Marls as an Ecological Substitute for Cement with Lower Energy Consumption. Mortars Research

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Abstract

This work suggests how to reduce the negative impact of cement production on the natural environment. Marl rock was milled to granulation less than 1 mm, dried at 105°C, calcined at 800°C and 1000°C. The mass content of clay phase in marls was 16%, calcium carbonates 75%. Mortars of marl (m) and cement (c) in m:c proportions of 50:50, 30:70, 25:75 and 0:100 were made, in order to compare their compressive strength values after 1st, 4th and 15th week of hardening. The compressive strength of samples using marl calcined at 1000°C and dried at 105°C were similar, but lower than in the case of samples with marl calcined at 800°C. Unlike in other cases marl calcined at 800°C contained 34% of the amorphous phase. The obtained strength values ranged from 20 to 75% in relation to the cement reference samples. These low values were caused due to granulation of the marl, dilution effect, presence of non-binding phases or mechanically weak hydrates, weak microstructure of the dried and calcined marls themselves. Although these mixtures are not suitable for high-performance concrete, they had warm colour and texture that may be useful in the reconstruction of architectural details or for other decorative purposes.

Keywords: *marls, ecological cement production, sustainability, calcination, compressive strength, architectural use*

1. Introduction

The production of cement clinker is extremely energy-intensive and has a large carbon footprint. As concrete production grows worldwide, more ecological solutions must be sought. In the era of decreasing amounts of industrial pozzolan resources and deficit of hydraulic additives, marls, the rocks that are mixtures of clays and carbonates, are the hope for reducing costs in cement industry. Manufacturing instability in the steel and energy industries caused by europe's move towards a zero-emission economy has consequences for the cement industry, as well. Regardless of the future legal conditions, the most ecological solutions for energy consumption and deposit exploitation should be sought. Replacing clinker in cement with non-clinker components is an effective way to reduce greenhouse gas emissions. In the era of decreasing pozzolanic resources of combustion by-products (e.g. silica fly ash) and hydraulic additives (ground granulated blast furnace slag), more and more attention is now being paid to calcined clays, clay minerals and even marls (Kurdowski 2022). Marls are a raw material in the production of cement clinker, although separately they can be sintered at lower temperatures than 1450°c, and depending on the phase composition, they can constitute a very effective pozzolan, because marls are sedimentary rocks, transitional between carbonate and clay, occurring in nature in quite large quantities. The well known diagram regarding the quantitative ratios of the most important sedimentary rocks (sand-clays-limestone), marls occupy the middle field (Turnau-Morawska 1954), which means that their deposits are quite heterogeneous. It is generally assumed that marls contain 75–25% clay phase and 25–75% calcium carbonates. However, there are also other classifications. For example, according to haldar (Haldar 2014), marl is considered a rock containing from 20% to 80% clay and from 80% to 20% calcite. Therefore, due to the amount and type of clay and carbonate phases and the SiO_2 content, there is a huge variety of marls in the world. Geological and chemical variability also occurs within a given deposit. Consequently, different calcined and hydrated marl mixtures will have different chemical and phase compositions (Danner 2019, Bahhou 2021). Even though the content of the clay phase in marl may be high, it is the so-called "bad clay" due to the content of calcium carbonate. Such a raw material is undesirable in the production of ceramic materials (e.g. fired clay bricks). Marls are the main raw material in the production of portland clinker. They can also become efficient pozzolana after calcination, containing both a dehydroxylated clay phase and calcium compounds obtained as a result of calcination of calcite. Marl can also be used to produce mixed portland cements (Kurdowski 2022, Bahhou 2021).

Calcined, or sintered marl, is a marl rock that has been thermally activated. The most commonly used calcination temperatures range from 700 to 900°C. Under such conditions, the calcium and magnesium carbonates present in the marl thermally dissociate according to the equations (Bahhou 2021):

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \quad (1)$$

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \uparrow \quad (2)$$

The consequence of which is the emission of carbon dioxide, which should be captured and used. The ecological friendliness of the production of such binders consists in the use of lower calcination temperatures, compared to the temperatures needed to prepare portland clinker. Then, the marl prepared in this way can be added to cement, but it can also act as a binder on its own, depending on its pozzolanity (Østnor 2014).

Tab. 1. Characteristics of MG marls preparation
Tab. 1. Charakterystyka preparatu MG marls

Marl name	Method of drying, calcination and grain size
MG.105.S3	Drying to constant weight at 105°C. Grain size 0.25-0.5 mm before calcination
MG.800.M4	Calcination at 800°C for 30 minutes. Grain size < 1mm before calcination
MG.1000.M4	Calcination at 1000°C for 30 minutes. Grain size < 1mm before calcination

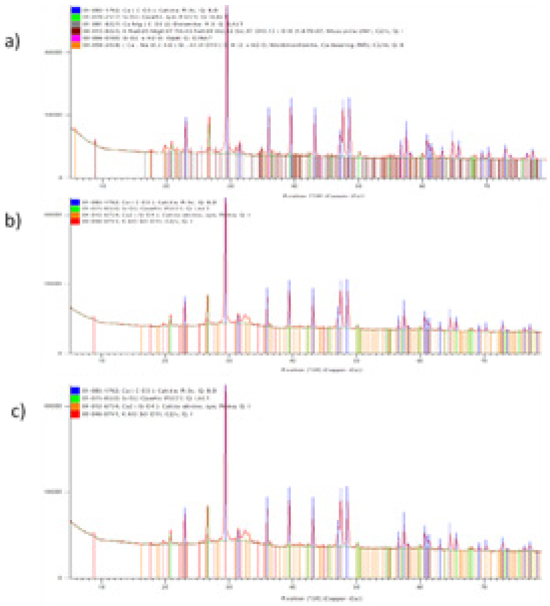


Fig. 1. Diffractograms of marl: a) dried, named MG.105.S3; b) calcined at 800°C, named MG.800.M4; c) calcined at 1000°C, named MG.1000.M4
Rys. 1. Dyfraktogramy margli: a) suszonych, o nazwie MG.105.S3; b) kalcynowanych w temperaturze 800°C, o nazwie MG.800.M4; c) kalcynowanych w temperaturze 1000°C, o nazwie MG.1000.M4

The mixtures with a similar composition, but three-component, called lc3, with lime, calcined clay and clinker with gypsum are examined by prof. Scrivener and her team (Scrivener 2017). The share of clinker substitution in these cements is up to 50%, and in the hardened state they have desirable and satisfactory properties. However, each of these substrates is sintered separately. Marl, in turn, is a rock consisting of these two phases – clayey and carbonate, so an effective calcination temperature should be sought for each type of marl rock. The binder should contain active silica from clay dehydroxylation and lime oxide from carbonates dissociation, calcination – according to equations (1) and (2) (Danner 2019, Bahhou 2021).

