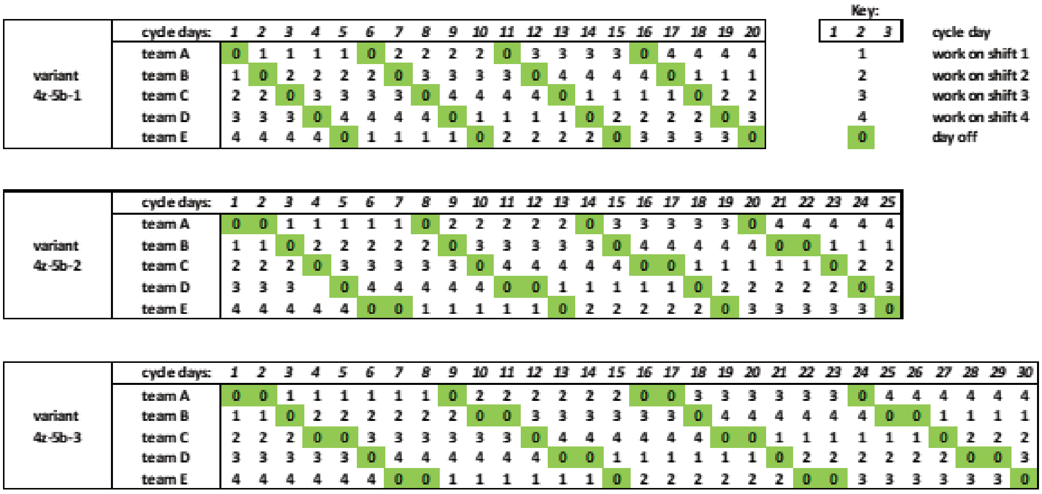
The analysis of the annual work time balance of working teams in the four-shift system with five working teams [1,3] showed that it comprises 281 ÷ 283 work shifts per year and, on average, includes 30 shifts more than the traditional four-shift system (with work performed only on working days). For work in such a system, an employee should receive an additional allowance taking into account the increased number of shifts during the year and work on Saturdays and Sundays.

Data on production costs by type for Variant I with a breakdown into fixed and variable costs in relation to the volume of production, in accordance with the accounting method, were treated as input data for the calculation of production costs for the other variants. The following assumptions were made:

1. Amortization costs (fixed and variable) are proportional to the number of production days.
2. The costs of equipment lease and rent, drilling and mining services, methane drainage services, training services, mining damage adjustment services, transport services and mining fee are proportionate to the volume of production.
3. The costs of materials, energy, other mining services, repair services, taxes and other charges are divided into a fixed part, independent of the volume of coal production, and a variable part proportional to that volume.
4. In Variant II, gross labour costs, social insurance (ZUS) surcharges and union benefits take into account the wage-related consequences of extending the working time of a mine from five to six days a week (a conversion rate of 1.14) and, in Variant III, of transition to continuous operation (a conversion rate of 1.52).
5. Real estate tax, environmental and PFRON (National Disabled Persons' Rehabilitation Fund) fees, insurance and other costs are fixed, regardless of the volume of coal production.
6. Unit variable costs are the same in all variants.

Results of sample calculations

Analytical tests were carried out on a sample coal mine characterised by average daily coal production of 19200 Mg/day, with the application of the work organisation variants



variant		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	cycle days:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
variant 4z-5b-1	team A	0	1	1	1	1	0	2	2	2	2	0	3	3	3	3	0	4	4	4	4
	team B	1	0	2	2	2	2	0	3	3	3	3	0	4	4	4	4	0	1	1	1
	team C	2	2	0	3	3	3	3	0	4	4	4	4	0	1	1	1	1	0	2	2
	team D	3	3	3	0	4	4	4	4	0	1	1	1	1	0	2	2	2	2	0	3
	team E	4	4	4	4	0	1	1	1	1	0	2	2	2	2	0	3	3	3	3	0

Key:

1 2 3	cycle day
1	work on shift 1
2	work on shift 2
3	work on shift 3
4	work on shift 4
0	day off

	cycle days:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
variant 4z-5b-2	team A	0	0	1	1	1	1	1	0	2	2	2	2	2	0	3	3	3	3	3	0	4	4	4	4	4
	team B	1	1	0	2	2	2	2	2	0	3	3	3	3	3	0	4	4	4	4	4	0	0	1	1	1
	team C	2	2	2	0	3	3	3	3	3	0	4	4	4	4	4	0	0	1	1	1	1	1	0	2	2
	team D	3	3	3		0	4	4	4	4	4	0	0	1	1	1	1	1	0	2	2	2	2	2	0	3
	team E	4	4	4	4	4	0	0	1	1	1	1	1	0	2	2	2	2	2	0	3	3	3	3	3	0

	cycle days:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
variant 4z-5b-3	team A	0	0	1	1	1	1	1	1	0	2	2	2	2	2	2	0	0	3	3	3	3	3	3	0	4	4	4	4	4	4
	team B	1	1	0	2	2	2	2	2	2	0	0	3	3	3	3	3	3	0	4	4	4	4	4	4	0	0	1	1	1	1
	team C	2	2	2	0	0	3	3	3	3	3	3	0	4	4	4	4	4	4	0	0	1	1	1	1	1	1	0	2	2	2
	team D	3	3	3	3	3	0	4	4	4	4	4	4	0	0	1	1	1	1	1	1	0	2	2	2	2	2	2	0	0	3
	team E	4	4	4	4	4	4	0	0	1	1	1	1	1	1	0	2	2	2	2	2	2	0	0	3	3	3	3	3	3	0

Fig. 1. The work-rest pattern in a 4-shift system with five work teams [Source: 2, p. 49]
Rys. 1. Układ dni pracy i odpoczynku w systemie czterozmianowym z pięcioma zespołami roboczymi [Źródło: 2, s. 49]

described above. The daily mining capacity of the mine (the maximum level) is 24000 Mg/day and its use reaches 80% on average.

The most important assumptions and input data are as follows:

- Variant I: – the mine extracts coal 5 days a week in a four-shift work organisation system (three production shifts and one maintenance and repair shift) – the length of the work shift is 8 hours, the time spent at the coal face – 6 hours, the time spent specifically on mining – 18 hours/day, and the annual number of mining days assumed for calculations – 250.
- Variant II – the mine extracts coal 6 days a week (excluding public holidays), in a four-shift work organisation system (three production shifts and one maintenance and repair shift) – the length of the work shift is 8 hours, the time spent at the coal face – 6 hours, the time spent specifically on mining – 18 hours/day, and the annual number of mining days assumed for calculations – 300.
- Variant III – the mining plant extracts coal 7 days a week (excluding public holidays and several days for shaft inspections), in a four-shift work organisation system (three production shifts and one maintenance and repair shift) – the duration of the working shift is 8 hours, the time spent at the coal face – 6 hours, the time spent specifically on mining – 18 hours a day, and the annual number of mining days assumed for calculations – 350.

It has been assumed that the mine's annual mining capacity, which is the smallest amount resulting from the combination of production capacities – the extraction operations, the mine ventilation system, horizontal transport (haulage), vertical transport (hoisting), mineral processing plant – does not limit the annual coal production volume which can be as follows:

- Variant I: 4.8 million Mg/year
- Variant II: 5.76 million Mg/year
- Variant III: 6.72 million Mg/year

Number of employees:

- Variant I: 8000 people
- Variant II: 8000 people
- Variant III: 9500 people – this figure is based on the assumption that part of the current crew working at the main extraction operations (75% of the staff, i.e. 6000 people) must be expanded in a 5:4 ratio, i.e. by 1500 people, with the remaining 2000 people working under the regular Monday-to-Friday system.

The total annual costs and unit costs for each variant are presented in Table 1.

The data on total costs in Table 1 together fixed and variable for Variant I were adopted as data for the model coal mine. On the basis of this data and the assumptions listed above, appropriate calculations were carried out for Variants II and III. Their results are presented in the respective columns.

In Table 1 the results of the calculation of unit production costs for the individual variants of work organisation obtained by dividing the annual production costs by the volume of annual mining volume are presented as well.

Table 2 presents a relative percentage comparison of the selected values that apply to the respective calculation variants, assuming that the values for Variant I are at the level of 100%.

On comparing selected Variant I and II figures, it can be stated that the extension of the mine's operation time from five to six days a week will result in:

- a 20% increase in production volume,
- a 14% increase in total costs,
- a 14% increase in personnel costs,
- a 5% decrease in unit costs.

On comparing selected Variant I and III figures, it can be stated that the implementation of a continuous work system will result in:

- a 40% increase in production volume,
- a 40% increase in total costs,
- a 52% increase in personnel costs,
- the unit costs remaining at a comparable level.

Fig. 1. The work-rest pattern in a 4-shift system with five work teams [Source: 2, p. 49]
Rys. 1. Układ dni pracy i odpoczynku w systemie czterozmianowym z pięcioma zespołami roboczymi [Źródło: 2, s. 49]

No.	Specification	Costs [PLN thous./year]			Unit costs [PLN/Mg]		
		Variant I	Variant II	Variant III	Variant I	Variant II	Variant III
1	Amortization	278428	334113	389799	58.01	58.01	58.01
2	Materials	194589	219097	243606	40.54	38.04	36.25
3	Energy	127210	132470	137730	26.50	23.00	20.50
4	Equipment lease and rental	37173	44607	52042	7.74	7.74	7.74
5	Drilling and mining services	64630	77556	90482	13.46	13.46	13.46
6	Methane drainage services	14884	17861	20838	3.10	3.10	3.10
7	Other mining services	55432	61377	67323	11.55	10.66	10.02
8	Training services	22482	26978	31474	4.68	4.68	4.68
9	Mining damage services	11149	13378	15608	2.32	2.32	2.32
10	Repair services	81481	97772	114064	16.98	16.97	16.97
11	Transport services	59214	71057	82900	12.34	12.34	12.34
12	Other services	45767	45800	45833	9.53	7.95	6.82
13	Labour costs brutto	761976	868333	1158204	158.75	150.75	172.35
14	Welfare securities	162791	185513	247442	33.91	32.21	36.82
15	Union benefits	63043	71842	95825	13.13	12.47	14.26
16	Real property tax	8686	8686	8686	1.81	1.51	1.29
17	Royalties (exploitation fee)	10240	12288	14336	2.13	2.13	2.13
18	Environmental fee	283	283	283	0.06	0.05	0.04
19	PFRON charge	9218	9218	9218	1.92	1.60	1.37
20	Other taxes and charges	1455	1464	1472	0.30	0.25	0.22
21	Insurances	8467	8467	8467	1.76	1.47	1.26
22	Other costs	715	715	715	0.15	0.12	0.11
	Total sum	2019313	2308877	2836346	420.69	400.85	422.08

Tab. 2. Comparison of selected values characterising calculation variants [Source: own study]
Tab. 2. Porównanie wybranych wielkości charakteryzujących warianty obliczeniowe [Źródło: opracowanie własne]

Specification	Unit	Variant I	Variant II	Variant III
Production volume	million Mg/year	100%	120%	140%
Total costs	million PLN/year	100%	114%	140%
Personnel costs (gross labour costs, welfare securities, union benefits)	million PLN/year	100%	114%	152%
Unit costs	PLN/Mg	100%	95%	100%

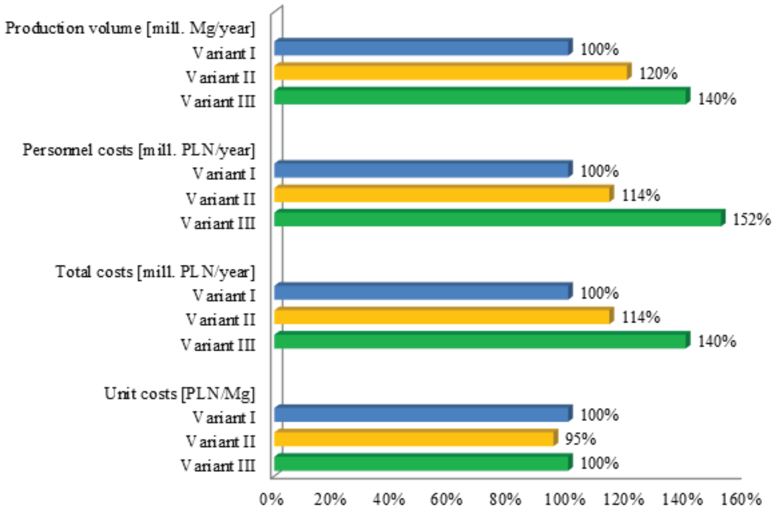


Fig. 2. Illustration of a relative comparison of the selected values characterising calculation variants [Source: own study]

Rys. 2. Ilustracja porównawcza wybranych wielkości charakteryzujących warianty obliczeniowe [Źródło: opracowanie własne]

Summary

Based on the obtained results of calculations, it can be concluded that extending the mine's operation time from five to six days a week is the preferred solution in terms of minimisation of unit production costs. With regard to the example at hand, this solution is characterised not only by a 20% increase in the production volume (which also entails revenue higher by approx. 20%, assuming no changes to the average fixed price of coal), but also a 5% decrease in the unit production costs.

The deployment of a continuous work system can result in the mining volume higher by 40% (which will also increase sales revenue), with the unit cost kept at a comparable level.

The obtained sample calculations regard the adopted, simplified model assumptions, as well as a good market situation guaranteeing the sale of any quantity of coal produced by the mine. In practice, the problem is more complex, the market situation is changing, and the largely unpredictable nature of mining production, in the context of an underground hard coal mine, further limits the possibility of assessing how various cost components will develop. Each case should be considered individually. The paper presents an example of assessing the benefits that can be derived from extending the working time of a coal mine during an economic upturn on the hard coal market. The results of simulation calculations presented in the article are deterministic and simplified. Further, more detailed research into the topic should be based on modelling and stochastic simulation.

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Ocena wybranych wariantów organizacji pracy w podziemnej kopalni węgla kamiennego w aspekcie jednostkowych kosztów wydobycia

Celem publikacji jest porównanie dwóch form organizacji pracy, z których pierwsza zakłada wydłużenie czasu pracy kopalni z pięciu do sześciu dni w tygodniu, a druga - wdrożenie systemu organizacji pracy ciągłej, na przykładzie pewnej, modelowej kopalni węgla kamiennego w aspekcie kształtowania się jednostkowych kosztów wydobycia. Obok aktualnego rozwiązania organizacyjnego, które stanowi punkt wyjścia dla analizy porównawczej, zaproponowano rozwiązania zmierzające do wzrostu stopnia wykorzystania posiadanego potencjału produkcyjnego w zakresie obejmującym przede wszystkim techniczne środki produkcji i zasoby ludzkie. Zaproponowane rozwiązania zakładają intensywniejsze wykorzystanie technicznych środków produkcji w skali roku poprzez wydłużenie rocznego czasu pracy niektórych załóg górniczych. Na potrzeby analizy porównawczej przyjęto trzy warianty funkcjonowania zakładu górniczego w aspekcie systemu organizacji produkcji. Wariant I, potraktowany jako wariant bazowy, zakłada dotychczasową organizację produkcji przez 5 dni w tygodniu (praca od poniedziałku do piątku, z wyłączeniem dni ustawowo wolnych od pracy). Wariant II zakłada wydłużenie czasu pracy niektórych załóg górniczych do 6 dni w tygodniu (praca od poniedziałku do soboty, z wyłączeniem dni ustawowo wolnych od pracy). Wariant III zakłada pracę ciągłą przez 7 dni w tygodniu (z wyłączeniem dni ustawowo wolnych od pracy i kilku dni przeznaczonych na przeglądy szybowe). Przyjmując odpowiednie założenia podstawowe do obliczeń symulacyjnych oraz zbiór danych wejściowych odpowiadających warunkom pewnego zakładu górniczego wykonano obliczenia symulacyjne, których wyniki użyto do analizy porównawczej wybranych rozwiązań organizacyjnych.

Słowa kluczowe: górnictwo węgla kamiennego, zarządzanie kopalnią, ekonomika produkcji górniczej, jednostkowe koszty produkcji

Opportunities for Making Production-Related Decisions on the basis of Shadow Prices

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Abstract

This article describes how shadow prices can be used as active constraints (in this case constraints of mine production capacity) to address and support production-related decision-making. This is an algorithm from a post-optimal analysis developed by the author as part of a method for rationalising production decisions for a formal group (PGG, a company) of hard coal mines. Opportunities for using shadow prices are presented using examples of actual mines. The developed algorithm provides a quick way of obtaining information, with no need to solve the problem again, about possible gains or losses resulting from an increase or a decrease in a selected production limit, to determine how changes to such constraints will affect the profits and production and sales structures for specific coal sizes.

Keywords: shadow prices, post-optimal analysis, simplex algorithm

Introduction

The method presented here relies on what is known as the simplex tableau, generated on the basis of an optimisation model developed by the author. It constitutes an optimum solution for the production and sales of coal by mines [2, 3, 4, 5].

The tableau contains a complete set of balance-sheet equations and coefficients representing objective function sensitivity to changes in decision variables. In addition, it is a starting point for the post-optimal analysis, where shadow prices play a very important role, since they help assess the extent and direction of changes to the optimum value of the criterion function as constraints change. Shadow prices make it possible to predict, with no need to solve the problem again, the possible gains or losses resulting from an increase or a decrease in a selected (production or sales) limit [7]. This is particularly important for hard-coal mining, where mines frequently have spare production capacities. The practical example of using shadow prices to make rational production decisions, as presented here, shows how specific decisions could affect companies' or mines' optimum coal production and sales plans.

This method can be successfully used in the decision making process for planning mining works in hard coal mines [1].

The nature of shadow prices

The coal production and sales optimisation model, as developed by the author, has the following canonical form [2, 3, 4, 5]:

$$A \cdot X = B, \tag{1}$$

$$J = c^T \cdot X, \tag{2}$$

$$X \geq 0\ , \tag{3}$$

where:
A – constraint matrix (simplex tableau),
X – vector of decision variable values together with inequality constraint slack variables (1),
B – vector of the right-hand sides of the equation;
c – vector of objective function coefficients and zero coefficients for slack variables,
J – objective function (quality coefficient).

The solution to the problem (1-3) is vector X divided into sub-vectors of basic variables with positive values, and vector of the other variables, referred to as non-basic, whose optimum values are zeroes. This solution is a simplex tableau.

The optimal solution, which – in relation to the basic and nonbasic variables and the quality coefficient – is represented by the following equations [4, 5, 6]:

$$x^B = \left[A^B\right]^{-1} \cdot B - \left[A^B\right]^{-1} \cdot A^N \cdot x^N \tag{4}$$

$$J = c^{BT} \cdot \left[A^B\right]^{-1} \cdot B - [[c^{BT} \cdot \left[A^B\right]^{-1} \cdot A^N]^T - c^N]^T \cdot x^N \tag{5}$$

where:
A^B, A^N – submatrixes of the A matrix (A – matrix of the constraint coefficients);
c^B, c^N – subvectors of objective-function coefficients;
x^B, x^N – vectors of basic and nonbasic decision variables, respectively.

In the index maximisation task (2) optimum coefficient values in formula (5) with non-basic variables are non-positive.

With x^{NO} and x^{BO} representing, respectively, optimum values of basic and non-basic decision variables, and the following symbols:

$$A^O = \left[A^B\right]^{-1} \cdot A^N \tag{6}$$

$$c^O = [c^{BT} \cdot \left[A^B\right]^{-1} \cdot A^N]^T - c^N \tag{7}$$

and disregarding all non-basic variables x^{NO} (as in the opti-

Tab. 2. Comparison of selected values characterising calculation variants [Source: own study]
Tab. 2. Porównanie wybranych wielkości charakteryzujących warianty obliczeniowe [Źródło: opracowanie własne]

Problem:	Kopalnia	XM0301	X040107	X040113	X040116	X050116	QS01	QS05
OBJ	3,3E+08	54,332	2,206	17,496	14,946	0,0	3,42	20,791
XM0101	160 022,5	0,0	0,0	0,0	0,0	0,0	0,11	0,0
XM0201	21 821,3	0,0	0,0	0,0	0,0	0,0	0,015	0,0
X030113	264 764,5	1,0	0,0	0,0	0,0	0,0	0,182	0,0
X040109	0,0	0,0	1,0	1,0	1,0	0,0	0,0	0,0
XM0401	675 004,0	0,0	0,0	0,0	0,0	0,0	0,464	0,0
X050113	317 135,5	0,0	0,0	0,0	0,0	1,0	0,218	0,0
X060115	16 002,3	0,0	0,0	0,0	0,0	0,0	0,011	0,0
X010214	112 672,7	0,012	0,0	−0,001	−0,001	0,0	0,005	0,011
XM0202	250 787,5	0,027	0,0	−0,002	−0,002	0,0	0,011	0,024

mum solution these take zero values) the result is:

- optimum values of basic variables in the form:

$$x^{BO} = \left[A^B \right]^{-1} \cdot B \tag{8}$$

- optimum value of quality indicator:

$$J^O = c^{BT} \cdot \left[A^B \right]^{-1} \cdot B = W^T \cdot B \tag{9}$$

where:
W - weight vector, which represents the impact of individual constraint values B on the quality indicator.

When correlations (4) and (5) are substituted to equations (6-9), we obtain formulas directly used in post-optimal analysis [5, 6]:

$$x^B = x^{BO} = x^{BO} - A^O \cdot x^N \tag{10}$$

and

$$J = J^O - c^{OT} \cdot x^N \tag{11}$$

where:
c^o – non-basic variable shadow prices, ≥ 0 for the maximisation of the quality indicator,
A^O – optimum solution coefficient matrix,
J^O – optimum value of the quality indicator.

Let us determine, using J(B), the optimum value of the objective function for the primal problem, as produced by the constraint $B = [B_i]$ adopted for the purposes of these calculations. The optimum value of shadow price is a partial derivative of function J(B) in relation to limit B_i [7]:

$$c_i^o = \frac{\partial J(B)}{\partial B_i} \tag{12}$$

and expresses a reaction of the optimum value of the primal problem objective function to slight (marginal) changes in limit B_i.

In practice, marginal interpretations are replaced with incremental interpretations. What the optimum variable value refers to here is a change in the optimum value of the objective function of the primal problem caused by a change in the absolute term B_i of the i-th primal problem constraint by a unit, namely:

$$c_i^o = \frac{\Delta J(x^o)}{\Delta B_i} \qquad przy \quad \Delta B_i = 1 \tag{13}$$

If in the i-th constraint of the problem the absolute term increases by a unit (while not causing the constraints to be not satisfied), then the optimum value of the objective function of the primal problem f(x^o) increases by c_i^o units, i.e., to J(x^o)+ and vice versa [7].

Generally, shadow price is treated as the measure of how efficiently a limited resource B_i of the i-th production factor is used. When shadow price is interpreted on the basis of the partial derivative in formula 12, shadow price c_i^o can be considered to be the marginal productivity of the i-th factor. The above interpretations are correct if they refer to certain production factors with predefined limits („≥" model constraints) [7].

Shadow prices for active inequality constraints (constraints on the productive capacity of the mine) directly show how changes to these constraints affect the quality indicator [6].

Let *k* denote constraint number in system (10) corresponding to the production capacity of the k-th mine, and j the number of the corresponding slack variable. Matrix A^N (Formula 4) has in its j-th column zero elements, except a single one in the k-th row (this results directly from the definition of the slack variable). Based on this and on correlation (5), it is possible to demonstrate that weight W in formula (9) is equal to the shadow price for variable j, i.e. $W = c_i^o$. Assuming a negative value of the j-th non-basic variable, one can calculate the increase in the quality indicator obtained by increasing the k-th constraint by the module of this value. The acceptable value of this increase and its impact on basic variables are determined in the same way as for positive increases in non-basic variables.

