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THE EFFECT OF THE POZZOLANIC ACTIVITY OF DIFFERENT MICRO-FILLERS ON PORTLAND CEMENT HYDRATION

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This study estimates the influence of the different pozzolanic activity micro-fillers on the hydration of Portland cement. Cements with binary blends of ordinary Portland cement and different micro-fillers (15 % by mass) were developed and their characteristics were investigated in terms of the fineness, chemical composition, mineral composition, setting time, particle distribution, hydration heat, water demand, changes in the mineral composition during the hydration, and the compressive strength. All the specific properties of the blended cement pastes were compared with the pure Portland cement paste. The study showed that the investigated micro-fillers (except for quartz sand) increase the initial hydration of the Portland cement. In addition to this, the inert limestone micro-filler mainly affects the initial hydration of the calcium silicates, whereas the pozzolanic active micro-fillers (calcined mica and kaolinitic clay and its mixture) affect both processes: the initial hydration of the calcium silicates and the reaction of the aluminate-bearing phase with the gypsum. The inert micro-fillers (especially limestone) are more effective at the early stage of hardening (up to 7 days), but later, after 28 days, the compressive strength of the samples directly depends on the activity of the micro-fillers. All investigated pozzolanic active micro-fillers promote the formation of the calcium silicate hydrates, however, only in the samples with the most active (kaolinitic clay) micro-filler after 28 days of hardening clearly identifies the pozzolanic reaction. In contrast to the active micro-fillers, the inert micro-fillers increase the amount of portlandite in the hardened cement paste.

INTRODUCTION

Most of the available studies on the properties of blended systems focus on the complex use of natural and artificial raw materials that lead to a significant reduction in CO_2 emissions per tonne of cementitious materials. Slag, silica fume, fly ash etc. are widely used in concrete either in blended cements or added separately in the concrete mix. A number of studies [1-5] have reported that various additives not only can lower the CO_2 emissions, but also improve its chemical, physical, and strength properties. In addition to this, the use of additives, such as micro-fillers, provides even greater opportunities to replace a part of the cement clinker in the cementitious systems. The researchers have stated that concrete provides microstructural changes due to the pozzolanic and filler action of the additives [6].

Although the main requirement for micro-fillers is the fineness, their impact on the cementitious systems also depends on many properties such as the pozzolanic activity, chemical or mineral composition, the method of preparation, and others. The micro-fillers are effective additives for Portland cement; however, in terms of their effect on the hydration of the Portland cement, differences of opinion still exist. Compared with ordinary additives, micro-fillers can be active or inert [7]. Inert micro-fillers are distinguished by their physical (filler) effect and do not change the qualitative composition of the cement hydrates, but can affect the rate of the hydration process [8]. Meanwhile, active micro-fillers react with the cement hydrates to form new compounds [8, 9]. In cementitious systems with micro-fillers, it is difficult to separate the effects of the physical and chemical origins. The study reports [4] that silica fume physically affects the concrete prior to its action as a pozzolanic material and the micro-filler effect enhances the strength of the concrete. Other researches show [5] that both the physical effect and chemical effect increase in the degree of the hydration and compressive strength. The research data on the effect of the fineness of the additives on their pozzolanic activity is quite different.

Cordeiro et al. [10] state that a clear correlation between the Chapelle reactivity and the fineness of sugar cane bagasse ash (SCBA) was observed and a direct relationship between the compressive strength of the mortar containing (SCBA) and the Blaine fineness of the ash exists. It was also reported [11] that the rice husk ash collected from a paper plant after grinding showed an accelerated activity compared to the silica fume. Another study [12] suggests that the pozzolanic activity of a mechanochemically activated biomass fly ash changes insignificantly.

Research [13] of the pozzolanic effect and the filler effect of the rice husk ash on the mechanical properties and microstructure of a brick aggregate concrete showed that the compressive strength, due to filler effect, are 58.56 - 94.62 % less compared to the pozzolanic effect for the 10 - 25 wt. % replacement of the cement. The tensile strength and flexural strength of the brick aggregate concrete due to the pozzolanic effect are 60 - 150 % and 25 - 150 % higher than that of the filler effect for the 10 - 25 wt. % replacement of cement, respectively [13].

A considerable amount of literature has been assigned to determine the influence of calcined clay additives on Portland cement properties. The kaolinite-rich clays are characterised by the best pozzolanic properties because calcined kaolinite obtains an active form – metakaolinite [14, 15]. Calcined kaolinite clay has proven to have very good pozzolanic activity and, therefore, it can drastically improve the strength and durability properties of the cement products [16]. In parallel, research into cement has brought attention to the pozzolanic properties of various calcined clay minerals: kaolinite, illite and montmorillonite. It was found [17] that the system containing calcined kaolinite was the most reactive, followed by calcined montmorillonite, which showed some reactivity at the later ages, and calcined illite, which functioned as an inert filler. The results of the investigation [18] revealed that the rates of the pozzolanic reaction and portlandite consumption in the silica fume-blended cement pastes are higher than in the illite clay-blended cement pastes. The scientists [17] concluded that kaolinite has the highest pozzolanic properties because of the higher content of the hydroxyl groups and their location in the crystal structure of the clay. Moreover, illite and montmorillonite kept the order of their structural layers after complete dehydroxylation.

It is important to note, that the activation temperature does not have a significant influence on the pozzolanic activity of the calcined clay minerals, except for montmorillonite, whose particle surface was changed by the increase in the calcination temperature [17]. However, the microstructures between the systems with the calcined illite or montmorillonite showed that these additions have low activity and do not influence the microstructural changes much, so they showed similar mechanical properties to the mix with the inert filler.

Clays are natural materials so they contain some impurities such as quartz, feldspars or other clay types. The composition strongly depends on the region of the original clay, therefore, the characterisation of the different clays plays an important role in the application of the new sources of raw materials. Although extensive research has been carried out on the dependence of the pozzolanic activity on the fineness or mineral composition, there is little information about the influence of the same fineness, but different pozzolanic activity, of the micro-fillers on the hydration of Portland cement. The new results supplement a better understanding about the mechanism of the influence of the different micro-fillers on the hydration of Portland cement.

