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The Effect of Different Admixture on the Properties of Refractory Concrete with Portland Cement

V. Antonovich[*], **S. Goberis**

VGTU Institute of Thermal Insulation, Linkmenų 28, LT-2600 Vilnius, Lithuania

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The effect of admixtures, such as disperse chamotte, microsilica, low – density liquid glass and alumina cement (Gorkal 40) on Portland cement hydration by measuring the temperature due to exothermic reaction is investigated. The admixtures differently affect Portland cement hydration: microsilica and alumina cement accelerate, while low density (1025 – 1050 kg/m^3) liquid glass retards Portland cement hydration. When the density of the liquid glass reaches 1100 kg/m^3, it accelerates the Portland cement hydration as well. Thermal shock resistance of refractory concrete with Portland cement, chamotte aggregates and various admixtures is studied. It was found that a complex admixture of disperse chamotte, microsilica and low – density liquid glass allows the thermal shock resistance of concrete to be increased, thereby indirectly demonstrating the capability of these admixtures to effectively bind CaO.

Keywords: refractory concrete, Portland cement, hydration, thermal shock resistance

INTRODUCTION

In thermally heating equipment the operating temperature usually does not exceed 1100 – 1200 ºC. Therefore, the lining of such units is made of refractory concretes with alumina cement, the amount of Al_2O_3 in which is no more than 40 per cent. One of the possible ways to reduce the cost of the above refractory concrete is the replacement of the alumina cement with Portland cement, which is approximately by four times cheaper than the alumina cement.

When determining thermal resistance of hardened Portland cement paste, the effect of $Ca(OH)_2$ formed during its setting on the fired cement paste and concrete failure should be taken into account [1, 2]. During heating the crystals of $Ca(OH)_2$ of the size 10^{-6}m turn into CaO crystals, usually of 10^{-9}m in size [3]. Since the surface area of CaO is very large, it often rehydrates in the humid environment. It has been shown [4] that during rehydration, the volume of $Ca(OH)_2$ expands by 44 %, leading to the complete failure of hardened cement paste.

In order to use Portland cement in refractory concrete, various disperse materials should be added into concrete (the size of their particles being close to this of cement particles). They are: refractory clay, disperse chamotte, metallurgical slag, etc. [5]. Under elevated temperatures, these admixtures partially bind CaO, thus reducing the amount of $Ca(OH)_2$ which may be formed during rehydration.

Portland cement concrete with refractory aggregates and disperse admixtures was used in the former USSR in 1950 – 1980 [1, 6, 7]. However, because of great disadvantages observed (sharp decrease of compressive strength, when firing under 600 – 800 ºC, rather low application temperature, poor thermal shock resistance, etc.) the above concrete had not found wide application in heating equipment.

Recent experiments have shown that the use of micro additives (e.g. aluminium hydroxide ($Al(OH)_3$) or Aloxil – type aluminium silica, with the particle size less than 3 μm) thermal properties of new materials may be practically the same as those of refractories with alumina cement (with the amount of Al_2O reaching 40 %) [8, 9].

One of the effective (pozzolana) admixtures is microsilica, which binds $Ca(OH)_2$ already at the stage of cement hardening. However, the reaction takes a long time, with the amount of $Ca(OH)_2$ considerably decreased only after 2 – 4 months, if the proportion of microsilica in the slurry with Portland cement >10 % [10].

It may be assumed that some complex materials may be used as the effective admixtures in the refractory concrete with Portland cement, which may affect its properties both under high temperatures and during the process of hardening.

The efficiency of admixtures in binding $Ca(OH)_2$ and CaO may be evaluated by determining the thermal shock resistance of concrete. In thermal shock resistance tests, when samples are heated up to 800 °C and then cooled in water, the unbound CaO rehydrates. This leads to concrete destruction as well as decreasing its thermal shock resistance.

The goal of the present investigation is to determine the effect of various admixtures (e.g. microsilica, liquid glass, alumina cement) on Portland cement hydration and thermal shock resistance of refractory concrete with chamotte aggregates.

EXPERIMENTAL

Portland cement CEM I 42.5 (*PC*) manufactured by "Akmenės cementas" (Lithuania) was used. Blaine surface area of the cement reaches 320 m^2/kg , while its chemical composition is given in Table 1.

