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Effect of Pozzolanic Additives on the Strength Development of High Performance Concrete

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Abstract

The aim of this research is to estimate the effect of pozzolanic substitutes on the temperature generated by the hydration and on the final strength of concrete. Differential thermal analyses (DTA) were conducted. Ternary cementitious systems with different ratios of Portland cement, silica fume and calcined illite clay were investigated. The results showed that the rates of pozzolanic reaction and portlandite consumption in the silica fume-blended cement pastes are higher than in the illite clay-blended cement pastes.

Keywords: High performance concrete; pozzolanic additives; silica fume; ternary systems.

1. Introduction

   Today, pozzolanic materials are enjoying a renaissance as supplementary cementing materials in Portland cements pastes and may replace part of the clinker in order to enhance the performance of the hydrated cement. When Portland cement clinker is produced there is a significant amount of CO_2 emitted from the calcination of the limestone. [1]. In order to reduce the emission of CO_2, reduction of the cement amount in concrete production and usage of pozzolans is an advantage [2].

   Pozzolans are materials that consist predominantly of silica and alumina [3] and are able to combine with portlandite in the presence of water to produce new reaction products exhibiting a binding character [4,5]. The amount of portlandite produced during the cement hydration will be reduced relatively to the percentage of pozzolans used in

the mixture, and it will vary depending on the type of cements. Amount of portlandite is also related to the ratio of cement hydration. It will depend upon the amount of C_3S and C_2S in the cement. Each of these compounds react with water to form C-S-H (calcium silicate hydrate) and portlandite – $Ca(OH)_2$. A small portion of portlandite enters into reactions with alumina and sulphates to form compounds such as ettringite. Therefore not all of the portlandite produced is available or free to react with pozzolans [6,7]. It has been noted in the research by Massazza, that approximately 22% of free portlandite is available in the system. [8] Moreover, it has been found that adding calcium to pozzolan, which has a low calcium /silica ratio, enhances the hydration reaction for the formation of calcium silicate hydrate (C-S-H) gels and improves the mechanical strength of high-performance concrete [9].

Materials that exhibit pozzolanic activity can decrease the hydration heat by means of cement substitution, which increases the heat generated during hydration due to the pozzolanic reaction [10].

Pozzolans are known to increase the durability [11], lower the hydration heat [12], increase the resistance to sulphate attack [13] and reduce the energy cost per cement unit [12].

In the scientific research work by other scientists [14-16] it has been proved that by addition of metakaolin with pozzolanic character to the PC (in the reaction with PC hydratation products calcium silicates appear in the structure), the binding time is accelerated in the early stage of hydration. Giergiczny has detected, that by replacing half of PC amount in the composition with metakaolin – the shrinkage and amount of cracks diminishes for the concrete samples [17].

Consequently, the present study focuses on modification of cement pastes with binary and ternary cement paste systems in order to determine changes of hydration heat. In addition, the hydration characteristics of the cement mortars prepared by blending cement with silica fume (SF) and calcined illite clay (CC) were examined at different curing ages.

2. Materials and methods

2.1. Test methods

Chemical composition of raw materials was determined according to LVS EN 196-2 with precision +/- 0.5%. Specific surface area has been detected by BET method. SEM was used for microstructural investigation of hardened specimens and for description of raw materials. To describe the hydration process of blended cement pastes, thermogravimetrical research was carried out by DTA. The temperatures of exothermic effects during the binding and hardening of concrete paste were registered according to the methodology devised by company Alcoa, (Calcium Aluminate Cement Test Methods. Exothermic Reaction (EXO). Alcoa Industrial Chemicals: 16 p.).

Properties of fresh mixes were determined according to LVS EN 1015-3:2000 with flow table for mortar. The initial cement setting time was determined according to LVS EN 196-3, the normal consistency was tested according to LVS EN 196-3. Compressive strength of specimens was determined according to standard LVS EN 1015-11 'Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar'.

