

Blended cements consisting of Portland cement–slag–silica fume–metakaolin system

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Abstract In the present study, hydration of four-compound systems consisting of Portland cement and three supplementary cementitious materials: silica fume, blast-furnace slag, and metakaolin, has been investigated by means of isothermal calorimetry and thermal analysis. Substitution of Portland cement was achieved at 25, 30, and 35 mass% by cementitious supplementary materials. Owing to the high specific surface, the silica fume eventuated in more distinctive demonstration of pozzolanic reactions. It decreased C/S ratio and led to the formation of hydration phases with $C/S \cong 1$, which is demonstrated by wollastonite crystallization at higher temperatures. Enhanced formation of gehlenite hydrate was proved by DTG when blended cements included higher content of metakaolin and blast-furnace slag. Pozzolanic materials increased the compressive strength of particular blended samples and thus overcame the dilution effect especially at long term of curing. Presented quaternary blended samples in comparison with ordinary Portland cement thus allowed the formation of more thermal stable hydration products

and can be considered as promising materials for the development of special concrete also for hydrothermal applications.

Keywords Blended cements · Metakaolin · Silica fume · Blast-furnace slag

Introduction

The development and the use of multicomponent blended cements are besides economic and ecological aspects driven by the requirements to enhance some properties of resulting materials in comparison with original ones. The most blended cements consist in addition to Portland cement of one or two compounds, so-called supplementary cementitious materials (SCM). The European Standard 197-1 has defined CEM II as ones that may contain up to 35 % of supplementary latently hydraulic materials. Binary blended cements based on blast-furnace slag (BFS), fly ash (FA), metakaolin (MK), limestone (L), silica fume (SF) and other pozzolanic materials were developed and used around the world [1–5]. In the last two decades, ternary systems combining two supplementary cementitious materials with Portland cement are also of growing interest [6–10]. Combination of two or more binders materials allowed the development of self-compacting concrete and high-performance cements [8–13].

The outcome of all the foregoing in the use of supplementary materials is the generation of additional hydrated products via pozzolanic reactions. The matrix of cement past with higher content of $\text{Ca}(\text{OH})_2$ is a suitable environment for the activation of latently hydraulic materials. The reactivity of these materials will depend not only on the quantity, but also on the factors such chemical and

Cement nomenclature is used when C = CaO, S = SiO₂,
A = Al₂O₃, F = Fe₂O₃, \bar{S} = SO₃, H = H₂O.

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mineralogical composition, temperature, activator concentration, and particle size distribution [14]. The combination of two or more admixtures can present some advantages, owing to the synergetic effect and complementarity in some specific field of requirements. For example, authors [8, 15] have demonstrated that in PC–BFS–MK system, addition of BFS can improve flowability of fresh cement mixtures which is poorer due to the presence of MK.

Khan et al. [16] divided mineral admixtures added to cement into two groups: chemically active mineral admixtures (highly reactive pozzolan) and microfiller mineral admixtures (low- to moderate-reactive pozzolan). According their categorization, SF and MK are chemically active mineral admixtures, whereas BFS belongs to microfiller mineral admixtures. Results of Chapelle test [17] confirmed expected reactivity of mentioned materials in order: $MK > SF > BFS$. Higher reactivity of MK and SF accrues from their very fine microstructure that leads to the higher specific surface area. Resulting lower workability is usually offset by adding plasticizers. Contrary to BFS, MK and SF provide thanks to their nature highly dense and impermeable concretes. Duan et al. [18] demonstrated that MK enhances interfacial transition zone better than SF and BFS and thus can produce higher values of compressive strength. Supplementary cementitious materials affect not only final properties of concretes, such as porosity, related permeability, and strength, but also characteristics of fresh concretes: workability, setting time, bleeding, heat, and rate of hydration [19]. All of the mentioned characteristics are besides fundamental properties of used supplementary materials influenced by the level of their replacement and selected preparation conditions (e.g., water content, initial and curing temperature, dosage of plasticizer [20]).

The present study deals with the quaternary mixtures (Quatro) substituting high-energy intensive Portland cement (PC) with three locally available supplementary cementitious materials (SCM) namely granulated blast-furnace slag (BFS), silica fume (SF), and metakaolin (MK). It is expected that proposed system can serve as a fundament for development of new high-performance and high-strength concretes possibly suitable for hydrothermal applications, too. The total degree of Portland cement substitution by SCM (BFS, SF, and MK) was changed from 25 to 35 % by mass. At the same time, the composition of SCM varied. Each of the used materials possesses different characteristics and influences properties of concrete in different ways. They differ in chemical and phase composition, specific surface, and particle size distribution. Under hydrothermal conditions of applications, SF as a source of silicon dioxide helps to reverse the inconvenient conversion of C–S–H gel to highly crystalline and much denser, alpha dicalcium silicate hydrate (α -C₂SH) [21, 22].

