Utilization Range of By-Products from Coal Combustion in Earth Structures of Transport Infrastructure

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Abstract

In transportation engineering, earthwork is the main structural material which geotechnical properties can be positively modified with admixtures. This article focuses on the application of energy by-products in earthwork of transportation line structures and summarizes their advantages and define the scope of their utilization. Earthwork construction demands the considerable volume of quality material and therefore, the effort to optimize traditional material substitution is made. One possibility is to apply solid by-products emerging when combusting coal, which is referred to as secondary energy products. These include various types of fly-ash, slag, bottom ash or gypsum. Requisite for their widespread utilization is the application in the construction and modernization of transport infrastructure, including road and rail construction, or in the case of flood control dams within the framework of water management measures against flooding. They can be utilized also as municipal waste dumps covering. However, the application of fly ashes in earthwork constructions delivers certain limits. When contacting with rain ingress or groundwater, the leaching containing heavy and toxic metals depending on energy by-product type may occur. Alternatively, the limitation of their application can be relatively low mechanical resistance to cyclic saturation and frost effect and consequent volume changes. This article deals with long-term observation results of the energy by-products saturation and additivity influence on volume changes. For the investigation purpose of failure causes, the phase composition using X-ray crystallography and Raman spectroscopy was determined.

Keywords: coal combustion, fly ash, earth structures, transport infrastructure, volume changes, ettringite

Introduction

The cementing or modification of solid coal products is an effective method for using materials otherwise difficult to apply, often classified as waste. The secondary energy products (CCPs) coming from the combustion and desulphurisation technologies used in power stations and heating plants includes, among others, different kinds of fly ash, slag, ash or mineral gypsum (calcium sulphate). Every year around 15 million tons of secondary energy products are produced in the Czech Republic. Only 20 30% of this production is used in the construction industry. Most products are deposited or used to load excavated areas after mining (Fečko, 2005). Within the scope of applicability in the ground constructions of road structures, CCPs, often mixed with a binder (lime or cement) and water, are often used. These modified CCPs are referred to as fly ash based stabilizers (Lidmila, 2015). The fly ash based stabilizer can also be produced by wetting the mixture of fluid fly ash or bed ash (Kresta, 2012).

There are not so much experience with using of fly ash for constructing railway embankment.

The more detailed study for utilization of fly ash as a structural fill material for railway embankment for rail metro was done in Japan (Sunaga, 1992), another study for the railway substructure was done in Serbia (Vukićević, 2016). The real application of fly ash in railway structures in the form of fly ash based stabilizer was applied in the railway line at Smiřice station in 2005. The earthwork, which contains a layer of dangerously freezing and swellable clay limestone, was protected from the effect of frost and penetration of water by a layer of fly ash based stabilizer. After more than 13 years from the implementation of the fly ash based stabilizer layer in the track bed construction, all requirements of ŠZDC S4 regulation (Lojda, 2017) are still met.

The use of ash stabilizers for building earthworks brings major problems associated with volume changes (Yoon, 2007). When long term contacting the fluid fly ashes with water new secondary minerals are created, especially ettringite Ca₆Al₂(SO₄)₃(OH)₁₂·26(H₂O) and calcium carbonates, which can cause volume changes causing defects of road construction layers. In terms of the risk of loss of mechanical strength and ultimately of overall stability, the most dangerous is the formation and growth of ettringite minerals (Dermatas, 1995). Another risk factor for the use of fly ash based stabilizers in ground constructions is their relatively low resistance to repeated contact with water and frost (Chen 2009, Sear 2011) and the risk of partially unsatisfactory hygienic and ecological parameters (Vaniček, 2003).
In relation to the risk of undesirable volumetric changes, this article focuses on the issue of CCP swelling. The long-term influence of saturation and influence of used additives in the investigated mixtures on volumetric changes of CCPs were studied within experimental research.