The aim of the study is to assess the influence of the same fineness, but having different activity micro-fillers (Mica clay, Kaolinitic clay, its mix, Limestone and Quartz sand), on the early hydration of Portland cement.

EXPERIMENTAL

Ordinary Portland cement (OPC) CEM I 42.5 R, mica clay, kaolinitic clay, limestone, and quartz sand were investigated in this work. The chemical composition of the materials is shown in Table 1.

The mineral composition of the Portland cement was (wt. %): $3CaO\cdot SiO_2$ – 53.0; $2CaO\cdot SiO_2$ – 19.6; $3CaO\cdot Al_2O_3$ – 9.2; $4CaO\cdot Al_2O_3\cdot Fe_2O_3$ – 9.7; $CaSO_4\cdot 2H_2O$ – 5.4; the specific surface area – 350 $m^2\ kg^{-1}$.

Limestone from industrial quarries (Lithuania) was used. The mineral composition of the limestone was (wt. %): calcite ($CaCO_3$) – 92.2 %; dolomite ($CaMg(CO_3)_2$) – 3.0; quartz – 4.5; other – 0.3.

Quartz sand from industrial quarries (Lithuania) was used. The quartz content in the quartz sand was 99.15 wt. %.

Kaolinitic clay from a trade network (Czech Republic) and Mica clay from industrial quarries (Lithuania) was used.

Table 1. The chemical composition of the materials.

Component (wt. %)	OPC	Mica clay	Kaolinitic clay	Limestone	Quartz sand
SiO_2	19.52	48.02	60.04	4.38	99.35
Al_2O_3	5.03	13.33	27.95	0.22	0.6
Fe_2O_3	3.05	6.69	0.56	0.7	0.05
CaO	61.39	10.19	0.06	50.88	–
MgO	3.93	4.59	0.18	1.67	–
K_2O	1.06	2.75	1.27	–	–
Na_2O	0.12	0.376	0.10	–	–
SO_3	2.5	–	–	–	–
Loss on ignition	3.2	14.81	9.84	41.63	–

Based on the literature data and previous work [17, 19, 20], the kaolinitic clay was calcined at 600 °C, while the mica clay was calcined at 900 °C. The clays were crushed, dried for 24 h at 100 ± 3 °C, and ground in a ball mill. The granules (10 ± 2 mm) were formed from the wetted clay. The granules were burned 1 h at the chosen temperature. Then, all the samples, after the jaw crusher, were milled with a vibrating disc mill.

The mix of the kaolinitic and mica clays were obtained from the prepared mica clay and kaolinitic clay. They were homogenised with a ratio 1:1 in a homogeniser for 15 min.

The limestone and quartz sand were dried for 24 h at 100 ± 3° and milled with a vibrating disc mill.

All the samples of Portland cement were blended with 15 % (by weight) of the different additives. Each sample was homogenised in a homogeniser for 15 min. The cement paste samples were formed without sand ($30 \times 30 \times 30\ mm^3$) and used for the compressive strength and the instrumental analysis. The normal consistency of the cement paste was estimated according to Standard EN 196-3 [21]. The samples were kept in moulds for 1 day at 20 ± 1 °C and 100 % RH (relative humidity). Then, the samples were transferred to deionised water and treated there for 2, 6 and 27 days at 20 ± 1 °C. The compressive strength was determined using a Form+Test Mega 10-400-50 press. The hydration of the samples was stopped using a (1:1) methanol/acetone mixture: firstly, the samples were crushed, milled with a laboratory vibrating disc mill, washed with the methanol/acetone mixture and dried at 60 ± 5 °C for 6 hours. The milling of the samples was performed 5 times (5 sec each) to prevent a temperature increase.

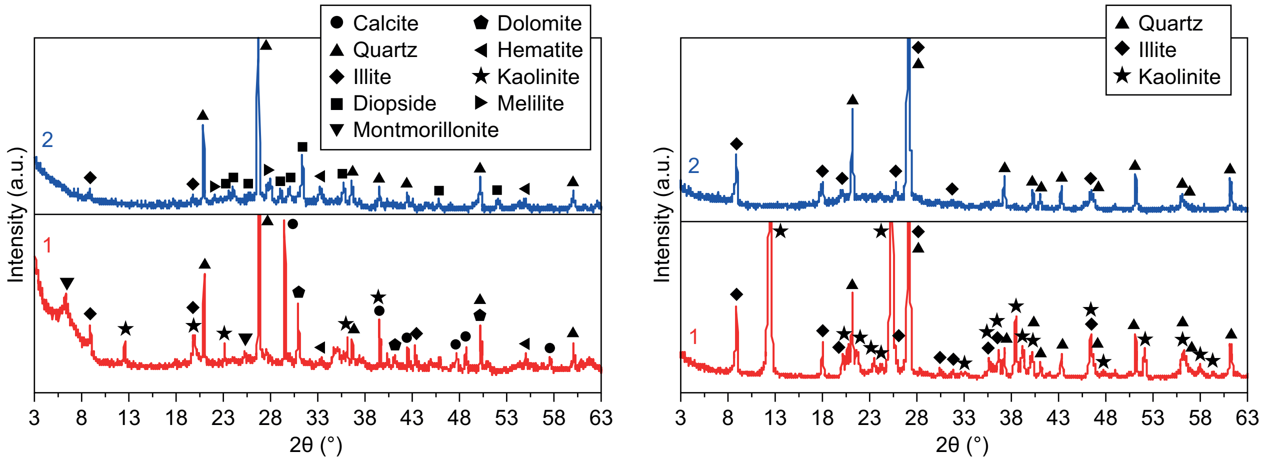
The pozzolanic activity was estimated by Chapelle's method (modified) [22]. According to this test, 1.000 g of material is mixed with 500 ml of lime solution ($1.200\ g\cdot l^{-1}$ CaO) and kept for 48 h at 45 °C in a thermostat. Then, 50 ml of the solution is titrated with 0.05 N hydrochloric acid (HCl) using methyl orange as the indicator for the evaluation of the CaO content. The results are expressed as milligrams of fixed CaO per gram of pozzolanic additive. The rest of the solution (450 ml) is stored in the thermostat for an additional 24 h at the same temperature. The process is repeated until the estimated value of the pozzolanic activity was insignificantly low.

