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BEHAVIOR OF BLENDED CEMENT PASTES AT ELEVATED TEMPERATURE

Fire can cause severe damage to building structures. This fact has increased the importance of the fire resistance of concrete. The consideration of the fire resistance of concrete requires the complete knowledge of the behaviour of each concrete component under elevated temperatures. The resistance of blended cement pastes upon heating was studied in the present paper. Natural pozzolana, fly ash, ground granulated blast-furnace slag, metakaolin and limestone were used as the main cement constituents. Blended cements were prepared by replacing a part of Portland Cement (PC) with the minerals mentioned above (10% w/w in the case of metakaolin, 20% w/w in the case of the rest materials). The specimens were water-cured for 3 months and then they were thermally treated at 200, 400, 600 800 and 1000°C for 1h. Visual inspection, mass measurements and ultrasonic pulse velocity measurements were carried out after each thermal treatment. It was concluded that the cohesion of the pastes was strongly affected by the kind of the main constituent, added to the Portland cement. The use of pozzolanic materials and especially metakaolin improved the fire resistance of the pastes, while the samples with limestone show the worst behavior.

Key words: Blended cement, Pastes, High temperature.

The development of Portland-composite cements, using traditional and modern mineral additions, is considered to be state of the art in cement production. The initial aim was, of course, the reduction of cost, but further objectives have been added, such as the improvement of performance, energy saving, the exploitation of conventional raw materials or industrial by-products and the ecological benefits [1–3].

The European Standard EN 197–1 (2000) identifies type II cements that may contain various materials as the main constituents, in percentages ranging from 6% to 35%. Pozzolana, fly ash, ground granulated blast-furnace slag (ggbs) and limestone are the main materials that are permitted by EN 197–1 [4].

A question that came out, after recent big fire outbreaks in buildings and tunnels, is the resistance of blended cements under extreme thermal conditions. Upon exposure to high temperature, cement and concrete undergo both chemical and physical changes, such as the evaporation of free water, the dehydration of hydrated compounds, the partial volatilisation of C–S–H and shrinkage. As a result, the material exhibits cracking, explosive spalling or both.

Previously published work is mostly concerned with the effect of high temperature on the performance of concrete [1–7] or the development of mathematical models for the evaluation of fire resistance of concrete structures [8–11]. There are only a few papers on the effect of high temperature on the structure of cement pastes [12–14]. However, the consideration of the fire resistance of concrete requires the complete knowledge

of the behavior of each concrete component under elevated temperatures. The behavior of blended cement pastes upon heating, was studied in the present paper.

EXPERIMENTAL

One sample of reference Portland cement and five samples of composite cements containing limestone, natural pozzolana from Milos Island, blast-furnace slag, fly ash and metakaolin were examined. The chemical composition of these materials is shown in Table 1, while the mineralogical composition and the moduli of the clinker are given in Table 2. The cements were produced by intergrinding clinker, the second main constituent, and gypsum in a pro-pilot plant ball mill. Metakaolin is a commercial ultra fine material and the cement with metakaolin was prepared by replacing 10% of the Portland cement with metakaolin. The mix proportions and the sample coding are given in Table 3.

The pastes were prepared with a water to solid ratio of 0.45 using carbon dioxide free distilled water. In the case of metakaolin, the water to solid ratio was 0.50. The pastes were cast in steel moulds where they

Table 1. Chemical analysis of the minerals (% w/w)

Oxide	Lime-stone (L)	Natural Pozzolana (P)	Fly Ash (F)	Slag (S)	Meta-kaolin (M)
SiO ₂	0.54	59.18	49.33	36.74	54.41
Al ₂ O ₃	0.43	16.12	20.72	10.44	43.94
Fe ₂ O ₃	0.20	6.14	7.98	1.20	0.35
CaO	53.61	4.92	10.26	40.32	0.37
MgO	1.29	1.96	2.19	7.60	–
K ₂ O	0.06	2.15	1.94	0.31	0.31
LOI	43.73	4.78	2.02	0.44	–
Total	99.86	95.25	94.44	97.05	99.38

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Table 2. Chemical and mineralogical composition of the clinker