Materials

For the purpose of experimental research of coal combustion by-products, samples (see Figure 1) were taken from three power stations in the Czech Republic, namely fly ash from the Mělník power station, fluid bed ash from the Ledvice power station, and filter fly ash from the Tisová power station. In addition, a fly ash-based stabilizer sample was taken from the trial section trackbed at the Smiřice railway station within the Pardubice–Liberec railway line, where stabilizer from the Chvaletice power plant (ECHV A) was used.

The above-mentioned power stations represent two basic types of desulphurisation and each produces by-products with other technical parameters. In Mělník, desulphurization is done by wet limestone solution. From Ledvice and Tisová have been used fluid combustion products. All three power stations burn brown coal.

High-temperature fly ash (Mělník) from wet limestone solution consists mainly of aluminosilicates (mullite, quartz). Fluid bed ash from Ledvice is mostly formed of CaSO₄, CaCO₃, CaO and aluminosilicates (mullite, quartz) (Mráz, 2015).

As additives the following materials were used:

- Calcitic-dolomitic crystalline limestone from Krty mine, which was subjected to mechanical activation in a two-rotor repulsion high-speed mill;
- Mechanically-chemically activated fluid ash from the Pilsen heating plant;
- Cement CEM II/B-M 32,5 R in accordance with ČSN EN 197-1.

The fly ash stabilizer from the Chvaletice Power Station was used as part of the test section verifying the use of fly ash stabilizer in the railway substructure construction, as described for example in (Lidmila, 2015). The fly ash stabilizer from Chvaletice Power Station was consisted (weight composition) of fly ash (52%), gypsum, (25%), calcium oxide mined in Kotouč Štramberk (3%) and water (20%). Furthermore, crystals of CaSO₄ (gypsum) and fragments of minerals of quartz, K feldspar, plagioclase, biotite, calcite, zirconium, BaSO₄ and KCl were present in fly ash stabilizer. Gypsum and mineral debris form accumulation sites.

Methodology

Laboratory compactibility determination of fly ash mixtures by Proctor standard tests according to ČSN EN 13286-2 were carried out at Czech Technical University in Prague, the Faculty of Civil Engineering. In order to verify the resistance to the effects of transport loads, the stress tests according to...
ČSN EN 13286-41 were performed. To determine the resistance to the effects of climatic conditions, suitability for water effect and reduction under freezing according to ČSN EN 14227-14 was assessed. The greatest attention was paid to the long-term influence of saturation and the influence of additives in examined mixtures on volume changes.

Mixtures of both combustion and desulphurisation technologies and with different binder ratios were tested separately. In the case of CCPs, commonly used binders were replaced by inorganic bulk binders obtained by mechanical-chemical activation of fluid fly ash or by mechanical activation of dolomitic limestones.

One of the purposes of applying mechanically-chemically activated materials to CCPs was to eliminate the formation of ettringite.

Methodology of analysis of elemental and phase composition
To describe the causes of volume changes was in the laboratory of University of Chemistry and Technology analysed the elemental composition by X-ray fluorescence spectroscopy (XRF) and determining the phase composition using X-ray diffraction analysis (XRD). XRD analysis was performed on 5 samples of fly ash mixtures. It was a fly ash bed ash from Ledvice without additives, a fluid bed ash with 10 wt. % of mechanically-chemically activated fluid fly ash, fluid bed ash with 6 wt. % mechanically-chemically activated dolomite limestone, slag from Mělník without admixtures, non-admixed fly ash from Tisová. XRD data were obtained at room ambient temperature using 0-0 powder diffractometer Bruker AXS D8’ Pert PRO in Bragg-Brentano para focusing with wave length CoKα radiation (λ = 1.7903 Å, U = 34 kV, I = 20 or 30 mA). Data were scanned using high-speed detector LynxEye in angle range of 30–80° (2θ) with measurement step of 0.0196° (2θ) and adding time of 19.2 per step. Data processing and evaluation was done in HighScore Plus 3.0e software.