Particle size distribution and the specific surface area of the materials were estimated using a particle analyser *CILAS 1090 LD* in intervals from 0.04 to 500 µm. The distribution of the solid particles in the air stream was 12-15 wt. %. Compressed air (2500 mbar) was used as a dispersing phase. The measuring time was 15 s.

The calorimetric analysis data were collected with a calorimeter – TAM AIR III. The range of the measurement was ± 600 mW, the sensitivity of the signal was 4 µW, the time constant was < 500 s, the temperature of the experiment was 25 ± 0.1 °C and the water-to-solid ratio was 0.5.

The XRD (X-ray diffraction) analysis was undertaken using a D8 Advance diffractometer operating at a tube voltage of 40 kV and a tube current of 40 mA. The X-ray beam was filtered with a Ni 0.02 mm filter to select the CuKa wavelength. The diffraction patterns were recorded in a Bragg–Brentano geometry using a Bruker LynxEye fast counting detector based on the silicon strip technology. The specimens were scanned over a range of 2θ = 3 - 70° using a coupled two theta/theta scan type.

STA (Simultaneous thermal analysis): the DSC (differential scanning calorimetry) and the TG (thermogravimetry) was measured with a Netzsch STA 409 PC Luxx instrument with ceramic sample handlers and platinum–rhodium crucibles (Pt–Rh). At a heating rate of $10 °C\cdot min^{-1}$, the temperature ranged from 30 °C to 1000 °C under the ambient atmosphere. The uncertainty in measurements for the DSC and for TG were ± 0.2 °C and ± 0.3 %, respectively.



a) mica clay

b) kaolinitic clay

Figure 1. The XRD patterns of the raw (1) and calcined (2) clays: a) the mica clay; b) the kaolinitic clay.

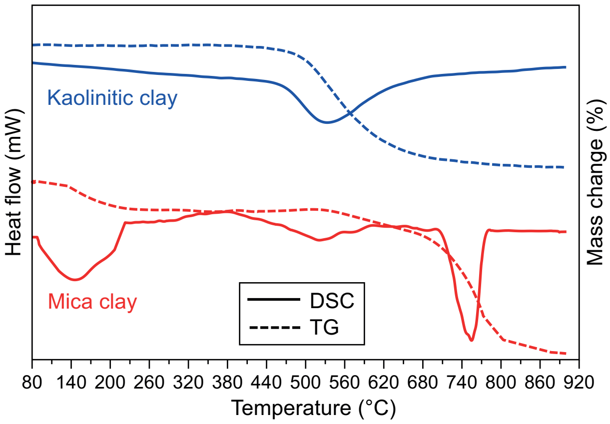


Figure 2. The STA analysis of the raw materials.

RESULTS AND DISCUSSION

The XRD and STA analysis data of the clays before and after the calcination are given in Figures 1 and 2. The XRD analysis data of the raw mica clay showed (Figure 1a, curve 1) kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) (*d*: 0.715, 0.447, 0.357, 0.249, 0.233 nm; ICDD 75-0938), montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$) (*d*: 1.400, 0.309, nm; ICDD 03-0016), hematite (Fe_2O_3) (*d*: 0.270, 0.251, 0.169 nm; ICDD 72-0469), illite ($K_{0.65\text{-}0.85}Al_2(Si,Al)_4O_{10}(OH)_2$) (*d*: 1.000, 0.502, 0.200 nm; ICDD 26-911), dolomite ($CaMg\,(CO_3)_2$ (*d*: 0.288, 0.219, 0.178 nm; ICDD 83-1766), quartz (*d*: 0.425, 0.334, 0.245, 0.181, 0.154 nm; ICDD 46-1045) and calcite ($CaCO_3$) (*d*: 0.302, 0.228, 0.209, 0.189, 0.186 nm; ICDD 72-1650); whereas kaolinite (*d*: 0.715, 0.447, 0.357, 0.249, 0.233 nm; ICDD 75-0938), quartz (*d*: 0.425, 0.334, 0.245, 0.181, 0.154 nm; ICDD 46-1045) and illite (*d*: 1.000, 0.502, 0.200 nm; ICDD 26-911) were found in the raw kaolinitic clay (Figure 1b, curve 1).

The DSC analysis of the mica clay is presented in Figure 2. The first thermal effect up to 200 °C is attributed to the removal of the free water from clay and the second one at 550 °C is due to the decomposition of the kaolinite [23]. The endothermic effect at ~780 °C occurred because of the decomposition of the calcite and dolomite. The exothermic effect at 300 - 450 °C is related to the burning out of the organic impurity, while the DSC of the kaolinitic clay (Figure 2) only showed an endothermic effect at 530 °C typical to the kaolinite decomposition.

Compared to the dried sample, the deterioration of illite, the complete decomposition of kaolinite, montmorillonite and calcite and the formation of melilite ($(Ca,Na)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$ (*d*: 0.318, 0.256, 0.191 nm; ICDD 72-1412) together with diopside ($MgCaSi_2O_6$) (*d*: 0.295, 0.289, 0.252, 0.197 nm; ICDD 17-0318) were observed in the XRD curve (Fig. 1a, curve 2) of the calcined mica clay.

The full decomposition of the kaolinite and the slight damage to the illite were observed in the kaolinitic clay calcined at 600 °C (Figure 1b, curve 2). In contrast to the mica clay, the blunt hill appears in the area of the diffraction angle between 18 - 26°, which is typical for amorphous phases.