This conversion is associated with volume reduction and therefore, it is deleterious for the hardened cement. Ratio of C/S approximately equals 1, leading to the formation of tobermorite that is stable also at higher temperatures [23, 24]. BFS contributes to the formation of CSAH phases that are at hydrothermal conditions even more stable than calcium silicate hydrates [4]. Partial replacement of cement by MK eventuates in the same products as the use of BFS and in the formation of ettringite [25].

Suitable stability, durability, and mechanical properties of concretes must be therefore achieved through optimization of processing parameters and input materials dosages. This paper presents first part of study of four-compound systems and it is devoted to the evaluation of the pozzolanic activity and the heat evolution by means of isothermal calorimetry and thermal analysis.

Experimental

The contents of Portland cement (CEM I 52.5 N, Holcim (Slovensko), a.s., Slovakia), ground granulated blast-furnace slag (Kotouč Štramberk, spol. s r.o., Czech Republic), silica fume (Oravské ferozliatinárske závody, a.s., Slovakia), and metakaolin L₀₅ (Mefisto, České lupkové závody, Czech Republic) in the samples were changed according to the Table 1. The results of chemical analysis and physical characteristic of the used Portland cement and supplementary cementitious materials are shown in Table 2. Mineral composition of the used cement is displayed in Table 3. In order to compensate the amount of sulfate ions consumed by metakaolin to form additional ettringite, gypsum was added to each mixture according to the metakaolin content in the amount corresponding to 1.25 mass% of metakaolin content.

Calorimetric measurements of cement pastes were conducted on TAM AIR 8-Channel calorimeter. It consists of an eight channel calorimeter block and data logging system required for use with the TAM AIR thermostat. The mixtures of blended cements were placed in ampoules with lid. The quantity of water to achieve water/cement ratio 0.5 was injected in the ampoule using syringe. The samples

Table 1 Composition of prepared samples (in mass %)

Sample	w _{PC} /%	w _{BFS} /%	w _{SF} /%	w _{MK} /%	w/c
Quatro0	100	–	–	–	0.27
Quatro1	75	5	15	5	0.25
Quatro2	70	10	10	10	0.24
Quatro3	65	15	5	15	0.25

The mentioned w/c ratio was used only to prepare the samples selected for compressive strength measurements

Table 2 Oxide composition (in mass %) and specific surface (in $\text{m}^2 \text{kg}^{-1}$) of the used Portland cement and supplementary cementitious materials

	Oxide composition/%						Specific surface/ $\text{m}^2 \text{kg}^{-1}$	
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃		
CEM I 52.5 N	64.01	20.39	4.85	2.88	2.06	2.85	Blaine	464.3
SF	0.50	97.10	0.21	–	0.40	–	BET	15,000
MK	0.24	49.70	42.36	0.79	0.22	0.08	Blaine	2586
BFS	36.53	35.76	9.39	0.24	14.0	0.03	Blaine	469.9

Table 3 Mineral composition (in mass %) of CEM I 52.5 N given by producer

	Mineral composition/%						
	C ₃ S	C ₂ S	C ₃ A (ort.)	C ₃ A (cub.)	C ₄ AF	Free lime	MgO
CEM 52.5 N	61.49	15.44	3.85	5.48	8.76	0.93	1.35

C₃A is present in orthorhombic and cubic form, MgO as periclase (cubic form)

were gently stirred after adding of water and placed in the calorimeter. The measurement started few seconds after adding the water. Hydration of samples was after 2 days stopped by immersing them in acetone, and residual acetone was removed by evaporating for thermal analysis.

The phase changes taking place in the samples were after calorimetric measurements monitored by TG/DSC technique (TGA/DSC—1, STARe software 9.30, Mettler Toledo). The 50.00 (± 0.03) mg of powdered samples was heated in the open platinum crucibles up to 1000 °C at the heating rate of 10 °C min^{-1} in the atmosphere of synthetic air (purity 5.0).

The in situ X-ray diffraction analyses of referential sample Quatro0 were conducted on Bruker D8 Advance diffractometer equipped with Cu anode ($\lambda K\alpha = 0.15418 \text{ nm}$), 1-D position sensitive detector, and variable divergence slits at convention Bragg–Brentano parafocusing θ – θ reflection geometry. Step size—0.04° 2θ and time per step—188 s were used. The duration of individual scans was approximately 20 min. The measured data were processed using Diffrac plus software. For the XRD, the sample with the standard was mixed with water ($w/c = 0.5$). The paste was placed in a sample holder and covered with kapton foil to prevent carbonation.