Analysis of shadow prices

Having an optimum solution in the form of a simplex tableau, one can quickly see the measurable effect produced by tapping into the unused production capacities in mines. Moreover, it is possible to analyse the consequences (to the optimum production and sales plans) to which such an increase by a specific value could lead. This was presented on the basis of the coal company Alfa [5].

Shadow prices for active inequality constraints (constraints on the productive capacity of the mine) directly show how changes to these constraints affect quality indicator levels. In Table 1, production capacity constraints correspond to non-basic variables QS01 and QS05, (for mines „A" and „E"

Tab. 2. Optymalny plan produkcji po korekcie zdolności produkcyjnych; Źródło: opracowanie własne

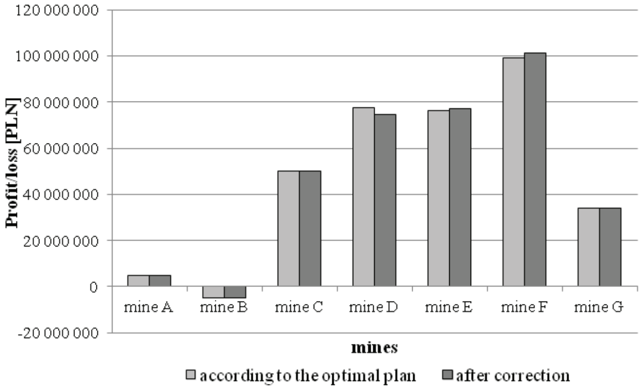
Tab. 2. Optimal production plan after the correction of the production capacity; Source: Own elaboration

Company „Alpha"				
Max. Extraction: 15,949,350 ton		Profit: 336,778,099 PLN		
Sold: 11,423,865 ton		Company reserves: 1,896,203 ton		
Mine „A"				
Max. Extraction: 1,454,750 ton		Profit: 4,843,298 PLN		
Sold: 597,902 ton		Mine reserves: 0 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Dust kettles	fine coal I	264,764	264,764	0
Dust kettles	fine coal II	317,135	317,135	0
Grates 4	slurry	16,002	16,002	0
Dumping coal	cobble	160,023	160,023	0
Dumping coal	nut coal	21,821	21,821	0
Dumping coal	fine coal IIA	675,004	675,004	0
Mine „B"				
Max. Extraction: 793,500 ton		Loss: -4,873,866 PLN		
Sold: 112,783 ton		Mine reserves: 429,690 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Grates 3	fine coal II	112,783	112,673	110
Dumping coal	coaking coal	251,027	250,787	240
Mine „C"				
Max. Extraction: 1,110,900 ton		Profit: 49,931,963 PLN		
Sold: 996,546 ton		Mine reserves: 114,354 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Export 5	coaking coal	130,74	130,74	0
Coking plants 3	coaking coal	865,806	865,806	0
Mine „D"				
Max. Extraction: 3,174,000 ton		Profit: 74,459,137 PLN		
Sold: 1,801,825 ton		Mine reserves: 1,352,159 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Export 1	coaking coal	24,324	24,324	0
Export 2	coaking coal	287,249	287,359	–110
Export 3	coaking coal	233,299	233,299	0
Indv. consumers 2	cobble	40,042	40,512	–470
Indv. consumers 3	fine coal IIA	695,179	703,929	–8,750
Grates 3	fine coal II	9,097	9,207	–110
Coking plants 2	coaking coal	78,136	78,136	0
Coking plants 1	coaking coal	387,109	398,899	–11,790
Chamber grates 1	fine coal IIA	47,39	47,39	0
Dumping coal	fine coal I	20,016	20,256	–240

Mine „E”				
Max. Extraction: 2,988,850 ton		Profit: 76,944,673 PLN		
Sold: 2,962,438 ton		Mine reserves: 0 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Export 2	coaking coal	32,987	32,877	110
Export 8	nut coal	38,985	38,855	130
Indv. consumers 2	cobble	215,917	215,197	720
Dust kettles	fine coal I	206,921	206,231	690
Dust kettles	fine coal IIA	1,550,405	1,545,235	5,17
Dust kettles	fine coal II	866,668	863,778	2,89
Grates 4	slurry	47,178	47,178	0
Chamber grates 2	slurry	3,377	3,377	0
Dumping coal	slurry	36,412	36,122	290
Mine „F”				
Max. Extraction: 3,385,600 ton		Profit: 101,119,561 PLN		
Sold: 3,027,320 ton		Mine reserves: 0 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Export 7	cobble	175,801	175,551	250
Export 8	nut coal II	51,751	51,881	–130
Export 9	fine coal II	998,845	998,845	0
Indv. consumers 2	cobble	67,718	67,968	–250
coking plants 1	coaking coal	263,03	251,24	11,79
Dust kettles	fine coal I	243,52	243,52	0
Dust kettles	fine coal IIA	23,675	23,675	0
Dust kettles	fine coal II	1,202,980	1,202,980	0
Dumping coal	coaking coal	274,742	286,532	-11,79
Dumping coal	nut coal	9,129	8,999	130
Dumping coal	slurry	74,409	74,409	0
Mine „G”				
Max. Extraction: 3,041,750 ton		Profit: 33,978,285 PLN		
Sold: 1,925,051 ton		Mine reserves: 0 ton		
Name of consumer group	Coal size grade	adjusted amount of sales [ton]	The basic amount of sales [ton]	Difference + increase – decrease [ton]
Export 7	cobble	62,32	62,57	-250
Export 9	fine coal IIA	206,632	206,632	0
Indv. consumers 3	fine coal II	619,903	611,153	8,75
Dust kettles	fine coal IIA	12,155	12,155	0
Dust kettles	fine coal II	990,615	999,365	-8,75
Chamber grates 2	fine coal II	33,426	33,426	0
Dumping coal	cobble	44,035	43,785	250
Dumping coal	nut coal	15,194	15,194	0
Dumping coal	coaking coal	1,057,470	1,057,470	0

respectively). An increase in the production capacity of any of these mines causes its profit to increase by an amount equal to the value of the increased production capacity multiplied by the shadow price for that variable. As can be seen, the most beneficial option is to increase the production capacity in mine „E”, as this generates an additional PLN 20.8 for every additional tonne [5].

For example, we calculated the increase in the quality indicator that can be achieved as a result of increasing the production capacity in mine „E” by 10,000 tonnes. The results of these calculations are presented as adjusted coal production and sales plans for company Alfa in Table 2 and Figure 1.



Rys. 1. Zysk/strata kopalń według planu optymalnego I po korekcie zwiększenia zdolności produkcyjnej kopalni „E” ; Źródło: opracowanie własne
Fig. 1. Mining profit/loss according to the optimal plan and after adjusting the production capacity of the „E”; mine; Source: Own elaboration

Impact assessment of the conducted dual price analysis

The applied adjustment has caused the following changes in comparison to the optimal plan [3]:

1. The company's profit earned owing to the applied adjustment increased by 0.06% (increase by PLN 208,000); sales remained unchanged; production reserves increased by 1.1%.
2. As for the „A” and „C” mines, the optimal plan remained unchanged.
3. In the “B” mine, the loss rate decreased slightly by 0.13%. The volume of coal sales by 0.1%, the mine's production reserves decreased by 0.08%.
4. The profit of „D” mine decreased by 4.8%. Sales decreased by 1.16% and production reserves decreased by 1.6%.
5. In the “E” mine, as a result of the increase in production capacity, the profit increased by 1.1% and the sales volume increased by 0.32%.
6. In the “F” mine there was an increase in profit by 2.08% as a result of an increase in the sales volume by 0.39%.
7. In the “G” mine, profit decreased by 1.6%, and the sales volume by almost 0.02%.

Summary

The presented adjustment and the solutions described in [5] make it possible to adjust production plans to reflect the actual internal and external conditions in which mines are expected to function. This can help significantly reduce computation time while not requiring the optimisation procedure to be run again with new constraints.

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Możliwości podejmowania decyzji produkcyjnych z wykorzystaniem cen dualnych

W artykule zaprezentowano sposób wykorzystania cen dualnych aktywnych ograniczeń (w tym przypadku ograniczeń zdolności wydobywczych kopalń) do rozwiązywania i wspomagania decyzji produkcyjnych. Jest to jeden z algorytmów opracowanej przez autora analizy postoptymalnej opracowanej w ramach metody racjonalizacji decyzji produkcyjnych dla sformalizowanej grupy (spółki, PGG) kopalń węgla kamiennego. Możliwości wykorzystania cen dualnych przedstawiono na rzeczywistym przykładzie kopalń. Dzięki opracowanemu algorytmowi można szybko uzyskać informację, bez konieczności ponownego rozwiązywania zadania, co uzyskalibyśmy lub stracili zwiększając lub zmniejszając wybrany limit produkcji, i określić wpływ zmian tych ograniczeń na osiągany zysk i strukturę wielkości produkcji i sprzedaży poszczególnych sortymentów węgla.

Słowa kluczowe: ceny dualne, analiza postoptymalna, algorytm Simpleks

An Overview of Data Mining and Process Mining Applications in Underground Mining

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Abstract

The underground mining process can be analysed with a data-oriented or process-oriented approach. The first of them is popular and wide known as data mining while the second is still not often used in the conditions of the mining companies. The aim of this paper is an overview of data mining and process mining applications in an underground mining domain and an investigation of the most popular analytic techniques used in the defined analytic perspectives ("Diagnostics and machinery", "Geomechanics", "Hazards", "Mine planning and safety"). In the paper two research questions are formulated: RQ1: What are the most popular data mining/process mining tasks in the analysis of the underground mining process? and RQ2: What are the most popular data mining/process mining techniques applied in the multi-perspective analysis of the underground mining process? In the paper sixty-two published articles regarding to data mining tasks and analytic techniques in the mentioned domain have been analysed. The results show that predominatingly predictive tasks were formulated with regard to the analysed phenomena, with strong overrepresentation of classification task. The most frequent data mining algorithms is comprised of the following: artificial neural networks, decision trees, rule induction and regression. Only a few applications of process mining in analysis of the underground mining process have been found – they were briefly described in the paper.

Keywords: data mining, process mining, analysis, mining process, underground mining

Introduction

The Industry 4.0 concept has a strong impact on the analytic activities of companies, which are willing to implement various solutions being an inherent part of modern smart factories. Nowadays, companies all over the world and across industries actively recognize and implement 4.0. solutions i.e. intelligent sensors, mobile devices or IoT platforms. Therefore, as result very fast growth of data gathered in organisations that need processing can be observed. These data are a potential source of new, useful knowledge for the decision-making process, that should be discovered. The knowledge discovery process in data can be supported by IT systems of different types (i.e. databases, analytic software, and cloud computing) and the data analytics domain. That is why big data and advanced analytics are the key features of today's companies.

The mining industry is also strongly involved in the implementation on Industry 4.0. solutions and the development of analytic competences. The analytics of the mining process should take into account the specific conditions of the mining process realisation as well as the nature of the mining process itself. The mining process, especially underground, is a complex system of people and machinery activities carried out in changeable working conditions. The occurrence of natural hazards, climate conditions as well as deposit geology have great impact on mining process performance.

The underground mining process can be analysed with the data-oriented or the process-oriented approach. The data-oriented approach is called data mining (DM) and is comprised of various tasks, algorithms and techniques that are very popular and wide known whilst the process-oriented approach is still not widely used in mining process analytics. This rather new research discipline is called process mining (PM) and enables modelling, diagnostics and the enhancement of the business processes using event data from IT systems supporting and monitoring the process execution.

The aim of the paper is an overview of data mining and process mining applications in an underground mining domain and investigation of the most popular analytic techniques used in the defined analytic perspectives. In the paper the following research questions are formulated:

RQ1: What are the most popular DM/PM tasks in the analysis of the mining process?

RQ2: What are the most popular DM/PM techniques applied in the multi-perspective analysis of the underground mining process?

These questions will be answered with an overview of data mining and process mining applications in the multi-perspective analysis of the underground mining process.

The paper's structure is as follows. In Section 2 the main analytic approaches are characterised. An overview of the DM and PM application in mining process analytics is presented in Section 3. Section 4 concludes the paper and provides the answers to the formulated research questions.

The main analytics approaches

In a modern business analytic two main approaches can be distinguished:

1. data-oriented analytics,
2. process-oriented analytics.

Data-oriented analytics offers new capabilities of knowledge discovery from data with the use of classic and advanced algorithms of data science (namely data mining - DM). The

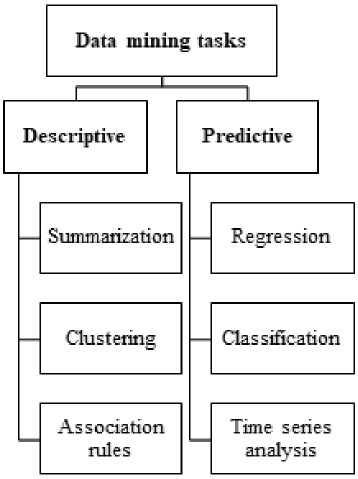

Fig. 1. Main tasks of DM
Rys. 1. Główne zadania DM

main tasks of data mining can be divided into descriptive and predictive tasks (Fig.1).

The main descriptive tasks include: summarization, clustering and association rules. Summarization enables the characterization of the dataset with the use of statistics and visualization techniques. Clustering is used for the segmentation of observations from a dataset into groups based on similarities among the selected attributes. Association rules (often used in a basket analysis) indicate the patterns in a dataset between the observations in a form of simple or complex rules. The mentioned tasks concentrate on a description and grouping or pattern findings in an available dataset.

Predictive tasks include regression, classification and time series analysis. The main distinctive feature from the descriptive tasks is that the obtained models built on the available dataset can be used for prediction. Regression enables the finding of a function describing the dependency between the selected variables (mainly of the numerical type). Classification is used for building the model describing rules for data mapping into predefined classes or groups (mainly of the categorical type). Time series analysis regards to analysis of variable values changes in the time.

Data-oriented algorithms are mainly a part of the machine learning domain and in dependency on the analytic tasks various techniques are used (Table 1).

In general, machine learning can be divided into supervised and unsupervised learning. The distinction is based on the necessity of target variable indication (in supervised learning a target variable should be indicated). From this point of view, in descriptive tasks unsupervised learning is used, while in predictive tasks supervised techniques are applied.

The data mining approach is nowadays wide known and used in the analytic community, however very fast growth of process-oriented analytics cannot be disregarded (Fig.2).

The number of papers on process mining in the Scopus database has tripled in the last 8 years.

Process-oriented analytics offers new capabilities of knowledge discovery about process execution from event logs with the use of process mining techniques. Process mining (PM) is a relatively new analytic discipline and is characterized as a bridge between data and process science (van der Aalst 2016).

The main tasks that could be proceed with process mining techniques include (van der Aalst 2016): the discovery of process models, conformance checking and enhancement. Their characteristics are presented in Table 2.

The basic data structure for process mining – namely event log – includes: case id, the timestamp of an event and an event name. These data can be extended with other contextual information related to resources, costs etc. The process models built on the top of the event log can be expressed in a form of dependency graphs, Petri nets or BPMN models. Process models enable conformance checking and in-depth process analysis in time, resource or case perspectives.

The presented approaches establish a complementary source of potentially new and useful knowledge in an organization for process improvement and optimization of the economic or production results. In the next sections an overview of their applications in the multi-perspective analysis of the underground mining process is presented.

An overview of the data mining and process mining applications in underground mining process analytics

Data Mining applications

An overview of data mining applications in the underground mining process analysis has been based on 62 papers searched with use of the Science Direct, Scopus, IEEE Explore and Google Scholar databases (examples of used terms: "analysis+mining+process+underground", "prediction+underground+mine", "data+analysis+longwall", "machine+learning+longwall").

In the paper, for the purpose of a more detailed description of data mining applications in underground mining process analytics, the following perspectives have been introduced: "Diagnostic and machinery", "Geomechanics", (other) "Hazards" and "Mine planning and safety".

The distributions of the papers in terms of publication year and defined analytic perspective are presented in Fig.3 and Fig. 4.

Most of the analysed papers have been published in the last 5 years. The distribution of the papers in relation to de-

Tab. 1. Example techniques used in DM tasks. Source: based on (Larose and Larose 2014)
Tab. 1. Przykładowe techniki wykorzystywane w zadaniach DM

Data mining task	Example techniques
summarization	statistical analysis, histograms, plots
clustering	K-means, Kohonen, k-NN
association rules	A priori, FP Growth
regression	linear regression, neural networks,
classification	decision trees, neural networks, support vector machine (SVM), Bayes classifiers
time series analysis	ARMA, ARIMA, models ARCH models, HMM models, trend estimation, decomposition, spectral analysis

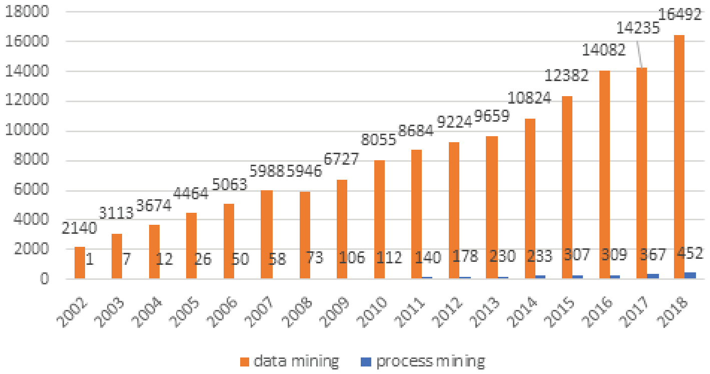

Fig. 2. The number of papers in the Scopus database (query for “data mining” or “process mining” in the title, abstract or keywords).
Rys. 2. Liczba artykułów w bazie Scopus (zapytanie dla “data mining” lub “process mining” w tytule, streszczeniu czy słowach kluczowych).

fined analytics perspectives is rather regular. In the “Diagnostic and machinery” and “Mine planning and safety” perspectives 15 papers were analysed per group, while in the “Geomechanics” and “Hazards” 16 papers were analysed per group.

In most publications, concerning the analysed phenomena, predictive tasks were formulated, with strong overrepresentation of the classification task (Fig.5).

The distribution of data mining tasks in various analytic perspectives of the mining process is presented in Table 3.

Except for the classification task, as popular data mining tasks regression and rule induction can be found. The multitask label introduced in the table indicates the presence of predictive and descriptive tasks in the published papers.

In the mentioned data mining tasks various techniques have been applied. A detailed overview with regard to the defined analytic perspectives is presented in the following part of the paper.

In the first analytic perspective – “Diagnostic and machinery” - the analysed papers have been related to strictly diagnostic problems (8) i.e. belt conveyor diagnostic, as well as machinery performance and its prediction (7), i.e. longwall powered support capacity. The applied data mining techniques in this perspective are presented in Table 4.

As it can be clearly observed the most popular techniques are artificial neural networks (8) and time series analysis (4). ANN are also popular (6 findings) in papers included in the “Geomechanics” perspective (Table 5).

This collection is extended with decision trees algorithms (4 papers). Tree classifiers used in the analysed sample are comprised of some simple algorithms as i.e. CART as well as more sophisticated i.e. boosted trees.

It is worth of mentioning that the “Geomechanics” perspective contains papers related to: rock mechanics (2 papers), rock mass characteristic (2), seismic (9) and subsidence (3). Analysing the papers in the scientific databases it can be observed that the prediction of seismic events in underground mines is very often the subject of research.

Other “Hazards” perspective collects papers related to natural hazards (except seismic), namely: methane (7 papers), rock burst (5) coal combustion (2), gas and rock outburst (1) and roof fall (1).

The data mining techniques used in the “Hazards” analytic perspective are presented in Table 6.

In the analysed papers the most often mentioned DM techniques were ANN (5 papers), decision trees (5) and regression (5). Simple CART algorithms as well as the more advanced XGBoost were used. In the regression task simple models and logistic regression have been applied.

The last analytic perspective “Mine planning and safety” comprises of papers from a wide scope of issues related to mine planning i.e. equipment selection, production costs, coal

Tab. 2. PM tasks. Source: based on (van der Aalst 2016; Augusto et al. 2019; Carmona et al. 2018)
Tab. 2. Zadania PM

Process mining task	Description	Example algorithms
Process model discovery	create a model without using any a-priori information on top of the event log	Alpha Miner Heuristic miner Inductive miner Fuzzy miner
Conformance checking	an existing process model is compared with an event log in order to detect and locate deviations between the process model and the real process execution	casual footprints matrix rule checking token replay alignments
Enhancement	The extension of the analysis or improvement of the process by the use of the additional information recorded in the event log i.e. involved resources or adding other perspectives to the process model (i.e. organizational, time or case perspective)	performance analysis data-aware heuristic miner social networks

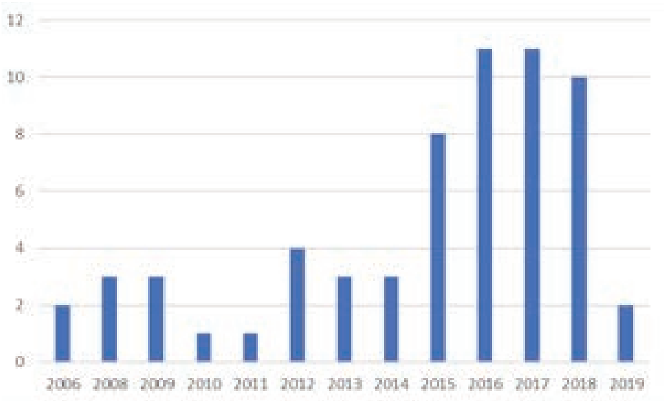

Fig. 3. Papers – year of publication distribution
Rys. 3. Artykuły – rozkład wg roku publikacji

prices (9 papers) and safety, mainly related to the analysis of occupational accidents (6). The main data mining techniques applied in this analytic perspective are presented in Table 7.

In the table, it can be observed that the most popular techniques are regression models (6 papers) and decision trees algorithms (4). The variety of the used techniques results from the specificity of the analysed issue. In some cases several techniques have been applied i.e. (Krzemień, A. et. al. 2015).

A holistic view of the DM techniques application in various analytic perspectives of the underground mining process is presented in Fig. 6.

A strong presence of "black-box" techniques can be found in "Diagnostic and machinery" and "Geomechanics" perspectives, where complex phenomena are analysed, very often without full available context information.

The presentation of the most popular DM techniques in the analyzed papers is shown in Figure 7.

The most popular DM techniques applied in the analytics of the mining process are: artificial neural networks, regression, tree models and rule induction.

An analysis of the mining process can be also supported with soft computing techniques. An example of their overview is presented in (Jang and Topal, 2014).

Process Mining applications

Papers with process mining applications in the underground mining process analysis have been searched with the use of the Science Direct, IEEE Explore, Scopus and Google Scholar databases. Due to the characteristic word play – "process mining" and "mining process", the following search terms have been used: "event+logs+process+underground", "event+logs+longwall+mining", "event+logs+ underground+process+analysis".

The results of searching in the mentioned databases are presented in Table 8.

Process mining applications in underground mining are rare and only several papers focus on this type of analytics of a mining process.