2.2. Materials

All materials used in this study were commercially available raw materials - silica fume (SF) ("Elkem Microsilica® Grade 971-U"), calcined illite clay (CC) (brick factory "Lode"), Portland cement (CEM) ("Kunda®" CEM I 42,5 N) and superplasticizer (SP) admixtures ("Sikament® 56"). Chemical compositions of raw materials are given in the Table 1. The initial setting time of cement was 182 min and the final setting – 224 min, the normal consistency was 28.2%.

According to technical data sheet the density of granulated silica fume is 300 kg/m^3. Specific surface area of the material is 18-20 m^2/g (technical information obtained from the commercially available data sheet), 99.8% of silica fume particles are smaller than 45µm. 90% of silica fume particles had dimensions ranging from 20 nm to 0.5 µm. It is confirmed by SEM image (Figure 1).

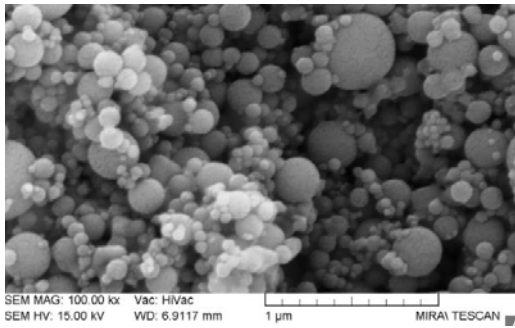Table 1. Chemical composition of Portland cement, silica fume and calcined clay, [wt, %].

Oxides	SF	CEM	CC
SiO_2	98.4	18.85	73.15
Al_2O_3	0.20	4.37	11.72
Fe_2O_3	0.01	3.09	6.15
CaO	0.2	61.98	-
MgO	0.1	3.64	-
SO_3	0.1	3.18	-
Na_2O	0.15	0.22	-
K_2O	0.2	1.25	-
Other	0.6	3.42	10.21

Fig. 1. SEM photograph of the silica fume (SF), magnification x 100 000.

Industrially prepared illite clay was used as the second substitute from the range of pozzolanic additives. Illite clay was calcined in the rotary furnace in laboratory at 700°C temperature for 30 min. CC was ground in the planetary ball mill Retsch 300 for 30 min with a speed 300 ppm. BET for illite clay is 21.4 m^2/g. Chemical composition is given in Table 1.

Natural dried and graded sand from "SAULKALNE S" Ltd with fraction from 0 to 1.0 mm, humidity less than 0.2%, bulk density 1425 kg/m^3 was used for mortars. Highly effective water amount reducing SP additive "Sikament ® 56" ("Sika Baltic" Ltd) was used to increase workability of fresh HPC mortars.

2.3. Sample preparation

The composition of prepared cement pastes and cement mortars is given in table 2 and table 3.

Table 2. Cement pastes.

	Composition, %				
	Cement paste			SP	W/C
	CEM	SF	CC		
CEM100	100	0	0	0.5	0.21
SF10	90	10	0	0.5	0.27
SF20	80	20	0	0.5	0.29
SF30	70	30	0	0.5	0.34
SF10CC20	70	10	20	0.5	0.25
SF20CC10	70	20	10	0.5	0.31

Table 3. Cement mortars.

	Composition, %					
	Cement paste			SP	Sand	W/C
	CEM	SF	CC			
CEM100	100	0	0	0.5	100	0.26
SF10	90	10	0	0.5	100	0.27
SF20	80	20	0	0.5	100	0.29
SF30	70	30	0	0.5	100	0.36
SF10CC20	70	10	20	0.5	100	0.32
SF20CC10	70	20	10	0.5	100	0.38

The mixing procedure of materials was the following: all dry materials were mixed by a high speed mixer until a homogenous mixture was obtained (for 1 min). Then water and superplasticizer (SP) was added in two steps. During the first step 50% of water with superplasticizer was added and the batch was mixed for 1.5 minutes. During the second step the rest of the water was added. Total mixing time was approximately 6 minutes. Natural sand was used for preparation of mortar specimens but was not used for preparation of cement paste specimens.