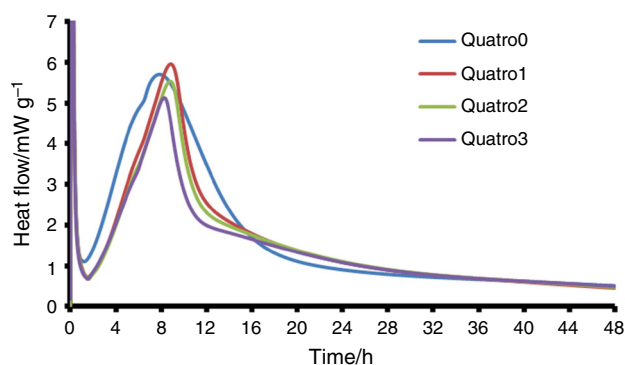
For compressive strength measurements, mixtures were homogenized along with the gradual adding of water using the cement mixer. Quantity of water was adjusted to achieve suitable workability of pastes (water-to-cement ratio depends on BFS/SF ratio in the mixtures; Tab. 1). Plasticizer Stachment® 2353 (Stachema Bratislava, Slovakia) was applied to reduce the demand for water. Plasticizer concentration in water of 0.05 vol% was kept constant. After the whole amount of water was added, 10 min of additional homogenization followed. Three prisms with the dimensions of 160 × 40 × 40 mm were

prepared from the paste of each composition. Compressive strength of hardened samples was estimated using WPM WEB Thüringer Industriewerk Raustein 11/2612 (up to 25,000 N). Each displayed data represents arithmetic mean of 6 experimental measurements.

Results and discussion

Isothermal calorimetry

Figure 1 shows the calorimetric curves in terms of heat flow. The general feature of calorimetric curve is its different periods and peaks with different intensities. The first peak that intensities were reduced in Fig. 1 (separately presented in Fig. 2) characterizes the fast exothermic process (1st period) that leads to the formation of protective layer engendering the dormant period (2nd period) after which hydration is accelerated (3rd period) to maximal rate before it decreases (4th period) to steady state (5th period). Each calorimetric curve can be described by the peak

**Fig. 1** Heat flow development in time of the samples

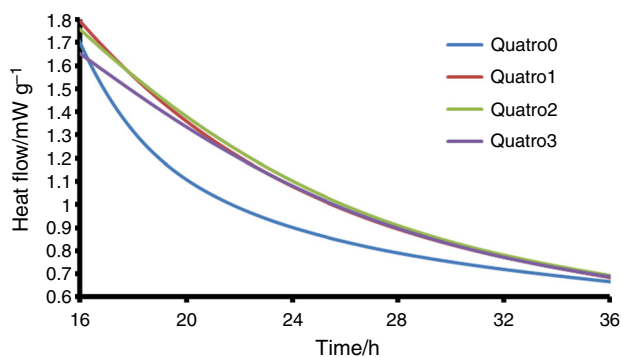


Fig. 2 Influence of SCM on the hydration at deceleration period

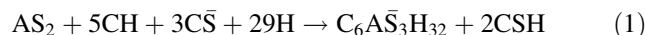
velocity and the time position, duration of induction period and the end of hydration process. Chemical reactions occurring at each period were deeply described elsewhere [26]. Though the duration of induction period seems to be less influenced, the intensity of the main peaks depends on the composition of the samples.

The highest overall heat flow displays the sample denoted as Quatro1 prepared with 15 mass% of SF and the quantity of cement reduced for 25 mass% in comparison with the referential sample Quatro0 (Fig. 1). Other decrease in PC content and increase in BFS and MK content at the expense of SF lead to the drop of heat flow under the level measured for pure Portland cement paste. Mostafa et al. [26] declared that there are two effects which affect behavior of material: the pozzolanic activity and the influence of substituting PC. The first is expected to increase the heat output owing to the reaction of pozzolans with calcium hydroxide. The later may decrease the heat output due to the reduction in the main cement compounds (C_3S) and it is also known as dilution effect. In accordance with these statements, the lowest substitution level together with the highest content of SF as very reactive pozzolanic material (Quatro1) results in the highest overall heat flow. Higher substitutions levels of PC cause the decrease in overall heat flow. The reduction in material able to hydrate and thus capable to produce the heat together with related decrease in calcium hydrate as cement hydration product needed for pozzolanic reactions overcome the effect of pozzolanic materials activity.

Depending on the chemical composition and the pozzolanicity of the supplementary cementitious materials, pozzolanic reactions contribute to the total heat output, but generally after the main hydration peak [27]. This is confirmed also by heat flow development after approximately 16 h when the blended cement pastes display in certain sector higher heat flow as pure PC paste (Fig. 2). More significant contribution of sample Quatro1 to the heat flow of the first peak (Fig. 3) can be attributed also to the highest specific surface of SF among other pozzolan

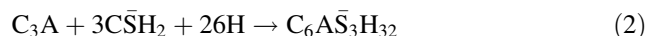
materials [28, 29]. Higher specific surface as a result of the smallest particle size ($0.1 \mu\text{m}$ [30]) improves the wetting as one from the main factor influencing heat of initial reaction.