XRF analysis was performed using the ARL 9400 XP sequenced wave-dispersive X-ray spectrometer. This spectrometer is equipped with an X-ray tube with Rh anode type 4GN with an end Be window of 50 μm thickness. All intensity of the spectral lines of the elements were measured in vacuum by WinXRF. The combination of generator-collimator-crystal-detector settings has been optimized for 82 measured elements with a time of 6 seconds per element. The obtained intensities were processed by Uniquant 4 without the need to measure standards. The analysed powder samples were extruded into tablets of 5 mm thickness and 40 mm in diameter without the use of a binder (or using Dentacryl as a binder) and with or without a 4 μm thick polypropylene film (PP). The time of measuring of one sample was approximately 15 minutes.

Analysis by Raman microspectroscopy method were conducted at several randomly selected locations individu-}

![Tab. 1. XRF elemental analysis of fluid filter fly ash and slag from wet limestone scrubbing
Tab. 1. Analiza elementarna XRF popiołu lotnego i żużla z filtra z przemywania wapnia](image1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fluid filter fly ash from Tisová</th>
<th>Slag from wet limestone solution from Mělník</th>
<th>Fluid filter fly ash without additives from Tisová</th>
<th>Slag from wet limestone solution without additives from Mělník</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>14,4</td>
<td>15,4</td>
<td>14,3</td>
<td>11,4</td>
</tr>
<tr>
<td>Si</td>
<td>16,0</td>
<td>17,7</td>
<td>16,8</td>
<td>13,5</td>
</tr>
<tr>
<td>Ti</td>
<td>6,5</td>
<td>2,0</td>
<td>4,1</td>
<td>2,5</td>
</tr>
<tr>
<td>Fe</td>
<td>4,5</td>
<td>6,4</td>
<td>4,6</td>
<td>4,4</td>
</tr>
<tr>
<td>Mg</td>
<td>0,5</td>
<td>0,3</td>
<td>0,7</td>
<td>0,5</td>
</tr>
<tr>
<td>Sr</td>
<td>3,8</td>
<td>4,3</td>
<td>6,4</td>
<td>5,9</td>
</tr>
</tbody>
</table>

![Fig. 3. Testing bodies of fly ash based stabilizers after the volume changes monitoring, a) fluid fly ash without additives from Tisová after 28 days of curing - (ETI_mineral), b) fluid bed ash without additives from Ledvice after 28 days of curing, c) fly ash without additives from Mělník after 28 days of curing](image2)

Rys. 3. Badanie stabilizatorów na bazie popiołu lotnego po monitorowaniu zmian objętości, a) płynny popiół lotny bez dodatków Tisová po 28 dniach utwardzania - (ETI_mineral), b) popiół fluidalny bez dodatków Ledvice po 28 dniach utwardzania, c) popioły lotne bez dodatków z Mielnika po 28 dniach utwardzania
Verification of volumetric stability of ash stabilizer

The purpose of measuring the volume changes of ash stabilizer was the determination of the volume swelling coefficient. For this test, the CBR mortar and other equipment used for the preparation and execution of the CBR test according to ČSN EN 13286-47 was used. The mixture moisturized to optimal moisture was compacted in the CBR by the energy Proctor Standard. The ash stabilizers were aged for 7 or 28 days in a mold at 20°C in a sealed package and then saturated with water until the deformation subsides. In time intervals, the change in the height of the surface of the compacted, saturated sample loaded with load was measured.

The volume swelling coefficient $B_t$ was determined according to the following relationship (1) (see appendix 3 of TP 93):

$$B_t = \frac{\Delta V}{V_1}$$

where: $V_1$ (m$^3$) is the original volume of the sample and $\Delta V$ (m$^3$) is the change of volume of the sample in the time $t$.

In the experiment, fluid bed ash samples, non-additive fluid filter fly ash, and various admixtures (10 wt.% of mechanically chemically activated fluid fly ash, 3 wt.% of cement CEM II/B 32.5 R, 6 wt.% of micronized dolomite limestone) were subjected to laboratory testing. Additionally, samples of high-temperature fly ash and slag without additives and with 6 wt.% of cement CEM II/B 32.5 R were tested.