3. Results and discussion

3.1. Effect of silica fume (SF) and calcined illite clay (CC) used to determinate hydration temperature
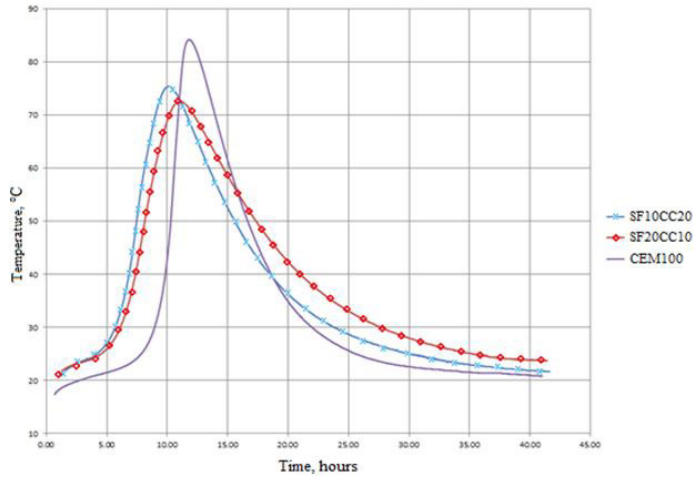

Fig. 2. Curves of the hydration temperature for cement paste specimens – CEM100 (CEM I), SF10 (CEM I+10%SF), SF20 (CEM I+20%SF), SF30 (CEM I+30%SF).
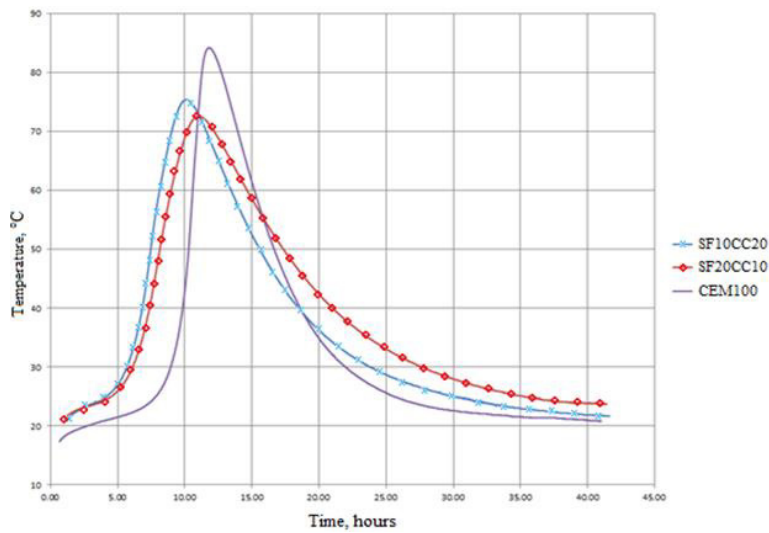

Fig. 3. Curves of the hydration temperature for cement paste specimens – CEM100 (CEM I), SF10CC20 (CEM I + 10%SF + 20%CC), SF20CC10 (CEM I + 20%SF + 10%CC).

Hydration temperature curves are shown in the Figure 2, which characterise the hydration process of different cement pastes (with or without SF – Table 2). The maximum hydration temperature for the reference composition CEM100 is 83°C and it was reached after ~13 hours. For SF10 cement paste hydration temperature reached the maximum point of ~85ºC after around 11 hours of reaction (Figure 2). For sample SF20 beginning of hydration process started earlier than for SF10 and the hydration process is longer, maximum hydration temperature has dropped till ~78ºC.

For SF30, hydration temperature is diminished for 15ºC and maximum was reached after ~12.5 hours, outperforming composition CEM100. Reduction of hydration temperature has a positive influence on cement composites hardening process and the risk of having micro cracks in the early age of concrete decreases. All compositions reached maximum temperature in the 11-13 hour interval.