Besides binding phases resulting from the reaction of pozzolans with calcium hydroxide ($C-S-H$, C_4AH_{13} , C_3AH_6 and C_2ASH_8 [31–33]), MK and BFS can contribute to the formation of ettringite by the reaction of Al_2O_3 with gypsum or other sulphate bearing compounds in aqueous environment containing calcium ions according to Eq. 1 [34].



The formation rate of ettringite deriving from the reactive alumina in pozzolans is much higher than that from clinker minerals C_3A and C_4AF [35]; thus, it should manifest at earlier times of hydration, especially in the case of reactive MK. Non-demonstrated effect of this rapid formed ettringite supports the idea of dominant dilution effect in blended cement pastes. Boháč et al. [25] proved the acceleration effect of MK on the rate of hydration reaction when higher replacement amounts as in this study were applied. At 50 mass% replacement of PC by MK, the intensity of hydration peak was similar to that of pure PC.

In addition to the two mentioned main peaks, little shoulder appears during acceleratory periods of hydration of all samples. This shoulder is most visible in the case of sample without supplementary materials additions (Quatro0) and becomes less noticeable when lower amounts of cement were used to prepare samples. The presence of these shoulders can be attributed to the formation of ettringite that results from the hydration of C_3A in the presence of gypsum (Eq. 2; [26]).



Formation of ettringite is in the case of commonly used cement strength class 42.5 often noticed after the maximum rate of $C-S-H$ formation is attained (second peak) [36]. Because the milling effectiveness of C_3A and gypsum

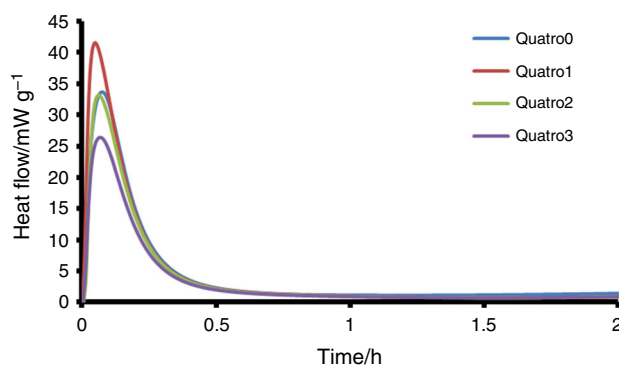


Fig. 3 Time-dependent heat flow during the first peak occurrence

are higher than that of C_3S , they acquire higher specific surface area and thus improved reactivity in the cement of strength class 52.5. Higher reactivity consequently leads to the shift of C_3A hydration to the earlier times—before hydration of C_3S .

The time corresponding with the maximal heat flow (first peak) gets slightly shorter with the increasing level of SF in the samples. Maximum of second peak is reached the soonest in the case of referential PC paste (Quatro0). Blended samples attain this maximum faster when higher amounts of BFS and MK substituted cement. However, the biggest difference between these samples does not exceed 35 min. As BFS belongs to the supplementary materials with low pozzolanic activity, it can be supposed that its influence was compensated by high pozzolanic activity of metakaolin.

In order to clearly emphasize the pozzolanic activity of the supplementary materials, measured heat flow of sample Quatro0 was modified considering the dilution effect in the blended samples (reduced for 25, 30 and 35 %, respectively). The difference between real and particular calculated heat flow of these samples is demonstrated in the Fig. 4. The strongest demonstration of pozzolanic influence observed during initial reaction can be primarily explained by finer specific surface of pozzolanic materials and relevant improved wetting when compared with cement particles. Displayed differences between heat flow of pozzolanic reactions among samples correspond to the amount of SF as the finest supplementary material. As it was expected, the intensity of the peak corresponding with C–S–H formation decreased with increasing substitution level of PC. The lower amount of PC used to prepare the samples, the smaller amount of primary hydration products was formed. At the end of deceleration period, the heat flow of pozzolanic reactions attains negative values. Reactions taking place during deceleration period are controlled by diffusion instead of previously asserting chemical control and their rate due to the depletion of small particles slows down [37]. The amount of calcium

hydroxide is in the case of blended samples consumed by pozzolanic reactions. At the end of deceleration period is the amount of precipitated calcium hydroxide too little and because the heat of pozzolanic reaction is lower than that of primary hydration, the spotted difference lead to the negative values.

Heat produced by samples as the hydration proceeds demonstrates the clear dependence on the cement content (Fig. 5). Also other authors [26, 38, 39] expressed that the pastes containing pozzolanic material or slag decreased heat of hydration compared to the cement mainly during the period of C_3S hydration, i.e., the main hydration peak. However, when the overall heat generated by samples up to monitored 48 h is taken into account, it can be clearly demonstrated that it does not display direct proportionality to the substitution level. Dilution effect caused by replacement of 25, 30 or 35 mass% of PC by SF, BFS and MK is therefore compensated by pozzolanic effect of the used substitution materials. The difference between quantity of heat that should be released after the partial substitution of cement and real heat produced by particular samples represents 24 % for Quatro1, 26 % for Quatro2 and 27 % for Quatro3.