There is not much research on marl, and each deposit has a different composition, but it is known that marl roasted to the appropriate temperature is an effective pozzolan that ensures adequate strength of mortars (Kurdowski 2022, Bahhou 2021, Østnor 2014). In a sense, it can actually be said that marl research is local research. Calcined marl is called “ordinary blue clay” containing calcium carbonate. According to research by østnor and justnes (Østnor 2014), mortars in which the cement was replaced by calcined marl by volume at the levels of 0, 20, 35, 50 and 65% obtained satisfactory strength values both on the 1st and 28th day in relation to the reference values. For example, replacing 50% of the volume of cement gave a compressive strength of 63 mpa after a year (Østnor 2014). However, the calcination conditions of this marl are unknown, although it is known that it contained only 20% calcium carbonates and 70% clay minerals, and the rest was quartz and feldspar. It seems that this composition of marl is very beneficial and undoubtedly broaden the variety of available supplementary cementitious materials (SCMS) especially with the accessibility of this type of material in the world (Bahhou 2021). Marls are often waste during the extraction of minerals, such as brown coal, for example in Southern Poland, but they also accompany phosphate sedimentary deposits (Poussardin 2022) and contain a quite unusual clay phase, palygorskite ($(Mg,Al)_2$-$Si_4O_{10}(OH)\cdot 4H_2O$, 2:1 clay), which dehydroxylates at 600°C. The suitability of this calcined marl as an SCM has been tested in mortars at 20 wt% portland cement replacement. Specimens revealed nearly the same compressive strengths after 7 and 28 days as the reference made of pure portland cement (Poussardin 2022). The results of the study by mahdi et al. (Mahdi 2022) showed that the pozzolanic reactivity of marls increased with the formation of an amorphous phase during the calcination of clays containing large amounts of calcite. The resulting amorphous phase leads to structural disturbance and depends mainly on the clay mineralogy (Mahdi 2022). However, Bahhou et al. observed that the pozzolanic activity of marl decreased when the sintering temperature exceeded 900°C. This was related to the crystallization of inactive phases, for example gehlenite, and other calcium and magnesium phases (Bahhou 2021). Therefore, the appropriate method of activation must be selected separately for each type of marl. Marl can be activated thermally, mechanically and chemically. Thermal activation leads to the parallel decomposition of calcium carbonates, which results in the formation of lime and small amounts of poorly crys-

Tab. 2. Phase composition of marls and cement

Tab. 2. Skład fazowy margli i cementu

Phase	**Chemical formula**	**Content, %mas.**			
		MG.105.S3	**MG.800.M4**	**MG.1000.M4**	**CEM I 52,5 R**
Montmorillonite	$Al_2O_3 \cdot SiO_2 \cdot nH_2O$	7.7	-		-
Dolomite	$CaMg(CO_3)_2$	2.7	-	-	-
Opal	$SiO_2 \cdot H_2O$	1.2	-	-	-
Illite Muscovite	$K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$: $KAl_2(AlSi_3O_{10})(OH)_2$	8.1	1.9	-	-
Quartz	SiO_2	5.7	5.7	3.5	-
Calcite	$CaCO_3$	74.6	53.6	11.2	-
γ-C_2S calcio-olivine	$2CaO \cdot SiO_2$	-	6.7	3.3	-
β-C_2S Larnite (belite)	$2CaO \cdot SiO_2$	-	-	30.0	11.1
Spurite	$Ca_5(SiO_4)_2(CO_3)$			5.0	
Portlandite	$Ca(OH)_2$	-	-	11.7	-
Gehlenite	$Ca_2Al_2SiO_7$			6.8	
C_3S (alite)	$3CaO \cdot SiO_2$	-	-	17.8	64.5
C_4AF Brownmillerite	$2CaO \cdot (Fe,Al)O_3$	-	-	10.6	8.9
C_3A	$3CaO \cdot Al_2O_3$	-	-	-	9.8
Gypsum	$CaO \cdot SO_4 \cdot H_2O$	-	-		2.6
Bassanite(Na)	$Ca_{0,98} \cdot Na_{0,03} \cdot SO_{4(0,47)} \cdot H_2O$	-	-	-	2.6
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$				0.6
Amorphous	~ ~	-	33.6	-	-

tallized belite (β-Ca_2SiO_4), therefore producing a dual system with pozzolanic and a hydraulic component in one (Bahhou 2021). After reaction of the calcined marls with water, ch is forming which reacts further with the amorphous phases produced by calcination of the clays. C-(A)-S-H is forming, as the main hydrate phase. According to 29Si NMR measurements approx. 30% of the silicon was present in the C-(A)-S-H phase after seven days of hydration and roughly 60% after 180 days (poussardin 2022). Chemical activation was applied by Mabroum et al. (Mabroum 2023), who presented the possibility of making cementless, alkali-activated binders from marl calcined at 650°C, 750°C and 850°C, and the highest strength, of 38 MPa, was obtained after 120 days of curing with marls calcined at 750°C. This kind of marls were characterized by a high content of silicon, magnesium and calcium, and a trace amount of aluminum. As can be seen, calcination temperatures of marls are much lower than during cement production, so less energy is needed to sinter this raw material. Therefore it would seem that this solution is more ecological, however, the CO_2 footprint of alkaline activator production in the total ecological calculation should be considered as well.