The first paper (Brzychczy and Trzcionkowska 2017) focuses on the analysis of mechanized roof support operations in underground mines. In the paper all three PM tasks can be found. Log Explorer, Mine Petri Net with Inductive Miner as well as Replay A Log on Petri Net for Performance/Conformance Analysis, plug-ins were used. In the paper (Brzychczy and Trzcionkowska 2019) a general idea of the underground mining process analysis based on sensor data and the creation of suitable event logs for process mining purposes are presented. Available data from

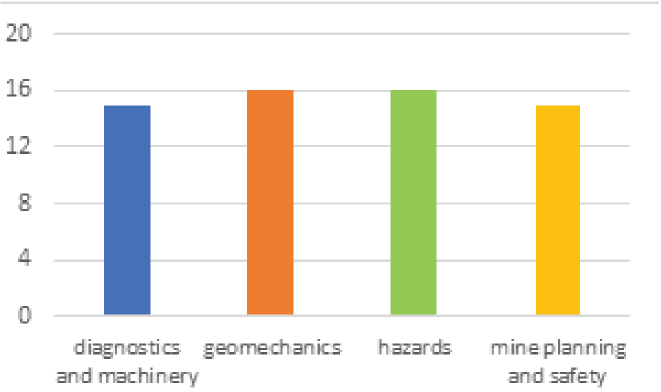

Fig. 4. Number of papers in the defined analytic perspectives
Rys. 4. Liczba artykułów w zdefiniowanych perspektywach analitycznych

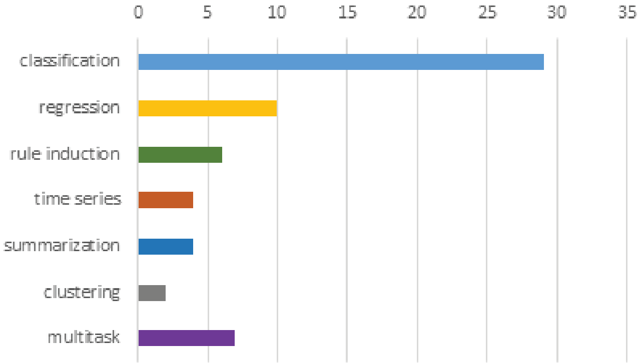

Fig. 5. Distribution of DM tasks in the analysed papers
Rys. 5. Zadania DM w analizowanych artykułach

Tab. 3. DM tasks by defined mining process analytic perspectives
Tab. 3. Zadania DM w zdefiniowanych perspektywach analitycznych procesu wydobywczego

Perspective	**classification**	**regression**	**rule induction**	**time series**	**summarization**	**clustering**	**multitask**	**number of papers**
Diagnostics and machinery	8	1	3	1	1	-	1	15
Geomechanics	9	1	1	2	-	1	2	16
Hazards	9	3	1	1	-	1	1	16
Mine planning and safety	3	5	1	-	3	-	3	15
Total	29	10	6	4	4	2	7	62

longwall monitoring systems are on a low-level of abstraction, that its direct analysis with process mining tools is pointless. Data in its existing form requires preprocessing with the use of supervised and unsupervised data mining techniques. These aspects were extended in papers (Brzychczy and Trzcionkowska 2018; Trzcionkowska and Brzychczy 2018).

The paper (He et al. 2019) presents process mining application to the emergency rescue processes analysis of fatal gas explosion accidents in China. In the paper process model discovery as well as other PM tasks were presented. Among others the following PM techniques were applied: Mine Petri Net with Inductive Miner, Check Conformance using ETConformance, Dotted charts and Social Networks Analysis.

The main reasons for a little number of PM applications in mining process analysis are: a lack of process mining tools awareness in the mining community and, what is more important, a lack of suitable event logs for process modelling and analysis. However, an observation of process mining discipline development as well as the interest of mining companies in advanced analytics of their processes entitles the

Tab. 4. DM techniques in the "Diagnostics and machinery" analytic perspective
Tab. 4. Techniki DM w perspektywie analitycznej „Diagnostyka i maszyny"

Author(s)	**TSA**	**BM**	**ANN**	**DT**	**RI**	**REG**	**CLS**	**kNN**	**SVM**	**STAT**
Deb, D., Kumar, A. and Rosha, R.P.S. (2006)			●							
Bongers D.R. and Gurgenci H. (2008)			●							●
Chatterjee, S. and Bandopadhyay, S. (2012)			●							
Al-Chalabi, H. et al. (2014)			●							
Michalak, M., Sikora, B. and Sobczyk, J. (2015)	●				●	●				
Moczulski, W. et al. (2016)		●	●	●						
Michalak, M., Sikora, B. and Sobczyk J. (2016)					●					
Trzcionkowska A. and Brzychczy E. (2016)					●					
Verma, A.K., Kishore, K. and Chatterjee, S. (2016)			●							
Kesek, M. (2017)						●				
Kucharczyk, D., Wyłomańska, A. and Zimroz, R. (2017)	●					●				
Hargrave, Ch., James, C. and Ralston, J. (2017)	●									
Kashnikov, A., Levin, L. (2017)			●							
Wodecki, J., Stefaniak, P., Polak, M. and Zimroz R. (2018)	●						●			
Jedliński, Ł. and Gajewski, J. (2019)			●					●		

TSA - time series analysis, BM – Bayesian models, ANN – artificial neural network, DT – decision tree models, RI – rule induction, REG – regression, CLS – clustering, kNN – k-nearest neighbour, SVM – support vector machine, STAT– probability distributions, multivariate analysis

Tab. 5. DM techniques in the "Geomechanics" analytic perspective
Tab.5. Techniki DM w perspektywie analitycznej „Geomechanika"

Author(s)	**TSA**	**BM**	**ANN**	**DT**	**RI**	**REG**	**CLS**	**kNN**	**SVM**
Leśniak, A. and Isakow, Z. (2009)							●		
Sikora, M. and Wróbel (2010)					●				
Li, P., Tan, Z., Yan, L. and Deng, K. (2011)									●
Kabiesz, et al. (2013)				●	●				
Lee, S. and Park, I (2013)				●					
Zhou, J. et al. (2013)									●
Jakubowski, J. and Tajduś, A. (2014)			●	●					
Iannacone J.P. et al. (2015)	●								
Jamróz, D. and Niedoba, T. (2015)			●						
Boullé, M. (2016)		●							
Kurach, K. and Pawlowski, K. (2016)			●						
Hussain, S. et al. (2016)			●			●			
Polak, M. et al. (2016)	●						●		
Janusz, A. et al. (2017)				●		●			●
Mahdevari, S., Shahriar, K., Sharifzadeh, M. and Tannant, D. D. (2017)			●						
Huang, L. et al. (2018)			●						

Tab. 6. DM techniques in the “Hazards” analytic perspective
Tab. 6. Techniki DM w perspektywie analitycznej „Zagrożenia”

Author(s)	**TSA**	**BM**	**ANN**	**DT**	**RI**	**REG**	**CLS**	**kNN**	**SVM**	**STAT**
Borowski, M. and Szlązak, N. (2006)			●							
Özgen Karacan, C. (2008)			●							
Krauze, E., (2009)							●			
Sikora, M. and Sikora, B (2012)	●				●			●		
Özgen Karacan, C. and Goodman, G.V.R. (2012)				●						
Grzegorowski, M. and Stawicki, S. (2015)										●
He, M. et al. (2015)			●			●			●	
Manowska, A. (2015)						●				
Wojtecki, Ł. and Konicek, P. (2016)						●				
Javadi, M., Saeedi G. and Shahriar, K. (2017)		●								
Ribeiro e Sousa, L. et al. (2017)		●	●	●				●	●	
Li, N. and Jimenez, R. (2018)						●				
Lei, Ch. et al. (2018)			●	●		●				
Bodlak, M., Kudełko J. and Zibrow, A. (2018)				●						
Kozielski, M., Matyszok, P., Sikora, M. and Wróbel Ł. (2018)					●					
Lei, Ch. et al. (2019)				●					●	

Tab. 7. DM techniques in the “Mine planning and safety” analytic perspective
Tab. 7. Techniki DM w perspektywie analitycznej „Projektowanie kopalń i bezpieczeństwo”

Author(s)	**TSA**	**BM**	**ANN**	**DT**	**RI**	**REG**	**CLS**	**kNN**	**SVM**	**STAT**
Gawlik, L. (2008)						●				
Sari, M. et al. (2009)										●
Cheng, J. and Yang, S. (2012)									●	
Gernand, J.M. (2014)				●						
Kopacz, M. (2015)										●
Krzemień, A. et. al. (2015)	●		●			●				
Niedoba, T. and Ranosz, R. (2016)						●				
Snopkowski, R., Napieraj, A. and Sukiennik, M. (2016)										●
Brzychczy, E., Kęsek, M., Napieraj, A. and Magda R. (2017)				●	●					
Jonek-Kowalska, I. and Turek, M. (2017)						●				
Fuksa, D. et al. (2017)						●				
Duany, A. A., Lilford, E. and Topal E. (2018)				●						
Sanmiquel L. et al. (2018)					●					
Wyganowska, M. (2018)						●				
Qiao, W. et al. (2018)				●	●					

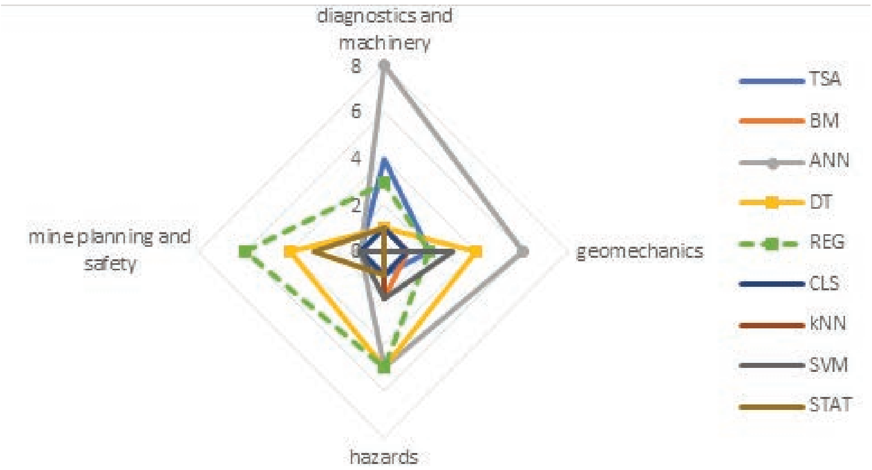

Fig. 6. The DM techniques applied in the analysed papers and defined perspectives
Rys. 6. Techniki DM zastosowane w analizowanych artykułach w ujęciu zdefiniowanych perspektyw

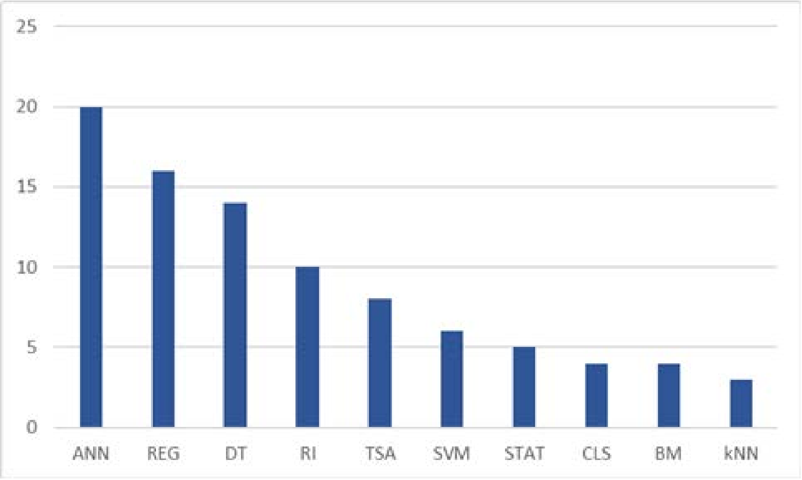

Fig. 7. The DM techniques applied in the analysed papers
Rys. 7. Techniki DM wykorzystane w analizowanych artykułach

Tab. 8. The results of searching PM applications in underground mining process analysis. Source: own searching – date 10.04.2019, * - only used in Google Scholar for result limitation
Tab. 8. Wyniki poszukiwania zastosowań PM w analizie podziemnego procesu wydobywczego

Searched terms	Science Direct results (hints)	IEEE Explore results (hints)	Scopus results (hints)	Google Scholar app. results (hints) since 2015
event logs process underground (mining*)	5 (1)	2 (0)	9 (2)	16 400 (5 in first 100 results)
event logs longwall mining	1 (0)	19 (0)	5 (2)	899 (3)
event logs underground (mining*) process analysis	2 (0)	1 (0)	6 (2)	16 700 (5)

author to state that the number of these applications in the mining domain will increase in the next years.

Conclusions

An analysis of the gathered papers regarding data mining and process mining applications in the underground mining domain enabled to formulate the following conclusions and answers for the research questions:

- DM techniques are widely used for mining process analysis, mainly in the predictive kind of DM tasks, with strong overrepresentation of classification task (RQ1),
- the most popular DM techniques in the underground mining process analysis include: artificial neural networks, tree models, rule induction and regression (RQ2).

The different sophistication degree of used techniques can be found - from simple models (CART tree, linear regression, naïve Bayesian) to more complex (XGboost, Random Forrest, multi regression or Bayesian fuzzy models). The interest in various techniques is rather comparable in defined analytics perspectives with an exception of economics related papers (in the mine planning and safety perspective), where the over presence of regression models can be observed.

Due to small presence of process mining applications in the underground mining process analysis, only general conclusions can be drawn. Process mining is still not discovered by the mining community. However, several found papers have shown, that it can become a new potentially useful analytics in mining companies aiming in process improvement and efficiency increasing.

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Przegląd zastosowań technik drążenia danych i procesów w górnictwie podziemnym

Celem artykułu jest przegląd zastosowań eksploracji danych (data mining) i procesów (process mining) w analizie procesu wydobywczego w kopalniach podziemnych oraz identyfikacja najpopularniejszych technik analizy danych w tym zakresie. W artykule sformułowano dwa pytania badawcze: P1: Jakie są najpopularniejsze zadania eksploracji danych/eksploracji procesów w analizie procesu wydobywczego w kopalniach podziemnych? oraz P2: Jakie są najpopularniejsze techniki eksploracji danych/eksploracji procesów stosowane w wielowymiarowej analizie procesu wydobywczego w kopalniach podziemnych? W artykule przeanalizowano sześćdziesiąt dwie opublikowane prace dotyczące eksploracji danych w ujęciu zdefiniowanych perspektyw analitycznych ("Diagnostyka i maszyny", "Geomechanika", "Zagrożenia", "Projektowanie kopalń i bezpieczeństwo"). Wyniki pokazują, że w odniesieniu do analizowanych zjawisk formułowano głównie zadania predykcyjne, z silną nadreprezentacją zadania klasyfikacji. Do najczęściej wykorzystywanych technik eksploracji danych należą: sztuczne sieci neuronowe, drzewa decyzyjne, indukcja reguł i regresja. Eksploracja procesów w analizie procesu wydobywczego w kopalniach podziemnych została opisana tylko w kilku artykułach, które pokrótce omówiono.

Słowa kluczowe: eksploracja danych, eksploracja procesów, analiza, proces wydobywczy, górnictwo podziemne

An Analysis of Selected Benchmarks and Evaluation Methods to Test the Replacebility of Mathematical-Statistical Methods in Benchmarking by Solvency and Bankruptcy Models: A Case Study in Assessing Gravel-Sand Mining Companies in the Czech Republic

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Abstract

Benchmarking is a useful managerial tool to identify opportunities in order to improve the efficiency and effectiveness of a company via the application of benchmarks to assess and compare the company efficiency with the leader in the field or other selected companies. For this reason, it is vital to conveniently select the different benchmarks and adequate methods for the evaluation. Having benchmarked five selected mining companies exploiting gravel-sand in the Czech Republic, CEMEX Sand, k.s., Českomoravský štěrk, a. s., LB MINERALS, s.r.o., CEMEX Cement, s.r.o., and ZEPIKO, spol. s r.o., the article aims to consider mutual replacebility of mathematical-statistical methods used for evaluation in benchmarking. Next, it verifies the agreement in results rendered by the solvency and bankruptcy models and those rendered by mathematical-statistical methods. We used eleven benchmarks (EBITDA, ROA, ROS, WACC, Quick ratio, Total assets turnover, Net working capital turnover ratio, Interest coverage, Altman's model, Index IN05, and Taffler's model), and seven evaluation methods. The research study shows that the majority of the examined benchmarking methods may be mutually replaced. Based on the results, we determined two groups of methods, out of which one method may be chosen and mutually combined with a method from the other group, and vice versa. The first group contains the Rank ordering weighting method, Point allocation method, Standardised variable method, Method of the distance from a fictitious object, Weighted sum method and TOPSIS method. The second group contains Weighted average method. The research also proves that selected benchmarks, such as Altman's model and Taffler's model, may be used on their own.

Keywords: benchmarking, mathematical-statistical methods, solvency and bankruptcy models, mining companies

Introduction

One of the key challenges company management must face is the attainment and maintenance of the competitive advantage. Considering the variety of businesses and managers' creativity, there are an endless number of ways how to fulfil the challenge, and this usually constitutes a chain of decisions taken by managers. The quality of the decisions is conditioned, inter alia, by the quantity and quality of information that managers have available during the decision-making process.

Managers or decision makers may apply benchmarking to gain the crucial knowledge. Benchmarking has its roots in the 1970s in the company XEROX (Camp, 1995). In the 21st century, according to Stapenhurst (2009), organisations benchmark because of performance improvement, budgeting, testing ideas, technical problem solving and resolving disputes. The popularity of benchmarking in business and the industry may be explained by its usefulness as well as by the fact that comparison especially with others and with the best is natural to people. By analogy, we may approach comparison from the point of view of company management.

Moreover, benchmarking may contribute to the company's goodwill and its positive image on its surroundings, including the environmental impacts. The environmental aspects may be the benchmarks (e.g. the budget for environmental improvements, both absolute and relative). The fact that a company is the economic leader is not only a reflection of its commercial fitness, but also of its abilities to minimize the consumption of energies, materials, and production of waste during the production processes. If other companies aim to improve their results in the complex evaluation and approximate the leader, they cannot overlook positive attitudes to environmental aspects.

Company management is responsible for the decisions and choices. Apart from benchmarking, company managers may rely on other methods to help them decide. Still, the decisions

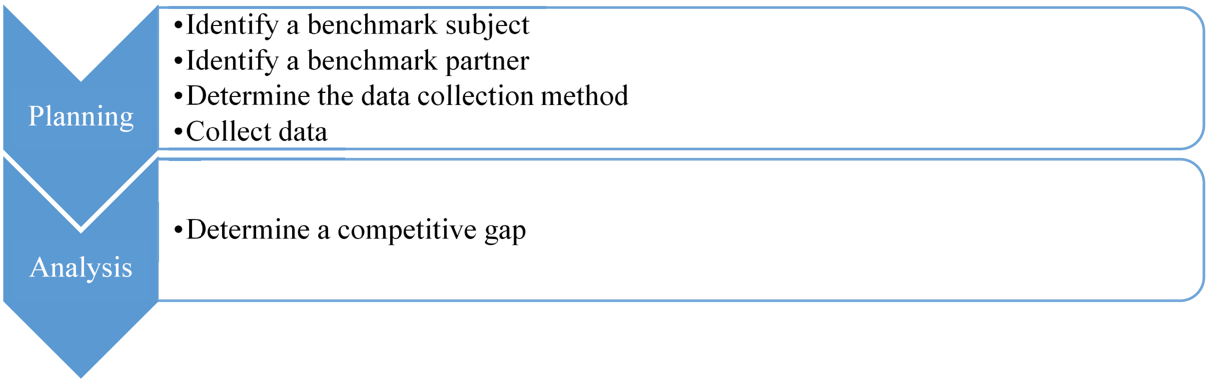

Fig. 1. Modified benchmarking process (modified according Camp, 1995)
Rys. 1. Zmodyfikowany proces benchmarkingu (zmodyfikowany według Camp, 1995)

Tab. 1. Brief characteristics of benchmarked mining companies. Source: Mining Yearbook, 2015 + company websites
Tab. 1. Krótka charakterystyka benchmarkingu spółek

Company name	**Volume mined [m^3]**	**Brief characteristics**
CEMEX Sand, k.s.	876 600	The company was established under the name GZ - Sand, s.r.o. in 1993. The major business is extraction and processing of sand and gravel. In the Czech Republic the company offers high-quality sorted and unsorted stone and sand, both for customers and the needs of other members of CEMEX group. In the Czech Republic CEMEX Sand operates 11 gravel-pits and 7 stone quarries.
Českomoravský štěrk, a.s.	954 539	The company belongs to the multinational group Heidelberg Cement. The company belongs among the biggest producers of aggregate in the Czech Republic. They operate 14 stone quarries and 11 sand-pits. They sell a wide spectrum of fractions applicable in all branches of the building industry.
LB MINERALS, s.r.o.	682 000	The company is a member of the multinational concern LASSELSBERGER Group. The mines and processing plants are distributed around the Czech Republic, where gravel and sand are extracted as major or accompanying raw materials.
CEMEX Cement, s.r.o.	361 671	CEMEX Cement, k.s. has been a member of CEMEX group since 2015. The major business is the production of cement and special products to stabilise soils.
ZEPIKO, spol. s r.o.	282 000	The founding company of ZEPIKO GROUP is a purely Czech mining enterprise that started in Brno in 1992. The company deals with mining, mining of non-reserved minerals and waste management. They operate sandpits. Fro example, the sand-pit in Oblekovice u Znojma has reserves for next 20 years.

should be made based on a number of criteria. Multicriteria decision making (MCDM) is also popular to screen, prioritise, rank or choose alternatives grounded in human judgment from a limited number of alternatives (Roszkowska, 2013), who dealt with MCDM and compared ranking methods of weight determination. Adding multicriteria decision making methods to benchmarking, managers have plentiful means to arrive at exact conclusions and may thus formulate measures for further development of their companies. However, we realise that benchmarking may be a challenge for many managers as the topic has been approached from many points of view and the efforts resulted in a number of publications.

Considering the high number of literature dealing with benchamarking, we may classify it into two groups. The first is constituted by books or textbooks, such as Camp, 1995; Rolstadas, 1995; Stapenhurst, 2009; Zairi, 2009, which acquaint readers with benchmarking, but naturally the books are characteristic of certain generalisation in the approaches. The second group comprises of benchmarking applications in specific disciplines and areas (Henriksson, 2017; Kołodziejczuk, 2016; Sweis, 2016; Talebi, 2014; Magd, 2011). Moreover, the study of multicriteria decision methods offers a wide range of specific methods that may be applied in benchmarking. Rozskowská (2013) refers to many such methods (ranking ordering method, DEA, AHP, DR, PA, LINPAC, SD, etc.) and authors in her comparative overview. It is clear that the stated methods vary in their intensity for data and processing. A question arises, though, whether simpler methods may render comparable results as many data-intense and time-consuming methods.