In further investigations, the pozzolanic activity of the calcined clays and their mixture was determined. The results are presented in Figure 3.

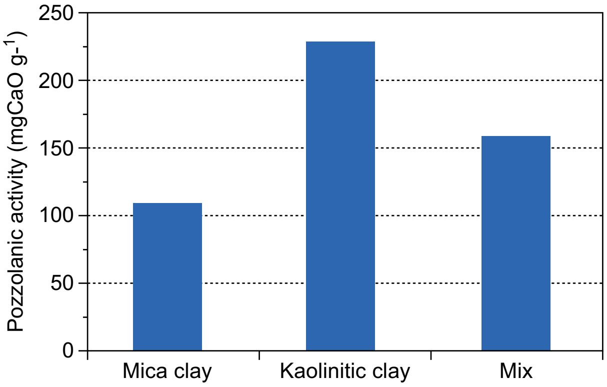


Figure 3. The pozzolanic activity of the calcined mica and the kaolinitic clay and its mixture.

The pozzolanic activity of the calcined kaolinitic clay is more than twice as much as (230 mg CaO/g) the pozzolanic activity of the calcined mica clay (109 mg CaO/g), whereas the mixture has an average activity (160 mg CaO/g).

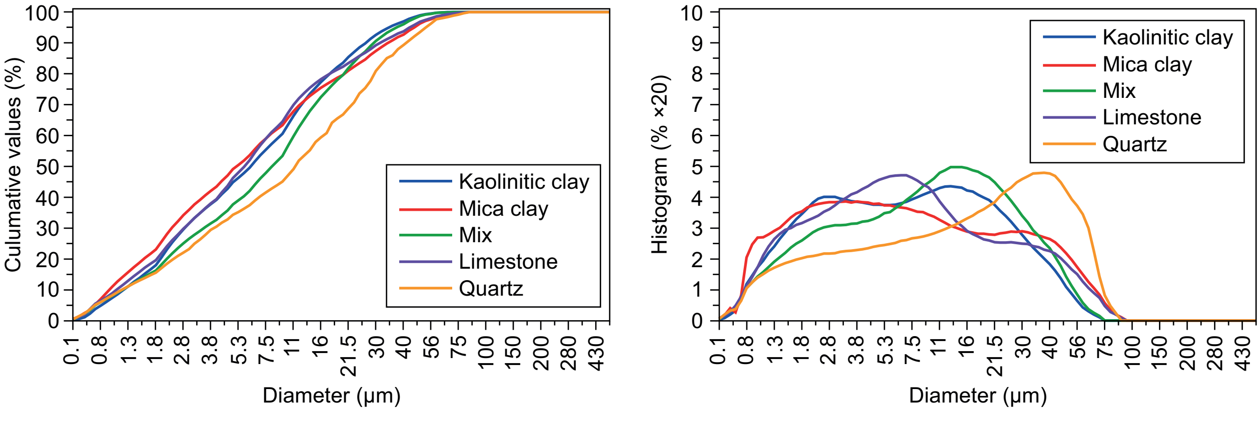
These results showed that the pozzolanic activity of the calcined kaolinitic clay is smaller than the activity of the pure metakaolinite (300 - 350 mg CaO/g), but it is higher than the natural pozzolan (180 mg CaO/g) [24]. Meanwhile, the pozzolanic activity of the calcined mica clay is equal to the activity of the natural volcanic pozzolan (110 mg CaO/g) [25].

During the next stage of the investigation, these three additives were milled until 70 wt. % of the material until it passed through a 63 μm sieve. To compare the results, two different milled inert materials such as quartz sand and limestone were used. The data of the particle size distribution analysis is presented in Figure 4.

The data of the particle analysis show that all the micro-fillers are quite similar: in all the materials, there are no particles larger than 100 μm in diameter and 90 % of all the particles have a diameter less than 34 μm. The value of the specific surface area of all the tested micro-fillers is shown in Table 2.

Table 2. The specific surface area of the micro-fillers.

Additive	Specific surface area ($m^2{\cdot}kg^{-1}$)
Kaolinitic clay	465
Mica clay	481
Clay Mix	468
Limestone	480
Quartz sand	472



a) b)

Figure 4. The particle size distribution of the materials used.

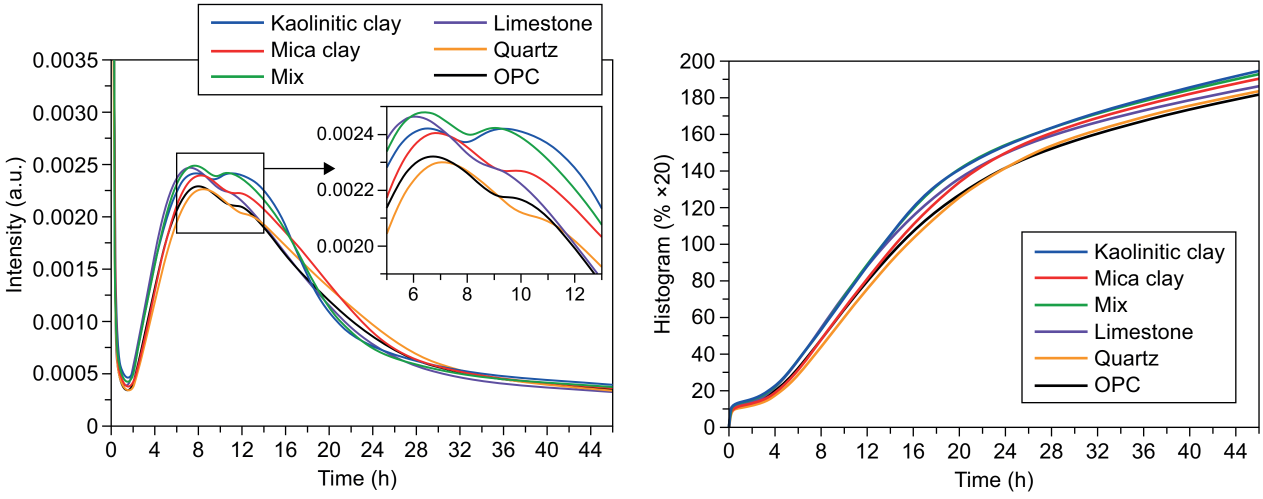
The surface area of all the tested micro-fillers is very similar and the difference does not exceed more than 5 %, therefore, the hydration process of the Portland cement should be affected only by the pozzolanic activity or the chemical composition.