Marls are a raw material in cement production, during which the entire batch is calcined at a temperature of 1450°C. In this work the assumption of reducing costs based on the use of marl additives, ground in a shorter time and calcined at a lower temperature than cement clinker. The use of marl as a cement substitute will also reduce the carbon footprint associated with the transportation of cement substitutes from other industries, as the marl mine is located close to the cement plant. Due to the fact that it is not known how plasticizers interact with the clay phase, their addition was abandoned. This influenced the excessive use of water, as might be expected. It was decided to examine what effect would be achieved in order to preparation ecological mortars with coarse-grained cement supplements. The aim of this work was realized through investigation the differences in the phase composition of dried and calcined marls, and then to characterize the differences in the obtained compressive strength values of mortars prepared from marls: dried at 105°C or calcined at 800°C or 1000°C.

The mixtures were also differentiated in terms of marl content (m) in relation to the mass of cement (c). Mortars with m:c = 25:75, 30:70, 50:50 were prepared. Marls had a granulation larger than that of cement (< 1 mm), which was supposed to be justified by reducing the costs of energy consumption needed in the grinding process (without the use of grinding additives). The choice of the temperature of 800°C was justified by the formation of the glass phase at this temperature, while avoiding the recrystallization of new minerals (Bahhou 2021). Temperatures: 105°C and 1000°C were selected for comparison purposes. Another attempt to reduce energy costs involved a short calcination time in a ceramic furnace of 30 minutes. The study also suggests potential future research directions.

2. Methods

In order to examine the phase composition of cement and marls prepared at temperatures of 105°C, 800°C and 1000°C, diffractometric and thermo-gravimetric methods were used. The tests were carried out in the X'Pert Pro MPD diffractometer by PANalytical. Qualitative analysis was performed using HighScore v4.9 software and the ICDD PDF4+ database. The phases were quantitatively determined using the Rietveld method using the Siroquant computational program. The amorphous phase in calcined marl was determined by the Rietveld method with the addition of an internal standard for the quantitative determination of the amorphous phase. Spinel $MgAl_2O_4$ was added as an internal standard.

In order to determine the range of characteristic phase transformation temperatures of the tested raw materials, thermal tests were carried out. The DTA, DTG and TG techniques were used, using a Hungarian Paulik-Paulik-Erdey derivatograph, while maintaining the following measurement conditions: heating rate: 10°C/1min, atmosphere: air, reference substance: Al_2O_3, TG: 500 mg, DTG: 1/15, DTA: 1/10; ms (sample): 500 mg.

Microscopic observations of the microstructure of the polished specimen sections reflected the mechanical conditions of the mortars. In order to examine polished sections with a SEM (scanning electron microscope), samples were vapor-coated with carbon. During this work, the scanning electron microscope EVO MA 15 from Zeiss was used, which is equipped with a Zeiss backscatter electron detector (BSE) and an INCA DryCool detector (X-ray EDS chemical microanalysis) from Oxford Instruments.

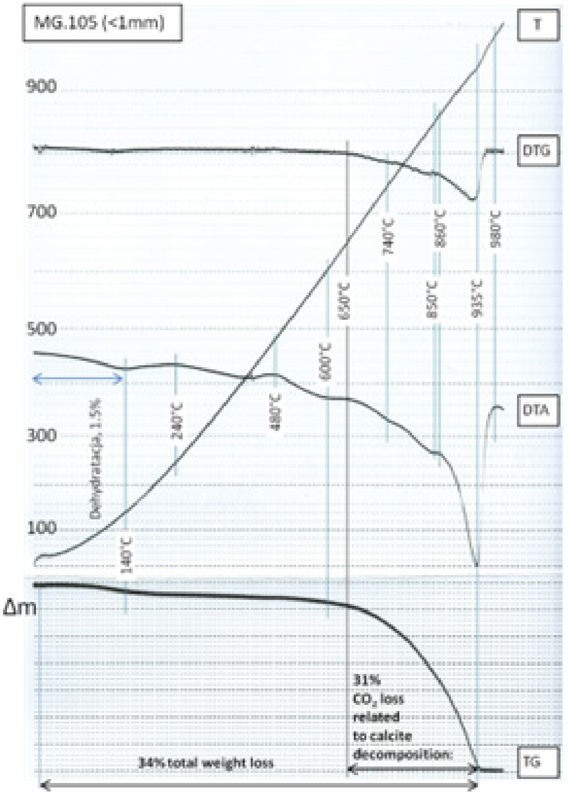


Fig. 2. DTA, DTG, TG Thermograms of MG marl dried in 105°C
Rys. 2. Termogramy DTA, DTG, TG margla MG suszonego w 105°C

3. Materials

Mortars were made in the standard ratio of binder to sand = 1:3 (according to EN 196-1), the amount of water was dosed according to the workability of the mortars. Mortar samples were made using marl and CEM I 52.5R cement, which together were considered to be a binder components. The proportions of marl to cement (m:c) were selected as in the standards for testing the hydraulic activity index (EN 15167-1) m:c = 50:50, for testing the pozzolanic activity index (EN 450-1) m:c = 25: 75 and water demand (PN-EN 450-1) m:c = 30:70. The consistency of the mortars was also checked using a flow table (PN-EN 1015-3).

The marls came from the Chalk Marl Mine (of Cretaceous era) in Southern Poland, where were initially crushed to a granulation of approximately 10 cm and delivered for testing and was abbreviated with the symbol "MG". The MG marls were then dried in a building materials dryer, crushed in a jaw crusher with a jaw spacing of up to 1 cm, dried again to constant weight, and then milled in a Los Angeles drum. Milled material was sieved through a set of sieves to obtain several fractions.