Thermal analysis

DTG curves of the samples prepared with and without supplementary cementitious materials are displayed in Fig. 6. The first endothermic peak between 70 and 130 °C corresponds with the release of water due to the decomposition of nearly amorphous hydrates (mainly C–S–H) [40, 41]. The height and the spread of the peak decrease with increasing substitution of cement in blended samples. Correspondingly, maximum intensity and width of the peak is reached in the case of sample Quatro0 which points out on the highest amount of C–S–H formed in this sample.

Following endothermic peak located approximately between 140 and 200 °C can be attributed to the decomposition of gehlenite hydrate (C_2ASH_8) [42] and its

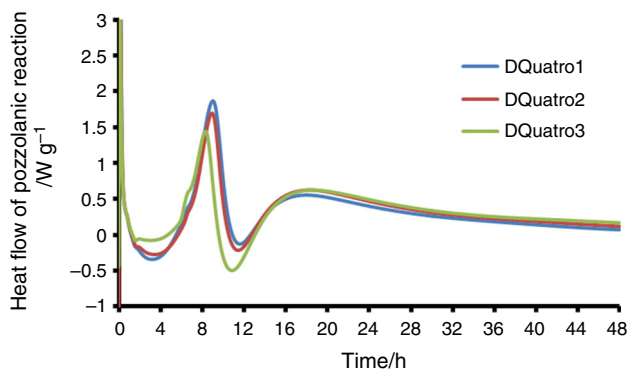


Fig. 4 Heat flow of pozzolanic reaction

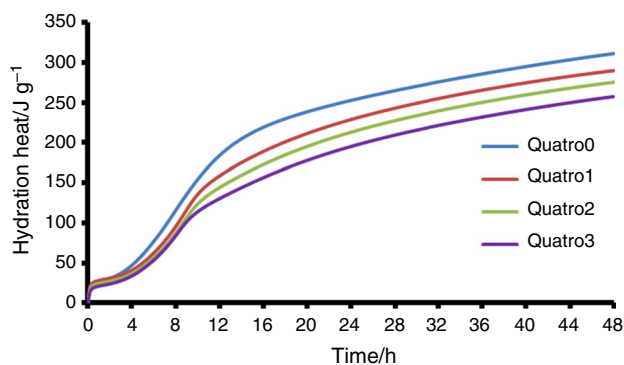


Fig. 5 Heat produced by samples in time

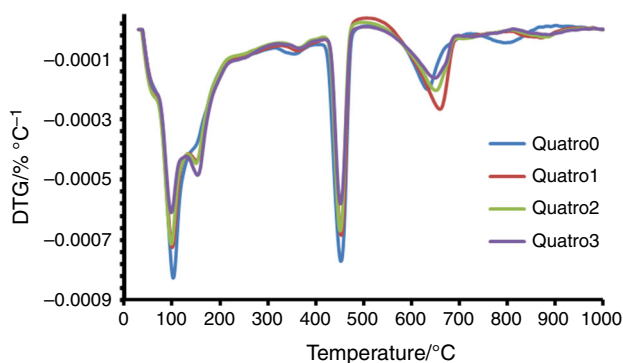


Fig. 6 DTG curves of referential and blended samples after 2 days of curing

intensity in blended samples increases with rising amount of MK, thus reflecting the amount of aluminous ions. Small endothermic maximum between 310 and 390 °C belongs to the hydrogarnet series [42]. Referential sample Quatro0 displays the most significant intensity, and maximum of this peak is moved to the lower temperatures.

Quantity of portlandite (CH) documented by its decomposition into free lime between 400 and 500 °C [40, 43] depends on the initial amount of Portland cement in the samples. Referential sample Quatro0 demonstrates the highest appropriate endothermic effect, whereas the sample Quatro3 prepared with the highest content of supplementary materials shows the lowest one. As well as in the case of peak belonging to C–S–H decomposition, decreasing peak intensity with descending amount of PC in the samples clearly suggests the dilution effect in the hydration of blended cements. In addition to the mentioned, CH is consumed by pozzolanic reaction in blended samples.

Degree of carbonation in the samples can be considered on the basis of endothermic peak between 550 and 700 °C that appertains to the calcium carbonate decomposition [44]. Increasing amount of supplementary materials results in less notable peak. Sample Quatro0 shows intensity of this peak comparable with that of sample Quatro2; however, the maximum of peak shifts to the lower temperature. Endothermic peak occurring on the curve of sample Quatro0 between 730 and 830 °C can be attributed to the decarbonation of other carbonates present in modest quantities or to the decomposition of other polymorph modification of calcium carbonate.