Chemical composition (%)		Mineralogical composition (%)	
SiO ₂	21.47	C ₃ S *	65.0
Al ₂ O ₃	5.00	C ₂ S	12.6
Fe ₂ O ₃	3.89	C ₃ A	6.7
CaO	65.67	C ₄ AF	11.8
MgO	1.89	Modulii	
K ₂ O	0.68	Lime Saturation Factor (LSF)	95.79
Na ₂ O	0.16		
SO ₃	1.04	Silica Ratio (SR)	2.42
Total	99.70	Alumina Ratio (AR)	1.29
fCaO	1.15	Hydraulic Modulus (HM)	2.18

*Cement chemistry notation: C: CaO, S: SiO₂, A: Al₂O₃, F: Fe₂O₃

Table 3. Codes and composition of the produced mixes

Code	Composition
PC	Clinker: 100%w/w, (gypsum: 5% of clinker by mass)
PFC	Clinker: 80% w/w, 20% fly ash (gypsum: 5% of clinker by mass)
PPC	Clinker: 80% w/w, 20% natural pozzolana (gypsum: 5% of clinker by mass)
PLC	Clinker: 80% w/w, 20% limestone (gypsum: 5% of clinker by mass)
PSC	Clinker: 80% w/w, 20% ground granulated blast-furnace slag (gypsum: 5% of clinker by mass)
PMC	PC: 90% w/w, metakaolin: 10% w/w

remained for 24 h. Then, the specimens were demolded and cured in water for 3 months. After the curing period, the specimens were oven-dried at 105°C for 24h. Finally, the specimens were cooled and kept in airtight bags at room temperature.

The thermal treatment of the specimens was carried out in a laboratory electric furnace at 200°C, 400°C, 600°C, 800°C and 1000°C. The temperature was raised gradually and the specimens were left at the final temperature for 1 hour. The cooling took place slowly, inside the furnace and lasted for 24 hours.

The specimen weight was measured before and after each thermal treatment and the % mass loss was determined.

The visual examination of the samples was performed after the thermal treatment and all significant modifications, such as changes in surface color and texture, deterioration, expansion and cracking were recorded.

The ultrasonic pulse velocity test (apparatus: 58-E48, Controls Testing Equipments Ltd) was used as a measure of the internal soundness of the samples. The measurements were carried out before and after each thermal treatment.

RESULTS AND DISCUSSION

Mass loss measurements

The total mass loss of the specimens after thermal treatment at each temperature is shown in Table 4. The mass loss at specific temperature ranges can be attributed to the following reactions:

T < 200°C: loss of pore water,

200°C < T < 400°C: removal of water from hydrated compounds,

400°C < T < 600°C: dehydroxylation of Mg(OH)₂ and Ca(OH)₂,

T > 600°C: decomposition of carbonates.

Table 4. Mass loss in relation to the temperature of thermal treatment (%)

Sample	200°C	400°C	600°C	800°C	1000°C
PC	2.04	5.38	9.67	11.02	11.47
PFC	2.55	7.30	10.90	12.68	14.87
PPC	3.28	7.33	11.49	13.08	15.26
PLC	2.85	6.03	10.04	17.24	17.65
PSC	2.80	6.48	11.45	13.22	13.83
PMC	3.74	8.92	12.34	13.66	13.91

Figure 1 presents the mass loss of the specimens in each temperature range. As shown, in all the samples, with the exception of the sample with the limestone (PLC), most of the weight was lost up to 600 °C. This loss is attributed to the removal of chemically bound water. The limestone specimen has the highest mass loss in the range of 600–800 °C, due to the decomposition of limestone and the removal of CO₂.

As is obvious, the mass loss of the specimens takes place in two well-defined stages. The first one (T < 600°C), is associated with the decomposition of the hydrated compounds and the removal of chemically bound water. The mass loss at this stage depends on the kind and amount of hydrated compounds. The second stage (600 < T < 1000 °C), is associated with the thermal decomposition of minerals present in the added materials. In this case the mass loss depends on the type and percentage of added material. Figure 2 shows the mass loss of the specimens in the higher temperature range. In the first range, the highest mass loss was observed in the sample with metakaolin, while in the second range in the sample with limestone. In both cases the PC sample showed the lower mass loss.