The process of marl roasting in steamers in a ceramic furnace consisted of heating for 3 hours, sintering for half an hour at a target temperature of 800°C or 1000°C, and unforced cooling to 25°C. It was decided to use a short calcination time for economic and ecological reasons and to examine its stimulation effectiveness. The method of marl preparing is presented in Table 1.

The tests used distilled water and secured and stored in tightly closed containers:

- marl rock
- Portland cement CEM I 52.5R (EN 197-1)
- standard sand from Kwarcmix (certified for compliance with EN 196-1).

The results of XRD tests of the phase composition of marls are presented in Fig. 1. The phase composition of marls and cement is presented in Table 2. The main phase of dried marl was calcite, muscovite and montmorillonite. The main phase of marl calcined at 800°C was calcite and the amorphous phase, and illite (muscovite) existed in the dedehydroxylated form. Montmorillonite, dolomite and opal were no longer present in the marl calcined at 800°C. At this temperature γ-C_2S appeared, the amount of which decreased in the sample roasted in 1000°C. Consistently, the content of β-C_2S has increased significantly, mainly at the expense of the amorphous phase. In turn, the main phases of marl calcined at 1000°C were belite and alite with disturbed structures, portlandite and calcite.

The presence of alite obtained at such low temperatures is not confirmed by literature data, but it is not rhombic alite, which occurs in Portland clinker, but its monoclinic polymorph JII. Alite polymorphs are described in more detail by Kurdowski, among others, in (Kurdowski 1981, 2003, 2014). Kurdowski also describes research on the formation of alite at the interface of SiO_2 and CaO as a result of diffusion, and not crystallization from the melt (Kurdowski 2014). This issue is further developed in the "Discussion" section. MG.1000 did not contain lime, only portlandite, because calcium oxide obtained by firing limestone at a temperature lower than 1050°C reacts very quickly with water. This is the so-called soft quicklime. Hydration probably occurred during unforced cooling of the ceramic furnace and sample preparation in air (Kurdowski 1981).

Tab. 3. Endothermic and exothermic effects of minerals, according to (Hatipoğlu 2010, Wyszomirski 2007, Borkowska 1973)

Tab. 3. Efekty endotermiczne i egzotermiczne minerałów według (Hatipoğlu 2010, Wyszomirski 2007, Borkowska 1973)

Reaction extreme temperatur, °C	**Endothermic effect**	**Exothermic effect**
140	Mica (illite): dehydration	
240		Organic substance: oxidation - combustion
480		Effect demonstrated by selected types of Kaolin, decomposition of organic matter
600	Kaolinite: dehydroxylation	
650	Calcite: the beginning of decomposition	
740	Decomposition of dolomite into MgO, CaO and CO_2 with simultaneous formation of $CaCO_3$	
850	Montmorillonite: dissociation - disintegration of the crystal lattice	
860		Formation of spinel from montmorillonite
935	Calcite: dissociation associated with the release of a gas phase - decomposition of carbonates	
980		Kaolonite: synthesis of the spinel phase

Tab. 4. Differences in weight loss during sintering and TG tests

Tab. 4. Różnice w utracie masy podczas spiekania i testów TG

Marl	**Calcination temperature, °C**	**Loss of weight in the oven, %mas.**	**Loss of weight according to TG, %mas.**	**Obtained material**
MG.105	800	12.5	11	MG.800.M4
MG.105	1000	29.3	34	MG.1000.M4

Tab. 5. Characteristics of mortar mixtures

Tab. 5. Charakterystyka mieszanek zapraw

Specimens name	**Marl preparation temperature, °C**	**Marl (m) %mas.**	**Cement (c) %mas.**	**The amount of water in relation to the binder (b=m+c) w/b**	**The amount of water in relation to marl (w/m)**	**Flow, cm**
Z0-cem	-	0	100	0.5	-	18.0
Z23.MG105(W)	105	30	70	0.62	0.89	16.7
Z24.MG105(AH)	105	50	50	0.64	0.78	16.0
Z25.MG105(AP)	105	25	75	0.57	0.80	15.8
Z29.MG800(W1)	800	30	70	0.6	0.82	18.5
Z32.MG800(W2)	800	30	70	0.55	0.68	16.0
Z30.MG800(AH)	800	50	50	0.63	0.77	16.4
Z31.MG800(AP)	800	25	75	0.56	0.74	17.5
Z26.MG1000(W)	1000	30	70	0.86	1.70	17.0
Z27.MG1000(AH)	1000	50	50	0.80	1.09	16.0
Z28.MG1000(AP)	1000	25	75	0.66	1.12	16.3

Based on the results of the X-ray analysis of the examined material from the marl mine dried at 105°C, it appears that over 77% of its content are carbonate phases and less than 16% of the mass share are clay phases. Therefore, according to the previously given classification (Turnau-Morawska 1954), it can be concluded that the material is marly limestone. However, it will be called "marl", which corresponds to Haldar's classification (Haldar 2014).

The process of drying and calcining MG marl in the temperature range of 105–800–1000°C resulted in a reduction in the calcium carbonate content in the mass of the raw material from 74.6% to 53.6%, and then to 11.2% (according to XRD), respectively. It should be emphasized, however, that these are relative values, each time referring to a new mass after calcination. Compared to the initial sample, MG.105, these losses are larger.

The DTA/TG/DTG thermograms presented in Fig. 2 indicate the transformations described in Table 3. First of all, the mass loss caused by roasting was examined, but thermo-gravimetric tests also help determine the method of phase formation. It should be noted that thermal analysis of multiphase materials is difficult and therefore should be supported by the results of diffractometric tests.

The most important mass loss in the MG.105 sample resulting from the thermal dissociation of calcite (reaction 1) according to the thermograms (Fig. 2) was 31% of the sample mass, with the total mass loss of the sample equal to 34%, up to a temperature of 1000°C. Based on diffractometric studies, gamma-C_2S was present in the sample calcined at 800°C. The most likely substrates for C_2S synthesis were, among others, dissociated opal, which according to (Małolepszy 2022) reaches its maximum decomposition between 342°C and 722°C, and montmorillonite, which decomposes in the range from 650°C to 750°C (Hatipoğlu).