It is concluded that the reduction of the amount of cement in the composition and the proportional increase of SF in the composition results in the reduction of the maximum temperature of the heat of hydration.

The hydration temperature for ternary systems is given in Figure 3. Comparing to CEM100 the highest maximal hydration temperature for the composition SF10CC20 was ~75ºC after around 10 h of reaction. For the composition SF20CC10, beginning of hydration process is delayed comparing to SF10CC20 and the hydration process is longer, maximum hydration temperature has dropped till ~72ºC (Figure 3). Both compositions reached maximum temperature in the 10-11 h interval and generally it is earlier than for compositions blended just with SF.

According to the theory of hydration of cement, three periods of micro-structural development in cement pastes are usually distinguished: an early, middle and a late period, with divisions at 3 and 24 hours of hydration time. As it has been discovered in the early researches by several scientists that in the middle period of hydration after ~4 h the dissolving clinker grains are completely covered by cracked shells of C-S-H, which show a thickness of 0.5 - 1 µm after ~12 h [18,19]. These shells are separated from the clinker grains through spaces up to 0.5 µm wide. Precipitation occurs inside these spaces in the pore solution but also on the surfaces of inert grains. From ~18 h onwards but basically in the late period of hydration, these spaces become progressively filled with C-S-H. Released hydration heat for pure cement paste decreases rapidly after 18 h; this is explained by the fact that the C-S-H layer around the cement grains has increased to 8µm and the hydration process is limited but released heat decreases rapidly. When adding pozzolans, apparently this C-S-H layer is not formed as compact or dense, so the cement hydration may continue for a longer period of time, which is displayed in the charts in Figure 3. In contrast to the through-solution processes (dissolution, aqueous diffusion and precipitation from solution), further hydration was suggested to occur very slowly by a topochemical mechanism due to the lack of a true liquid phase in contact with the dissolving surfaces.

Hydration heat maximum temperature reduces, possibly it is caused by formation of C-S-H layer around the cement particles; SF absorbs calcium ions in its structure and it reduces the Ca^{2+} concentration in the composition [20], and it is observed, when PC is diminished by 10% in the composition, that it has influence on lowering the hydration temperature.

According to literature [20] the prolonged dormant period at the low w/c ratio can be explained by the water absorption behavior of SF and the formation of a SF layer on the cement particles. Silica fume (SF) is composed of very small particles which may form agglomerations, when mixed with water, and are soon covered with a gel-like layer. Water may become enclosed in this layer, which has been suggested as the cause of the rapid water consumption of SF mixtures. If the w/c ratio is low, cement and water do not come into full contact initially, as the voids may not be full of water. Absorption decreases the water content available for the cement hydration resulting in less cement taking part in the hydration process. Thus, SF acts as a retarder to the process. The formation of SF layers on the surface of the cement particles also contributes to the delay of the hydration speed which decreases maximal hydration temperature of the paste.

For the low w/c ratios silica fume (SF) reduces the rate of heat of hydration during the acceleration period and increases the rate after the acceleration period.

Recently, some activated materials, such as metakaolin, which is produced by heating kaolinite, have been found to be an excellent pozzolanic material. In the recent studies by other scientists (Mohamed S. Morsy et al. [20]), the utilisation of calcined clay in the form of metakaolin and silica fume (SF) as a pozzolanic additive for cement paste has provoked considerable interest focusing on removal of the calcium hydroxide, which is produced by the hydration of cement and which is associated with poor durability. Calcium hydroxide removal has a major influence on resistance to fire, which is derived from the additional cementitious phases generated by reaction of calcium hydroxide and metakaolin and also due to the filler effect in the poor system. Studies of concrete based on Portland cement showed that addition of metakaolin develops pozzolanic properties (calcium hydrosilicates are formed) and accelerates concrete hardening, particularly in the early period of hardening. Replacement of part of Portland cement by metakaolin reduces concrete shrinkage and the number of cracks in it [21].