Visual inspection

Visual inspection of the specimens was carried out after each thermal treatment. The observations are summarised in Table 5. Photos of the specimens thermally treated at 600 and 800°C are presented in Figures 3 and 4, respectively. The thermal treatment of the samples up to 400°C does not cause any visible

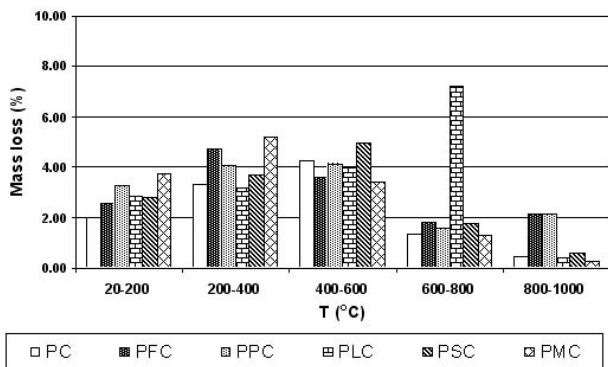


Figure 1. Mass loss of the samples

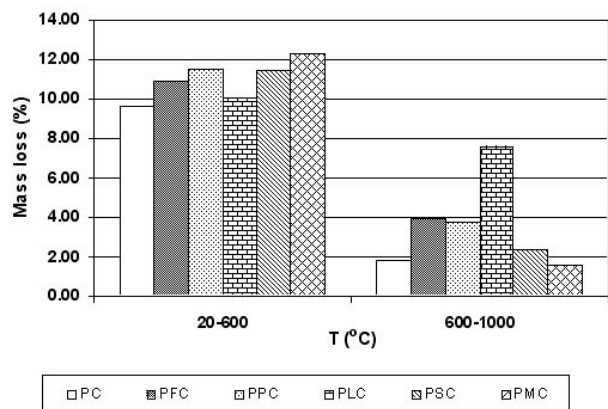


Figure 2. Mass loss of the samples in the temperature ranges 25-600°C and 600-1000°C

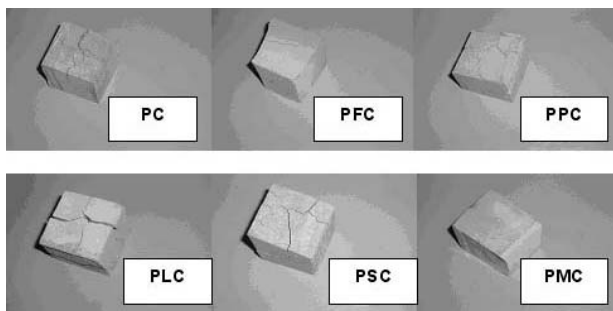


Figure 3. Photos of specimens thermally treated at 600°C

Table 5. Appearance of the specimens after thermal treatment

T (°C)	PC	PFC	PPC	PLC	PSC	PMC
200	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration
400	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration
600	Cracking	Some cracking	Some cracking	Extensive cracking	Cracking	No visible deterioration
800	Extensive cracking	Some cracking	Some cracking	Cracking and spalling	Extensive cracking	No visible deterioration
1000	Cracking and spalling	Some cracking	Some cracking	Cracking and spalling	Extensive cracking	Some cracking

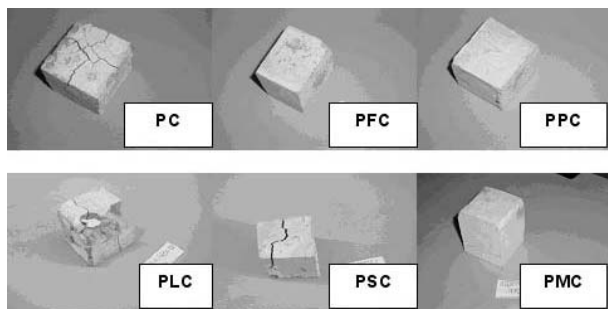


Figure 4. Photos of specimens thermally treated at 800°C

deterioration. At 600 °C some surface cracking appears on the surface of most samples. The sample with the limestone exhibits extensive cracking, due to the start of limestone decomposition and the evolution of CO₂, while the sample with metakaolin does not have any visible deterioration. At 800 °C, the extensive cracking of PC sample and the spalling of PLC sample are the only observed changes. At 1000 °C, PC and PLC samples exhibit extensive cracking and spalling, while the rest of the samples have surface cracking. The sample with metakaolin continues to have the best behavior. It must be noticed that the deterioration of the specimens is not related with the mass loss. Although, half of the total mass loss has already occurred up to 400 °C, no cracking was observed at this temperature.