The γ-C_2S has no hydraulic properties and may be formed during cooling from the β-C_2S in 500°C (Kurdowski 1981). However, it is also known (Kurdowski 2003) that the reaction of calcium carbonate with silica starts at 500°C, so dicalcium silicate appeared as the first clinkerization product. Larnite (belite, β-C_2S) is formed in a range of 675–1450°C temperatures (Bolewski 1975). Noticeable weight loss started from a temperature of about 550°C and amounted to 33% up to a temperature of 935°C. This was mainly related to the decomposition of calcite at the level of 31% from a temperature of 650°C to 935°C, according to (Wyszomirski 2007). Thermal curves of quartz show a clear endothermic effect corresponding to the polymorphic transformation of β-quartz into α-quartz, usually occurring at a temperature of 573°C, according to (Hatipoğlu 2010). However, in the case of these studies, it coincides with the endothermic effect of kaolin dissociation. An organic substance is usually marked on DTA curves in the form of an extensive exothermic combustion effect, which is accompanied by a loss of mass. This effect was compensated by an endothermic effect corresponding to the dehydroxylation of clay phases. As a consequence, weight losses were obtained: 2.5% in the temperature range of 200÷500°C and 0.5% up to 650°C, according to (Hatipoğlu 2010).

In the case of the analyzed thermogram, this effect is not extensive, but is shown in the form of two larger ones, probably due to the presence of sulfur and iron compounds, ac-

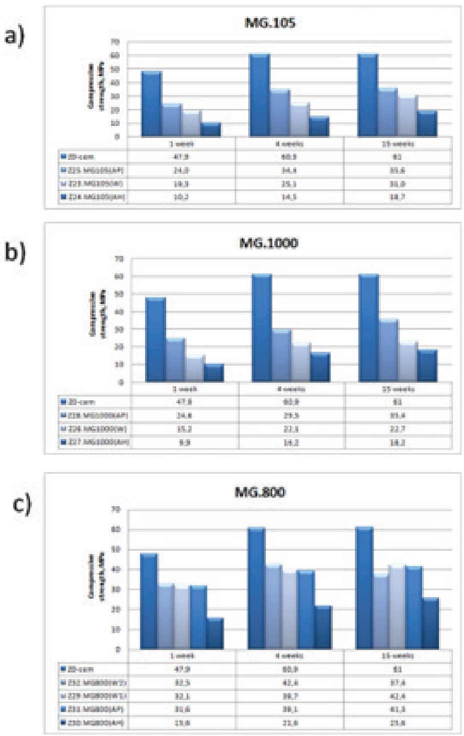


Fig. 3. Comparison of compressive strength after 1, 4 and 15 weeks of marl-cement mixtures hardening with marls:
a) dried, b) calcined at 800°C, c) calcined at 1000°C

Rys. 3. Porównanie wytrzymałości na ściskanie po 1, 4 i 15 tygodniach mieszanek cementowo-marmurowych utwardzanych marglem:
a) suszonym, b) kalcynowanym w temperaturze 800°C, c) kalcynowanym w temperaturze 1000°C

cording to (Hatipoğlu 2010) (the raw material contains 1.35% Fe_2O_3 and 0.16% S). Endothermic effects are also observed in the loss of water from montmorillonite, between 100°C and 250°C, indicating the separation of interpack water, and 450–500°C, reaching a maximum at 700°C, indicating the separation of constitutional water, according to (Borkowska 1973). At a temperature of 740°C, the endothermic effect concerns the formation of an additional amount of calcium carbonate from simultaneously thermally degraded dolomite:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \rightarrow CaCO_3 + MgO + CO_2$$

Then, endothermic (at 850°C) and exothermic (at 860°C) effects occur, which are related to the breakdown of the montmorillonite structure and then spinel is formed (Borkowska 1973).

The endothermic extreme at 935°C indicates the decomposition of calcite. Above 940°C, the mass did not change, but a well-developed exothermic peak on the DTA curve at 980°C is the result of the formation of spinel or other phases from the decomposition of illite and montmorillonite.

Attention was also paid to the differences in mass loss in gravimetric tests of portions of marl roasted in the furnace in relation to the mass loss observed during TG tests. Table 4 below shows a comparison, therefore it is recommended to diffractometrically test the material after calcination and not rely solely on the thermogravimetric test result.

4. Preparation of Mortar Mixtures for Strength Tests

Table 5 shows the composition of the prepared mortar mixtures. Each time, the total amount of marl and cement (m+c) was 450 grams, and the standard sand was 1350 grams (according to EN 196-1). Water was added in varying amounts depending on workability. The proportions of marl to cement (m:c) were selected in the ratios 50:50 (designation AH), 25:75 (designation AP) and 30:70 (designation W). Table 5 also shows the ratio of water to marl (w/m) assuming that w/c = 0.5. Mixing consisted of first combining the marl with water, 225 grams of water each time, and mixing for 3 minutes, then adding cement and mixing for another 3 minutes. During adding sand, additional amounts of water had to be poured in, in the same time, due to difficulties in workability of the mixtures and was stopped when the desired consistency was achieved. Flow was determined after 11 minutes of mixing.

In the case of one of the mixtures, a smaller amount of water was deliberately added, which was marked as W2 in the name (Table 5). The smaller amount of water in Z32.MG800(W2) compared to Z29.MG800(W1) consequently resulted in reduced flow. It was noticed that the highest water demand was for marl calcined at 1000°C, and the lowest for marl calcined at 800°C (Table 5).

The bars were demolded after 7 days and their strength was immediately tested. Then they were stored in string bags to prevent carbonation and water evaporation. Water could be used for further hydration reactions. Compressive strength was tested after 1, 4 and 15 weeks of hardening.