Microsilica (*MS*) is manufactured by the Polish plant "Huta Lasiska SA". Sodium liquid glass (*LG*) modulus (SiO_2/Na_2O) is 3.3, while its density was varied (from 1025 to 1100 kg/m^3) by diluting it with water. The alumina cement "Gorkal 40" (*AC*), with the content of Al_2O_3 not

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[*] Corresponding author. Tel.: + 370-5-2752231; fax: + 370-5-2731230.
E-mail address: *valentin@centras.lt* (V. Antonovich)

less than 40 %, was manufactured at “Gorka” works (Poland). Disperse chamotte and chamotte concrete aggregates were obtained from chamotte scrap (Al_2O_3 ~30 %).

Table 1. The chemical composition of Portland cement

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	L.O.I.
54.9	20.5	5.41	4.41	3.62	0.12	0.89	0.98	2.73

Bogue calculation, %: C_3S – 25.02; C_2S – 33.91; C_3A – 11.52; C_4AF – 13.41.

The temperature of exothermic reaction (EXO temperature) of cement paste was determined according to the “Alcoa Industrial Chemicals" method [11]. The binder paste was prepared by mechanical mixing (2 min) and casted in the moulds (100 × 100 × 100 mm) under light vibration (10 sec). The cast sample (EXO specimen) weighted about 1.5 kg. The mould with the binder paste was put into the insulating box. The recording of the exothermic heat development was done by a thermocouple stuck into a freshly mixed binder paste. The temperature inside the mix was recorded with the help of a data logger connected with thermocouple. The collected database was monitored in the connected PC workstation.

The cubes of the size 70 × 70 × 70 mm were formed for all types of concrete. After 3 days of normal curing, the samples were dried at a temperature of 105 ±5 °C for 48 hours. Next, they were kept for three hours under the investigated temperatures 800 °C, 1000 °C and 1200 °C respectively in an electronic controller furnace and cooled. Then the shrinkage of samples was measured.

GOST 20910-90 method to determinate the concrete thermal shock resistance was used. In this approach a concrete sample (70 × 70 × 70 mm) is being heated for 40 min. at 800 °C and then cooled for 5 min. in water. Such cycles are repeated until the samples break or lose 20 % of their mass.

RESULTS AND DISCUSSION

The hydration of Portland cement undergoes several phases: the solution of cement minerals, the release of Ca^+ ions, the induction period, intense ions sedimentation and the formation of hydrate crystals [12]. In cement hydration, a considerable amount of heat is released, which varies depending on the particular stage of the process.

The admixtures which may affect the hydration of Portland cements were tested in the present investigation. Their effect was assessed by determining the kinetics of the temperature of the heat released in exothermic reaction. The compositions of the binders tested are given in Table 2.

Not a few researchers [13 – 15] emphasized the capability of microsilica (with its amount in the paste being >10 %) to accelerate the hydration of Portland cement by intensifying the formation of calcium hydrosilicates and ettringite. However, the above MS quantity in refractory castables is too high, impairing their thermal and mechanical properties. Therefore, the effect of MS additive on the development of exothermal reaction heat in Portland cement (when MS proportion is <10 %) (Fig. 1) was investigated.

Table 2. Binder composition, %

Binder grade	Binder components, %				
	PC	MS	AC	Water*	LG*
PC	100	–	–	35	–
PCMS-2.5	97.5	2.5	–	35	–
PCMS-5	95	5	–	35	–
PCMS-7.5	92.5	7.5	–	35	–
PCAC-5	95	–	5	35	–
PCAC-10	90	–	10	35	–
PCAC-15	85	–	15	35	–
PCLG-1025	100	–	–	–	35
PCLG-1050	100	–	–	–	35
PCLG-1100	100	–	–	–	35

*over 100 % of dry components.

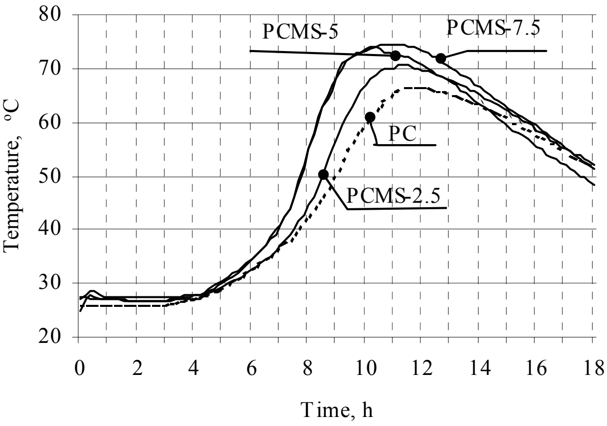

Fig. 1. The dependence of Portland cement EXO temperature on the amount of MS added: PC – pure Portland cement; PCMS – 2.5 – 2.5 % MS is added into the cement mix; PCMS – 5 – 5 % MS added; PCMS – 7.5 – 7.5 % MS added