Calcined illite clay (CC) was introduced in the composition to test the qualities of the local fillers such as pozzolan and ingredients contributing to reducing the necessary amount of the Portland cement together with silica fume (SF). Comparing the compositions, which consisted only SF (Figure 2) and compositions with SF and CC (Figure 3), it can be concluded that the lowest hydration temperature was for the specimen SF30, where maximum hydration temperature is ~70°C (Figure 2). Further results show that the hydration heat temperature rises by reducing the amount of SF and increasing the amount of CC in the composition: for SF20CC10 – max. hydration temperature is around 72°C and for SF10CC20 – max. 75°C, subsequently for the SF20 – max. 78ºC (Figure 3).

Chatterji et al. stated that around each cement particle there were approximately 100 000 grains of SF [22]. Clearly, this number depends on the size of the cement and SF particles, and the percentage of SF in the mixture. Water required for the hydration of the cement grains have to percolate through the layers of SF. The resistance to this water flow will increase with an increase in the thickness of the SF layer, i.e. with lowering of the w/c ratio. In the dormant period, the SF layer inhibits the diffusion of water to the cement particle surface.

Silica fume (SF), even though it adsorbs some water, does not reduce the amount of water available for the cement hydration. The higher the w/c ratio, the more the SF is dissolved and remains in solution for rapid dissolution reaction. Therefore, the retarding effects reduce as the w/c increases [23].

3.2. The effect of pozzolanic additives on the amount of free portlandite

 Systems using SF and CC (Figure 4 and 5) were prepared to prove that addition of SF diminishes the hydration heat and lowers the amount of portlandite in the composition.

As selected pozzolans contain low amount of CaO, this component must be added in the exact proportions required for the reaction, CaO is either added as portlandite or, in a composite cement, provided by the portlandite formed during cement hydration. Pozzolans react with a saturated solution of calcium hydroxide under the formation of calcium silicate hydrates (C-S-H gels) and hexagonal aluminates C_4AH_{13}. Similar results were observed during the reaction of zeolitic compounds with calcium hydroxide. Other products of pozzolanic reaction can be also C_3AH_6, $C_3AS_2H_2$, $C_3A \cdot CaCO_3 \cdot 12H_2O$ and C_2ASH_8 [24].
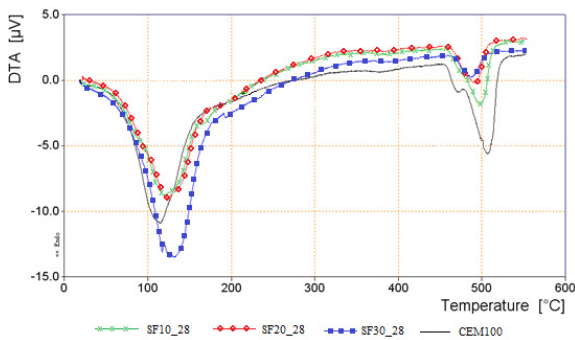

Fig. 4. DTA results for the 28 days old specimens with 10%, 20% and 30% silica fume (SF) in the composition.
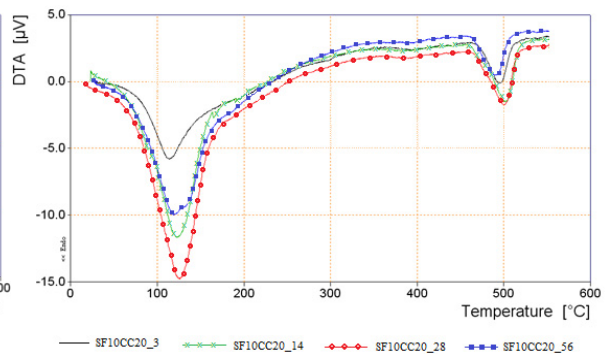
Fig. 5. DTA results for ternary cementitious compositions (silica fume SF 10% and calcined clay CC 20%) for all ages.