5. Results and Analysis of Strength Tests

Figure 3 show the compressive strength values after 1, 4 and 15 weeks for mixtures with marl at the selected preparation temperature. Table 6 shows the percentage of the strength of mortars in relation to 100% of the strength of mortar made of cement - the reference sample at a given curing time. Figure 4 summarizes all the results, and Fig. 5 show only the results

Tab. 6. Percentage of the strength of the base mixture (Fig. 3)
Tab. 6. Procent wytrzymałości mieszanki bazowej (rys. 3)

Sample name	**Percentage value of compressive strength, %**		
	1 week	4 weeks	15 weeks
Z0-cem	100.0	100.0	100.0
Z25.MG105(AP)	50.1	56.5	62.1
Z23.MG105(W)	40.3	41.2	54.0
Z24.MG105(AH)	21.3	23.8	32.6
Z31.MG800(AP)	66.0	64.2	72.1
Z29.MG800(W1)	67.0	65.2	74.0
Z32.MG800(W2)	67.8	69.6	65.2
Z30.MG800(AH)	32.6	35.5	44.7
Z28.MG1000(AP)	51.4	48.4	35.1
Z26.MG1000(W)	31.7	36.3	22.7
Z27.MG1000(AH)	20.7	26.6	18.2

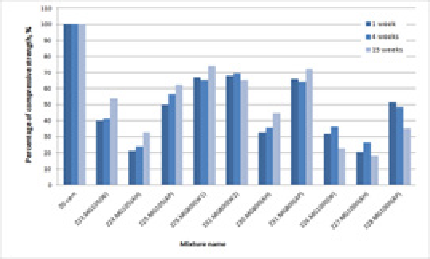


Fig. 4. Comparative compressive strength values of all tested samples
Rys. 4. Porównanie wartości wytrzymałości na ściskanie wszystkich badanych próbek

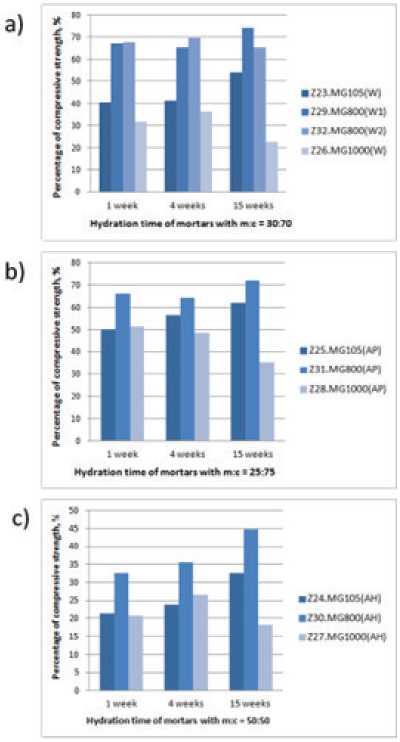


Fig. 5. Comparison of the strength values of mixtures with: a) m:c = 30:70, b) m:c = 25:75, c) m:c = 50:50
Rys. 5. Porównanie wartości wytrzymałości mieszanek: a) m:c = 30:70, b) m:c = 25:75, c) m:c = 50:50

for specific m:c ratios in the mixtures. The terms pozzolanic activity testing or hydraulic activity testing of calcined marls are not used because marls were not milled to the appropriate standard granulation.

None of the cement-marl mortar strength values were greater than the value of cement mortar strength. In the case of mixtures using marl dried at 105°C and calcined at 1000°C (Fig. 3a and 3c), logically the highest strengths had samples marked AP (where m:c = 25:75) and W (where m: c = 30:70), because they contained the most cement, while the lowest compressive strength values were obtained for AH samples (where m:c = 50:50) – Table 5. It is worth noting that the strength values of samples containing marly rocks calcined at 1000°C or dried at 105°C were almost the same, and sometimes even higher in the case of those containing MG.105 marls. In turn, mixtures containing rock calcined at 800°C, MG.800, were characterized by the highest values of compressive strength.

The development of the strength of Z29.MG800(W1), Z32.MG800(W2), Z31.MG800(AP) mixtures is interesting. The visible great similarity between Z29.MG800(W1) and Z31.MG800(AP) suggests that there is a slight difference be-

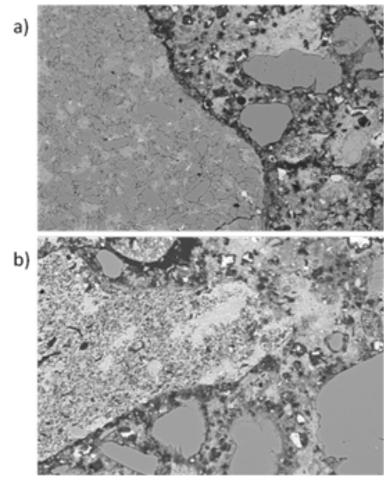


Fig. 6. Microstructure of mortar with m:c = 50:50. SEM-BSE photo taken at 500× magnification: a) marl grain dried at 105°C on the left, porous cement matrix with quartz on the right; b) marl grain roasted at 1000°C on the left, and a porous cement matrix with quartz grains around

Rys. 6. Mikrostruktura zaprawy o stosunku m:c = 50:50. Zdjęcie SEM-BSE wykonane przy powiększeniu 500×: a) ziarno margla suszone w temperaturze 105°C po lewej, porowata matryca cementowa z kwarcem po prawej; b) ziarno margla prażone w temperaturze 1000°C po lewej, porowata matryca cementowa z ziarnami kwarcu wokół

tween the amount of water and the m:c ratio. However, in the case of Z32.MG800(W2), the strength increased for up to 4 weeks, but later there was most likely no water left for further hydration reactions to occur. However, it is intended to repeat this study.

In order to illustrate the strength of the mixed samples in relation to the reference sample, the strength of which was tested at the same maturation time, a graph was made in Figure 4. Here it is clearly visible that only mixtures with MG.800, the m:c of which were 30:70 and 25:75 (W and AP), reached over 60% of the strength value of the reference sample.