To assess the influence of the different micro-fillers (15 wt. %) on the initial hydration of the Portland cement, the measurement of the generated heat of the hydration was performed (Figure 5). During the hydration of the samples, the released heat flow ($W\cdot g^{-1}$) (Figure 5a) and heat ($J\cdot g^{-1}$) (Figure 5b) were determined. The generated heat was normalised per gram of Portland cement.

The curves exhibit an initial exothermic peak, attributed to the complex reactions, during which the SiO_4^{4-}, OH^-, Ca^{2+}, SO_4^{2-} ions dissolve into the solution. After the induction period, the second peak of the heat evolution mostly related to the calcium silicates hydration is observed, while the additional peak (shoulder) corresponds to the aluminate-bearing phase reaction with the gypsum. The results show that the limestone micro-filler shortened the induction period (until 1 h 40 min), while the induction period lasted from 1 h 50 min up to 2 h for all of the other samples.

Comparing with the Portland cement samples, the slight delay in the second exothermic reaction period of the heat flow was identified for the samples with the quartz micro-filler (Figure 5a). The maximum heat flow was generated after 7 h 40 min of hydration, whereas, in the Portland cement sample, it was reached after 7 h 22 min. In the samples with the kaolinitic clay and the clay mix, a slightly earlier heat flow was identified (7 h 15 min), while in the sample with mica clay, it remained the same as in the Portland cement. The earliest second peak was reached in the sample with the limestone micro-filler – at 6 h 34 min. The intensity of the second peak was the highest of all (except for the quartz sand) samples with the micro-fillers when compared with the Portland cement sample.

The main heat flow difference was identified for the aluminate-bearing phase reaction with the gypsum, which is characterised by the shoulder intensity of the second period. This shoulder of the heat flow was clearly



a) heat flow b) heat

Figure 5. The heat flow (a) and heat (b) curves of the Portland cement hydration with the different micro-fillers.

observed in mixtures with active micro-fillers only. The third maximum was reached after 11 h 50 min in the Portland cement and with the mica clay micro-filler samples, while, in the samples with the kaolinitic clay and the clay mix, it occurred after 10 h 40 min. The shoulder was more intensive than the second peak in the sample with the kaolinitic clay, but slightly smaller in the sample with the clay mixture.

Overall, a higher heat hydration (186 - 192 $J \cdot g^{-1}$) was measured (Figure 5b) in all the samples with the micro-fillers (except for the quartz sand sample) when compared with the Portland cement sample (181 $J \cdot g^{-1}$) up to 45 hours in duration. The hydration heat increased with the increase in the pozzolanic activity of the additives. The highest heat hydration is released in the samples with the kaolinitic clay and the clay mix.

According to the obtained results, it can be assumed that all the investigated micro-fillers (except the quartz sand) increased the primary hydration of the Portland cement, but their influence on the hydration process is different: the limestone micro-filler mainly affects the initial hydration of the calcium silicates as the crystallisation centres, whereas the active micro-fillers affects the initial hydration of the calcium silicates and the aluminate-bearing phase reaction with the gypsum. These results correlate with the data of other researchers [26, 27].

The results of the setting time and the W/C ratio for the normal consistency of the samples are summarised in Table 3. An increase in the water content in the samples with the calcined clay was observed. This could be explained by the large water absorption in the calcined clay. The W/C ratio of the samples with the inert micro-fillers remained the same when compared with the Portland cement. Besides, no noticeable effect was determined with the micro-fillers on the setting time.

Table 3. The W/C and setting time of the Portland cement with the micro-fillers.

Additive	W/C ratio for normal consistency	Setting time (min)	
		initial	final
–	0.30	86	138
Kaolinitic clay	0.36	80	132
Mica clay	0.33	82	134
Clay Mix	0.35	82	132
Limestone	0.30	80	130
Quartz sand	0.30	85	138

The compressive strength of the samples mostly depends on the micro-filler type. It was estimated (Figure 6) that the Portland cement samples had the highest compressive strength throughout the entire investigated period of the hydration. The compressive strength of the mixtures with the inert micro-fillers (quartz sand and limestone) up to 7 days (especially after 1 and 3 days of hydration) was higher compared to the mixtures containing the active mineral micro-fillers (kaolinitic clay, mica clay and mixtures of these clay). In contrast, after 28 hydration days, a higher compressive strength was identified in all of the samples with the active micro-fillers. The highest increase in the compressive strength from the first day (34.5 MPa) up to 28th day (76.7 MPa) was measured in the samples with the kaolinitic clay active mineral micro-filler. After 28 days of hydration, the compressive strength of these samples was the same as the Portland cement samples (76.8 MPa), while the lowest value (70.0 MPa) was determined in the samples with the inert micro-fillers: the limestone and quartz sand. Summarising the obtained results, the inert micro-fillers (especially limestone) are more effective at an early stage of hardening (up to 7 days), however, after 28 days, the compressive strength of the samples directly depends on the activity of the micro-fillers: the higher pozzolanic activity ensures the greater compressive strength of the samples.