It has been found that immediately after mixing the cement (with or without MS added) with water (W/(C+MS) ratio is 0.35), the EXO temperature in the sample rose by 6 – 8 °C. This occurs due to the heat released during the adsorption of water by cement particles and in early hydration [12]. When the temperature has risen to 26 – 28 °C, it remains constant for about 3 – 3.5 hours. This time corresponds to the induction period of cement hydration when high concentration of ions is achieved and some more minerals are solved. In 4 hours EXO temperature in the sample starts to rise sharply, reaching 66 – 75 °C. This takes place in the period of intense ions sedimentation and the formation of hydrate crystals. Having reached the maximum value, the temperature begins to fall. It is observed [12] that, at this stage, the hydration reactions are retarded and the last period of slow reaction begins.

It has been found (Fig. 1) that even a small amount of MS promotes the hydration of Portland cement: the time of EXO temperature is shorter by 1 – 2 hours, the temperature is by 5 – 10 °C higher compared to that of MS – free Portland cement. This shows that the cement paste with

MS added generates much more heat, though the sample contains by 2.5 – 7.5 % less cement. This also shows that the exothermal effect depends not only on the reaction between cement and water, but on pozzolana reaction as well.

The addition of the alumina cement (from 5 % to 15 %) greatly accelerates the hydration of Portland cement. One can see that the maximum time of EXO temperature in PCAC binder is by 4 – 6 hours shorter (Fig. 2), while its value is 10 – 14° higher compared to that of pure Portland cement. It has been stated [16] that quick setting of the mixed binder is caused by premature formation of etringite minerals.

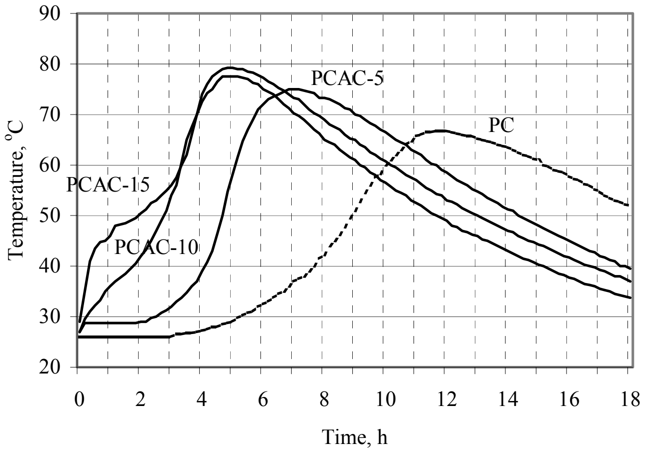

Fig. 2. EXO temperatures of PC – AC binder during setting: PC – pure Portland cement, PCAC – 5 – a mixture with 5 % of AC, PCAC – 10 – a mixture with 10 % of AC, PCAC – 15 – a mixture with 15 % of AC

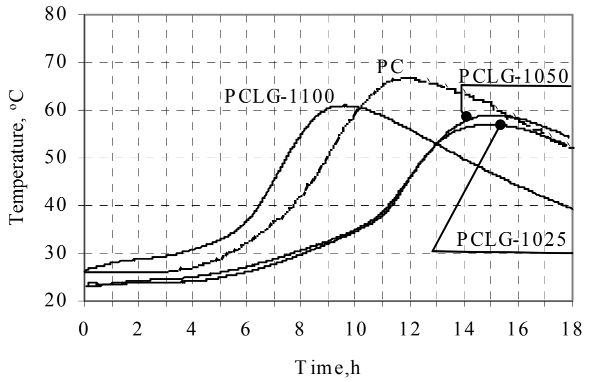

Fig. 3. The dependence of EXO temperature during cement hardening on liquid glass density: PC – Portland cement with water, PCLG – 1025 – a mixture with liquid glass of 1025 kg/m^3 density, PCLG – 1050 – a mixture with 1050 kg/m^3 density liquid glass and PCLG – 1100 – for 1100 kg/m^3 density

When mixing Portland cement with liquid glass of various density (liquid glass and cement ratio being 0.35) it has been found that the maximum EXO temperature time is about 3 hours shorter when the liquid glass density is 1100 kg/m^3, increasing by about 2 hours for the density of 1025 – 1050 kg/m^3 (Fig. 3).