In the group of samples with the ratio m:c = 30:70 (Fig. 5a), the compressive strength of samples from the series with dried marl Z23.MG105(W) was in the range of 40–53% of the reference sample and increased in time. The compressive strength of the MG.800 series samples was in the range of 65–74% of the reference sample and did not have a stable behavior. The compressive strength of the MG1000 series samples was in the range of 32–23% of the reference sample and first increased and then decreased during hydration compared to the reference sample.

A smaller amount of water in Z32.MG800(W2) compared to Z29.MG800(W1) resulted in an increase in strength in the first 4 weeks, and then, probably, the mixing water was needed for the reaction to occur, which in turn was reflected in the increase in the strength of the Z29.MG800(W1) mortar.

In the group of samples with the ratio m:c = 25:75 (Fig. 5b), the compressive strength of samples from the series with dried marl Z25.MG105(AP) was in the range of 50–62% of the reference sample and increased over time. The compressive strength of the Z31.MG800(AP) series samples was in the range of 64–72% of the reference sample and was growing. The compressive strength of the Z28.MG1000(AP) series samples was in the range of 48–35% and decreased during hardening compared to the reference sample.

In the group of samples with the ratio m:c = 50:50 (Fig. 5c), the compressive strength of samples from the series with dried marl Z24.MG105(AH) was in the range of 21–33% of the reference sample and increased over time. The compressive strength of the Z30.MG800(AH) series samples was in the range of 32–45% of the reference sample and increased over time. The compressive strength of the Z27.MG1000(AH) series samples was in the range of 27–18% of the reference sample and first increased and then decreased during hydration compared to the reference sample.

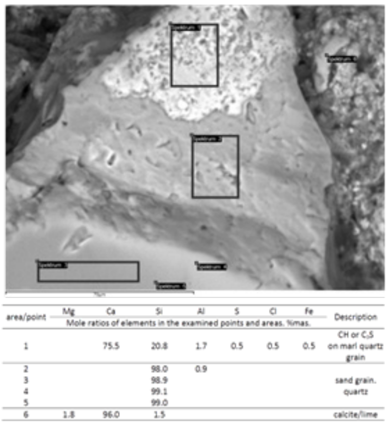
The obtained values did not exceed the requirements of the PN-EN 1567-1 standard for either 1 or 4 weeks of hydration, should be ≥45% and ≥70% of the strength of the reference sample, respectively.

The compressive strength of all mortars increased with hydration time. Strength increasing those with marl calcined at 1000°C were the slowest. This was probably the result of the largest share of CaO in the system, coming from marl roasted at 1000°C. This, in consequence, probably resulted in the formation of the largest amounts of portlandite, which significantly reduced the compressive strength of the tested samples. Moreover, the C-S-H phase could have been enriched with calcium, which also caused its weakening. On the other hand, this mixture was a cement-lime mortar, so its hardening required carbonation reactions, which were difficult because the samples were correctly insulated.

For such reasons, the hydration process should be monitored, at least by diffractometric technique, in order to draw more precise conclusions about the binding process. However, looking at an examplary microscopic image (Fig. 6a) of a mortar made with marl dried at 105°C, with mass quantity m:c = 1:1, it can be concluded that the larger the grain size of the marl, the lower the strength of the mortar will be, due to low strength of this sedimentary rock. Therefore, energy savings during grinding can be achieved depending on the needed compressive strength of mortars. The strength of marls decreases during calcination process because their porosity increases due to thermal decomposition of calcium carbonates. Porous marl grain calcined at 1000°C can be noticed in Fig. 6b, on the left.

6. Discussion

The fact that alite was detected in MG.800 can be controversial, so a discussion should be initiated on this subject. It



area/point	Mg	Ca	Si	Al	S	Cl	Fe	Description
	Mole ratios of elements in the examined points and areas. %mas.							
1		75.5	20.8	1.7	0.5	0.5	0.5	CH or C_3S on marl quartz grain
2			98.0	0.9				sand grain. quartz
3			98.9					
4			99.1					
5			99.0					
6	1.8	96.0	1.5					calcite/lime

Fig. 7. Quartz grain with calcium phase shell and EDS analysis. Mortar with MG.800
Rys. 7. Ziarno kwarcu z otoczką fazy wapniowej i analiza EDS. Zaprawa z MG.800

is possible that CaO formed in high concentration, as a result of calcination of marl, penetrated into the SiO_2 grains, but the calcination process was quickly interrupted, therefore the diffusion kinetics was inhibited. Therefore, transient, metastable C_3S crystallized at the edge or in the contact zone with SiO_2, what is probably shown in Fig. 7. This is how the obtained test result, which was also checked in another independent laboratory, can be explained. There was probably a rapid thermodynamic transformation of the CaO-SiO_2 system with a short-term temperature stimulus. However, if this result is not acceptable due to insufficient test data α'L-C_2S should be assumed to be detected. However, this phenomenon must be recognized more thoroughly.

Unlike most works, marls with much larger granulations than cement granulation were used, because it is known that granulation has a huge impact on their reactivity. It was therefore shown that marl added to cement caused a significant reduction in the strength of cement mortars, even below 50%. This applies in particular to mixtures with marl dried at 105°C and calcined at 1000°C, even though only 25%, 30% or 50% of the cement was replaced by it. The reason for this, among others, was a significant amount of water absorbed and not used by the marl for binding, which diluted the cement hydrates. The results of strength tests in the examined period up to week 15 suggest that the doses of marl added to the cement, with a grain size larger than cement, constituted a filler. The marls prepared in this way were insufficiently chemically active during the period under study, which may lead to the conclusion that such a waste of cement is not justified. A lime-cement mortar was produced from marls calcined at 1000°C, which lost strength as it dried, so it should work in a humid environment. An increase in strength of up to 14 weeks is not much for such mixtures. It is known that marl binders set much slower than cement binders (Danner 2019), therefore their strength should be further tested for at least 2 years, as recommended by the authors of the paper (Østnor 2014). However, in order to more precisely describe the processes occurring during hardening, changes in phase composition should be monitored. Marl is a rock consisting of limestone and clay, so an effective calcination temperature must be found for each type of marl.