Ultrasonic pulse velocity

The ultrasonic pulse velocity was measured before and after each thermal treatment. The decrease of the ultrasonic pulse velocity indicates the formation of cracks in the interior of the specimens. Figure 5 shows the ultrasonic pulse velocity of the specimens, in relation to the temperature of thermal treatment. As seen, the pulse velocity remains practically constant up to 400 °C and then gradually decreases up to 800 °C. The high decrease in the ultrasonic pulse velocity of the samples PC and PSC and the highest in PLC after heating at 800 °C indicates the extensive cracking of these samples.

The results drawn from each one of the above-mentioned techniques are in good accordance with each other. As was confirmed, most of the mass loss in all the specimens was observed up to 600 °C. However, deterioration of the specimens took place at

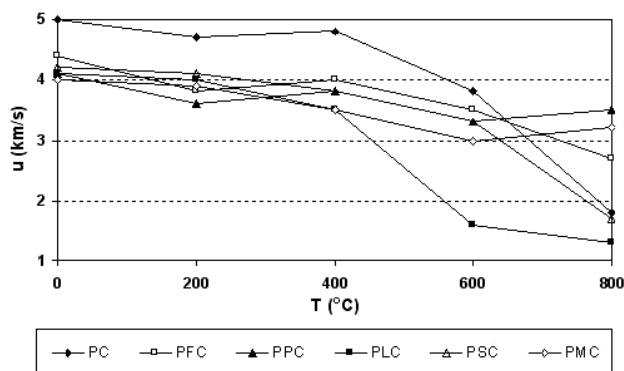


Figure 5. Ultrasonic pulse velocity of the specimens

higher temperature and is most probably related to the high content of free CaO which is transformed to $\text{Ca}(\text{OH})_2$ during cooling. This is the reason for the extensive deterioration of the samples with a higher content of CaO (PC, PLC and PSC).

CONCLUSIONS

This work led to the following conclusions:

- The cohesion of the pastes at high temperature is strongly affected by the type of main constituent added to the Portland cement.
- The use of pozzolanic materials, and especially metakaolin, improves the fire resistance of the pastes, while the samples with limestone show the worst behavior.
- The damage of the specimens was due mainly to the transformation of free CaO to $\text{Ca}(\text{OH})_2$ and took place during the cooling rather than the heating.

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IZVOD

PONAŠANJE MODIFIKOVANIH CEMENTNIH PASTI NA POVIŠENIM TEMPERATURAMA

(Naučni rad)

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Visoke temperature koje se stvaraju tokom požara mogu da prouzrokuju teška oštećenja strukture materijala od kojeg je izgrađena neka građevina, na pr. betona. Ova činjenica značajno utiče na značaj poboljšanja karakteristika betona i njegove otpornosti na visokim temperaturama. Razmatranje ovih osobina betona, otpornosti na visokim temperaturama, zahteva potpuno poznavanje ponašanja na visokim temperaturama svake komponente koja ulazi u sastav betona. U ovom radu je analizirano ponašanje na visokim temperaturama modifikovanih cementnih pasti tj. cementa sa određenim dodacima kao na primer, prirodna pocolana, lebdeći pepeo, samlevena i granulirana vatrostalna opeka, metakaolin i kreč. Modifikovan cement sa navedenim dodacima je iskorišćen u cilju zamene jednog dela Portland cementa (PC) sa navedenim mineralima (10% w/w u slučaju dodatka metakaolina, 20% w/w u slučaju dodatka ostalih materijala). Pripremljen uzorak je vlažen vodom 3 meseca, a zatim termijski tretiran na 200, 400, 600 800 i 1000°C u toku 1 sata. Nakon termijskih tretmana pristupilo se vizuelnoj analizi uzoraka kao i merenju njegove mase i ultrasoničnom-pulzirajućom metodom brzine zvuka. Zaključeno je da je kohezija paste u znatnoj meri promenjena dodatkom glavnog konstituenta u PC. Upotreba pocolanita, a posebno metakaolina, povećava otpornost cementnih pasti na visokim temperaturama, dok se u slučaju upotrebe kalcijum oksida njegove karakteristike pogoršavaju.

Ključne reči: Modifikovan cement, Cementne paste, Karakteristike, Otpornost na visokim temperaturama.