The latest detected exothermic effect at about 880 °C visible on DSC curves (Fig. 7) is caused by the formation of wollastonite [24]. The formation of wollastonite can be assigned to the thermal transformation of hydration phases with C/S \cong 1, such as tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$) [45]. Tobermorite and other similar phases arise in the present systems mainly due to the addition of silica fume that as a source of silicon dioxide changes C/S ratio to

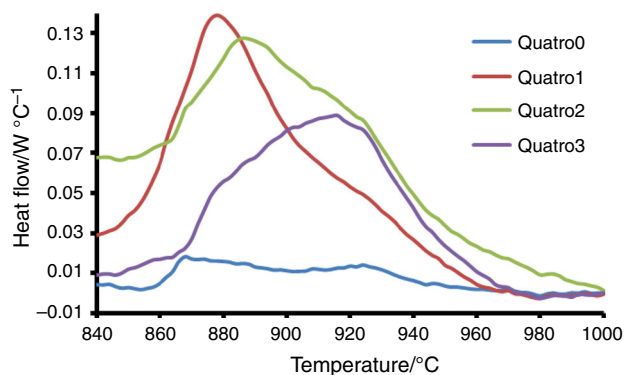


Fig. 7 Influence of supplementary materials type and content on DSC curves in the temperature interval 840–1000 °C

approximately 1. Accordingly, the highest intensity of relevant exothermic peak belongs to the sample Quatro1. In the case of samples prepared with higher content of MK (Quatro2 and Quatro3), the shift of exothermic peak to higher temperatures as well as its spreading can be explained also by accompanying mullite formation [46]. Crystallization of mullite reflects the higher content of aluminous ions from MK addition.

Thermogravimetric curves of 2days' samples can be divided into several zones (Fig. 8) with three rapid mass losses. The first up to approximately 200 °C corresponds with dehydration of various hydrates, mainly C–S–H but also carboaluminates and ettringite. The second significant mass loss can be observed between 450 and 500 °C and it is caused by dehydration of portlandite. The last major mass loss in the temperature range of 550–700 °C appears due to decarbonation of calcium carbonate.

In order to evaluate the dependence between different supplementary materials and resulting hydration products in more details, relative mass loss (%) was calculated from the overall mass loss (%) of thermally decomposed samples (Table 4). The largest mass loss up to 1000 °C (cca 12 mass%) demonstrates the sample Quatro0 not

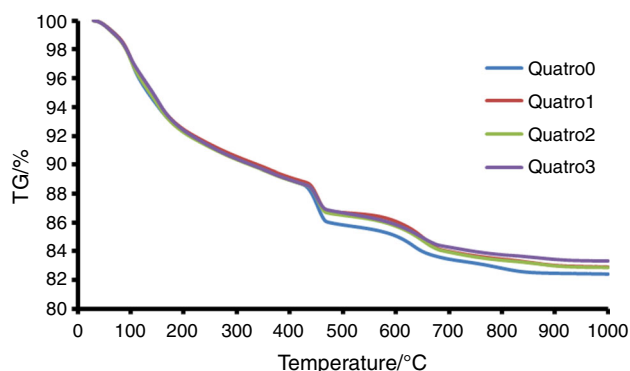


Fig. 8 Influence of supplementary materials type and content on TG curves of samples

containing supplementary materials. On the contrary, the smallest mass loss achieves the sample Quatro3. However, recorded extent of mass loss differs a little between samples in particular temperature regions. It can be observed that the difference among mass loss of referential and blended samples becomes more significant during the period belonging to the dehydration of portlandite. Previous more distinctive dehydration of C–S–H in the case of Quatro0 was compensated by lower extent of CSAH decomposition. Following mass loss due to decarbonation of calcium carbonate in this sample was affected by the presence of other carbonate compounds. Relative mass loss pertaining to the last distinguished temperature interval mentions the decomposition of natural limestone. Besides PC, other source of limestone in studied systems presents BFS. In accordance with this, the highest relative mass loss is determined for the sample Quatro2.

In situ XRD analysis

Small shoulder appearing on the calorimetric curves of samples approximately between 5 and 7 h of hydration (Fig. 1) was attributed to ettringite. In order to submit its origin, referential sample Quatro0 was subjected to in situ XRD analysis (Fig. 9). The beginning of hydration was not possible to record as each individual scan took 20 min. The characteristic peaks of C_3S and C_2S were cut from 3D graphs to show also crystalline phases with considerably lower intensities.

CH, ettringite, and calcium carbonate present the main crystalline hydration products within the duration of analysis. Besides them, mentioned unreacted clinker minerals— C_3S and C_2S with decreasing tendency of peak intensities can be detected on XRD patterns. Analysis of first scans revealed also small amount of brownmillerite ($C_2(A,F)$). The presence of C–S–H cannot be uniquely confirmed in such early times of hydration as it occurs mainly in amorphous state. Formation of ettringite in the

sample without supplementary cementitious materials addition takes place by the reaction of C_3A , C_4AF , and gypsum. Gypsum peaks occurring at the beginning of analysis decrease and finally disappear as it is consumed by the reaction with aluminous phases. Accordingly, intensity of peak belonging to ettringite increases in time. Also peak intensities of other hydration products—CH and calcite rise; however as evidenced by Fig. 9, their formation is delayed in comparison with ettringite, thus confirming the results of isothermal calorimetry.