It is difficult to conduct a detailed discussion on the research of marls from other mines because they are characterized by wide chemical and phase diversity. However, it is worth looking for similarities and establishing some common rules for creating mortars. These mortars do not have to be only a component of concrete, but can also serve architectural purposes due to their warm sandy or brick shade, like belite or roman cements (Gnisci 2022).

7. Conclusions

The paper describes research of the phase composition of marls and tests of the strength of cement-marl mortars. Marl with a large amount of calcium carbonates (75%) and a small amount of clay phases (16%) was used. The marls were calcined at 800°C and, for comparison, they were also calcined at 1000°C and dried at 105°C. The following conclusions were drawn.

- XRD spectra of calcined marls in 800°C showed that raw materials were converted mainly in amorphous phase and γ-C_2S
- XRD spectra of calcined in 1000°C marls showed that raw materials were converted mainly in larnite (β-C_2S), CH (portlandite), brownmillerite (C_4AF), alite (C_3S) or belite (α'L-C_2S), gehlenite ($Ca_2Al_2SiO_7$) and spurite ($Ca_5(SiO_4)_2(CO_3)$)
- The relatively large grain size of milled marls increased the demand for water in mortars due to the large development of their internal surface.
- The porosity of the marl grains increased as a result of calcination, especially at 1000°C.
- To improve the workability of mortars, larger amounts of water were added during mixing, which in turn led to the effect of diluting the clinker phases and consequently low strength of cement-marl mortars in relation to cement mortars.
- The carbonation-limiting method of curing cement-lime mortars prepared with marl calcined at 1000°C may have contributed to the reduced strength gain.
- The incomplete decomposition of calcium carbonate in calcined marls was a filler, not a binder in the mortar, in examination period.
- The total 55% mass content of alite and belite in the sample calcined at 1000°C did not give such a satisfactory effect as the almost 34% of the amorphous

phase in the sample calcined at 800°C. This statement mainly refers to the strength values of mortars with a higher cement content, i.e. W and AP.

- Marls prepared at temperatures of 105°C and 1000°C gave similar strength values of mortars up to 4 weeks of hardening, and then increased (MG.105) and decreased (MG.1000), respectively. Therefore, roasting at 1000°C with such granulation has no economic or ecological justification. Moreover, the demand for water for these mortars increased significantly, which was also the reason for low strength.
- The higher strength of mortars with dried marls (MG105) was due to the fact that calcium carbonate had greater strength than portlandite, which was created as a result of hydration of marl roasted at 1000°C (MG1000).
- Increasing the calcination temperature of marl, along with the loss of CO_2, increased the content of calcium and other elements, such as Al, Mg, Fe and Si, in the material.
- Initially, low strength values of mixtures with marl dried at 105°C increased faster during hydration, which could mean that the limestone filler acquired binding properties and was activated by alkali components of cement.
- Marls calcined at 800°C contained a very large amount of amorphous phase, therefore mixtures containing them had the greatest strength. Therefore, in subsequent tests, MG marls calcined at around this temperature (from 700°C to 900°C) should be used.
- The prepared mortars can be used in the reconstruction of monuments, for this purpose other properties (fracture, roughness, porosity) are needed than high mechanical strength.
- Further research should be aimed at optimizing the marl preparation process along with:
  - increasing the specific surface of marl and reducing the amount of added water
  - increasing the calcination time and varying temperatures in the range of 700–900°C
  - testing the pozzolanic activity of the prepared marls
  - determining the water demand of a given marl granulation
  - testing the concentration of calcium ions in the solution in the pores of the cement paste; which is related to the molar C/S ratio in the C-S-H phase
  - testing of free lime and volume stability
  - examining phase changes during hardening to explain changes in strength over time
  - recognizing quartz from marl and undecomposed calcite as a filler, not a binder component
  - preparing mortars with an additional amount of metastable clay phase, for example metakaolin or silica fly ash, because the calcined MG marl used in these studies contained too much carbonate phase and too little clay phases. It would also be worth considering adding an additional amount of gypsum to create ettringite and considering chemical activation to create a geopolymer matrix rich in lime without cement.

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Margle jako ekologiczny zamiennik cementu o niższym zużyciu energii. Badania nad zaprawami

Niniejsza praca sugeruje, jak zmniejszyć negatywny wpływ produkcji cementu na środowisko naturalne. Skała marglista została zmielona do granulacji mniejszej niż 1 mm, wysuszona w temperaturze 105°C, kalcynowana w temperaturze 800°C i 1000°C. Masowa zawartość fazy ilastej w marglach wynosiła 16%, węglanów wapnia 75%. Wykonano zaprawy z margla (m) i cementu (c) w proporcjach m:c 50:50, 30:70, 25:75 i 0:100 w celu porównania ich wytrzymałości na ściskanie po 1, 4 i 15 tygodniu twardnienia. Wytrzymałość na ściskanie próbek z marglem kalcynowanym w temperaturze 1000°C i suszonym w temperaturze 105°C była podobna, ale niższa niż w przypadku próbek z marglem kalcynowanym w temperaturze 800°C. W przeciwieństwie do innych przypadków, margiel kalcynowany w temperaturze 800°C zawierał 34% fazy amorficznej. Uzyskane wartości wytrzymałości wahały się od 20 do 75% w stosunku do próbek referencyjnych cementu. Te niskie wartości były spowodowane granulacją margli, efektem rozcieńczenia, obecnością faz niewiążących lub słabych mechanicznie hydratów, słabą mikrostrukturą samych wysuszonych i kalcynowanych margli. Chociaż mieszanki te nie nadają się do betonu o wysokich parametrach, miały ciepły kolor i teksturę, które mogą być przydatne w rekonstrukcji detali architektonicznych lub do innych celów dekoracyjnych.

Słowa kluczowe: *margle, ekologiczna produkcja cementu, zrównoważony rozwój, kalcynacja, wytrzymałość na ściskanie, zastosowanie architektoniczne*