Results

The results of volumetric changes in fly ash based stabilizers are shown in the Figure 2. The evolution of volumetric changes in fly ash mixture made of wet limestone solution without additives technology and their values indicate that most volume changes occurred during the first week. At mixtures of high-temperature fly ash without additives, it has occurred to volumetric changes after watering. Volume changes of high temperature fly ash without additives in saturation of compacted samples can be attributed to the release of negative pore pressures. This value was up to 4%. Since it is not a swelling, i.e. a change in volume due to chemical reactions, it is not necessary to modify by binders the fly ash tested for applications in transport structures. Sample fly ash samples with 6 wt.% of cement can be considered as volume-stable. In the case of slag from wet limestone solution, it has been shown that the test procedure does not change its volume.

The largest increase in volume (more than 10%) show fly ash based stabilizers from fluid bed ash from Ledvice and fluid fly ash without additives from Tisová. Even after 160 days, there are no signs of stabilization. In the case of the additive mixtures, the volume increase occurs more slowly with approximately linear growth. It can be assumed that for all other tested fly ash based stabilizers the maximum permissible volume changes for use in earth structures (<3% swelling in the CBR cylinder according to TP 93) will be achieved after longer observation.

An important finding of swelling measurements during solidification and hardening of the ash stabilizer prepared from fluid combustion technology products is that the addition of mechanically-chemically activated additives into the fly ash mixture results in a decrease in swelling. For example, the effect of mechanically-chemically activated fluid fly ash and mechanically activated dolomite limestone applied to the mixture with fluid bed ash indicates a decrease of swelling to about half.

The XRF and XRD analysis was then performed on the tested fly ash mixtures. XRF analysis showed that the fly ash mixture is significantly represented by Al, Si, (Ti, Fe). The elemental composition of fly ash mixtures remains virtually unchanged during curing. XRD and XRF analyses show a heterogeneous distribution of iron FeOt concentrations. In the case of slag from wet limestone solution, the iron concentration is reduced during the sample curing, probably due to precipitation reactions. Examples of XRF analyses for fluid fly ash and slag from wet limestone solution are given in Table 1.

From made XRD analyses, the crystallic phases are in fly ash mixtures represented mainly by anhydrite (CaSO₄), quartz (SiO₂), anortitis (CaAl₂Si₂O₈), mullite (Al₆Si₂O₁₃) and calcium (CaCO₃). The results of XRD analysis showed that
due to swelling, the phase composition of the studied samples changed. Expansive behaviour of fly ash based stabilizers can be therefore attributed to the formation of ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_12\cdot26(\text{H}_2\text{O})$ and thaumasite $\text{Ca}_6[\text{Si}(\text{OH})_6]_2(\text{CO}_3)_2(\text{SO}_4)_2\cdot24\text{H}_2\text{O}$.

XRD analysis of fly ash-based stabilizer extracted from structural layer of trackbed from the trial section showed that most of the fly ash material is represented by $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ particles, with variable $\text{Ca}$, $\text{Fe}$, $\text{Mg} +/- \text{Ti}$ and $\text{K}$ contents. The particles are mostly porous with many "bubbles", or smaller spherical particles are present. Heavy particles are $\text{Fe}$ oxides and silicates, or they are rich in $\text{Ti}$. Other particles consist of amorphous glass, some of them contain automorphic, sometimes skeletal growths of $\text{Fe}$ (magnetite) oxides. To a small extent, $\text{Fe}$ sulphide (corresponding to pyrhotine) is present in these particles.