Tab. 2. Input data of the 5 selected mining companies – part I (calculated by authors based on company annual reports). Source: Calculated by authors based on company annual reports

Tab. 2. Dane wejściowe dla 5 spółek górniczych – część I (wyliczone przez Autorów na podstawie raportów rocznych)

Year	**Company**	**Benchmarks**					
		ROA	**WACC**	**ROS**	**Quick ratio**	**Net working capital turnover ratio**	**Interest coverage**
2010	**CEMEX Sand. k.s.**	9.30%	10.13%	11.32%	1.7327	3.7635	638.08
	Českomoravský štěrk. a.s.	8.79%	8.69%	10.34%	3.5058	2.0945	198,771.00
	LB Minerals. s.r.o.	6.91%	7.26%	9.68%	1.0518	13.4552	13.20
	CEMEX Cement. s.r.o.	8.33%	11.00%	7.60%	0.2252	-2.7560	4.932
	ZEPIKO. spol. s r.o.	5.69%	7.60%	7.40%	0.6213	-12.5636	31.69
2011	**CEMEX Sand. k.s.**	3.00%	3.43%	2.00%	1.5808	4.3494	2.14
	Českomoravský štěrk. a.s.	5.88%	6.52%	6.49%	1.6348	3.5514	118,132.00
	LB Minerals. s.r.o.	5.50%	5.59%	6.99%	1.3402	7.5377	10.77
	CEMEX Cement. s.r.o.	7.63%	6.68%	7.44%	1.5755	-3.4261	4.76
	ZEPIKO. spol. s r.o.	5.18%	6.96%	6.62%	0.7534	-19.2722	49.52
2012	**CEMEX Sand. k.s.**	5.43%	2.34%	0.00%	1.1225	7.7048	3.14
	Českomoravský štěrk. a.s.	3.58%	3.65%	3.87%	1.5800	3.5976	171.42
	LB Minerals. s.r.o.	4.95%	4.93%	5.96%	1.4464	6.3654	7.58
	CEMEX Cement. s.r.o.	5.78%	5.41%	5.10%	1.1368	8.8981	2.38
	ZEPIKO. spol. s r.o.	-11.41%	-19.69%	-14.75%	1.0896	36.9906	-58.39
2013	**CEMEX Sand. k.s.**	2.13%	1.58%	0.00%	1.1310	6.1356	1.94
	Českomoravský štěrk. a.s.	3.76%	4.02%	5.06%	2.0063	2.6230	819.94
	LB Minerals. s.r.o.	4.52%	4.42%	5.08%	1.3980	5.9412	7.05
	CEMEX Cement. s.r.o.	0.89%	1.19%	-2.92%	0.2027	-1.6283	0.33
	ZEPIKO. spol. s r.o.	-4.15%	-9.98%	-5.35%	0.7205	-13.0973	-15.81
2014	**CEMEX Sand. k.s.**	0.40%	2.86%	0.00%	1.2193	5.8897	0.21
	Českomoravský štěrk. a.s.	6.34%	6.91%	7.58%	2.1401	2.8471	125,759.00
	LB Minerals. s.r.o.	6.21%	6.24%	7.23%	1.5313	5.7888	9.69
	CEMEX Cement. s.r.o.	6.55%	5.61%	4.52%	0.9652	14.7030	2.67
	ZEPIKO. spol. s r.o.	5.74%	14.22%	6.47%	0.7257	-11.7739	27.71

Tab. 3. Input data of the 5 selected mining companies – part II (calculated by authors based on company annual reports). Source: Ccalculated by authors based on company annual reports

Tab. 2. Dane wejściowe dla 5 spółek górniczych – część II (wyliczone przez Autorów na podstawie raportów rocznych)

Year	**Company**	**Benchmarks**				
		Total assets turnover	**EBITDA**	**Altman's model**	**Index IN05**	**Taffler's model**
2010	**CEMEX Sand. k.s.**	0.6571	79,598	1.2605	26.3770	0.4754
	Českomoravský štěrk. a.s.	0.6829	309,012	2.6742	7,952.3128	0.8542
	LB Minerals. s.r.o.	0.5301	381,561	1.4191	1.2393	0.3841
	CEMEX Cement. s.r.o.	0.6660	481,965	1.0559	0.8797	0.2974
	ZEPIKO. spol. s r.o.	0.6004	15,129	1.0951	1.8353	0.3516
2011	**CEMEX Sand. k.s.**	0.6849	45,183	1.1074	0.6781	0.2447
	Českomoravský štěrk. a.s.	0.7348	217,782	2.0233	4,726.2944	0.4946
	LB Minerals. s.r.o.	0.5727	316,486	1.5765	1.1251	0.3761
	CEMEX Cement. s.r.o.	0.6308	472,068	1.2293	0.8928	0.5282
	ZEPIKO. spol. s r.o.	0.6157	15,358	1.1370	2.5451	0.3231
2012	**CEMEX Sand. k.s.**	0.7054	65,594	1.1620	0.7702	0.2954
	Českomoravský štěrk. a.s.	0.6715	170,663	1.8573	7.7315	0.3942
	LB Minerals. s.r.o.	0.5733	288,103	1.4097	0.9601	0.3511
	CEMEX Cement. s.r.o.	0.5633	413,932	0.9228	0.6462	0.3507
	ZEPIKO. spol. s r.o.	0.6380	-8,321	0.6094	-2.2997	-0.2298
2013	**CEMEX Sand. k.s.**	0.6792	48,310	1.0353	0.5860	0.2547
	Českomoravský štěrk. a.s.	0.6000	174,590	2.0340	33.7780	0.4362
	LB Minerals. s.r.o.	0.5822	290,647	1.4707	0.9425	0.3309
	CEMEX Cement. s.r.o.	0.5611	250,275	0.4995	0.3454	0.1860
	ZEPIKO. spol. s r.o.	0.6736	3,234	0.7470	-0.3903	0.0493
2014	**CEMEX Sand. k.s.**	0.7744	48,310	1.0516	0.4642	0.2362
	Českomoravský štěrk. a.s.	0.6840	174,590	2.1384	7,952.3128	0.5472
	LB Minerals. s.r.o.	0.6123	290,647	1.5142	1.1319	0.4190
	CEMEX Cement. s.r.o.	0.6374	250,275	2.3317	1.1310	0.4083
	ZEPIKO. spol. s r.o.	0.6839	3,234	1.0424	1.6738	0.3087

Tab. 4. Benchmarking results of the examined companies between 2010 and 2014 using the benchmarking evaluation methods and selected benchmarks. Source: own

Tab. 4. Wyniki benchmarkingu badanych spółek w latach 2010-2014 z wykorzystaniem metod oceny i benchmarkingu

1.	**Rank ordering weighting method**	**2010**	**2011**	**2012**	**2013**	**2014**	**Rank based on the sum of ranks throughout the period**	**Rank based on the coefficient of variation**
CEMEX Sand, k.s.		2	4	3	3	4	3	4
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		3	3	2	2	2	2	3
CEMEX Cement, s.r.o.		4	2	4	4	2	3	5
ZEPIKO, spol. s r.o.		4	5	5	5	5	5	2
2.	**Weighted average method**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		3	5	4	5	4	5	1
Českomoravský štěrk, a.s.		2	2	3	3	1	1	3
LB Minerals, s.r.o.		1	4	1	4	3	2	4
CEMEX Cement, s.r.o.		4	3	2	2	2	2	2
ZEPIKO, spol. s r.o.		5	1	5	1	5	4	5
3.	**Point allocation method**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		3	4	4	4	4	4	2
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		2	2	2	2	3	2	4
CEMEX Cement, s.r.o.		4	3	3	5	2	3	5
ZEPIKO, spol. s r.o.		5	5	5	3	5	5	3
4.	**Standardised variable method**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		2	4	3	3	4	3	4
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		3	3	2	2	3	2	3
CEMEX Cement, s.r.o.		4	2	4	4	2	3	5
ZEPIKO, spol. s r.o.		5	5	5	5	5	5	1
5.	**Method of the distance from a fictitious object**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		2	4	3	3	4	3	4
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		3	3	2	2	3	2	3
CEMEX Cement, s.r.o.		4	2	4	4	2	3	5
ZEPIKO, spol. s r.o.		5	5	5	5	5	5	1

6.	**Weighted sum method**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		2	4	3	3	4	3	4
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		3	3	2	2	3	2	3
CEMEX Cement, s.r.o.		4	2	4	4	2	3	5
ZEPIKO, spol. s r.o.		5	5	5	5	5	5	1
7.	**TOPSIS method**	**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		3	3	4	3	4	4	3
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		2	2	3	2	3	2	4
CEMEX Cement, s.r.o.		4	4	2	4	2	3	5
ZEPIKO, spol. s r.o.		5	5	5	5	5	5	1
Altman's model		**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		3	5	3	3	4	3	3
Českomoravský štěrk, a.s.		1	1	1	1	2	1	4
LB Minerals, s.r.o.		2	2	2	2	3	2	2
CEMEX Cement, s.r.o.		5	3	4	5	1	3	5
ZEPIKO, spol. s r.o.		4	4	5	4	5	5	1
Index IN05		**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		2	5	3	3	5	4	4
Českomoravský štěrk, a.s.		1	1	1	1	1	1	1
LB Minerals, s.r.o.		4	3	2	2	3	2	3
CEMEX Cement, s.r.o.		5	4	4	4	4	5	2
ZEPIKO, spol. s r.o.		3	2	5	5	2	3	5
Taffler's model		**2010**	**2011**	**2012**	**2013**	**2014**		
CEMEX Sand, k.s.		2	5	4	3	5	4	3
Českomoravský štěrk, a.s.		1	2	1	1	1	1	4
LB Minerals, s.r.o.		3	3	2	2	2	2	2
CEMEX Cement, s.r.o.		5	1	3	4	3	3	5
ZEPIKO, spol. s r.o.		4	4	5	5	4	5	1

Tab. 5. Comparison of results and statistical testing of the benchmarking evaluation methods based on Spearman's coefficient of rank correlation

Tab. 5. Porównanie wyników i testów statystycznych metod oceny benchmarkingowej w oparciu o współczynnik korelacji rang Spearmana

Method No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	0	.7 (IND) 0	.95 (PR) 1	(PR)	1 (PR) 1	(PR)	0.95 (PR)
2		0	.85 (IND) 0	.7 (IND) 0	.7 (IND) 0	.7 (IND)	0.85 (IND)
3			0	.95 (PR) 0	.95 (PR) 0	.95 (PR)	1 (PR)
4				1	(PR)	1 (PR)	0.95 (PR)
5					1	(PR)	0.95 (PR)
6							0.95 (PR)
7							

where IND – insignificant coefficient of rank correlation (independent results of benchmarkingmethods); NR – significant coefficient (negative ordinal relation); PR – significant coefficient (positive ordinal relation) R_(S,0.,95) (5)=0.9

Source: own

Tab. 5. Comparison of results and statistical testing of the benchmarking evaluation methods based on Spearman's coefficient of rank correlation

Tab. 5. Porównanie wyników i testów statystycznych metod oceny benchmarkingowej w oparciu o współczynnik korelacji rang Spearmana

Method No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	0	.7 (IND) 0	.95 (PR) 1	(PR)	1 (PR) 1	(PR)	0.95 (PR)
2		0	.85 (IND) 0	.7 (IND) 0	.7 (IND) 0	.7 (IND)	0.85 (IND)
3			0	.95 (PR) 0	.95 (PR) 0	.95 (PR)	1 (PR)
4				1	(PR)	1 (PR)	0.95 (PR)
5					1	(PR)	0.95 (PR)
6							0.95 (PR)
7							

where IND – insignificant coefficient of rank correlation (independent results of benchmarkingmethods); NR – significant coefficient (negative ordinal relation); PR – significant coefficient (positive ordinal relation) R_(S,0.,95) (5)=0.9
Source: own

To obtain reliable results, it is crucial to choose the benchmarking criteria conveniently along with the different evaluation methods. It is the financial health of a company and its status among the competition that are valuable pieces of information for managers. Financial indicators are popular benchmarks, which is also supported by a relatively good availability of primary data. Financial health of a company may also be evaluated by means of the so-called solvency and bankruptcy models. Altman and Eisenbeis (1978) established the final Z-score model which considered, inter alia, new standards of financial reporting. This final model is called Zeta analysis. Before 1980 Multiple Discriminant Analysis (MDA) prevailed in use in the majority of studies dealing with bankruptcy models of companies, and MDA has become a recognised standard method (Vochozka, 2010). In the Czech Republic, the most commonly applied methods are Altman's model, Taffler's index, Grünwald Solvency Model, etc. (Vochozka, 2010). Another question is whether solvency and bankruptcy models may fully substitute benchmarking carried out on the backgrounds of financial analysis indicators.

As the available literature does not provide satisfactory answers to the questions stated above, we claim that it is desirable to continue in the attempts to specify benchmarks and related evaluation methods. Our efforts aim to make the evaluation process easier for decision makers and accelerate the different phases of benchmarking evaluation. Referring back to the financial indicators, we may quote Benjamin Franklin and his famous quote that time is money.

In order to answer the questions above, we need to benchmark. As we specialise in economics in the mining industry, we selected mining companies for the benchmarking, namely five selected mining companies exploiting gravel-sand in the Czech Republic, CEMEX Sand, k.s., Českomoravský štěrk, a.s., LB MINERALS, s.r.o., CEMEX Cement, s.r.o., and ZEPIKO, spol. s r.o.

To direct the research, we formulated two hypotheses: H1- There are evaluation methods applied in benchmarking that are mutually replaceable. H2 - Some solvency and bankruptcy models render comparable results to the mathematical-statistical methods examined herein in benchmarking evaluation.

The research was carried out by means of a case study of five selected mining companies exploiting gravel-sand in the Czech Republic using mathematical-statistical methods and solvency and bankruptcy models for the evaluation. The major objective was to determine whether the different evaluation methods are mutually interchangeable and whether the selected methods and solvency and bankruptcy models render identical results and conclusions. Because of the high number of different approaches and methodologies applied, this may be useful for the managers in the roles of decision-makers to make the process simpler and more straightforward.

Methods and materials

Bechmarking is not a standardised method, which leads to a variety of definitions, concepts and methodological approaches (Nenadál, 2011). The starting point to answer the hypotheses was the benchmarking process comprising of five stages (planning, analysis, integration, action, and maturity) (Camp, 1995). The first two stages were key for the research and thus the benchmarking process was modified as below – see Figure 1.

We assumed that benchmarking of performance parameters (Nenadál, 2011) would be most suitable for the purpose as it focuses on the comparison of different performance parameters. We selected mining companies with volume mined of over 280,000 m3 of gravel-sand and sand for the benchmarking. Another criterion was the availability of accounting books during the period under observation. As the volumes mined vary in the different years, the reference year was the year 2015. The data on mining are available in the Mining Yearbook 2015 (Hornická ročenka, 2015). Table 1 displays the five mining companies that met the conditions stated above.

We compared the performance of the selected mining companies using benchmarks based on the financial analysis indicators and the so-called solvency and bankruptcy models. We used the following 11 benchmarks: (1) Earnings before Interest, Taxes, Depreciations and Amortization Charges – EBITDA; (2) Return on assets – ROA; (3) Return on sales – ROS; (4) Weight avarage cost of capital – WACC; (5) Quick ratio; (6) Total assets turnover; (7) Net working capital turnover ratio; (8) Interest coverage; (9) Altman's model (Paolone et al., 2015); (10) Index IN05; (11) Taffler's model (Bordeianu et al., 2011).

We realize that it is very difficult to determine the weights of the different benchmarks unambiguously. Therefore, we decided to attribute an identical weight to each used benchmark. The data for the analyses were obtained from the Annual Reports of the selected mining companies between 2010 and 2014 (the Annual Reports are publically available at www.justice.cz).

Tables 2 and 3 below provides the matrix of the input data for the benchmarking process.

Evaluation methods of benchmarking

Despite each benchmarking phase being important for its successful implementation, we may claim that the core of the benchmarking process lies in the analytical phase. This is because via the application of specific methods we obtain the final information not only on the ranking of the compared companies, but also on the differences among the companies in question.

According to Nenadál (2011), for the analysis to render relevant outputs, before own data processing it is vital to structure and classify the obtained data, to quantitatively verify the data, to clean the data from deformations, and finally to normalise the data (Nenadál, 2011).

The analytical phase is characteristic of many methods and tools applied (Nenadál, 2011), (Camp, 1995). With regard to the limits of an academic article, we tested the following five mathematical-statistical methods with the aim to determine whether they are interchangeable: (1) Rank ordering weighting method; (2) Weighted average method; (3) Point allocation method; (4) Standardised variable method; (5) Method of the distance from a fictitious object.

Apart from the mathematical-statistical methods, we also used two multi-criteria decision analysis methods: (1) Weighted sum method; (2) Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) (Kobryń, 2016).

A unifying feature of the first five methods above is the fact that the methods transform and synthesise various indicators into one, the so-called integration indicator. This subsequently expresses the level of the selected set of different companies in a complex manner (Sedláček, 2011; Triantaphyllou, 2000).

With regard to the application of various methods to benchmark companies, the methods may have different informative values when determining the final ranking order. At the same time, different methods work with different benchmarks. Some of these, the so-called "solvency and bankruptcy models" (Altman's model, Index IN05, Taffler's model) are more complex in their structure (they contain more indicators) than the remaining 9 benchmarks. There is a question whether Altman's model, Index IN05, or Taffler's model have an analogous informative value as the examined benchmarking evaluation methods. In case the different examined benchmarking methods have analogous informative capacities based on statistical testing, they may be mutually interchangeable. At the same time, if selected benchmarks (solvency and bankruptcy models) have a similar informative value as the examined benchmarking methods, the selected benchmarks may be applied as evaluation methods on their own.

The final evaluation of the selected mining companies is carried out using the ranking order method (1st rank – the best evaluated company, 5th rank – the worst evaluated company). As the majority of companies achieve different ranks in the course of the evaluated period, the final evaluation of the selected mining companies is made via adding the ranks during the period under observation and by means of ranking according to the coefficient of variation. The ranking indicator based on adding the ranks during the period under observation is arranged in the ascending order (the minimum sum represents the best value – 1st rank; the maximum sum represents the worst value – 5th rank). The indicator of the order according to the coefficient of variation is arranged in the same manner as mentioned previously.

To verify the hypotheses, it is advisable to examine the so-called level of rank correlation, for example, using the Spearman's coefficient of rank correlation coefficient defined as below (Sedláček, 2011; Wilcox et al., 1979):

$$R_s = 1 - \frac{6\sum_{i=1}^{n} d_i^2}{n \cdot \left(n^2 - 1\right)} \tag{1}$$

where: d_i is the difference obtained between the rank gained via the first method, and rank obtained via the second method out of the two methods; n is the extent of the selected set (number of benchmarked companies).

The coefficient gains the values from the interval <-1; +1> and the interpretation of results is the same as in case of the well-known Pearson's coefficients of pairwise correlation (Sedláček, 2011). The level of rank correlation (results) obtained using a benchmarking evaluation method and using selected benchmarks (solvency and bankruptcy models) must be statistically tested. The testing statistics to verify the order independencies of the ordinal quantities may be the above mentioned Spearman's coefficient of rank correlation RS (Budíková et al., 2010). The testing is carried out as below:

On the significance level α we test H0: The results of methods X and Y are order independent random quantities as opposed to:

- bilateral alternative HA: The results of methods X and Y are order-dependent random quantities. The critical region fro the bilateral alternative is $W=[-1\dashv, \vdash R_{S,1-\alpha/2}(n)] U [R_{S,1-\alpha/2} \dashv (n), \vdash 1]$,
- left-handed alternative HA: Between the results of methods X and Y there is an indirect order dependency. The critical region for the left-handed alternative is $W=[-1\dashv, \vdash R_{S,1-\alpha}(n)], \vdash 1]$,
- right-handed alternative HA: Between the results of methods X and Y there is a direct order dependency. The critical region for the right-handed alternative is $=[R_{S,1-\alpha} \dashv (n), \vdash 1]$.
- $R_{S,1-\alpha/2}(n)$ or $R_{S,1-\alpha}(n)$ are critical values that we find in the statistical tables for α=0.05 or 0.01 and n≤30. The hypothesis on the order independency of the results of methods X and Y is thus rejected on the level of significance α, when $R_S \epsilon W$(Budíková at al., 2010).

Results and discussion

The research results are summed up in Tables 4 – 6 that evaluate the different examined companies using the herein defined benchmarking evaluation methods and selected benchmarks (solvency and bankruptcy models) during the period under observation (2010-2014).

Using all the evaluation methods and selected benchmarks, the benchmarking results clearly imply that adding up the ranks for the given period the leader is Českomoravský štěrk, a.s., followed by LB Minerals, s.r.o. The third and forth came CEMEX Cement, s.r.o. and CEMEX Sand, k.s. The fifth was ZEPIKO, spol. s r.o. According to the indicator "Rank based on the sum of ranks throughout the period" we may find 2 groups of benchmarking evaluation methods and selected benchmarks that provide identical results. The first group of methods include Rank ordering weighting method, Standardised variable method, Method of the distance from a fictitious object, Weighted sum method and Altman's model. The second group contains Point allocation method, TOPSIS method and Taffler's model.

As for the "Rank based on the coefficient of variation" we may rank the companies based on the majority of evaluation methods and selected benchmarks as follows: Českomoravský štěrk, a.s., ZEPIKO, spol. s r.o., LB Minerals, s.r.o., CEMEX Sand, k.s. and CEMEX Cement, s.r.o. On the grounds of this indicator there is a group of benchmarking evaluation methods that render identical results. These are Standardised variable method, Method of the distance from a fictitious object, and Weighted sum method.

Nevertheless, the best method to determine the so-called level of rank correlation is Spearman's coefficient of rank correlation. This coefficient was calculated for n=5 observations (5 benchmarked companies). For pairwise correlation of all benchmarking evaluation methods (Table 5) the coefficient value did not fall below 0.7, which shows a high value of rank correlation. In the pairwise comparison of the methods with selected benchmarks (Table 6), the situation is different. When compared with all the benchmarking evaluation methods, Altman's model and Taffler's model reach high values of this coefficient (at least 0.7). When compared with all the benchmarking evaluation methods, Index IN05 reaches only mean values of the Spearman's coefficient of rank correlation (at least 0.45). In pairwise comparison we identified 2 groups of methods that render identical results. The first group includes 4 methods: Rank ordering weighting method, Standardised variable method, Method of the distance from a fictitious object, and Weighted sum method (Table 5). The second group comnprises Point allocation method, and TOPSIS method. In the case of pairwise comparison of selected benchmarks and evaluation methods, we found identical results in Altman's model and the first group of benchmarking evaluation methods as well as between the Taffler's model and the second group of benchmarking evaluation methods (Table 6). This way, both Altman's model and Taffler's model may be considered separate benchmarking evaluation methods.

Based on the carried out test of rank independence of ordinal quantities that was on the significance level α=0.05 (being a common value in the economic and technical practice), we clearly proved a strong ordinal relation among the majority of the benchmarking evaluation methods (Table 4) as well as among the majority of the methods and majority of the selected benchmarks (Table 5).

Considering the obtained results of the first and last mining company, a possible conclusion may be that the company rank corresponds to its extraction volumes. The company Českomoravský štěrk, a. s. had the best results between 2010 and 2014, and it extracted the highest volumes of materials. The last company ZEPIKO, spol. s r.o., based on the benchmarking results, extracted the smallest volumes of gravel-sands among the benchmarked companies. However, this construct does not hold true for LB Minerals, s. r. o., who came second, but would be third as for the extraction volumes. The volumes of extracted materials are an important factor affecting the overall results, but effective and economical utilisation of input factors of production is undoubtedly decisive in success.

Going back to the hypotheses formulated at the beginning, let us first look at the mutual interchangeability of the benchmarking evaluation methods. Our research results prove that 6 out of 7 mathematical-statistical methods show a high level of agreement, which is represented by Spearman's coefficient of rank correlation (Rs □ 0.9). The only exception was the Weighted average method, in which Spearman's coefficient of rank correlation was 0.7.

As we benchmarked only five mining companies we may speak about a positive correlation only in case of a high coefficient value. In the case of a higher set of compared companies, the cricitical region of the tested criterion would expand. If we benchmarked X companies, the coefficient of 0.7 would be acceptable and we could speak of an agreement of the Weighted average method with the remaining tested mathematical-statistical methods used in benchmarking evaluation. The expansion of the set of the benchmarked companies is questionable, though, because of choosing suitable companies. On one hand, if we benchmark more companies, we may accept all the evaluation methods; on the other hand, it may not be sensible to include companies with low volumes of extraction and are thus incomparable as for the observed parameters.

The second hypothesis asked about the applicability of solvency and bankruptcy models. The results imply that 2 out of 3 models, namely Alman's model and Taffler's model, may be used for benchmarking evaluation. However, based on the statistical testing results herein, Index IN05 cannot be applied in benchmarking evaluation on its own. We may, therefore, claim that both the hypotheses were confirmed.