Compressive strength measurements

The results of compressive strength measurements from 2 up to 28 days are shown in Fig. 10. Whereas the sample Quatro0 displays the value of 2 days' compressive strength similar to other blended ones, continuing curing resulted in more visible demonstration of pozzolanic reactions. Already after 7 days, the compressive strength of this sample is the lowest among the prepared ones. The best values of 7 and 28 days' compressive strength were measured for the sample Quatro1 prepared from the highest content of silica fume, while Quatro3 demonstrates the lowest compressive strength within the blended samples. Nevertheless, one should be aware that also dilution effect due to the lowest cement content in this sample is the highest.

It is obvious that the decrease in Portland cement content in blended samples leads to the lower amount of hydration products yielding compressive strength of final materials. The evolution of compressive strength in these samples is, however, influenced also by the presence of pozzolanic materials that react with arising C–S–H and CH to form other cementitious phases. In order to distinguish between the dilution effect and the pozzolanic one, the so-called coefficient of pozzolanic activity (CPA; in %) in relation to Quatro0 as reference sample was defined (Eq. 3) and calculated for all blended samples (Fig. 11).

$$CPA = \frac{CS_{\text{Quatro}} - CS_{\text{Quatro0}} \cdot D}{CS_{\text{Quatro0}}} \quad (3)$$

CS_{Quatro} presents the compressive strength of particular blended sample (MPa) and CS_{Quatro0} is the compressive strength of the sample Quatro0 (MPa). Dilution coefficient D (%) is calculated from the percentage of Portland cement replacement by pozzolanic materials.

As it can be seen from Fig. 11, in the case of two days' cured samples, Quatro2 with equivalent content of all the used pozzolanic materials demonstrates the most significant pozzolanic activity. When the hydration reactions go on, the strongest pozzolanic effect on compressive strength indicates the sample Quatro1 prepared with the highest silica fume content. After 28 days of curing, the situation

Table 4 Total and relative mass loss (%) of samples in different temperature intervals corresponding with particular hydration products

Sample Temperature interval/°C	Relative mass loss/%			
	Quatro0	Quatro1	Quatro2	Quatro3
0–130 (C–S–H)	27.32	26.51	27.32	26.15
140–390 (CSAH)	14.17	33.24	33.39	35.99
400–500 (CH)	17.79	14.28	14.24	13.80
550–705 (carbonate 1)	12.11	14.98	13.54	12.48
730–830 (carbonate 2)	3.75	2.63	2.63	2.52
850–970 (carbonate 3)	0.63	1.81	1.87	1.62
Total mass loss/%	17.59	17.09	17.13	16.67

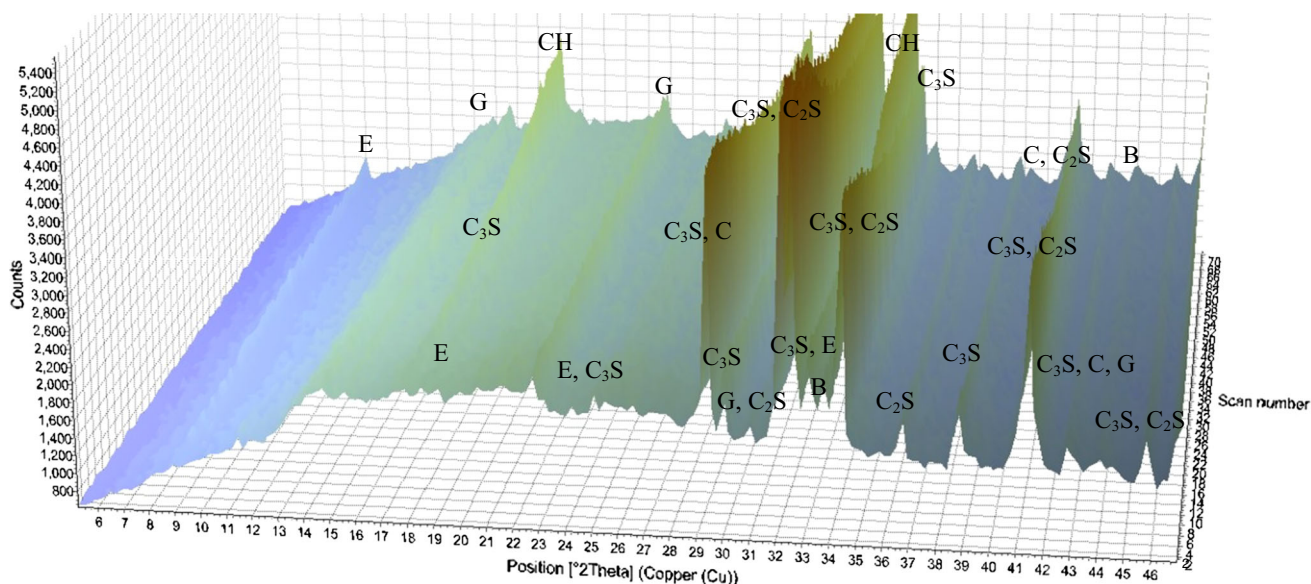


Fig. 9 Hydration of referential sample Quatro0 monitored by in situ XRD analysis up to 34 h and 50 min