**Raman’s spectroscopy**

All of the analysed samples were in the form of a coarse powder material consisting of a complex mixture of minerals and amorphous phases. This fact is reflected in the obtained spectra which, even when a microscope and a micrometric laser track is used, often contain Raman strips of several different minerals. Using a 785 nm wavelength laser often has a large amount of luminescence/fluorescence, which corresponds to previous experience in analysing similar samples containing anhydrite or silicate minerals. This luminescence can be caused by the presence of trace amounts of elements from the REE group and sometimes completely overlaps the Raman’s mineral signal. The presented spectra (Figures 4 and 5) are therefore cases where negative fluorescence occurred only to a limited extent. In the spectra obtained from the sample from Ledvice power station (Figure 4A) before swelling, the following minerals were identified in the white base mass: anhydrite, aragonite/calcite, portlandite. Quartz has also been identified. Dark minerals have been identified as anatas and hematite. In addition to the Raman strips corresponding to the aragonite/calcite, basanite, quartz, and anatase minerals, the strip 988 cm$^{-1}$ was identified in the samples obtained from Ledvice power station (Figure 4B, C) after swelling and from Ledvice power station with addition of milled fluid fly ash (Figure 4D), which corresponds to the ettringite mineral. This strip is related to symmetrical valence vibration in $\text{SO}_4$ tetrahedra and corresponds to a reference value of 988 cm$^{-1}$ (Deb et al., 2003). Other Raman strips of ettringite have much less intensity and were not detected in the samples.

Samples from Tisová power station were also analysed. In the sample of fluid fly ash from Tisová power station before swelling (Figure 5A), the calcite, anatase, anhydrite and portlandite minerals were clearly identified. The aragonite was dominated by spectra obtained from the sample taken after swelling from the outside of the base of the test form (Figure 5B). Significant changes, however, were recorded in the spectra obtained from the sample from Tisová power station after swelling. As can be seen from Figure 5C, D spectra are dominated by a strong Raman strip at the 900 cm$^{-1}$ position. This strip shows the presence of thaumasite and ettringite minerals. Additional bands corresponding to the thaumasite mineral were identified at 1072, 658 and 454 cm$^{-1}$, and for the ettringite mineral at 605, 553 and 454 cm$^{-1}$. Figure 5D shows a spectrum of almost exclusively thaumasite, and the positions of the Raman strips are in very good agreement with the reference values (Brough and Atkinson, 2001). The strip at 1074 cm$^{-1}$ (1072 reference value) is assigned to a symmetrical valence vibration of the $\text{CO}_3$ group, the 991 cm$^{-1}$ (990) strip corresponds to the symmetrical valence vibration of the $\text{SO}_4$ group, and the 659 cm$^{-1}$ (658) to the vibration of the $\text{Si}(\text{OH})_4$ group. Strips at 455 and 422 cm$^{-1}$ are probably to exhibit a deformation vibration of the $\text{SO}_4$ group.

**Conclusions**

The strip at 1074 cm$^{-1}$ (1072 reference value) is assigned to a symmetrical valence vibration of the $\text{CO}_3$ group, the 991 cm$^{-1}$ (990) strip corresponds to the symmetrical valence vi-
bration of the SO₄ group, and the 659 cm⁻¹ (658) strip to the vibration of the Si(OH)₆ group. Strips at 455 and 422 cm⁻¹ are probably to exhibit a deformation vibration of the SO₄ group.

From the results obtained from the XRD method and the Raman spectroscopy analysis, it is clear that the samples after swelling from Ledvice power station contain the newly formed ettringite mineral, and the samples after swelling from Tisová power station contain a larger amount of newly formed thaumasite mineral and a smaller amount of ettringite mineral. As for the realization of the fly ash stabilizer layer in the sleeper structure, all requirements of the SŽDC S4 regulation are still fulfilled after more than 10 years of implementation. The ash stabilizer layer performs its protective and insulating function in the structure and does not show a vertical alignment by measuring the track geometry parameters, which means that the stabilizer does not swell.

One of the ways to avoid the creation of ettringite and consequently the degradation of road construction layers is to use suitable additives. By performing the above-mentioned experiments, it has been shown that by adding additives, especially micronized fly ash or micronized dolomitic limestone, volume changes can be significantly reduced. When installing CCPs into the ground, other factors, especially the geological, hydrogeological and mechanical properties of the underlying earth, must be considered. An additional saturation of the earth structure with built-in CCPs with water can cause a further increase of the newly formed sulphate and carbonate crystals, which can cause a degradation of the road construction layers.

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Literatura – References


Zakres wykorzystania ubocznych produktów spalania węgla w infrastrukturze transportowej


Słowa kluczowe: spalanie węgla, popioły lotne, struktura gruntu, infrastruktura transportowa, zmiany objętości, ettringit