The next piece of knowledge arising from our research is the fact that by pairwise statistical comparison of results when studying the mathematical-statistical methods and solvency and bankruptcy models based on Spearman's coefficient of rank correlation (Table 4 and 5), there is no negative rank relation (NR). It means that it is possible to mutually combine the results of the mathematical-statistical methods and solvency and bankruptcy models.

All the tested models have different internal architectures, and thus we cannot herein identify the causes for the results. It is though clear that it is vital to test other solvency and bankruptcy models, such as Tamari's Index, Kralicek Quick Test, Grünwald Solvency Model, Solvency Index, etc. in the benchmarking evaluation.

Conclusion

The case study studied five selected mining companies exploiting gravel-sand in the Czech Republic using mathematical-statistical methods and solvency and bankruptcy models for the evaluation. It aimed to determine whether selected evaluation methods are mutually interchangeable. Next, it compared these method with solvency and bankruptcy models.

Within the case study we determined two groups of methods, out of which one method may be chosen and mutually combined with a method from the other group, and vice versa. The first group contains the Rank ordering weighting method, Point allocation method, Standardised variable method, Method of the distance from a fictitious object, Weighted sum method and TOPSIS method. The Weighted average method belongs to the second group. The research results also prove that selected benchmarks, Altman's model and Taffler's model, may be used on their own.

There are many different approaches and methodologies company managements may use, and thus the research results are useful for the managers in the roles of decision-makers to make the process simpler and more straightforward. Considering the number of available methods, we plan to continue in the comparison and research in mutual replaceability of benchmarking methods, different benchmarks and models.

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Analiza wybranych metod oceny w celu przetestowania zastępowalności metod matematyczno-statystycznych w benchmarkingu za pomocą modeli wypłacalności i upadłości: studium przypadku dla kopalń piasku i żwiru w Republice Czeskiej

Benchmarking jest użytecznym narzędziem do zarządzania, umożliwiającym identyfikację możliwości poprawy wydajności i skuteczności firmy poprzez zastosowanie testów porównawczych do oceny i porównania wydajności firmy z liderem w tej dziedzinie lub innymi wybranymi firmami. Z tego powodu konieczne jest wybranie punktów odniesienia i metod oceny. Przeprowadzono analizę porównawczą pięciu wybranych przedsiębiorstw wydobywczych eksploatujących złoża żwiru w Republice Czeskiej, CEMEX Sand, k.s., Českomoravský štěrk, a. s., LB MINERALS, s.r.o., CEMEX Cement, s.r.o. i ZEPIKO, spol. s r.o. Artykuł ma na celu przedstawienie zastępowalności metod matematyczno-statystycznych stosowanych w benchmarkingu. Zeryfikowano zgodność wyników dla modeli wypłacalności i upadłości oraz modeli matematyczno-statystycznych. Wykorzystano jedenaście benchmarków (EBITDA, ROA, ROS, WACC, Quick ratio, łączny obrót aktywów, wskaźnik rotacji kapitału obrotowego netto, pokrycie odsetek, model Altmana, indeks IN05 i model Tafflera) oraz siedem metod oceny. Badanie pokazuje, że większość badanych metod benchmarkingu może być wzajemnie zastępowana. Na podstawie wyników określono dwie grupy metod, z których jedna może zostać wybrana i połączona z metodą z drugiej grupy i odwrotnie. Pierwsza grupa zawiera metodę rankowania, metodę alokacji punktów, metodę zmiennej standardowej, metodę odległości od umownego obiektu, metodę sumy ważonej i metodę TOPSIS. Druga grupa zawiera metodę średniej ważonej. Badania dowodzą również, że wybrane testy porównawcze, takie jak model Altmana i model Tafflera, mogą być stosowane samodzielnie.

Słowa kluczowe: benchmarking, metody matematyczno-statystyczne, modele wypłacalności i upadłości, spółki górnicze

How Will the 4th Industrial Revolution Influences the Extraction Industry?

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Abstract

Even the third industrial revolution has never been officially finished, from some time an expression Fourth Industrial revolution got viral. It has started in 2011 with a project of German government, called Industrie 4.0, which was initiated during the Hanover Expo in 2012. In 2013 an official report on that project was issued.

The article explains the term of 4th industrial revolution and tries to foresee influence of that phenomena on extraction industry. The big challenge of digitalization and cybernetic systems implementation carries a large saving potential, estimated to astonishing 321 Bio. USD till 2025 but also risks and challenges to overcome. Discussion in the paper includes the most important technologies with their state of development and existing implementations including autonomous machines in both underground and open pit mining, technology of self-operating drilling rigs and driverless trucks in open pits.

Briefly description of current situation and a picture of the mining industry after extended automatization is presented. It touches also the challenges of the new industry concept and highlights a road map for the full digital mine.

Introduction

The question about the future is probably one of the oldest the humanity ever asked. People were using various methods to get closer to the mysterious knowledge of the future facts. At the very beginning those questions were rather personal, like "When I will find a husband/wife?" or related to a significant upcoming event of their tribe or nation, like "Will we win the war?". With the development of technology, especially during the second industrial revolution, people started to ask more general questions related also to the technological development in near and far future. That's how science fiction was born. Authors, like Julius Verne started to extrapolate the current development into the future, predicting next inventions or steps in technological journey. Of course, they could not predict facts, like the Hindenburg disaster or I and II World War which kind of derailed the future of the world.

Science fiction is still very popular, as well as fortunetellers, however none of them can accurately predict the future. But we live again in the times of the revolution and the desire to try is too big to resist. Let's think than which influence may the fourth industrial revolution have on the extraction industry.

Industrial revolutions

It is not the first time when the planet experiences the industrial revolution. The first happened in the second half of XVIII, related mostly to mass application of steam and waterpower in the textile industry. Later, growth of steel industry reised demand on iron and coal, causing rapid development of mining industry. As a result, former rural communities changed were urbanized and industrialized alternating life of millions of people. Mining industry was an important part of that changes, generating new workplaces and delivering raw materials, but also using the leverage of new technologies for own growth.

The second Industrial revolution started in 1870 and last till the beginning of the first World War (1914). It was the time of rapid development of mass production, electricity and crude oil extraction and processing. The revolution cut the dominance of steam engines in introducing much more efficient and less cumbersome diesel and electric engines.

Next, third revolution has started in 1980, when computers become small enough to leave large rooms constructed especially for them and entered our houses, where they stayed till today. Thanks to that, industrial digitization become possible. Beside that major achievement, it opened the door for communication technologies development, with its so far most advanced medium – the internet.

Even the third industrial revolution has never been officially finished, from some time an expression Fourth Industrial revolution got viral. It has started in 2011 with a project of German government, called Industrie 4.0, which was initiated during the Hanover Expo. In 2013 an official report on that project was issued. The project considers 4 elements which defines projects aligned with the idea of Industrie 4.0:

1. Interconnection: With wireless communication technology and the capabilities of the IoT, you can now connect machinery, sensors, and other devices to the people tasked with monitoring your process for effectiveness and efficiency.
2. Information transparency: The transparency afforded by Industry 4.0 technology provides operators with vast amounts of useful information needed to make appropriate decisions. Interconnectivity allows operators to collect immense amounts of data and information from all points in the manufacturing process, thus aiding functionality and identifying key areas that can benefit from innovation and improvement.
3. Decentralized decisions: Interconnection and information transparency allow for operators to make decisions both inside and outside of production facilities. This ability to combine local and global information at the same time helps to drive better decision-making and increase overall productivity.

Fig. 1. Drone model of Rzepka Quarry, rehabilitated in a recreational area, mapped using DJI Phantom 4 on 30.09.2018. Field work of approximately 5 minutes and 1 hour of data processing

Rys. 1. Model stworzony za pomocą drona, dla kamieniołomu Rzepka, zrekultywowanego w kierunku rekreacyjnym, zmapowany za pomocą drona DJI Phantom 4 w dniu 30.09.2018. Czaslotuokoło 5 minut, czas obróbki danych około 1 godziny

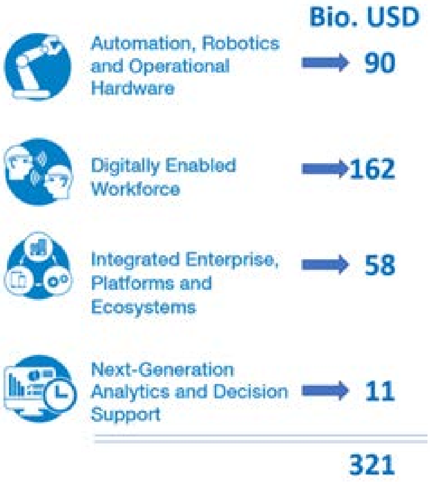

Fig. 2 Benefits of 4th Industrial Revolution according to [7]

Rys. 2. Korzyści z wprowadzenia rozwiązań 4-ej rewolucji przemysłowej wg. [7]

4. Technical assistance: Industry 4.0 shifts the role of humans from an operator of machines to a problem solver and decision maker. Assistance systems are designed to support operators that need to make informed decisions to solve urgent problems on short notice [2]

The above can be summarized by the key words so popular nowadays: Big Data (processing and large data analytics, also Data Mining), IoT (Internet of Things) and AI (Artificial intelligence) including machine learning. Supporting technologies are Virtual and Augmented Reality, which are essential for some applications, but on the other hand stay apart as they are mostly dedicated to people not machines. Machines does not need any visualization.

The term itself, 4th Industrial revolution has been used first during World Economic Forum in Davos in 2016. So, we are just at the very beginning of that journey, which shell change a lot also in the extraction industry. From that moment it caught the attention of all big consulting companies and become priority of all major equipment producers, data safety companies, and even other countries.

How possible is the digitalization of the extraction industry?

Digitalization per se is a part of 3rd Industrial revolution and is happening now and for a longer time. It is without any doubt a first step towards cybernetic systems application. Except from large international corporations, large part of the extraction overslept implementation of modern technologies. Especially in small quarries and pits job is done in the best case like it was 20 or even 40 years ago. Partially we may blame stiff regulations which impose certain solutions and are not open for moderner alternatives, but mostly it is due to people who in that branch are very conservative. As it is said, the good is an enemy of the better. Well, why to change something which works, and proved its reliability?

There is at least one reason. Being stubborn to ignore changing world, one may wake up once in an environment which is not understandable and almost hostile. That happens nowadays to elderly people who are pushed out of the new digital society and suffer trying to live like before. For the companies it is simply a way to become not competitive enough to keep the market share and find itself on the descending ramp. Being a rather basic industry, mining is not in a situation of for example Blockbuster. This large chain of DVD selling and renting stores, was once the market leader in the US. Somehow, they did not see the upcoming change and didn't react on time. Development of streaming technologies and internet as such, lead them to the bankruptcy. Now their place is filed by Netflix, Amazon or other internet streaming companies. Blockbuster become known only as an example of a company which failed to keep up with the changing world.

Is it a danger for Rio Tinto or KGHM? No, it's not, if there is no alternative for copper or other metals mined by them, but they are in danger to fail in keeping up with their competitors. Those companies as well as many others producing metals, rear earth and industrial minerals may gain a lot on the new industrial revolution, as a supplier of basic raw materials without which, the revolution would not happen.

One of the first thing which has happen when personal computers appeared was the development of modeling and designing packages which allowed using properly the geological data. Software like Surpac, Vulcan, Maptec, or most recently Deswik, open opportunity to store, visualize and use data for deposit modeling. That was the first step for applied usage of created models for the deposit evaluation and production planning and scheduling. Algorithms like Lerchs-Grossmann (LG) become mandatory standards for stock mining companies, to avoid frauds and misinterpretations. Recently, thanks to 64 bits functionality and growing performance of computers, a new method arises -Direct Block Scheduling (DBS). Having its roots in 1960's the method could not get through due to technical restrictions. Nowadays it has a potential to take over the role of LG.

Already from 2006 most of the OEM (Original Equipment Manufacturers) install telematic systems on their machines. The origin of that solution lays in the desire to acquire operational data for better storage and maintenance planning. With the time those systems evolved into more operations focused. Simultaneously the market complimented some solutions like CAT ProductionLink, Komtrack of Komatsu or Caretrack of Volvo with independent solutions, universal for all the machines, like Polish TMS MES which has a large market share among quarries in Poland. The main task of all above listed systems is to gather vital production data as a decision base for mobile fleet management. As a back site, the full utilization of the system capabilities requires a person who is almost fully dedicated to that task. Many smaller quarries cannot handle that, thus focuses only on the most important part. In many countries it is simply diesel consumption and thief avoidance. In the best-case idle time is also followed.

Recently a new technology appeared got warmly welcome in the industry. Drones are used more and more often, but mainly for topographical situation update. They can save time and money, but like in case of telematic system, deliver more information than the mine operators can process.

Those examples show, that digitalization simply happens. There are well developed, robust, commercial solutions which are in the reach of once hand. The only thing to do is to reach for it and establish a system which will take an advantage of acquired digital data. And it is not an easy task, at least not for humans…

The mine of the future

Before we get to the technical part, let's set an important benchmark. The one sure thing is, that the mine of the future will be green. Of course, not in the meaning of the color, but its impact on the environment. One may say it is a truism but lookat the following examples.

Jura Cement operates a small very compact and extremely clean plant in Wildegg, Switzerland. The limestone quarry delivering materials for cement production is located close to the plant and extremely well design and operated. Like in any case Jura needs to renew their mining lease which among others is a subject of extensive community consultations. And here is the problem. Having already the governmental clearance, the plant cannot agree with the local community which is opposing blasting as an extraction method. It does not matter that they do the blasting better than required, being below vibrations and airblast limits. Alternatives? There are a few but none of them will be as economically efficient as explosives [10].

In 2010's Holcim demolished an old cement plant in Miskolc, Hungary, planning to replace it with a new, modern one with marginal environmental impact. Mining strategy was prepared accordingly. At the end, the extensive community protests and never-ending negotiations pushed the company to abandon the investment. Simultaneously Hungary suffered a deficit of cement and needed to import it from Slovakia and Romania.

The last example is from the Netherlands. This country with 26% of land below the sea level is almost without any mineral resources but sand and gravel. Those commodities are extracted from below water level, creating water reservoirs which are anyway common in the landscape of the country. It should not be a problem to get a license though. The company Royal Smals, one of the biggest sands and gravel producers in the area waited 25 years to get a clearance for a new extraction area… Negotiations included extensive environmental impact assessments, community consultations and even resettlement of a beaver family which costed some million Euro.

This happens now and won't be any better in the future. Thus, if the new operation is not in the middle of nowhere, like Kamchatka in Russia or Australian Interior, it will need to be environmentally friendly, or will not exist.

Economic impact of the 4th revolution

In 2017 the consulting company Accenture published the report prepared for World Economic Forum (WEF) [7] stating that mining and metal industry globally can save till 2025 almost 321Bio. USD , out of which 189 Bio. USD the mining separately. It is equal to 2-3% of annual revenue .

Moreover, the report states, that thanks to digital solutions 1 000 fatalities and over 44 000 injuries can be avoided. Next to heavy social and private impact of that events, each fatality or lost time injury is a subject of high cost related to legal, compensation, medical and other expenses. According to [3] average cost of a fatality in US amounts to no less than 2.5 Mill. USD and non-fatal injuries around 50 000 USD. Assuming the above values and earlier stated number of accidents, it gives an additional value of 4.7 billion USD in next 10 years![6]

The report of Accenture divides sources of savings into four groups, let's check which technology in every group have the potential of the highest impact.

Automation and Robotic

Automation and robotic has a potential of 90Bio. USD savings in the global scale. The key technology in that group is autonomous vehicles and machines. Two group of machines has the larger potential for automation: drilling rigs and loading and hauling machines. Both on surface and underground there are thousands of loaders, excavators and dumpers hauling extracted material every day. This work, especially in underground mines is one of the most dangerous, and a subject of many injuries. Out of 12 fatalities in US surface mining, according to MSHA 6 were related to haulage. Similar values are reported in Australian mining (42% vehicle collisions, according to [1]). In case of autonomous machines, not only those fatalities could not happen, but most likely many of accidents would not have a place. It is due to the nature of autonomous vehicles, which are equipped in multiple sensors and able to handle information coming from all of them in a fraction of a second. Those technology is already tested by many automotive companies, just to mention Volvo and Tesla in a normal street traffic, much more demanding environment than isolated roads of open pit or corridors of underground mining. Thus, that technology is already used from many years in underground mines and enters in open pits as well.

First report on autonomous underground loaders are dated on 2004, so are more than a decade old! Underground mines are favorable environment for autonomous machines, as a large part of their cruise happens on a fixed and not changing tunnels. It gives an opportunity to place reflectors or other localization supporting devices on the fixed areas and limit number of sensors on the machine itself. Beside rare events of inspections or natural phenomenon's, almost nothing disturbs their travel. Additionally, it increases the safety!

Open pits are here slightly behind, due to more complex environment, but slowly catching up. Rio Tinto uses 80 autonomous Komatsu dumpers, in their Australian operations. Those trucks, which are 20% of their fleet delivered 25% of production showing 15% lower costs than maned ones [8]. That convinced Rio Tinto to double their autonomous fleet till the end of 2019.

Another interesting project has been recently undertaken by Volvo. The project called Free from emission quarry, considers not only autonomous dump trucks but also electric or hybrid powered machines. The project is in the early stage (started in August 2018) but considers at least 25% operational cost reduction. Beside emission reduction, the important part of the project is to prove, that autonomous concept make sense also in case of smaller operations [4]. Since then, the press releases on autonomous mining and construction equipment pops-up every month (eg. [9])

If we take an average quarry production limestone for cement production, with an average cost of 2 USD/t and production of 1.5 Mio. t (the Author has reliable data about that sector of extraction industry), it would result in 750 thousand USD per year, which scaling up to a multinational concern with 100 operations worldwide gives astonishing 750 Mio. USD!

Drilling in underground is more complex, but open pits mastered already also this activity. BHP Billiton and Rio Tinto use autonomous drill rigs since 2014 and basing on the experience decided that it is the way to go. O-Pitblast the modern blast design platform has capability to export designs into Hole Management System (HMS) of Epirock drill rigs. The system is available also on the small, quarry rigs. The machine equipped with the HMS system gets the design from O-Pitblast and can position itself over a future blasthole. It is not autonomous yet, but already close.

There is also one more economic aspect of autonomous or remote operations. Many big mines located either underground or in the remoted areas must transport and encourage employees to accept this demanding lifestyle. Working on the base of fly in, fly out (FIFO) is difficult, usually very few accepts in a long run. Cost related are not only higher salaries but also cost of camp and transport, often imposing private planes, airports and all the related infrastructure. If the mine won't be fully autonomous, a part of that cost needs to be paid, but there is a large optimization area.

Touching the topic of fully autonomic mine, Syama gold mine in Mali, which is being constructed by Australian Resolute Mining will be the first fully autonomous underground mine. Secluded location in unstable politically country encouraged the company to use recent technological novelty. The main should be fully operational till the end of the year! [11]

Digital enable workforce

With 162Bio. USD saving potential digital enabled workforce is the most promising out of 4 sectors. In the other words we can talk about the connected worker, an employee who all the time has access to work relevant data, like production, safety, environment and many more.

Imagine that there is no need to train the new employee, who during his task gets online support from augmented reality-based platform. Using a googles or another device, platform recognizes machine and task to be done and guides the employee in each task.

From the safety point of view, it is be possible to localize every employee. It would avoid traffic accidents, as connected machine could see the employee, as well as help to control access to areas of a plant. Preheater tower is an area of a cement plant, which is especially dangerous. It contains preheaters, high temperature gases installation and supports flow of tones of hot raw materials. Entering there is restricted and limited to the employees who have special training and authorization. Simply beacon based system may warn, once somebody enters the area without permission, as well as warn the employee that he is trespassing border of a dangerous zone.

But why at all go into a dangerous zone or perform a dangerous task if a machine can do it instead? The problem is, that not always autonomous machine would be able to do it alone. Here come the remote-control capabilities. Again, it is a technology already used in many operations, especially underground. LHD's and Jumbos are already for years operated remotely. The operator located on the surface has a direct control over machine which is underground. Beside obvious safety related benefits, it influences also an effective working time of

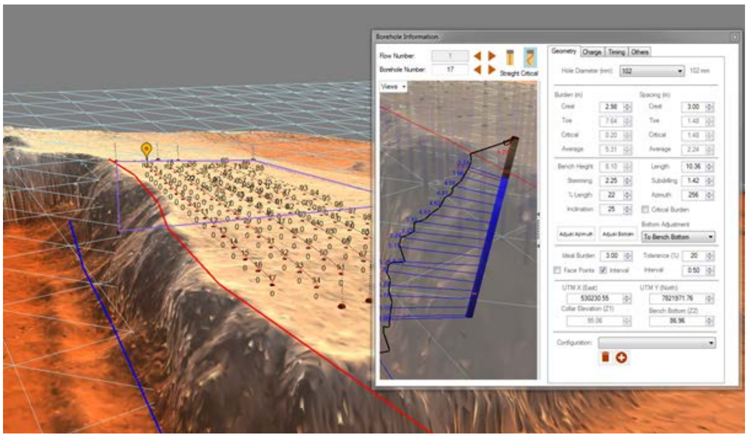

Fig. 3. Blast design using O-Pitblast, model created following [4]

Rys. 3. Projekt robót strzałowych z zastosowaniem O-Pitblast

Fig. 4.AugmentedQuarry – project of Kawalec Consulting GmbH

Rys. 4. AugmentedQuarry – project autorski Kawalec Consulting GmbH

the machine and the operator, who does not need to get underground. Recently there are investigations on remote or autonomous solutions for long walls and other coal mining systems.

Remote control would be also a solution to attract more people to work in mines in the future. Youngsters prefer to do other jobs, which are not really exposed to harsh weather conditions or dangerous confine space of underground mines. Additionally, it gives a potential for gamification – the operator may have an option to gain batches and is informed about his achievements, like in a computer game. Looking at popularity of different simulation games it shells significantly change the perception of the mining jobs, but also have a direct influence on the working performance. Many operators nowadays are just train to do a job safely and without damaging the machine, while work performance is far behind. Gamification would foster continuous development without expensive trainings.

The last to mention is the author's project related to Virtual and Augmented reality for quarry planning and operation support. It is partially connected with decision support platforms, but still more in connected employee. The project is on an early stage, with a major idea to create VR and AR platform which eventually will replace paper maps in normal quarry operations.

Integrated enterprises, platforms and ecosystems

This block of actions with the value over 58 Bio. USD is mostly about connecting and improving business processes and technological operations. Taking as an example an open pit mine, in case of overload on the crushing system, the connected trucks can be either sand on standby, or reassigned to transport overburden. The system would also have capacity to learn and adjust number of vehicles to optimize crusher throughput considering the distance to the crusher, road conditions or even weather or time of the day. With the scope to be as close to the nominal output or the best demonstrated practice, system would shuffle reevaluating options and strategies.

Another possibility is to shorten the distance between the producer and a final client. Using internet purchasing platforms big foundries and steal plants would be able to cut some middle levels of the supply chain, which would be beneficial for both sides.

Similar solution is used already by the OEMs like CAT or Komatsu, which use their telematic systems to predict possible breakdowns and supply spear parts on time, avoiding unnecessary stocks at the client, but also in the regional distributor.

The area covered by that block is wide, starting from internal processes optimization to Social Media application for company image improvement.

Special place is reserved for cybersecurity solution, which do not cut costs, but help to avoid loses related to cyberattacks and other kinds of cybercrime.

Next generation analytics and decision support

Already now each mining operation or any other industrial object collect vast amount of data, which very often are not properly analyzed and rarely used for process optimization. It is mostly due to the large amount of data which are collected. To make a proper decision we need to analyze the right data in the right time, which is hard being overflooded with the data waterfall. It requires extensive data analytic capabilities and won't be done without a person or a team dedicated to do that. A solution would be to delegate that task to AI which unlike people can work 24/7 and analyze more data per second than even the best trained human brain.