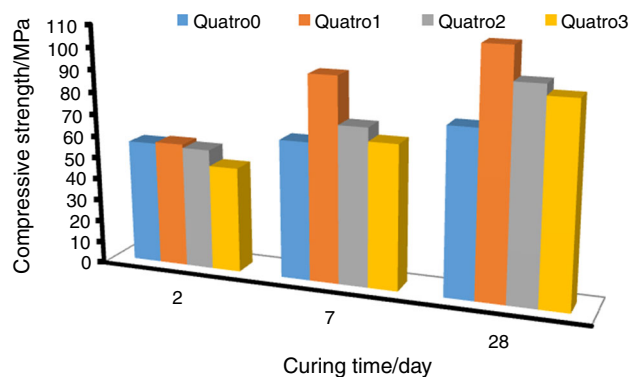


Fig. 10 Compressive strength (MPa) after 2, 7, and 28 days of curing

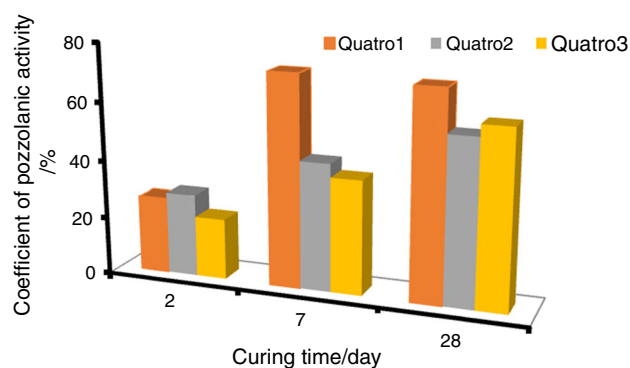


Fig. 11 Coefficient of pozzolanic activity (%) calculated from the values of compressive strength determined after 2, 7, and 28 days of curing

changes again and the pozzolanic effect of sample Quatro3 becomes more evident that the influence providing by sample Quatro2.

It is clearly evidenced that especially in the case of 7 and 28 days' cured samples, pozzolanic effect overcomes the influence of lower Portland cement content. Pozzolanic activities in the samples Quatro2 and 3 become more evident from 7 days after preparation mainly due to the delayed reactions of BFS. As can be assumed from the time-dependent CPA of sample Quatro1, initial rapid reactivity of SF slows down in time and 28 days after the preparation its contribution to compressive strength is even decreased when compared with 7 days' value. However, because all the three pozzolanic materials were used to prepare blended samples, their contribution to the compressive strength development cannot be univocally differentiated from each other and presents the synergetic effect.

Conclusions

Present study was devoted to the preliminary evaluation of pozzolanic activity of quaternary mixtures consisting of PC and three supplementary cementitious materials—BFS, SF, and MK.

Both, isothermal calorimetry and TG/DSC analysis, confirmed rising dilution effect as portion of pozzolanic materials replacing PC increased in the order 25, 30, and 35 mass%. Correspondingly, higher substitution levels led to the lowering amount of C–S–H and CH, and subsequently to lower degree of carbonation.

Dilution effect was in the case of blended cements compensated by pozzolanic reactions of the used supplementary cementitious materials. Demonstration of

pozzolanic reactions on the calorimetric curves differed according to the particular stage of hydration and also the amount of specific pozzolans. Evidence of pozzolanic activity using DTG analysis was uniquely able by gehlenite hydrate decomposition peak together with exothermic effect visible on DSC curves and belonging to the wollastonite and mullite formation. Decomposition of gehlenite hydrate as well as the formation of mullite was more pronounced in the case of sample with the highest content of MK. Presence of wollastonite was more obvious when larger amounts of SF were used. Wollastonite arose in the present systems from hydration phases with $C/S \cong 1$, such as tobermorite, which are much more thermally stable as commonly formed α - C_2SH arising from transformation of C–S–H gel in ordinary PC.

Contribution of pozzolanic materials to the compressive strength evolution overcame the dilution effect especially in the case of longer curing. Whereas higher SF activity influenced mainly the early-stage compressive strength, delayed reactivity of BFS demonstrated later and increased compressive strength of 7 and 28 days' cured samples.

On the basis of the above mentioned, it can be deduced that synergetic effect of three cementitious supplementary materials allows the formation of thermally stable products with improved compressive strengths and thus makes the present materials possibly suitable also for hydrothermal applications.

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