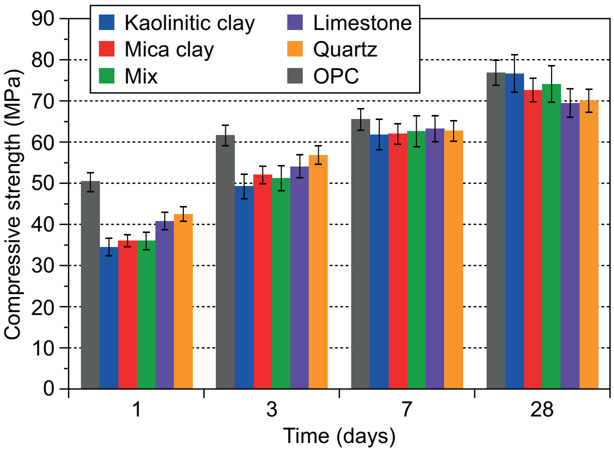


Figure 6. The compressive strength of the Portland cement samples with the different micro-fillers.

The mineral composition changes during the hydration of the samples with the micro-fillers that were evaluated by the XRD analysis (Figure 7).

The intensive XRD pattern peaks of the unhydrated cement minerals – tricalcium silicate (*d*: 0.304, 0.277, 0.260, 0.218 nm; ICDD 42-551), dicalcium silicate (*d*: 0.289; 0.277; 0.228; 0.163 nm) and brownmillerite (*d*: 0.727; 0.205 nm; ICDD 30-226) were identified in all the samples after 1 day of hydration (Figure 7a). Moreover, the ordinary products of the cement hydration, such as portlandite (*d*: 0.492, 0.311, 0.263, 0.193 nm; ICDD 84-1271) and ettringite (*d*: 0.972, 0.561, 0.387 nm) were determined. Additionally, in the sample with the quartz sand, quartz (*d*: 0.428; 0.336; 0.167 nm; ICDD 77-1060) and, in the sample with the limestone, calcite (*d*: 0.303; 0.228; 0.193 nm; ICDD 5-586) were marked.

No significant XRD curves changes (except for the diffraction intensity) were determined in all the samples after 7 hydration days (Figure 7b). However, the formation of calcite (*d*: 0.303, 0.228, 0.193 nm; ICDD 5-586), which is the result of the carbonation process, was identified in all the samples. After 28 days of hydration, the higher reduction in the main peak intensity typical with the unhydrated C_3S was identified in all the samples with the micro-fillers (Figure 7c). The highest decrease was observed in the Portland cement samples with the kaolinitic clay. This effect confirms that all the used micro-fillers stimulate the hydration of C_3S.

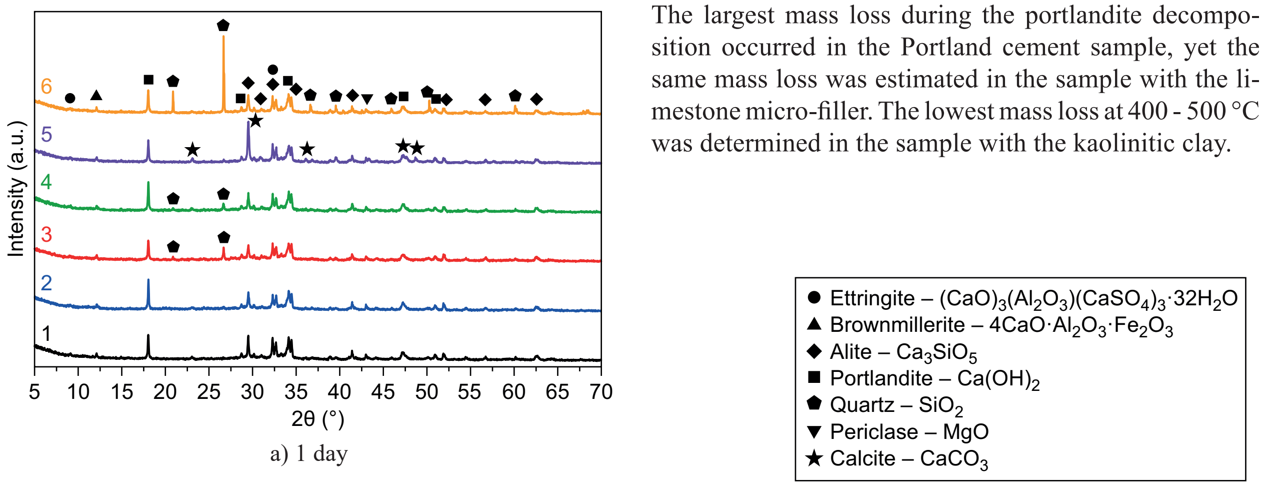
The data of the differential scanning calorimetry (DSC) are presented in Figure 8, while the data of the thermogravimetric analysis are showed in Table 4. The weight losses were calculated using a derivative method [28]. Three endothermic effects in the temperature ranges of 100 - 200 °C, 400 - 500 °C and 600 - 900 °C were detected. The endothermic effect at 100 - 200 °C is attributed to the dehydration of the main cement hydration products (ettringite, calcium aluminates, calcium silicate hydrates etc.), whereas the decomposition of portlandite and calcium carbonate is noticed at 400 - 500 °C and 600 - 900 °C, respectively.

The mass loss at the 600 - 900 °C temperature range was divided into two values: the total mass loss and the mass loss with an excluded effect of the evaluated decomposition of the carbonates in the additives. (Calculated from the TG data, taking into account that the mass loss of limestone sample at 600 - 900 °C was 41.38 % and mass loss of the mica clay sample was 5.85 %:

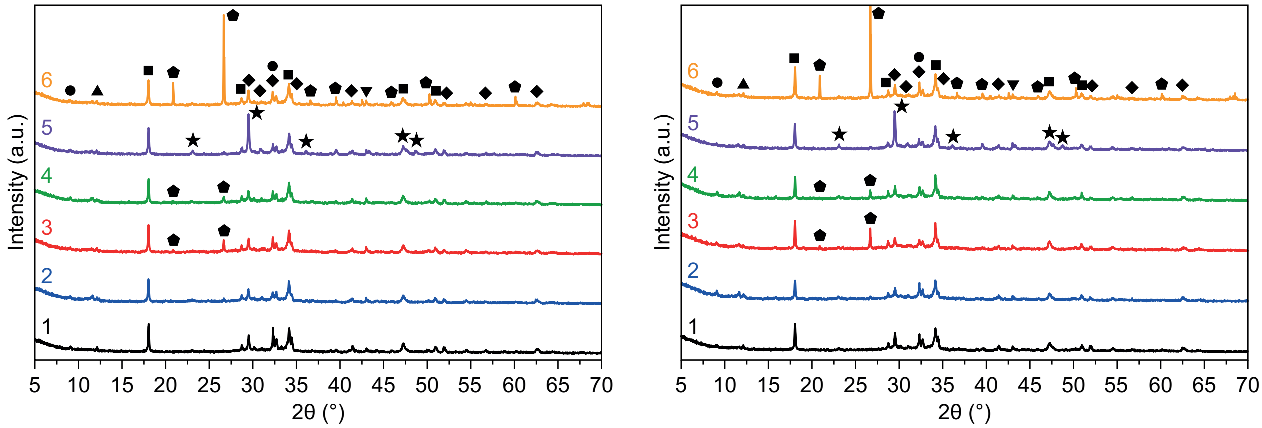
$$\Delta_{\text{mass loss of hydration products}} = \\ = \Delta_{\text{total mass loss}} - \Delta_{\text{mass loss of additive}} \times \text{wt. \% of the additive.}$$

After 1 day of hydration of the samples, the maximum mass loss at the temperature ranging from 100 - 200 °C was determined in the Portland cement sample, and the minimum – in the sample with the mica clay. At the temperature range due to the portlandite decomposition (a max. of approx. 450 °C), the largest mass loss was also identified in the Portland cement sample. However, in the samples with the inert micro-fillers, this decomposition effect was higher than in the samples with the active micro-fillers.

After 3 days of hydration, the mass loss changes, typical to the main cement hydration products, showed that the maximum mass loss was in the sample with the kaolinitic clay micro-filler, while the lowest mass loss remained in the sample with the mica clay micro-filler. The largest mass loss during the portlandite decomposition occurred in the Portland cement sample, yet the same mass loss was estimated in the sample with the limestone micro-filler. The lowest mass loss at 400 - 500 °C was determined in the sample with the kaolinitic clay.



a) 1 day



b) 7 days

c) 28 days

Figure 7. The X-ray patterns of the 1 (a), 7 (b) and 28 (c) day hydrated Portland cement samples with the additives: 1 – without the additives; 2 – with the kaolinitic clay; 3 – with the mica clay; 4 – with the clay mix; 5 – with the limestone; 6 – with the quartz sand.

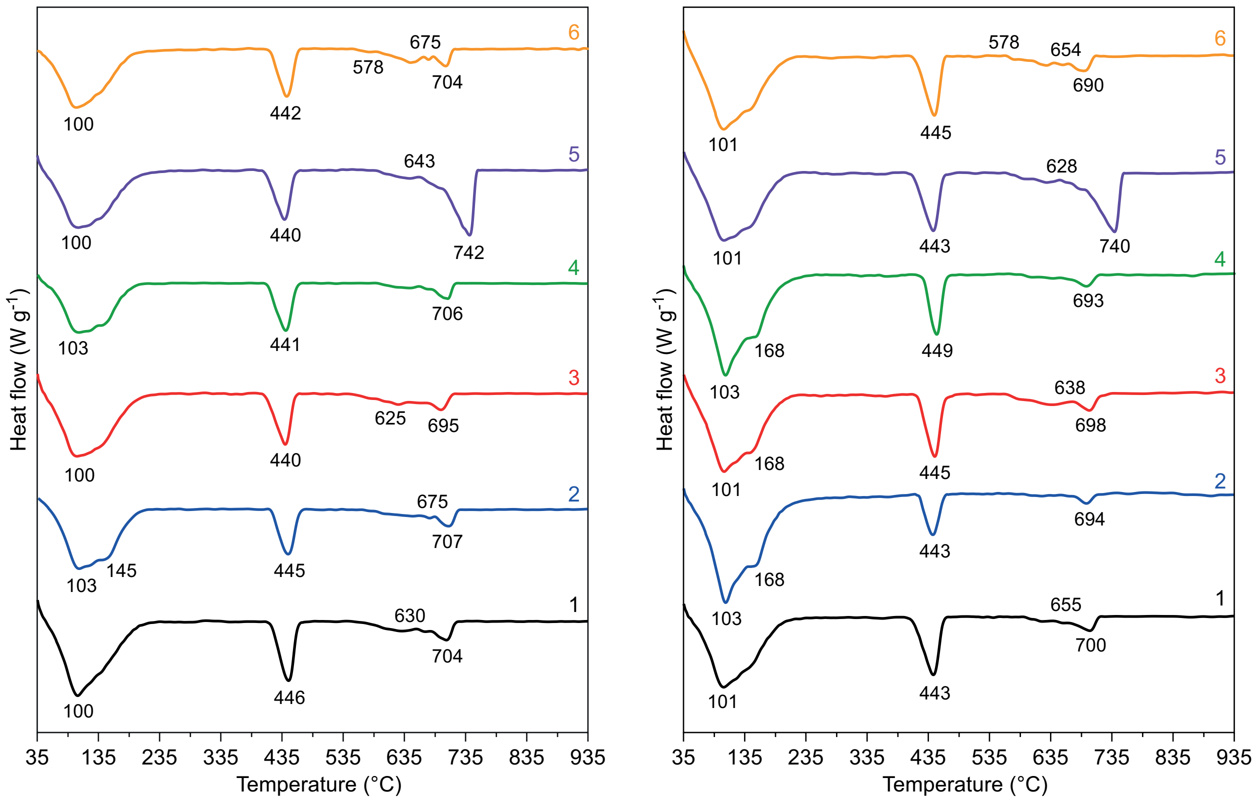
After proceeding with the hydration for 7 days, the thermogravimetric data showed that, in the temperature range of 100 - 200 °C, the maximum mass loss was determined in the sample with the kaolinitic clay: 24 % higher than in the Portland cement sample. Moreover, at this temperature range, the greater mass loss when compared with the Portland cement sample was observed in all the samples with the active micro-fillers. This increase in the weight loss can be associated with the formation of the additional calcium silicate hydrates, because less clinker minerals react in the samples with the micro-fillers.