The consumption of portlandite, followed by the precipitation of hydrated cement minerals with a lower density, is very efficient in filling up capillary pore space thereby decreasing porosity. This portlandite consuming process and the associated pore refinement process lead to increased strength, impermeability, durability and chemical resistance of cements with pozzolan additive.

In the reference composition mainly formed C-S-H, which decomposes at 95-120°C temperature. The peaks at 160-200°C, are due to decomposition of a complex mixture of hydrated silicate- and aluminate- type compounds [24]. The endothermic peaks below 200°C is mainly due to the dehydration of C-S-H (tobermorite - like phase and hydrogarnet $C_3A_1\text{-}xF_xS_yH_6\text{–}2y$ and gehlenite hydrate C_2ASH_8 [25] as well as ettringite [26].

Portlandite (C-H) also formed in the composition, which decomposes at 495-550ºC degrees temperature. In the reference specimen cement is 100%, so accordingly it has portlandite (C-H) in the largest amount. As the amount of cement was decreased by adding 10% of silica fume (SF) in the composition, C_2ASH_8 forms [27] as well as small amount of C_6ASH_{32}.

Table 4. Compound degradation temperature and intensity of endoeffect (µV).

	C-S-H	C_4ASH_{12}	CSH_2	C_6ASH_{32}	C-H
	95-120ºC	125-135ºC	160-185ºC	185-195ºC	495-550ºC
CEM100	11				7,8
SF10		8	1,5		5
SF20		8,5		1	2
SF30		14		1,5	1
SF10CC20		15		0,5	4,8
SF20CC10		12			2

For composition SF10, less C-H forms; this is proved by smaller endoeffect (36% smaller than for the reference composition) at 495-550°C temperature. This proves that part of Ca has reacted with silica fume (SF) and this is the reason why amount of C-H has diminished.

As the amount of silica fume (SF) in the composition (SF20) is increased till 20%, amount of C_2ASH_8 increases proportionally but the amount of C_6ASH_{32} and C-H has decreased by 75%, which shows that Ca reacts more intensively with the silica fume (SF) in this composition. For the specimen SF30 amount of C_4ASH_{12} increases significantly in comparison with C_6ASH_{32}. For specimen SF30 amount of C-H has decreased by 88%, this means that bigger amount of Ca has reacted with silica fume (SF). In case, when more SF reacts with Ca, smaller amount of C-H can be found in the structure of specimens.

For the specimen SF10CC20 amount of C_4ASH_{12} has risen twice in comparison with the other SF10 and SF20 specimens and approximately by 20% in comparison with SF20CC10 specimen, which shows that clay minerals react with the active aluminium and crystals of the calcium aluminium hydrosilicate form. Small amount of C_6ASH_{32} can be also determined. The amount of C-H for the compositions SF10 and SF10CC20 is nearly the same; therefore it can be concluded that Ca basically reacts only with silica fume (SF). The same tendencies can be observed for the specimen SF20CC10, where the amount of C_4ASH_{12} is decreasing, because the amount of the clay is diminished. Again, amount of C-H is the same for SF20 and SF20CC10 proving that the amount of C-H depends only of the amount of silica fume (SF) in the composition.

3.3. Mechanical properties

The mechanical properties of 3, 14, 28 and 56 days old specimens were tested. All specimens were taken out of the water shortly before testing and placed in the heating furnace for 15 min at 80°C, so the specimens were slightly dried. Bending strength and compressive strength results for all specimens are described in Figures 6 and 7.
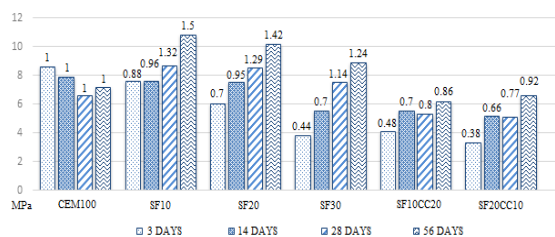

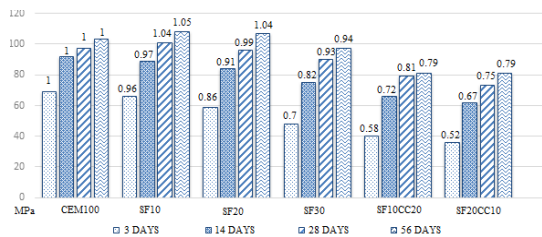Fig. 6. Bending strength results for 3, 14, 28 and 56 days old concrete.