The retarding of Portland cement hydration in alkaline environment has been demonstrated in [17]. However, when the concentration of sodium silicate in liquid glass is rather high (due to the increase of liquid glass density), sodium silicate violently reacts with C_2S of the cement [1]. It may be assumed that this reaction accelerates cement hydration. However, in any case, EXO temperature is reduced by 5 – 8 °C compared to that of Portland cement and water composition.

The effect of admixtures on thermal shock resistance of concrete with chamotte aggregates (Table 3) is shown in Fig. 4, providing the results of testing.

Table 3. Composition of refractory concrete, %

Concrete components	Composition, %					
	B1	B2	B3	B4	B5	B6
PC	20	20	19	19	19	19
Disp. chamotte	–	10	10	10	10	10
MS	–	–	–	1	2.5	1
AC	–	–	1	–	–	–
Chamotte agregates	80	70	70	70	68.5	70
Water*	16	16	16	16	16	–
Liquid glass (1050 kg/m^3)*	–	–	–	–	–	16

* - over 100 % of dry components

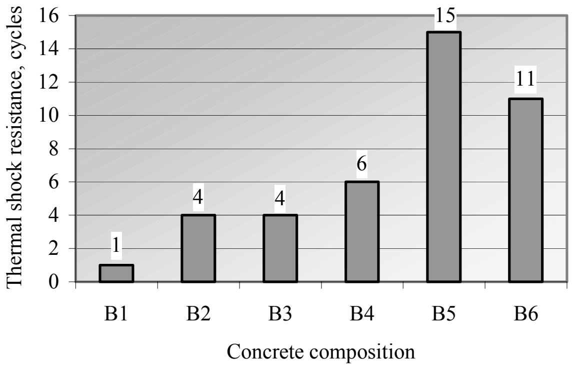

Fig. 4. Thermal shock resistance of concretes

Admixture free concrete (B1) can resist only one thermal shock because of the above mentioned CaO rehydration (when one heating – cooling cycle is complete). The addition of disperse chamotte in concrete (B2) allows its thermal shock resistance to be slightly increased (up to 4 cycles), because at 800 °C disperse chamotte (the component SiO_2) reacts with CaO, partly binding it.

Adding the admixture of the alumina cement into disperse chamotte concrete (B3) does not, in fact, improve its thermal shock resistance (4 cycles).

Thermal shock resistance of concretes (B4, B5) is considerably higher when highly effective microfiller – microsilica is added. With the addition of 2.5 % of MS, thermal shock resistance of concrete reaches as many as 15 cycles. It can be assumed that this admixture partially reacts with $Ca(OH)_2$ of concrete in curing. At the temperature of 800 °C it, together with disperse chamotte, effectively binds CaO. However, the increase of the admixture in concrete (B5) causes higher (by 2 %) shrinkage of the concrete under firing at 1200 °C (Fig. 5).

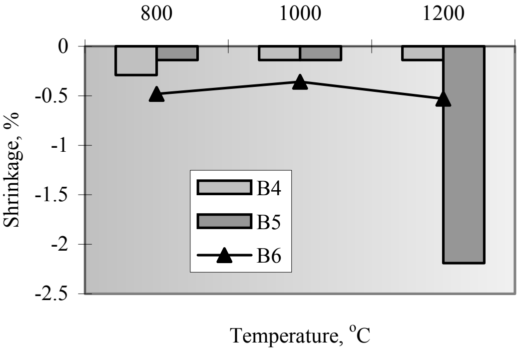

Fig. 5. Shrinkage of concretes fired under elevated temperatures

When liquid glass (of 1050 kg/m^3 density) is added into concrete B4 (with only 1 % of SiO_2) instead of water, the shrinkage of concrete (B6) is not higher than 1 % (Fig. 5), while its thermal shock resistance is also considerably high (11 cycles, Fig. 4). It should be noted, that ordinary concrete with alumina cement and chamotte aggregates can also resist about 10 cycles.

CONCLUSIONS

1. Unlike the commonly used various disperse admixtures, which bind CaO, the admixtures investigated differently affect Portland cement hydration: microsilica and alumina cement accelerate, while low density (1025 – 1050 kg/m^3) liquid glass retards Portland cement hydration. However, when the density of the latter reaches 1100 kg/m^3, it accelerates the Portland cement hydration as well.

2. A complex admixture of microsilica and low density liquid glass allows thermal shock resistance and other properties of Portland cement concrete with chamotte aggregate to be increased, thereby indirectly demonstrating the capability of these admixtures to effectively bind CaO.

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