Following that idea, simple or routine decisions can be done without human intervention and validated through so popular recently block chain.

On the other hand, visualization capabilities for both data and spatial information would efficiently support any interdisciplinary discussions and decision-making process.

Challenges and risks

Many of the above was about autonomous, automated, faster and easier processes. The first risk which is coming to once mind is no doubt related to the workforce which will face the danger of being unemployed. According to Accenture report, estimates the number of so-called displaced jobs to approximately 313 thousand. Among those are mostly the most risky and dangerous jobs, which requires the lowest skills and education.

Simultaneously the demand for data scientists, programmers, analytics, engineers and other highly educated specialists will rise drastically. Paradoxically the demand may rise faster than their training which will create lack of workforce as oppose to unemployment generated by jobs displacement.

Here the solutions described above may help as well. To reeducate a low skilled employee, it's possible to use augmented reality and gamification.

Another great risk is the safety of data transfer and protection of connected production lines against terrorism, sabotage or any other kinds of hacker attacks. Up to date it has been frequently done by creating an internal isolated network, which in the era of 4th revolutions does not look like a feasible solution anymore.

Talking about the safety it is also necessary to find a way to control the AI itself. The scenarios from movies like Terminator or Matrix looks very unlikely, but the rapidly developing new technology must not get out of control…

On the other hand, a great challenge lays in front of all the regulatory bodies and controlling institutions, as well as governments of countries, which will need to create a legislative environment capable to handle the new challenges.

Conclusions

Several interesting and ready to implements technologies is just waiting to be wider implemented. The ball is on mineral industry side and waits for initiative. Like in case of all other innovations, ore mining takes the lead but with high probability, others will follow soon.

The road to full digitalization contains two phases:

1. Preparation
   a. Digitization
   b. Data gathering (IoT)
2. Digitalization per se where advanced AI will start to take some decisions without human influence.

Change is inevitable, it happens all the time and cannot be ignored. It fosters an idea of continuous development. In our times, nobody can just simply finish education graduating college or university. It is a process which last through our entire life. Using the quote of marvelous American author:

"you got to figure out which end of the needle you're going to be, the one that's fastened to the thread or the end that pierces the cloth."

— Sue Monk Kidd, The Invention of Wings

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Jaki wpływ na przemysł wydobywczy będzie miała 4-ta rewolucja przemysłowa?

Mimo że trzecia rewolucja przemysłowa nigdy tak naprawdę oficjalnie się nie skończyła, od jakiegoś czasu określenie Czwarta Rewolucja Przemysłowa jest na ustach specjalistów branży technologicznej. Początków tejże upatruje się w projekcie rządu republiki Federalnej Niemiec, nazwanego Industrie 4.0, zainicjowanego podczas Hanower Expo w 2012 roku. W roku 2013 opublikowano oficjalny raport na temat ww. projektu.

Artykuł wyjaśnia pojęcie 4-tej rewolucji przemysłowej i podejmuje próbę przewidzenia wpływu tego fenomenu na przemysł wydobywczy. Olbrzymie wyzwanie jakim jest cyfryzacja i wprowadzenie systemów cybernetycznych do górnictwa niesie ze sobą ogromny potencjał ograniczenia kosztów, który ocenia się na 321 miliardów USD do roku 2025, ale także liczne wyzwania. Artykuł przedstawia najważniejsze technologie oraz ich stan rozwoju i istniejące już wdrożenia, uwzględniając maszyny autonomiczne w kopalniach podziemnych i odkrywkach, samosterujące maszyny wiertnicze czy pozbawione kierowcy samochody technologiczne w górnictwie odkrywkowym.

Prezentowany jest krótki opis bieżącej sytuacji oraz obraz górnictwa po wprowadzeniu pełnej automatyzacji. Poruszone są również zagadnienia związane z wyzwaniami związanymi z nowym konceptem przemysłu oraz nakreślona zostaje mapa drogowa dojścia do w pełni zautomatyzowanej kopalni.

The Use of Predictive Maintenance in the Production Processes

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Abstract

Failures are a problem for every company that causes the plant to stop working and thus incur losses. It is therefore obvious that companies want to eliminate unplanned downtime in the production process. In the wake of the still increasing demands in terms of productivity and safety requirements, cost reduction, the industry is forced to seek the optimum between economic requirements and an acceptable level of risk in terms of security. Modern factories equipped with computerized processes and extensive diagnostic tools often do not use all the information that is collected from the hardware level. It happens that some of the relationships between events are often overlooked or neglected.

The article presents an approach to increasing machine reliability through predictive data analysis. The assumptions of the predictive and preventive maintenance methods are presented. The threats and possibilities offered by this methodology implemented in the production process are presented.

Keywords: prediction, predictive maintenance, preventive maintenance

Introduction

Until the 40s of the twentieth century, the approach to the failure was based on the reactive approach, or principle: “broke down, so we fix.” The approach began to change during World War II, when the reliability of more and more complicated technical devices often decided about life or death. Smoothly began to undergo planned repairs, inspections and parts replacement. However, this solution also had some drawbacks. Among other things, it brought a high cost of maintenance, as the part that was in very good condition was often replaced. In particular, the aviation industry, as well as today, in the 1960s, analyzed the costs of maintaining the fleet of aircraft. With the arrival of the Boeing 747 with advanced technology, the Reliability Centered Maintenance (RCM) (Rausand 1998) method was developed, based largely on a predictive approach analyzing the condition of machines (called Condition Based Maintenance). Due to the rapid development of electronics, it became possible to more and more accurately analyze the parameters of machines and devices. On the other hand, the increasing share of electronics in machines caused that in addition to the traditional “bathtub” distribution of damage, several new ones appeared. Currently, the industry standard is vibroacoustic measurements, oil analyzes, and thermographic measurements of machines, electrical cabinets and substations. Various types of real-time measurements are also becoming more and more widely disseminated. Also thanks to the advances in technology, the sensor market has expanded its offer by testing many physical quantities, and at the same time the cost of a single sensor has dropped several dozen times (Piesik 2015). All this meant that modern production lines are equipped with hundreds and sometimes thousands of sensors that collect data on an ongoing basis and monitor the state and course of the production process.

It should be noted that research into the production process was carried out already in the second half of the nineteenth century, when the American engineer F.W. Taylor was the first to face the problem of production processes. He proposed the use of methods and techniques helpful in solving the problems of preparation and implementation of production by preparing the production process itself, eliminating unnecessary activities in the production process and establishing work standards. Further interest in the scientific sphere of production contributed to the foundations of the organization of production and the merit of the methods developed is attributed to: - L. and F. Gilbreth - methods of measuring working time, - H.L. Gantt - methods of planning and control of the production process, - H. Emerson - formulation of twelve principles of performance. This article, however, addresses the issue of failure in the production process and is devoted to the predictive approach to the analysis of the process in order to maintain its failure-free operation.

The concept of predictive maintenance and preventive maintenance

Prediction is rational, scientific anticipation of future events such as states of machines or industrial processes. It is a choice, within a given system, of the most likely way of changing the states of objects in the coming period, where the basis for this choice is the current course of this phenomenon and the current state of the system. Its aim is to reduce the risk in the decision-making process.

We base our prediction on the regularities that characterize the projected phenomenon or occur between it and other phenomena. Such existence of regularities, which are the result of mutual connections between various phenomena, is the ontological basis of forecasting, and their knowledge is the gnoseological basis. These can be regularities in the development of the forecasted phenomenon or causal relationships, similarities in development, symptomatic relationships between the predicted phenomenon and other phenomena.

Therefore, we can predict that:

- the event will occur because it occurred in the past,
- the event will occur because it is indicated by the frequency of its occurrence,
- the event will occur because it is strongly related to another event that occurred (Dittman 2016).

Among the many solutions recently, two approaches dominate - methods of machine maintenance: dependent on the state of the machine predictive maintenance/predictive testing and inspection (PdM/PTI) and proactive reliability centered maintenance (RCM). The basic assumption of predictive maintenance is to undertake preventive actions in the phase of deterioration of machine or process parameters, in order to prevent dangerous failures and associated downtime.

Predictive maintenance tools include: performance monitoring, non-invasive testing techniques and visual inspection. Within the scope of available methods, it is possible to use pattern recognition, trend analysis and correlation, statistical data analysis, and monitoring of alarm thresholds.

Implementation of online monitoring in relation to all machines is pointless (despite a marked improvement in safety and quality of work), and also results in a significant increase in investment outlays. In the case of the predictive maintenance method, it is important to conduct a criticality analysis, leading to the isolation of three groups of machines: critical, relevant and general application.

The classification can be made in terms of different criteria (Table 1) and depends to a large extent on the decisions of the maintenance services, diagnostics and management of the specific plant. Despite the strictly defined criteria, the assignment can lead to different results.

Critical equipment and machines whose failure affects the security of the industrial plant - machines important in the production process, failure of which results in a significant reduction in productivity,

- power units that cannot be duplicated or have high power output,

- machines with a high cost of purchase, maintenance and long-term renovation or repair,

- machines whose damage is caused by slight disturbances in the work process,

- machines for improving efficiency or improving the quality of production.

Essential equipment and machines whose failure may cause disturbance of the plant's safety and a significant reduction in the efficiency of the department or part of the production process:

- machines in which redundant units may or may not exist,

- the ability to start (after repair), which can affect the parameters of the production process,

- high power drive units and revolutions operating in an intermittent cycle,

- machines using a time-based exploitation model,

- machines with average cost and repair time,

- machines whose damage occurs as a result of progressive time (no sudden failures).

Equipment and general purpose machines whose failure does not affect the safety of the industrial plant - devices or machines not classified for a critical collection,

- duplicated or on-demand machines,

- machines with a low cost and short repair time (the risk of a subsequent failure after repair determined as minimal).

Prediction in technical systems makes sense if a favorable benefit-to-investment ratio is achieved. With reference to the presented classification and separate groups of machines:

- critical - online monitoring of parameters affecting the loss of quality and safety is required,
- significant - periodic measurements with trend analysis are recommended,
- general use - it is possible to implement periodic measurements, however, in many cases, it is sufficient to adopt a preventive method of operation (with scheduling repairs).

Predictive maitenance is one of the maintenance strategies based on the optimal use of machines. It is based on predicting the states of objects in the future and taking appropriate corrective, conservation and preventive actions in a timely manner. It is possible thanks to continuous monitoring of their technical condition and constant monitoring of the desired parameters.

Prediction allows to determine future states of objects thanks to continuous measurement (also in real time), analysis of current and historical states and estimation of future values. As a result, it is possible to optimally plan maintenance, overhaul, replacement and other work that minimizes the number of failures and allows you to achieve longer periods between failures. By taking action at the best of times, this method turns out to be more effective in preventing and removing failures than the preventive maintenance method (Levitt 2003).

The predictive maintenance strategy uses the CBM approach, that is, the exploitation of machines based on the technical condition. It is usually carried out on machinery and objects belonging to the high criticality group, because its use is demanding and for devices characterized by low production criticality would be unprofitable.

The effectiveness of the predictive maintenance model is closely dependent on the knowledge required at the stages (Birolini 2017):

1) planning the physical structure of the model - machine classification, selection of method for obtaining process data, identification of key parameters and determining the effectiveness of the tools used (including approximate payback period, cost of using tools, employee training, etc.),

2) implementation - proper configuration of the system with the condition of obtaining resistance to interference, determination of the diagnostic path and period of measurements,

3) use - knowledge and experience to determine the approximate time to failure and inference about possible causes, locations and the extent of failure or damage.

The advantages of implementing the predictive maintenance method include:

- reduction of failure costs and minimization of total downtime,

Tab. 1. Criteria for the division of machines enabling the identification of the measurement method and the variant of the implemented method of operation

Tab. 1. Kryteria podziału maszyn umożliwiające identyfikację sposobu pomiaru oraz odmiany wdrożonej metody eksploatacji

Machinery	Classification criteria
Critical equipment and machines whose failure affects the security of the industrial plant	- machines important in the production process, failure of which results in a significant reduction in productivity, - power units that cannot be duplicated or have high power output, - machines with a high cost of purchase, maintenance and long-term renovation or repair, - machines whose damage is caused by slight disturbances in the work process, - machines for improving efficiency or improving the quality of production.
Essential equipment and machines whose failure may cause disturbance of the plant's safety and a significant reduction in the efficiency of the department or part of the production process	- machines in which redundant units may or may not exist, - the ability to start (after repair), which can affect the parameters of the production process, - high power drive units and revolutions operating in an intermittent cycle, - machines using a time-based exploitation model, - machines with average cost and repair time, - machines whose damage occurs as a result of progressive time (no sudden failures).
Equipment and general purpose machines whose failure does not affect the safety of the industrial plant	- devices or machines not classified for a critical collection, - duplicated or on-demand machines, - machines with a low cost and short repair time (the risk of a subsequent failure after repair determined as minimal).

- the possibility of observation of current machine operation parameters and analysis of their condition,
- improvement of work safety and increase of production quality,
- no need to use complicated statistical models of machine reliability, in favor of the use of known diagnostic methods (based on standards) or relations between diagnostic signals,
- reducing the impact and elimination of secondary damage (i.e. resulting from the harmful effect of vibrations, elevated temperatures, enlargement of the looseness of damaged elements), which directly affects the extension of the machine's operating time,
- reducing the time needed for repair (registering a drop in the quality of work below the acceptable threshold, with the simultaneous location of the damage, allows you to order parts and prepare tools for the repair), developing procedures or actions to prevent further deterioration (including automatic safety devices).

An obstacle in the implementation of predictive maintenance is the costs associated with the need to use an advanced monitoring system, purchase of analyzers and continuous improvement of staff qualifications.

As determinants of the correct implementation of predictive maintenance, generally accepted indicators can be used, in the form of:

- OEE (Overall Equipment Efectiveness) Total Equipment Efficiency - implementation of predictive maintenance should cause a clear increase in the rate,
- MTBF (Mean Time Between Failure) Mean Time Failure-Free - increase the ratio while reducing the Mean Time To Repair (MTTR) Mean Time of Failure Removal.

In the case of OEE, using predictive maintenance techniques, it is possible to limit the loss of availability (failure and regulation), increase the use (stop times) and quality (gains, scrap, need for corrections). Other components of losses (conversion, idle time, start-up and machine shutdown) are included in the domain of management methods and adopted technology.

Tools, techniques and indicators of the predictive maintenance exploitation model

The basic tools used in the implementation of predictive maintenance strategies include primarily:

- monitoring performance and its parameters,
- non-interventional tests,
- visual observation,
- automatic state monitoring,
- IT systems supporting maintenance (CMMS systems).

Prediction in maintenance is also strongly related to the already mentioned basic performance indicators, i.e. OEE indicator and MTBF indicator, by means of which equipment performance and availability are measured. For a plant, they have a value that verifies whether the prediction is being carried out correctly (increase in the value of indicators), or whether it is necessary to re-plan/optimize the adopted strategy.

The main danger and distortion of the machine-dependent exploitation model is incorrect understanding of the possibilities hidden in predictive maintenance methods and tools.

Exceeding the set alarm threshold informing e.g. about the bearing's wear and making a decision on its replacement is the most correct procedure. At this point, however, a trap appears. Avoiding it requires checking the period between successive exchanges. It is worth observing groups of similar machines and periods of wear of individual components. Too frequent bearing replacement in one case can be caused by, for example, unbalance or other factors shortening the service life of a bearing node.

Monitoring the variability of parameters allows to define alarm thresholds. After exceeding the defined values, preventive or corrective actions are required.

One of the most popular methods of predictive maintenance is vibration diagnostics, most often used to assess the condition of machine bearings and drives. An important barrier to other methods is the still low level of knowledge and the high cost of implementing specialist tools.

Parameter monitoring is the basic element used to reduce the operating costs of technical systems. For drives:

- electrical - available methods focus on vibration diagnostics, monitoring of electrical parameters, state of brakes and lubricants,
- pneumatic and hydraulic - failure prevention can be carried out by scheduled inspections (replacement of filters, seals, hydraulic fluids), leak detection and the state of the working medium.

In many production plants, there is a disturbed exchange of information between departments and even groups of employees responsible for handling specific machines in one department. The implementation of the predictive maintenance model in such conditions will certainly not bring the expected results.

Diagnostics of machines and production systems must be supported by advanced equipment (not always of a closed structure, i.e. without the possibility of expansion) and the experience of employees.

If the team implementing the model of predictive maintenance is characterized by high knowledge of machines, an attempt can be made to build a diagnostic system based on online monitoring and diagnostic rules defined by maintenance services. The advantage of such a solution is the possibility of using universal tools that can be configured and freely expanded (as needed), according to the current user's requirements. In the development of a system for obtaining process data, attention should be paid to (Nash 2016):

– requirements related to architecture of the considered system of devices and machines:

• centralized - the possibility of using local data visualization in the form of HMI panels and diagnostic procedures stored in the PLC,

• distributed - using SCADA systems, IO modules and industrial networks bus,

– measurement sensors - the choice of process sensors should take into account the nature and type of the measured quantity (temperature, pressure, flow, displacement, presence, etc.), equipment with network interfaces, accuracy, measurement method, the need for calibration and purchase of additional equipment,

– accessibility to measured parameters - point (lights, displays, signaling towers) or decentralized (using industrial networks).

Documentation in the process of building a predictive model

Building a predictive maintenance model is a complex task that includes the need to include information contained in the documentation. The collection of basic elements includes documentation:

- technical and operational - including: specification of technical parameters, drawings (executive and assembly), lists (of normal and special equipment), diagrams (body, kinematic, electric and pneumatic), instructions (use, operation, maintenance and lubrication, health and safety), recommended manufacturer's repair norms, lists (spare and spare parts),
- operation history - including the history of the machine's operation and current records of operating notes of maintenance staff,
- the scope and expected values of monitored variables - sometimes deviating from norms.

A common case in industrial practice is exceeding the permissible thresholds defined by standards (e.g. ISO 10816 and ISO 7919 groups of standards), and yet the machines are not subject to rapid wear. The occurrence of such a state of affairs forces the necessity of a deeper analysis. The source of error is that in many cases the condition of newly installed machines is treated as a reference point for further evaluation. If all requirements (assembly, configuration and operation) are met, you can use the current work parameters of new machines as reference values. Irregularities can appear in every element (improper machine installation, power parameters, loose mechanical connections, inaccuracies etc.). It is therefore important to keep in mind three basic groups of errors related to the stages of construction, assembly and pre-operation.

Implementation of predictive maintenance

The implementation of the predictive maintenance system includes the following steps:

1) identification of needs - defining the current failure rate and the course of work of objects (e.g. on the basis of indicators), the number and range of variability of parameters uniquely identifying the state of the analyzed object,

2) an analysis of the reasonableness of implementation - taking into account the criticality of machines and the assessment of alternative methods projecting directly on the possibility of improving the safety, quality and productivity of production,

3) execution of statements (equipment, procedures, requirements) and determination of implementation costs - the decision stage in which the assumptions may change,

4) implementation - the stage requires defining the course of proceedings allowing the implementation of equipment and equipment, with the simultaneous possibility of a periodic decrease in the quality or performance of machines or entire lines,

5) assessment and correction - control of performance and effects, allowing identification of weak points of applied solutions and their removal.

The implementation of a comprehensive predictive diagnosis program requires close cooperation of maintenance services, managerial staff and machine operators. Many industry experts pay particular attention to the latter, as it is line workers and operators that in practice implement production and diagnostics management procedures at the lowest level of factory structures. In order to improve the operation of the system, it is also recommended to develop procedures for dealing with specific machine failures.

Summary

The implementation of the predictive maintenance model is possible in three mutually complementary variants:

- surveillance of trends - a diagnosis based on the basis of exceeding defined alarm thresholds, which necessitates the need to perform measurements at fixed time intervals and periodic control with non-invasive methods,
- qualitative measurements - a diagnosis based on the operator's knowledge, and the frequency of measurement depends on a visual assessment of the deterioration of the machine's operating parameters,
- quantitative measurements - based on the CM (Condition Monitoring) method, including the registration of online parameters, their archiving and analysis.

The progressive automation of industrial processes and the development of IT technologies are a determinant of the predominance of diagnostic systems operating on common historical databases (offering access to multiple users with different levels of authority). The presented forecasts indicate the importance of an additional criterion, which is the possibility of adapting the existing model of machine maintenance to new requirements and its extension, without the need to replace all diagnostic and monitoring equipment.

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Wykorzystanie predictive maitenance w procesie produkcyjnym

Awarie to problem każdego przedsiębiorstwa powodujący zatrzymanie pracy zakładu a przez to ponoszenie strat. Oczywistym zatem jest, że firmy chcą eliminować nieprzewidziane przestoje w procesie produkcji. W następstwie rosnących wciąż wymagań w zakresie produktywności i wymagań bezpieczeństwa, redukcji kosztów, przemysł zmuszony jest do poszukiwania optimum pomiędzy wymaganiami ekonomicznymi i akceptowalnym poziomem ryzyka w zakresie bezpieczeństwa. Nowoczesne fabryki wyposażone w skomputeryzowane procesy i rozbudowane narzędzia diagnostyczne często nie wykorzystują wszystkich informacji, które są zbierane z poziomu sprzętowego. Zdarza się, że niektóre z relacji pomiędzy zdarzeniami są często pomijane lub zaniedbywane. W artykule przedstawiono podejście do zwiększenia niezawodności maszyn poprzez predykcyjną analizę danych. Zaprezentowano założenia metodyki predictive i preventive maintenance. Przedstawiono zagrożenia i możliwości jakie daje ta metodyka zaimplementowana w procesie produkcyjnym.

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Słowa kluczowe: predykcja, predykcyjne utrzymanie ruchu, prewencyjne utrzymanie ruchu

Wydatki związane z pracami eksploracyjnymi – nakłady inwestycyjne czy koszty operacyjne?

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Abstract

W artykule przedstawiono sposoby ujęcia w rachunkowości wydatków związanych z pracami eksploracyjnymi. Zaprezentowano sposoby ich wyceny oraz wskazano regulacje rachunkowe oparte na MSSF 6, które dotyczą tego rodzaju wydatków. Ich ujęcie finansowe ma wpływ zarówno na zasoby jak również strumienie przychodów i kosztów przedsiębiorstw górniczych. Dla poparcia przedstawionych tez przytoczono badania przeprowadzone na firmach eksploracyjnych w Republice Południowej Afryki, która stanowi jeden z największych rynków firm poszukiwawczych na świecie.

Słowa kluczowe: projekt geologiczno-górniczy, prace eksploracyjne, nakład, koszty

Wstęp

Rachunkowość dla przemysłu wydobywczego były przedmiotem dyskusji w ciągu ostatnich 40 lat (Cortese & Irvine, 2010), jednakże wraz z rozpowszechnieniem się stosowania Międzynarodowych Standardów Rachunkowości (MSR) oraz Międzynarodowych Standardów Sprawozdawczości Finansowej (MSSF), Rada Międzynarodowych Standardów Rachunkowości (ang. International Accounting Standards Board, IASB) stwierdziła, iż działalność wydobywcza jest dziedziną, w której brak jest dostatecznych wytycznych oraz że została ona wykluczona z obszaru zainteresowań najważniejszych standardów. (KMPG, 2009). Odpowiedzią na ten problem było opracowanie MSSF 6. „Poszukiwanie i ocena zasobów mineralnych", określającego praktyki księgowe odnoszące się do nakładów na działalność w zakresie poszukiwania i szacowania złóż surowców mineralnych.