Fig. 7. Compressive strength results for 3, 14, 28 and 56 days old concrete.

Analyzing the results of compressive strength, it is visible that the highest early compressive strength for 3-day-old and 14-days-old specimens is for the reference composition of CEM100, 69 MPa and 92 MPa respectively. For sample SF10 compressive strength in the 14th day was 89 MPa (strength index 0.97). It was observed that according

to the strength in the early stage (3-14 days) compositions are ranked after the presented compressive strength indexes subsequently - CEM100, SF10, SF20 and SF30. Therefore it can be concluded that more cement in the composition leads to higher early strength for compositions (both bending and compressive strength) (Figure 6 and Figure 7). While testing the 56 days-old samples, the reference composition CEM100 was outperformed by SF10 with 108MPa and SF20 with 107 MPa (strength indexes 1.05 and 1.04). Ternary systems (SF10CC20 and SF20CC10) show the lowest bending and compressive strength results for all ages (3, 14, 28 and 56 days old concrete). It is possible to conclude that pozzolans (in this case SF) leads to increment of mechanical properties (especially bending strength) for specimens in prolonged curing period; however, more successful are compositions where no more than 20% of cement are replaced by SF. Ternary pozzolan systems do not prove to be efficient in this case. By replacement of PC by 30%, compression strength diminishes by 20% in comparison with CEM100.

4. Conclussion

It has been found that silica fume has a superior influence on the strength development of concrete in later stage. Portlandite (C-H) consumption in the silica fume blended cement pastes is higher than in the illite clay blended cement pastes.

It is concluded that SF accelerates the commencement of the cement minerals hydration process for approximately 1-2 hours. When increasing the amount of SF in the composition, beginning of hydration process starts earlier and the hydration process is longer. Reduction of hydration temperature has a positive influence on the concrete hardening process and decreases the risk of having micro cracks in the concrete at its early age. All compositions reached maximum temperature in 11-13 hour interval. SF leads to increment of mechanical properties, however, more successful are compositions where no more than 20% of cement are replaced by SF. Ternary systems show the lowest strength results for all ages and do not prove to be efficient in this case.

This paper concludes that pozzolanic reaction can significantly reduce the required amount of cement and make concrete more eco-friendly.

Acknowledgements

References

[1] D. Bajare, G. Bumanis, L. Upeniece, Coal combustion bottom ash as microfiller with pozzolanic properties for traditional concrete, Procedia Engineering 57 (2013) 149–158.
[2] E. R. Dunstan Jr., How Does Pozzolanic Reaction Make Concrete 'Green', 2011 World of Coal Ash (WOCA) Conference (2011) Denver, CO, USA.
[3] D. J. Cook, Natural pozzolanas, in: R. N. Swamy (Ed.), Cement Replacement Materials, Surrey University Press (1986) 200.
[4] S. Martinez-Ramirez, M. T. Blanco-Varela, I. Erena, M. Gener, Pozzolanic reactivity of zeolitic rocks from different Cuban deposits: characterisation of reaction products, Applied Clay Science 32 (2006) 40–52.
[5] G. Martens, R. Snellings, K. van Balen, B. Bicer-Simsir, P. Verlooy, J. Elsen, Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity, Cement and Concrete Research, 39 (2009) 233–240.
[6] N. Toropovs, D. Bajare, G. Sahmenko, L. Krage, A. Korjakins, The formation of microstructure in high strength concrete containing micro and nanosilica, Key Engineering Materials 604 (2014) 83–86.
[7] S. Popovic, Strength and Related Properties of Concrete, A Quantitive Approach, John Wiley and Sons, Inc, New York, 1998.
[8] F. Massazza, Pozzolana and Pozzolanic Cements, Lea's Chemistry of Cement and Concrete, Volume 4, edited by Peter Hewitt, Arnold, John Wiley and Sons Inc, New York.
[9] G. C. Isaia, A. L. G. Gastaldini, R. Moraes, Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete, Cement and Concrete Composites (2003) 25–69.
[10] M. Frias, M. I. Sanchez de Rojas, J. Cabrera, The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars, Cement and Concrete Research 30(2) (2000) 209–216.
[11] M. F. Rojas, J. Cabrera, The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin-lime-water systems, Cement and Concrete research 32 (2002) 133–138.
[12] C. Shi, Pozzolanic reaction and microstructure of chemical activated lime-fly ash pastes, ACI Materials Journal 95(5) (1998) 537–545.