The largest mass loss during the decomposition of the portlandite remains in the Portland cement sample, whereas, in the samples with the inert micro-fillers, it is greater than in the samples with the active micro-fillers.

Table 4. Results of thermogravimetric analysis after the different duration of hydration.

Additive	Duration of the hydration (days)											
	1			3			7			28		
	Temperature range (°C)											
	100-200	400-500	600-900	100-200	400-500	600-900	100-200	400-500	600-900	100-200	400-500	600-900
	Mass loss (%)											
–	5.65	2.19	3.16	6.09	2.2	3.31	6.27	2.57	3.70	7.52	2.92	4.23
Kaolinitic clay	5.32	1.81	3.04	6.57	1.85	3.24	8.23	1.93	3.69	9.37	1.91	3.75
Mica clay	4.42	1.88	3.98/3.10*	5.9	2.11	4.16/3.28*	6.55	2.28	4.38/3.50*	7.15	2.56	4.96/4.08*
Clay Mix	4.98	1.81	3.56/3.12*	5.83	2.02	3.66/3.22*	6.83	1.98	3.89/3.45*	9.29	2.29	4.25/3.81*
Limestone	4.92	1.90	9.32/3.12*	6.06	2.2	9.48/3.28*	6.27	2.30	9.75/3.55*	7.12	2.84	10.38/4.18*
Quartz sand	4.85	1.90	3.14	5.92	2.06	3.32	6.12	2.39	3.66	7.05	2.63	4.22

** the mass loss excluded the calcite content in the additives*



a) 3 days b) 28 days

Figure 8. The differential scanning calorimetry patterns of the 3 (a) and 28 (b) day hydrated Portland cement samples with the micro-fillers: 1 – without the micro-fillers; 2 – with the kaolinitic clay; 3 – with the mica clay; 4 – with the clay mix; 5 – with the limestone; 6 – with the quartz sand.

After 28 days of hydration, the mass loss at the temperature range of the dehydration of the main cement hydration products (100 - 200 °C) in the samples with the active micro-fillers (the kaolinitic clay and the clay mix) is more than 20 % higher than the mass loss in the Portland cement sample. The mass loss of the other samples with the micro-fillers at this temperature range was lower than of the Portland cement.

The mass loss of the portlandite decay after 28 days of hydration was an important indicator. Within the shorter hydration period of time, due to the portlandite decay, the most significant mass loss was in the Portland cement sample, and in the samples with the limestone micro-filler it was slightly lower. The most significant change was observed in the sample with the kaolinitic clay: only in this sample, the mass loss at the 400 - 500 °C temperature range decreased compared to the mass loss after 7 days of hydration, i.e., the portlandite consumption of the pozzolanic reaction was observed in this sample only. This statement can also be confirmed by evaluating the carbonation of the samples during the hydration. The carbonation of the samples is most intensive during the first three days of hydration. Later, this process slows down as the density of the samples increases and it is harder for the CO_2 to penetrate into the deeper layers. This is particularly noticeable in the sample with the kaolinitic clay micro-filler, because changes in the mass loss at 600 - 900 °C are minor (0.06 %) compared to the samples hydrated for 7 and 28 days. Therefore, the portlandite consumption for the pozzolanic reaction is visible rather than the carbonisation.

The level of the carbonisation of the other investigated samples is almost similar, except for the samples with the clay mix and the mica clay micro-fillers, which exhibited lower values. In the samples with the clay mix micro-filler, the mass loss due to the portlandite decomposition slightly increased and was lower than in the other samples with the micro-fillers. Considering a significantly higher mass loss in this sample at 100 - 200 °C, the traces of the pozzolanic reaction could be taken into account. Finally, in the sample with the least active micro-filler (the mica clay), no evidence of a pozzolanic reaction was determined.

Summarising the VTA analysis data, it can be stated that all the investigated micro-fillers of the calcined clay stimulated the formation of calcium silicate hydrates, however, only in the samples with the most active (the kaolinitic clay) micro-filler, the pozzolanic reaction was clearly identified after 28 days of hydration. In contrast to the active mineral micro-fillers, the inert micro-fillers increase the amount of portlandite. This indicates that despite the small difference in the compressive strength of the samples, a more reliable microstructure (a greater amount of calcium silicate hydrates) is formed in the cement stone with the low and medium pozzolanic activity micro-fillers. This structure ensures the durability of the cement stone at a longer period of curing.

CONCLUSIONS

All the investigated micro-fillers (except the quartz sand) increase the initial hydration of the Portland cement, but their impact on the hydration process is different: the inert limestone micro-filler mainly affects the initial hydration of the calcium silicates, whereas the active micro-fillers affect both of the following processes: the initial hydration of the calcium silicates and the aluminate-bearing phase reaction with the gypsum.

The inert micro-fillers (especially the limestone) are more effective at the early stage of hardening (up to 7 days), but later, after 28 days, the compressive strength of the samples directly depends on the activity of the micro-fillers: a higher pozzolanic activity ensures the greater compressive strength of the samples.

All the investigated micro-fillers of the calcined clay promote the formation of the calcium silicate hydrates, however, only in the samples with the most active (the kaolinitic clay) micro-filler, after 28 days of hardening, the pozzolanic reaction is clearly identified. In contrast to the active mineral micro-fillers, the inert micro-fillers in the hardening system increase the amount of portlandite.

The obtained results show that even the micro-fillers with a low and medium pozzolanic activity are suitable for the partial substitution of Portland cement. This expands the application possibility of the new sources of the raw materials.

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