Fazy cyklu życia projektu geologiczno-górniczego

MSSF 6 znajduje jednakże zastosowanie jedynie w odniesieniu do jednej z początkowych faz cyklu życia projektu geologiczno-górniczego, pozostaje zatem pytanie jak wyglądają praktyki księgowe w pozostałych fazach wśród podmiotów gospodarczych prowadzących działalność w sektorze wydobywczym.

W cyklu życia projektu geologiczno-górniczego wyróżnić można następujące fazy: (Kustra, 2013)

- prace przedposzukiwawcze (pre-exploration phase)
- prace poszukiwawcze, szacowanie i dokumentowanie złoża (exploration phase)
- udostępnienie złoża
- eksploatacja (wydobycie) złoża, wzbogacanie surowca
- likwidacja kopalni i rekultywacja terenu pogórniczego.

Spółki eksploracyjne typu junior mines

Dwie pierwsze fazy cyklu życia projektu geologiczno-górniczego są obecnie bardzo często realizowane przez osobne podmioty gospodarcze, specjalizujące się w poszukiwaniu i dokumentowaniu złóż, które jednak nie zajmują się działalnością wydobywczą oraz nie stanowią części koncernów wydobywczych czy też paliwowo-energetycznych. Podmioty te określane są mianem junior mines, lub krócej juniors, podczas gdy spółki prowadzące działalność w zakresie udostępniania złóż oraz wydobycia i wzbogacania surowca, nazywane są senior mines lub też spółkami typu seniors.

Charakterystyczną cechą spółek juniors jako podmiotów gospodarczych jest wysokie ryzyko prowadzenia działalności, wynikające z dużego prawdopodobieństwa niepowodzenia projektu, trudności w uzyskaniu finansowania działalności oraz braku realnych przychodów aż do momentu opracowania studium wykonalności i pojawienia się perspektywy kapitalizacji wyników dotychczasowych prac.

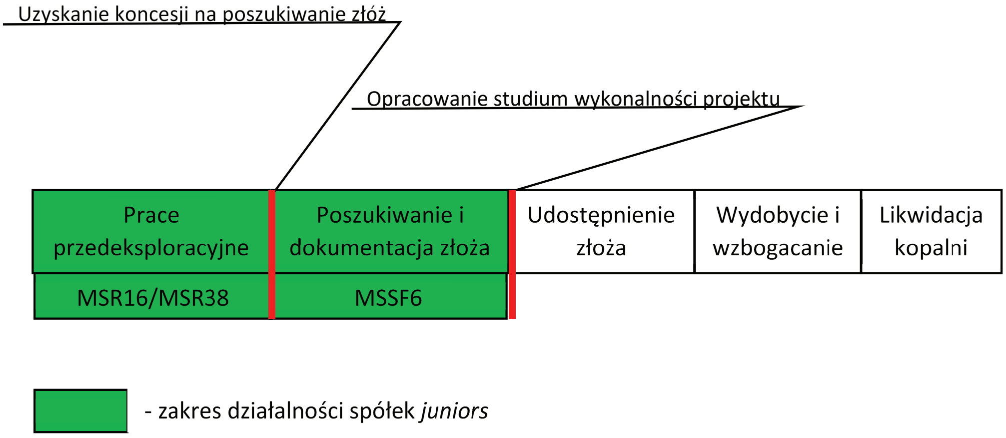
Rozwiązania w zakresie rachunkowości stosowane przez spółki juniors

Specyficzne warunki funkcjonowania spółek juniors wymagają od nich stosowania adekwatnego systemu rachunkowości. MSSF 6. obejmuje swym zakresem jedynie prace poszukiwawcze oraz szacowanie i dokumentowanie złoża, zatem nakłady poniesione przez spółki juniors we wcześniejszej fazie nie są przez niego regulowane. W fazie przedposzukiwawczej/przedeksploracyjnej (pre-exploration phase) zastosowanie znajdują natomiast międzynarodowe standardy rachunkowości – MSR 16 „Rzeczowe aktywa trwałe" oraz MSR 38 „ Wartości niematerialne".

Zakres działalności spółek juniors w cyklu życia projektu geologiczno-górniczego oraz regulacje w obszarze rachunkowości, znajdujące zastosowanie w fazach cyklu życia będących przedmiotem działalności tych spółek, został przedstawiony na rysunku 1.

Nakłady w pierwszej fazie obejmują wszystkie wydatki ponoszone przez podmiot do momentu uzyskania pozwolenia na prowadzenie prac poszukiwawczych (koncesji). Typowe nakłady w tej fazie obejmują: (Cronje, Sturdy, 2014)

- wydatki na akwizycję danych sejsmicznych oraz ich przetworzenie na potrzeby firmy,
- wydatki na badania i analizy geologiczne i geofizyczne oraz pozyskiwanie tego rodzaju danych ze źródeł zewnętrznych oraz opracowanie tych danych,



Tab. 1. Criteria for the division of machines enabling the identification of the measurement method and the variant of the implemented method of operation

Tab. 1. Kryteria podziału maszyn umożliwiające identyfikację sposobu pomiaru oraz odmiany wdrożonej metody eksploatacji

- wydatki związane bezpośrednio z uzyskaniem koncesji (opłaty administracyjne itp.)

Zgodnie z przedstawionym schematem w tej fazie nie ma jeszcze zastosowania MSSF 6. Politykę rachunkowości stosowaną przez podmioty na tym etapie regulują natomiast międzynarodowe standardy MSR 16 oraz MSR 38.

Ramy koncepcyjne definiują aktywa jako zasoby kontrolowane (posiadane) przez podmiot jako efekt przeszłych zdarzeń, z których posiadania przedsiębiorstwo spodziewa się przyszłych korzyści gospodarczych. (IASB, 2010) W odniesieniu do spółek juniors wymóg posiadania spełniony jest na etapie uzyskania przez podmiot koncesji na prowadzenie prac poszukiwawczych. Zwykle jednak nakłady w fazie przed-eksploracyjnej nie mogą zostać przypisane do konkretnego złoża surowców mineralnych, gdyż co do zasady mają one charakter spekulacyjny. (KPMG, 2005) Pomimo, iż możliwy jest wiarygodny pomiar takich kosztów, prawdopodobieństwo przyszłych korzyści gospodarczych może nie być wystarczająco wysokie w momencie poniesienia tych kosztów, by spełniona była definicja aktywów, stąd też wysoce rekomendowane jest traktowanie nakładów na tym etapie jako kosztów, nie zaś aktywów.

Pomimo, że MSR 16 wyklucza klasyfikowanie prac rozpoznawczych i pomiarowych jako aktywów związanych z poszukiwaniem i szacowaniem złóż, ma jednakże zastosowanie do składników rzeczowych aktywów trwałych użytych do wytworzenia tych aktywów. (IASB, 2010) Każdy składnik rzeczowych aktywów trwałych użyty podczas fazy przed-eksploracyjnej może być aktywowany w ramach rzeczowych aktywów trwałych oraz amortyzowany w okresie użytkowania. (PwC, 2012)

Wydatki związane z gromadzeniem, przetwarzaniem i analizą danych sejsmicznych oraz późniejsze analizy geologiczne oraz geofizyczne mogą być uznawane za wartości niematerialne w takim zakresie, w jakim wynika z nich wzrost wartości własnych, zastrzeżonych danych, kontrolowanych/posiadanych przed dany podmiot. (KPMG, 2005; MSR 16, 2008). Wiele z nakładów ponoszonych w fazie przed-eksploracyjnej może być związanych z nabyciem aktywu niematerialnego, jak na przykład wydatki związane bezpośrednio z ubieganiem się o uzyskanie prawa do prac poszukiwawczych (koncesji). Tego rodzaju nakłady będą traktowane w świetle MSR 38 jako składnik aktywów niematerialnych (np. koncesji na prace poszukiwawcze). (MSR 38, 2008)

Moment uzyskania przez podmiot pozwolenia na prowadzenie prac eksploracyjnych uznaje się umownie za początek drugiej fazy cyklu życia – fazy eksploracji/poszukiwania i dokumentowania złóż. Za jej zakończenie natomiast uznaje się moment opracowania studium wykonalności. Jest to faza, w której zasady rachunkowości są regulowane przez MSSF 6. Nakłady na tym etapie cyklu życia projektu geologiczno-górniczego związane są głównie z:

- nabyciem praw do wydobycia,
- analizami topograficznymi, geologicznymi, geomechanicznymi i geofizycznymi,
- wierceniami,
- pracami odkrywkowymi (trenching)
- próbkowaniem/rdzeniowaniem
- działaniami związanymi z oceną technicznej wykonalności i komercyjnej zasadności wydobycia zasobów mineralnych.

Rozliczanie nakładów prac eksploracyjnych w świetle MSSF 6.

MSSF 6 pozwala spółkom juniors na tworzenie własnego systemu księgowego w zakresie ewidencji nakładów ponoszonych w fazie poszukiwania i dokumentowania złóż. Główny problem podczas tworzenia polityki księgowej sprowadza się do ustalenia, czy nakłady ponoszone na tym etapie będą traktowane jako inwestycje i aktywowane, czy też jako koszty okresu, w którym zostały poniesione, obciążające rachunek zysków i strat. Najczęściej stosowane w praktyce metody księgowe zostały omówione poniżej.

- Metoda „w całości jako koszty" – jest metodą najbardziej konserwatywną (Catwright, 1991), zakłada traktowanie wszelkich wydatków na poszukiwanie i szacowanie złóż jako koszty w momencie ich powstania. Ze względu na rozłożenie w czasie tego rodzaju prac przysparza ona trudności w szacowaniu efektywności prowadzenia działalności przez podmiot w sektorze surowców mineralnych. Zdaniem Catwrightha (1991) metoda służy lepiej do maskowania rzeczywistych kosztów odnalezienia zasobów stanowiących aktywa niż ochronie przed przeszacowaniem wartości tych aktywów.

- Metoda „w całości jako nakłady inwestycyjne" – jest jedną z dwóch najpopularniejszych metod, obok metody nakładów zakończonych pozytywnym efektem gospodarczym. W metodzie tej, wszystkie nakłady niezależnie od ich efektu, są aktywowane do momentu ewentualnego odkrycia złoża a następnie amortyzowane w ciężar odkrytego złoża w sposób proporcjonalny. W metodzie tej nie traktuje się poszczególnych zasobów mineralnych jako centrum kosztów, w zamian za to uznając z nie rozległy obszar geograficzny, a nawet całe państwo. Metoda skutkuje wyższą wartością księgową aktywów niż metoda nakładów zakończonych pozytywnym efektem gospodarczym. (Malmquist 1989). W okresach wysokich odpisów, znacznie zniekształcony zostaje zysk netto, natomiast w okresach, kiedy odkryte zostanie więcej niż jedno opłacalne złoże, powstaje problem prawidłowej alokacji dotychczas aktywowanych nakładów. Metoda jest powszechnie stosowana przez spółki juniors nieposiadające aktywów generujących przychody w trakcie prac poszukiwawczych, których wynik nie jest jeszcze możliwy do określenia. Jest uznawana za najbardziej liberalną z metod.
- Metoda nakładów zakończonych pozytywnym efektem gospodarczym – jest obok w/w jedną z dwóch najpowszechniej stosowanych metod; zakłada aktywowanie nakładów na poszukiwanie i dokumentowanie złóż zakończonych pozytywnym efektem gospodarczym, dających się przypisać bezpośrednio do konkretnego złoża, podczas gdy nakłady niezakończone pozytywnym efektem są traktowane jako koszty okresu. Problem ze stosowaniem tej metody polega na tym, że do momentu odnalezienia złoże podmiot nie jest w stanie określić, które nakłady powinny być aktywowane. Z drugiej jednak strony, jedną z największych korzyści tej metody jest dawanie użytkownikom sprawozdania finansowego podmiotu możliwości oceny zarządzania w warunkach prac poszukiwawczych nie zakończonych pozytywnym efektem.(Venter, 2003)
- Metoda obszaru zainteresowania – w metodzie tej wyznacza się obszar geograficzny, mogący potencjalnie zawierać złoża surowców oraz aktywuje wszystkie nakłady związane z identyfikacją lub udowodnieniem istnienia złóż w danym obszarze. Nakłady są aktywowane do momentu udowodnienia pozytywnych efektów projektu (a zatem potwierdzona jest opłacalność wydobycia) lub przeciwnie, stwierdzenia braku opłacalności kontynuowania danego projektu. (Gerhardy, 1999) Metoda ta reprezentuje inne duże podejście do aktywowania nakładów na poszukiwanie i dokumentowanie złóż i jest dość powszechnie stosowana w przemyśle wydobywczym. (Epstein, Jermakowicz, 2009)
- Metoda kosztów i przywracania – w metodzie tej rejestruje się wszystkie nakłady jako koszty okresu, a następnie w momencie potwierdzenia rentowności odkrytego złoża, wcześniej przypisane do niego koszty zostają przeklasyfikowane na aktywa. Podmiot korzystający z tej metody potrzebuje sprawnego wewnętrznego systemu księgowego pozwalającego na rejestrowanie nakładów ponoszonych na poszczególne projekty aby zapewnić przeklasyfikowanie jedynie właściwych dla danego projektu kosztów.
- Metoda „szczególnego obszaru zainteresowania z rezerwą" – metoda ta zakłada aktywowanie wszystkich nakładów przypisanych do danego obszaru geograficznego, a jednocześnie tworzenie rezerwy tej samej wysokości obciążającej rachunek zysków i strat. Rezerwa ta jest utrzymywana do momentu kiedy zostaje oszacowana ekonomiczna rentowność danego obszaru. Rezerwa zostaje rozwiązana w rachunku zysków i strat w momencie, kiedy udokumentowana jest ekonomiczna opłacalność wydobycia. Efekt stosowania tej metody w sprawozdaniach finansowych będzie taki sam jak w przypadku metody kosztów i przywracania.

MSSF 6 wymaga klasyfikowania aktywów z tytułu prac poszukiwawczych jako aktywa materialne lub niematerialne zgodnie z ich naturą. Sposób klasyfikacji aktywów ma wpływ na późniejsze operacje księgowe z nimi związane. Praktyka firm w tym zakresie jest zróżnicowana. Część przedsiębiorstw traktuje aktywa powstałe w wyniku prac poszukiwawczych jako część rzeczowych aktywów trwałych, wiążąc je z bazowym aktywem trwałym w postaci udokumentowanego złoża, podczas gdy inne podmioty przypisują aktywa do odpowiednich koncesji na prowadzenie prac poszukiwawczych, traktując je w efekcie jako aktywa niematerialne. Wycena aktywów następuje w wysokości poniesionego kosztu, najczęściej w oparciu o model kosztu historycznego. Aktywa są następnie amortyzowane w okresie odpowiadającym przybliżonemu okresowi użytkowania rozpatrywanego zasobu. Obecna praktyka zakłada zwykle przyjmowanie jako okresu amortyzacji czasu trwania pozwolenia na prowadzenie prac poszukiwawczych.

MSSF 6 narzuca konieczność identyfikacji i oceny poziomy spadku wartości aktywów z tytułu poszukiwania i dokumentowania złóż, dokonywana jest ona jednak w oparciu o MSR 36 w sytuacji kiedy została stwierdzona utrata wartości. (Nichols, 2005) Do tych sytuacji zalicza się: (MSSF 6, 2008)

- okres, w którym jednostka miała prawo do prowadzenia poszukiwań na określony obszarze i który zakończył się w danym okresie obrotowym lub zakończy się w najbliższej przyszłości i nie oczekuje się, że prawo to zostanie wznowione,
- znacząca nakłady na dalsze poszukiwania i ocenę zasobów mineralnych na danym obszarze nie są ujęte w budżetach ani planach,
- poszukiwanie i ocena zasobów mineralnych na danym obszarze nie doprowadziły do odkrycia znaczących z komercyjnego punktu widzenia zasobów mineralnych i jednostka postanowiła zaniechać tych działań w danym obszarze,
- istnieją wystarczające dane, które wskazują, że mimo kontynuowania prac rozwojowych na danym obszarze, wartość bilansowa aktywów z tytułu poszukiwania i oceny zasobów mineralnych nie zostanie w pełni odzyskana z tytułu pomyślnego zakończenia prac rozwojowych lub sprzedaży.

Utrata wartości aktywów może być dokonywana na poziomie ośrodka lub grupy ośrodków wypracowujących środki pieniężne. Sposób przyporządkowania tych aktywów do określonego ośrodka musi zostać ustalony przez podmiot w ramach stosowanych zasad rachunkowości oraz stosowany konsekwentnie.

MSSF 6 narzuca jednocześnie na przedsiębiorstwa konieczność ujawniania stosowanych metod rachunkowych w zakresie wydatków na poszukiwanie i dokumentowanie złóż, łącznie z wartością aktywów z tytułu z tytułu tych prac. Podmioty powinny także ujawniać informacje dotyczące wartości aktywów, zobowiązań, przychodów oraz kosztów, poziomu operacyjnych i inwestycyjnych przepływów pieniężnych powstających w wyniku prowadzenia działalności w zakresie poszukiwania i szacowania złóż surowców mineralnych. MSSF nie wymaga za to ujawniania żadnych informacji dotyczących zasobów mineralnych lub rezerw spółek juniors.

Rozwiązania w zakresie rachunkowości w praktyce spółek typu juniors prowadzących działalność w Republice Południowej Afryki

Spółki junior mines koncentrują swoją działalność na rynkach krajów zorientowanych na rozwój sektora wydobycia surowców mineralnych. Wśród państw inwestujących w przemysł wydobywczy do najważniejszych i największych rynków należą obecnie Kanada, Australia oraz Republika Południowej Afryki. Dynamiczny rozwój segmentu poszukiwania, rozpoznawania i dokumentowania złóż, a co za tym idzie również gwałtowny wzrost zainteresowania tym regionem wśród spółek juniors został zapoczątkowany przez wprowadzenie w 2004 roku przez tamtejszy rząd ustawy o rozwoju przemysłu wydobywczego surowców mineralnych i ropy naftowej (MPRDA, Mineral nad Petroleum Resources Develompent Act). Zakładała ona poważne zmiany w zarządzaniu koncesjami górniczymi, mające na celu wspieranie rządu w działaniach zmierzających do zwiększenia zaangażowania ludności południowej Afryki w przedsięwzięciach związanych z poszukiwaniem i wydobyciem surowców mineralnych. W wyniku zmian w prawie, upraszczających uzyskanie koncesji na prowadzenie prac poszukiwawczych, na przestrzeni lat 2000-2004 liczba spółek juniors, posiadających w jednym momencie więcej niż 5 koncesji na poszukiwanie złóż, wzrosła od około 15 przed rokiem 2000 do około 60 po roku 2003. (Sturdy, Cronje, 2014)

Dynamiczny rozwój rynku spółek typu juniors w RPA oraz praktyki rachunkowości stosowane przez tamtejsze spółki był przedmiotem zainteresowanie dwojga naukowców – Christo Cronje oraz Joline Sturdy z Uniwerystetu Południowej Afryki. (Sturdy, Cronje,2014) Na podstawie ankiety przeprowadzonej wśród spółek junior mines prowadzących działalność na rynku RPA stworzyli oni zestawienie obrazujące praktyczne rozwiązania w zakresie rachunkowości, stosowane przez te spółki w zakresie ewidencjonowania i rozliczania nakładów ponoszonych w fazie przedeskploracyjnej oraz poszukiwania i dokumentowania złóż (eksploracji).

Wśród nakładów charakterystycznych dla fazy przedeskploracyjnej wyszczególnianych w praktyce firm na rynku RPA wyróżnić można:

- nabycie wyników badań stron trzecich dotyczących poszczególnych regionów kraju,
- gromadzenie informacji w zakresie historii poszukiwań na danym obszarze,
- nakłady na wyposażenie i infrastrukturę,
- prace zmierzające do przygotowania zespołu ekslproracyjnego,
- nakłady związane z ubieganiem się o prawa do poszukiwania i szacowania złóż,
- koszty ogólne związane bezpośrednio z fazą przedeksploracyjną,
- tworzenie hipotez geologicznych.

Spośród wymienionych kategorii nakładów, trzy pierwsze są traktowane przez większość spółek jako inwestycje i aktywowane, trzy kolejne stanowią w praktyce księgowości koszty okresu, zaś w odniesieniu do nakładów związanych z tworzeniem hipotez brak jest jednoznacznego podziału.

W odniesieniu do drugiej fazy cyklu życia projektu geologiczno-górniczego, regulowanej przez MSSF 6, w której możliwe jest korzystanie z wybranej metody ewidencjonowania nakładów, zdecydowana większość firm stosuje metodę „w całości jako nakłady inwestycyjne", natomiast pozostałe podmioty w przybliżeniu równych częściach ewidencjonują nakłady według metody „w całości jako koszty" lub metody obszaru zainteresowania z rezerwą. Badania autorów potwierdzają zatem zróżnicowanie w praktyce rozwiązań księgowych odnoszących się do nakładów na prace poszukiwawcze i dokumentowanie złóż. (Sturdy, Cronje, 2014)

Wśród nakładów, które są przez spółki juniors traktowane jako aktywa, wymienić można następujące kategorie wydatków:

- nabycie praw do prowadzenia eksploracji,
- badania topograficzne, geologiczne, geomechaniczne oraz geofizyczne,
- wiercenia,
- prace odkrywkowe,
- próbkowanie,
- opracowanie technicznego studium wykonalności,
- koszty personelu związanego z pracami poszukiwawczymi,
- koszty wyposażenia i infrastruktury,
- koszty ogólne związane bezpośrednio z fazą poszukiwania i szacowania złóż.

Praktyka przedsiębiorstw działających na rynku RPA ukazuje, iż oprócz nakładów związanych z wyposażeniem i infrastrukturą, uznawanych przez niemalże wszystkie przedsiębiorstwa za składnik aktywów materialnych, wszystkie z wyżej wymienionych nakładów są ewidencjonowane jako niematerialne składniki aktywów oraz przypisywane do odpowiednich praw do prowadzenia prac.

W zakresie amortyzacji powszechną praktyką jest natomiast amortyzowanie aktywów w okresie obowiązywania praw na prowadzenie prac poszukiwawczych.

Jeśli chodzi o testowanie aktywów pod kątem utraty wartości, wszyscy z dziewięciu respondentów przeprowadzają testy na utratę wartości w każdym okresie sprawozdawczym oraz potwierdzili posiadanie odpowiedniej polityki rachunkowości w zakresie przypisywania aktywów z tytułu poszukiwania i dokumentowania złóż do ośrodków wypracowujących środki pieniężne. Praktyka spółek działających na rynku afrykańskim pokazuje zatem stosowanie częstszego testowania na utratę wartości niż jest to wymagane przez MSSF6.

Praktyka spółek w zakresie ujawniania informacji wymaganych przez standardy rachunkowości pokazuje z kolei, iż większość spośród przebadanych spółek ujawnia część informacji dotyczących zasobów lub rezerw surowców mineralnych, podczas gdy pozostałe nie ujawniają żadnych informacji w tym zakresie.

Podsumowanie

Problem metod rachunkowych stosowanych przez spółki typu juniors, prowadzące działalność w dwóch pierwszych fazach cyklu życia projektu geologiczno-górniczego, tj. fazie przedeksploracyjnej oraz poszukiwania i dokumentowania złóż został tylko częściowo uregulowany poprzez wprowadzenie MSSF 6. Standard ten nie dotyczy pierwszej fazy, w której przedsiębiorstwa muszą opierać system rachunkowości na ramach koncepcyjnych MSR oraz MSR 16 Rzeczowe Aktywa Trwałe oraz MSR 38 Wartości niematerialne. MSSF 6 nie przyczynił się ponadto do wyeliminowania możliwości wyboru metod rachunkowych oraz do ujednolicenia stosowanych w praktyce polityk rachunkowości. Ankieta przeprowadzona wśród spółek typu juniors, prowadzących działalność na rynku afrykańskim, potwierdza rozbieżności w klasyfikowaniu ponoszonych nakładów, niezależni od etapu prac.