[13] I. Janotka, L. Krajci, Utilization of natural zeolite in Portland cement of increased sulphate resistance, ACI Special Publications 22 (2003) 223–229.

[14] A. Allahverdi, S. Vakilinia, P. Gharabeglu, Effects of RFCC spent catalyst on some physico mechanical properties of portland cement paste, Ceramics – Silikáty 55 (2) (2011) 161–168.

[15] R. Malathy, K. Subramanian, Efficiency factor for silica fume & metakaolin at various replacement levels, In: 32-nd Conference on 'Our World in Concrete & Structures' (2007) 1–10.

[16] E. Badogiannis, G. Kakali, G. Dimopoulou, E. Chaniotakis, S. Tsivilis, Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins, Cement and Concrete Composites 27 (2005) 197–203.

[17] Z. Giergiczny, Effect Of Some Additives On The Reactions in Fly Ash Ca(OH)2 system, Journal of Thermal Analysis and Calorimetry 76 (2004) 747–754.

[18] J. Justs, M. Wyrzykowski, F. Winnefeld, D. Bajare, P. Lura, Influence of superabsorbent polymers on hydration of cement pastes with low water-to-binder ratio: A calorimetry study, Journal of Thermal Analysis and Calorimetry 115(1) (2014) 425–432.

[19] C. L. Huang, R. F. Feldman, Hydration reactions in Portland cement – silica fume blends, Cement and Concrete Research 15 (1985) 585–592.

[20] M. S. Morsy, S. S. Shebl, Effect of silica fume and metakaoline pozzolana on the performance of blended cement pastes against fire, Ceramics – Silikáty 51(1) (2007) 40–44.

[21] R. Stonis, I. Pundiene, V. Antonoviè, M. Kligis, E. Spudulis, Study of the effect of replacing microsilica in heat-resistant concrete with additive based on metakaolin, Refractories and Industrial Ceramics 54(3) (2013) 232–237.

[22] S. Chatterji, N. Thaulow, P. Christensen, Pozzolanic activity of by product silica fume from ferro-silicon production, Cement and Concrete Research, 12 (6) (1982) 781–784.

[23] B. W. Langan, K. Weng, M. A. Ward, Effect of silica fume and fly ash on heat of hydration of Portland cement, Cement and Concrete Research 32 (2002) 1045–1051.

[24] P. Rovnaník, Supplementary Silicate Admixtures in The Context Of Calcium Hydroxide Content In Concrete, Brno University of Technology.

[25] N. Deneanu, M. Dulama, C. Diaconescu, A Thermal analysis study on proprietary quick-setting mixed binder system, Nuclear (2013)

[26] S. M. Morsy, Effect of Temperature on Hydration kinetics and stability of hydration phases of metakaolin-lime sludge-silica fume system, Ceramics – Silikáty 49(4) (2005) 225–229.

[27] R. Kaminskas, The Effect Of Pozzolana on The Properties Of the finest fraction of separated Portland Cement. Part 2, Ceramics – Silikáty 52(3) (2008) 183–189.