Zasadnym zatem wydaje się stwierdzenie, iż przemysł wydobywczy jest gałęzią gospodarki o wielu obszarach nieznajdujących odzwierciedlenia w międzynarodowych standardach rachunkowości, a co za tym idzie wymagającym dalszych prac w zakresie tworzenia regulacji podobnych do MSSF 6.

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The Expenses Related to Exploration Works – Capital Expenditures or Operating Costs?

The article presents the ways of accounting for expenditures related to exploration work. The methods of their valuation are presented and the accounting regulations based on IFRS 6, which relate to this type of expenditure, are indicated. Their financial treatment affects both assets and liabilities as well as revenues and costs of mining enterprises. The research carried out on exploration companies in South Africa, which is one of the largest markets of exploration companies in the world, was cited for support of the presented theses.

Keywords: geological-mining project, exploration works, capital expenditures, operational costs

Zachęty podatkowe stosowane dla spółek junior mines

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Abstract

W artykule przedstawiono specyfikę działalności spółek typu juniors, które realizują prace eksploracyjne w cyklu życia projektu geologiczno-górniczego. Z uwagi na wysokie ryzyko tych prac i dużą kapitałochłonność, państwa zainteresowane pracami poszukiwawczymi tworzą zachęty podatkowe dla takich firm oraz inwestorów chętnych do zaangażowania kapitałów w działalność eksploatacyjną. Rodzaje tych zachęt oraz ich charakter są głównym obszarem zainteresowań autorów.

Słowa kluczowe: górnictwo, spółki typu juniors, zachęty podatkowe

Wstęp

Sektor wydobywczy jest sektorem specyficznym, charakteryzującym się wysokim poziomem ryzyka operacyjnego oraz wysoką kapitałochłonnością. Dodatkowo charakterystyczną cechą jest sposób, w jaki zarówno ryzyko, jak również nakłady oraz przychody rozkładają się w cyklu życia projektu geologiczno-górniczego. Etap poszukiwania i dokumentowania złóż charakteryzuje się najwyższym poziomem ryzyka, co pociąga za sobą trudności w pozyskiwaniu zewnętrznego finansowania. Jednocześnie prace związane z poszukiwaniem i dokumentowaniem złóż wymagają wysokich nakładów.

Odpowiedzią rynku na wymienione wyzwania było powstawanie spółek specjalizujących się pracach eksploracyjnych, tzw. junior mining companies. Spółki te przejmują ryzyka i nakłady związane z poszukiwaniem i dokumentowaniem złóż a następnie sprzedają efekty swoich prac koncernom wydobywczym, posiadającym kompetencje górnicze.

Kraje zorientowane na rozwój sektora surowców mineralnych, takie jak Kanada, Australia, RPA, świadome barier, jakie sektor ten stawia potencjalnym inwestorom, stosują coraz częściej zachęty podatkowe zmierzające do stworzenia pozytywnego środowiska biznesowego dla spółek typu junior mines. Korzyści z tego rodzaju programów są obopólne – spółki obniżają nakłady ponoszone na prowadzenie eksploracji, państwa zaś zyskują informacje na temat rzeczywiście posiadanych zasobów surowców mineralnych.

W artykule omówiono cykl życia projektu geologiczno--górniczego ze szczególnym uwzględnieniem fazy eksploracji związanej z poszukiwaniem i dokumentowaniem złoża, charakterystykę spółek typu juniors jako przedsiębiorstw eksploracyjnych oraz przedstawiono stosowane w praktyce światowej formy zachęt podatkowych skierowanych do spółek juniors.

Cykl życia projektu geologiczno-górniczego

Projekt geologiczno-górniczy jest określany w literaturze najczęściej jako działalność realizowana w górnictwie oznaczająca poszukiwanie, udostępnienie, wydobycie, przeróbkę kopaliny oraz sprzedaż wzbogaconego produktu handlowego. Realizacja projektu geologiczno-górniczego jest związana ze złożem kopaliny, której eksploatacja jest przedmiotem działalności operacyjnej przedsiębiorstwa górniczego. (Uberman, 2006) Pojęcie złoża według Prawa geologicznego i górniczego jest identyfikowane jako nagromadzenie minerału czy też skały użytecznej, których eksploatacja może przynieść korzyści gospodarcze. (Lisowski, 2001)

Do specyficznych cech złoża zalicza się:

- unikatowość (rzadkość i niepowtarzalność występowania zarówno pod względem warunków geologicznych jak również lokalizacji),
- nieodnawialność,
- niepewność co do budowy zasobów i charakterystyki geologicznej.

Tym samym zasadność istnienia i realizacji projektu geologiczno- górniczego jest związana z posiadaniem złoża oraz uzyskaniem odpowiednich koncesji i pozwoleń na jego wydobycie. Realizacja wspomnianego projektu jest specyficzna w porównaniu do innych branż zarówno pod względem technicznym, technologicznym jak i finansowym i dotyczy w szczególności:

- długiego okresu przedprodukcyjnego obejmującego poszukiwanie, ocenę i udostępnienie złoża,
- długiego okresu produkcyjnego (eksploatacyjnego),
- zróżnicowanych warunków geologiczno-górniczych, gdzie prowadzona jest eksploatacja,
- dużej kapitałochłonności procesów,
- wysokiego kosztu kapitałów potencjalnie finansujących projekt z uwagi na długie okresy przed- jak i produkcyjne, a tym samym stosunkowo długie okresy zwrotu nakładów dla inwestorów,
- nieelastyczności produkcji wynikających z braku podjęcia działalności alternatywnej czy też wysokiego ryzyka operacyjnego obejmującego wysokie koszty stałe działalności,
- nieprzewidywalności cen na rynkach surowców mineralnych wykazujących co prawda pewną cykliczność zachowań, ale determinujących opłacalność eksploatacji.

Tab. 1. Przykłady zachęt podatkowych w ramach poszczególnych instrumentów fiskalnych. Źródło: opracowanie własne
Tab. 1. Examples of tax incentives in the range of individual fiscal instruments

Instrumenty fiskalne	**Możliwe zachęty podatkowe**
Podatki dochodowe	• okresowe z wolnienie z podatku dochodowego • przyśpieszona amortyzacja • ulga z tytułu inwestycji • możliwość przeniesienia straty na przyszłe okresy • ulga od podatku u źródła
Podatki od wydobycia (mining royalties)	• redukcja podatków górniczych • okresowe zwolnienie z podatków górniczych • stopniowa skala podatków górniczych
Opłaty od importu i eksportu	• zwolnienie z opłat celnych • strefy działalności ukierunkowanej na export
Inne	• stabilne warunki fiskalne

Długie okresy inwestycyjne oraz produkcyjne są niekorzystne z punktu widzenia czynnika czasu, który wpływa na wielkości finansowe (przepływy finansowe) generowane przez projekt. Tym samym opłacalność projektu górniczo-geologicznego musi uwzględniać przepływy generowane na każdym etapie realizacji projektu rozpatrywanego w całym cyklu swojego istnienia.

Z uwagi na przedstawione zależności istotnym jest ujęcie kosztów działalności geologiczno-górniczej i zarządzanie nimi w poszczególnych fazach cyklu życia projektu górniczego. Jak pokazuje praktyka sama ewidencja kosztów jest ważnym problemem tylko rachunkowości branży wydobywczej. Brak jednolitych standardów powoduje, że światowe koncerny górnicze stosują różne praktyki księgowe, co utrudnia porównywalność kosztów, a tym samym ocenę efektywności działania.

Wskazane problemy dotyczą ewidencji kosztów według zidentyfikowanych centrów utożsamianych z określonym złożem, czy też krajem lub nawet całym kontynentem. Ponadto kwestią sporną pozostaje odpisanie wydatków w koszty w okresie ich poniesienia czy też zatrzymanie ich w czasie poprzez aktywowanie, a następnie rozliczenie poprzez stopniową amortyzację.

Realizacja prac górniczo - geologicznych składa się najczęściej z kilka faz, które dotyczą kolejno: (PwC, 2000)

1. eksploracji i rozpoznania złoża kopaliny,
2. oceny złoża,
3. budowy kopalni,
4. produkcji górniczej,
5. likwidacji i rekultywacji terenu.

Prace eksploracyjne i ich charakterystyka

Eksploracja i rozpoznanie złoża kopaliny jest obciążone największym ryzykiem niepowodzenia, ale jednocześnie stanowi najmniej kapitałochłonny etap w stosunku do pozostałych faz procesu górniczo - geologicznego. Obejmuje ona najczęściej:

- analizę geologicznych danych historycznych, uzyskanych w ramach wcześniejszych badań wykonywanych przez firmy górnicze i geologiczne,
- analizy topograficzne, geologiczne, geochemiczne i geofizyczne,
- wiercenia poszukiwawcze,
- próbkowanie.

Prace eksploracyjne są wykonywane po uzyskaniu odpowiednich praw i koncesji (choć nie zawsze jest to czynnik determinujący) i koncentrują się na obszarach o największej mineralizacji złożowej.

Kolejnym etapem prac górniczo – geologicznych jest ocena złoża, przy czym do tej fazy dochodzi około 5% ilości projektów realizowanych w fazie eksploracji. (Wirth, 2006) Szczegółowe analizy mają zidentyfikować poszczególne parametry charakteryzujące złoże. Obejmują one wiercenia, wykonanie wyrobisk podziemnych lub odkrywkowych na małą skalę, przeprowadzenie prób przeróbki kopaliny oraz badania rynkowe i analizy finansowe pod kątem wymagań transportowych i infrastrukturalnych. W ramach oceny złoża prowadzone prace koncentrują się na stwierdzeniu technicznej wykonalności i komercyjnej zasadności wydobywania zasobów kopaliny, determinujących poniesienie nakładów na przygotowanie i udostępnienie złoża w celu prowadzenia eksploatacji. Jednocześnie, etap oceny kończy się w momencie zidentyfikowania złoża kopaliny, prowadzącego do podjęcia decyzji o budowie kopalni.

Ocena i finansowanie projektów geologiczno-górniczych jest szczególne złożona w porównaniu do tradycyjnych projektów inwestycyjnych. Potencjalni inwestorzy i dawcy kapitałów zwracają szczególną uwagę nie tylko na aspekty finansowe ale również na dane techniczne i technologiczne. Dotyczą one w szczególności informacji geologicznych i górniczych potwierdzonych przez doświadczonych geologów i licencjonowanych taksatorów złóż z bogatym doświadczeniem praktycznym. Wynika to z faktu, że inwestorzy chcą zarabiać zanim dany projekt górniczy zostanie uruchomiony, nie czekając na dywidendy z wypracowanych zysków pochodzących z działalności operacyjnej. Oznacza, to że już na etapach eksploracji i estymacji złóż akcje firm realizujących takie projekty podlegają obrotowi wtórnemu na giełdach finansowych. Dotyczy to spółek typu juniors mines, które są notowane na giełdach a wartość ich akcji zależy od ilości i jakości eksplorowanych i później zbywanych złóż. Tym samym potencjalni inwestorzy muszą uwzględniać nie tylko dane finansowe ale również brać pod uwagę dane geologiczno-górnicze charakterystyczne dla projektów górniczych.

Przedsiębiorstwa górnicze w poszukiwaniu źródeł finansowania muszą brać pod uwagę zainteresowanie potencjalnych inwestorów dotyczące: (Dow, 2007)

- jakości kadry zarządzającej,
- aspektów geologicznych związanych z danym złożem
- aspektów środowiskowych,
- lokalizacji przyszłej kopalni w stosunku do dróg transportu i portów przeładunkowych,
- sytuacji politycznej wpływającej na ryzyko projektu.

Potencjalni inwestorzy i dawcy kapitału udostępniają kapitał po określonym koszcie związanym z ryzykiem projektu górniczo geologicznego. Analizując cały cykl życia ryzyko to zmienia się w zależności od etapu realizacji projektu górniczo geologicznego.

Spółki typu junior mines jako spółki eksploracyjne

Działalność przedsiębiorstw górniczych typu junior mines polega na eksploracji nowych złóż, pozyskiwaniu koncesji i licencji na ich wydobycie oraz ich udostępnieniu w celu zapewnienia wydobycia na skalę przemysłową. Niejednokrotnie mogą one posiadać w swoich strukturach kilka zakładów górniczych zajmujących się eksploatacją kopalin, co zwiększa ich wartość rynkową.

Działalność przedsiębiorstw typu junior mines uchodzi za bardziej ryzykowną niż w przypadku dużych zdywersyfikowanych koncernów górniczych należących do grupy senior mines. Poszukują one nowych złóż ponosząc przy tym znaczne nakłady wymagające określonych źródeł finansowania. Często okazuje się, że prowadzone prace eksploracyjne nie przynoszą pozytywnych skutków gospodarczych, a ponoszone nakłady nigdy nie zostaną odzyskane, stając się kosztami generującymi określone straty finansowe. Finansowanie prac poszukiwawczych odbywa się najczęściej z kapitałów własnych pozyskanych w drodze publicznej oferty, prywatnego kapitału lub też poprzez joint ventures z dużymi przedsiębiorstwami górniczymi z grupy senior mines.

Dodatkowym ryzykiem rozpatrywanym przy działalności górniczej prowadzonej przez junior mines jest ryzyko finansowania prac po odkryciu i udokumentowaniu złoża nadającego się do eksploatacji. Pozyskanie koncesji na wydobycie i udostępnienie złoża wymaga kolejnych nakładów finansowych koniecznych do poniesienia.

Bardzo często duże przedsiębiorstwa górnicze posiadają udziały w junior mines, traktując je jako opcję z możliwością realizacji. Tym samym w każdej chwili mogą podjąć eksploatację jeżeli tylko prace prowadzone przez junior mines przyniosą pozytywne skutki w postaci odkrycia i udokumentowania złoża.

Zachęty podatkowe dla sektora wydobywczego w praktyce światowej

Zachęty podatkowe są specjalnymi udogodnieniami dla przedsiębiorstw, które mają na celu stworzenie środowiska sprzyjającego rozwojowi i nowym inwestycjom. W odniesieniu do sektora wydobywczego, zachęty podatkowe są definiowane jako wszelkie regulacje podatkowe, tworzone z myślą o inwestycjach górniczych, obejmujące odstępstwa od ogólnie stosowanych wobec wszystkich podmiotów gospodarczych przepisów podatkowych.

Zachęty podatkowe obejmują określone instrumenty fiskalne, które mogą byś identyfikowane w ramach następujących obszarów:

- w ogólnej ordynacji podatkowej – specjalne udogodnienia mogą być zapisane w osobnych rozdziałach i paragrafach, bądź mogą wynikać z ogólnych przepisów (np. niższa stawka podatku dochodowego),
- w prawie geologiczno-górniczym – które może regulować szczególne rodzaje opłat fiskalnych, charakterystyczne jedynie dla sektora górniczego (np. obniżona stawka podatku pobieranego od importowanych towarów dla górnictwa)
- w kontraktach górniczych – gdzie mogą zostać ustanowione specjalne ulgi charakterystyczne jedynie dla konkretnego projektu górniczego (np. całkowite zwolnienie z podatków przez pewien okres).

Formy zachęt podatkowych są zróżnicowane w zależności od instrumentów fiskalnych, do których mają odniesienie. W tabeli 1 przedstawione zostały przykłady zachęt stosowanych w ramach poszczególnych instrumentów fiskalnych.

Zachęty podatkowe odnoszące się do prac eksploracyjnych

Ze względu na wysokie ryzyko inwestycji, spółki typu juniors muszą nieustannie poszukiwać inwestorów i zewnętrznych źródeł finansowania. Rządy państw bogatych w zasoby naturalne takich jak Kanada, RPA czy Australia, wychodzą naprzeciw spółkom typu juniors i stosują liczne zachęty podatkowe, aby pobudzić inwestorów do zainwestowania swojego kapitału w proces eksploracji.

Spośród wymienionych w tabeli 1 kategorii zachęt podatkowych, następujące znajdują zastosowanie w odniesieniu do spółek juniors:

- w zakresie podatków dochodowych:
    - okres zwolnienia z podatku dochodowego - może przybrać formę kompletnego zwolnienia z podatku dochodowego, obniżonej stawki podatku dochodowego w założonym okresie lub kombinacji zwolnienia oraz obniżenia stawki. Czas trwania okresu zwolnienia z podatku dochodowego może być różny w zależności od przepisów krajowych. (Zolt, 2015)
    - przyśpieszona amortyzacja – przedsiębiorstwa zazwyczaj są zmuszone do rozliczania amortyzacji przez okres użytkowania danego składnika aktywów, narzucony przez standardy rachunkowości. Przedsiębiorstwa górnicze mogą natomiast liczyć na możliwość zastosowania przyśpieszonej amortyzacji i tym samym wcześniej rozliczać w kosztach poniesione nakłady,
    - ulga inwestycyjna – daje podatnikowi prawo do zrekompensowania części poniesionych wydatków inwestycyjnych poprzez odliczenie ich od dochodu podlegającemu opodatkowaniu w roku, w którym wydatki są ponoszone,
    - ulga podatkowa na inwestycje - w odróżnieniu od ulgi inwestycyjnej pozwala na odliczenie części wydatków inwestycyjnych od kwoty podatku, a nie od kwoty dochodu, w roku, w którym wydatki te zostały poniesione.
    - dłuższe rozliczanie straty - prawo podatkowe zwykle dopuszcza możliwość przeniesienia części straty netto na kolejny okres rozliczeniowy jako obciążenia przyszłego dochodu, aby zmniejszyć podstawę opodatkowania podatkiem

dochodowym w kolejnych latach, narzucając jednocześnie ograniczony okres, w którym możliwe jest przeniesienie straty. wysoki poziom kosztów ponoszonych z góry, charakterystyczny dla górnictwa przekłada się na zasadność zastosowania dłuższego okresu możliwości przeniesienia straty na kolejne lata fiskalne. Przekłada się ona na spadek poziomu podatku dochodowego w sytuacji, kiedy straty, które w normalnych warunkach by się przedawniły, mogą być w dalszym ciągu przenoszone na kolejne okresy w celu zmniejszenia podstawy opodatkowania.

o ulga od podatku u źródła – podatek u źródła wymaga od płatnika podatku zatrzymania części podatku dochodowego od płatności zagranicznych. Znaczenie tego rodzaju podatku w działalności wydobywczej sprawia, że z punktu widzenia państwa zarządzanie podatkiem u źródła jest kluczowe punktu widzenia w świetle wpływów budżetowych. Z drugiej zaś strony przekłada się ono na możliwość zastosowania wyjątków lub ulg, jak na przykład obniżenie stopy podatku u źródła dla płatności odsetkowych.

- w zakresie opłat celnych:

o ulga na cło importowe – cło importowe to podatki pobierane od importowanych towarów. Cło zazwyczaj opiera się na wartości importowanych towarów. Ulga przewiduje zmniejszenie stawki podatku.

o export processing zones - Typową cechą EPZ jest stosowanie specjalnych zachęt zmierzających do pozyskania inwestorów, głównie zagranicznych, zorientowanych na działalność związaną z eksportem. Zachęty mogą obejmować okresowe zwolnienia z podatków, zwolnienia z ceł eksportowych i importowych oraz wolną od podatków i opłat repatriację zysków.

- inne zachęty podatkowe:

o stabilizacja podatkowa - ma za zadanie zabezpieczyć poziom opodatkowania, podział produkcji, polityki cenowe oraz/lub poziom ingerencji państwa oraz rządu w podział korzyści pochodzących z projektu wydobywczego w czasie obowiązywania kontraktu górniczego. Głównym uzasadnieniem tej metody jest zapewnienie możliwości pozyskania finansowania bankowego (kredytu) projektów w krajach o wysokim poziomie ryzyka politycznego. Przepisy pomagają w ten sposób instytucjom finansowym w ocenie relatywnego ryzyka projektów. Wyróżnia się trzy podejścia to stabilizacji podatkowej (Daniel & Sunley, 2008):

o przepisy prawa (lub też warunki kontraktu) obowiązujące w dniu zawarcia umowy/kontraktu pozostają zamrożone,

o wszystkie przyszłe zmiany polityki fiskalnej, które wpłynęłyby na obciążenia podatkowe projektu nie będę miały zastosowania, jednakże projekt może czerpać korzyści z tytułu ewentualnego obniżenia podatków,

o zmiany w ordynacji podatkowej będą obowiązywały podmiot, ale rząd musi je z nim negocjować. Istnieje umowa z podmiotem gospodarczym, zakładająca negocjacje zmierzające do utrzymania równowagi ekonomicznej jeśli zmiana w prawie mogłaby mieć negatywne skutki dla przedsiębiorstwa..

Przykładem innej formy zachęt, odnoszącej się do potencjalnych inwestorów, nie zaś bezpośrednio do spółek juniors, są programy Flow-Through Shares (FTS) oraz Mining Exploration Depletion Allowance (MEDA), zapoczątkowane przez rząd kanadyjski na początku lat 80. Programy te miały za zadanie ułatwić spółkom prowadzącym działalność eksploracyjną pozyskanie finansowania. Były one skierowane do potencjalnych inwestorów i w przeciwieństwie do wcześniej wymienionych metod zakładały korzyści dla dawców kapitału, nie zaś bezpośrednio dla przedsiębiorstw.

Program MEDA został wycofany z realizacji w roku 1988, FTS jest wciąż kontynuowany.

W programie MEDA inwestor finansujący działalność spółki typu junior poprzez zakup udziałów, miał możliwość uzyskania znaczących umorzeń podatku. Na każdy 1 USD zainwestowany w udziały w spółce junior, przypadało 1,33 USD umorzenia podatku dla inwestorów.

Program FTS pozwala spółkom typu junior na „przeniesienie” (flow-through) nakładów związanych z działalnością eksploracyjną na akcjonariuszy (shareholders) w zamian za udziały w firmie. Udziałowcy mogą te „przekazane” (passed) w ten sposób nakłady odliczyć od podatku.

Podsumowanie

Odpowiedzią państw zorientowanych na rozwój własnego rynku surowców mineralnych jest tworzenie zachęt podatkowych zmierzających do obniżenia nakładów koniecznych do ponoszenia przez spółki typu juniors lub stanowiących zachęty dla potencjalnych inwestorów. Ze względu na charakterystykę zarówno całego sektora wydobywczego, jak również szczególnych warunków funkcjonowania spółek typu juniors, tworzenie tego typu zachęt wydaje się być zasadne i przynosić zamierzone skutki zarówno dla podmiotów gospodarczych jak i inwestorów.

Z punktu widzenia junior mines tego rodzaju korzyści pozwalają zmniejszyć poziom nakładów w fazie poszukiwania i dokumentowania złóż oraz zwiększyć potencjalne zyski ze zbycia efektów prac. Wiąże się to z mechanizmami stosowanymi przez państwa zorientowane na rozwój rynku surowców mineralnych, które niejednokrotnie obejmują swym zasięgiem także dalsze fazy cyklu życia projektu geologiczno-górniczego, co przyczynia się do zwiększenia zainteresowania wynikami pracy spółek typu juniors wśród koncernów wydobywczych. Z punktu widzenia państw stosujących zachęty główną korzyścią obok potencjalnego rozwoju sektora wydobywczego jest uzyskanie wiedzy na temat posiadanych zasobów surowców mineralnych.

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Tax Incentives Applied to Junior Mines Companies

The article presents the specificity of junior mines activities , which carry out exploration work in the life cycle of a geological and mining project. Due to the high risk of these works and high capital intensity, some countries interested in exploratory work, create tax incentives for such companies and investors willing to engage capital in exploration activities. The types of these incentives and their character are the main area of interest of the authors in the article.

Key words: mining, junior mines, tax incentives