The Investigation of Properties of Insulating Refractory Concrete with Portland Cement Binder

A Kudžma[1,2]**, V Antonovič**[1]**, R Stonys**[1] **and J Škamat**[1]
[1]Vilnius Gediminas Technical University, Scientific Institute of Thermal Insulation, Linkmenų Str.28, Vilnius, LT-08217, Lithuania

E-mail: andrius.kudzma@vgtu.lt

Abstract. The present work contains the results of experimental study on properties of insulating refractory concrete created on the basis of Portland cement (PC) binder and modified with microsilica (MS). The experimental compositions were made using Portland cement, lightweight aggregates (expanded clay and vermiculite) and microsilica additives. It was established that MS additives enable significant improvement of mechanical properties and thermal shock resistance of PC-based insulating concrete with values comparable to insulating refractory concrete based on calcium aluminate cement.

1. Introduction

In heating equipment, such as water boilers, boiler utilizers, etc., the operating temperature usually does not exceed 600–1000 ºC. Therefore, the lining of such units is made of insulating refractory concretes with calcium aluminate cement (CAC) with Al_2O_3 content not exceeding 40 percent. One of the possible ways to reduce the cost of the above-mentioned refractory concrete is the replacement of the alumina cement with Portland cement (PC), which is approximately by four times cheaper than the alumina cement.

Refractory concretes with PC and dispersive additives have been widely used in various countries from 1950 to 1980. Concretes were made with fireclay, expanded clay, vermiculite, perlite and other fillers. However, main disadvantages of these concretes are particularly high (70%) decrease of compressive strength after firing the concrete at 600–800 °C, relatively low operating temperature – 1100 °C [1], risk of explosion during first drying and heating [2]. Moreover, thermal shock resistance of these concretes is very low, it often reaches only 5–12 cycles of heating and cooling in water. For these reasons, the use of concrete fell considerably, and in most countries it is practically no longer used.

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[2] To whom any correspondence should be addressed.

When determining thermal resistance of hardened PC paste, the effect of $Ca(OH)_2$ formed during its setting on the fired cement paste and concrete failure should be taken into account [3, 4]. $Ca(OH)_2$ crystal hydrates with a size of 10^{-6} m lose water when heated and are replaced by CaO crystals with the characteristic size of 10^{-9} m [5]. Since CaO surface is very big, it relatively quickly re-hydrates. Under humid conditions, this process is even faster. It is stated in [6] that during the second hydration, the volume of $Ca(OH)_2$ increases by 44%. This causes full decomposition of cement stone.

In order to use PC in refractory concretes, the binder composites consisting of PC and various dispersive additives are used (average particle size is close to the average size of cement particles ~15 μm). At high temperature the dispersive additives react with CaO. The latter reacts with silica, alumina and iron oxides most easily.

The dispersive additives and combinations of heat-resistant binder are used with PC not only for CaO binding, but also for the improvement of physical and mechanical properties of composites and increase of fire resistance. Various additives were used for that purpose: quartz, refractory clay, dispersive fireclay, metallurgical slag, used ground refractory concrete, chromite, etc. [7].

Interesting results were obtained analyzing the PC mixtures with aluminium hydroxide additives ($Al(OH)_3$) [8], which showed that the thermal characteristics of such binder can match the properties of heat-resistant compositions with CAC. The paper reveals that during the hardening of the composition $Al(OH)_3$ with an average particle size of 4.5 μm reacts with cement components resulting in the formation of $Ca_3Al_2(SiO_4)(OH)_8$ crystalline hydrate. At temperature of 1200 °C $Al(OH)_3$ initiates the formation of calcium- and aliumo-silicates as well. Most importantly, in the composition with $Al(OH)_3$ during the curing and drying at 105 °C less calcium hydroxide than in the composition with pure PC is formed. After firing at 500 °C, free calcium oxide was not found in the substance.

PC compositions with SiO_2 and *Aloxil* additives (silica-aluminium compositions with different amounts of Al_2O_3, with particle size of ~3 μm) were analyzed in the paper [9]. It was found that fire resistance of the composition with *Aloxil* 80 (Al_2O_3 content 78%) has increased only slightly (~50 °C), and fire resistance of the composition containing the additive SiO_2 is much lower than that of Portland cement. It should be stated that all the components used improve the quality of refractory concrete matrix. However, when commenting on these works [8, 9], it should be noted that the dispersive components with aluminium oxide are very expensive compared with the price of PC, therefore, their use in large amounts is not economically justified.

As it is known, the SiO_2 micro-dust is an effective pozzolan which binds $Ca(OH)_2$ well. Moreover, this additive increases the strength characteristics of PC materials (mortars, concretes) [10, 11]. Most research on the effect of temperature on the properties of compositions of PC and SiO_2 micro-dust have been carried out to determine the impact of fire on simple building materials. However, the results obtained are also important when dealing with problems related to the application of Portland cement in heat resistant materials. Previous research by the authors [12] as well as the analysis of others publications showed that PC with an effective additive such as microsilica can be used for creation of various compositions of refractory concretes. The insulating refractory castable concrete with expanded clay and vermiculite filler and binder of Portland cement has been analyzed in this paper. The research results on concrete with fire resistant calcium aluminate cement are provided for comparison.

2. Experimental set-up

The following materials were used in the present work:

- Portland cement (PC) CEM I 42.5 R produced by "Akmenės cementas" (Lithuania): main mineral phase – C_3S (~59%); minor phases – C_2S (~14%), C_3A (~9%), C_4AF (~11%), where C denotes – CaO, A – Al_2O_3, F – Fe_2O_3, S – SiO_2. Specific surface by Blaine method – 3200 cm^2/g; chemical composition is given in Table 1.
- Calcium aluminate cement (CAC) "Istra 40" produced by "Calucem" (Croatia): main mineral phase – CA; minor phases – C_4AF, C_2AS and $C_{12}A_7$. Specific surface by Blaine method – 3000 cm^2/g; chemical composition is given in Table 1.
- Vermiculite (1-3 mm) produced by "Vermipu OY" (Finland): bulk density – 95–100 kg/m^3.
- Expanded clay (0-4 mm) produced by "Palemono keramika" (Lithuania): ~820 kg/m^3.
- Dispersive expanded clay produced by "Palemono keramika" (Lithuania): ~930 kg/m^3.
- Microsilica (MS) RW-Fuller produced by "RW Silicium GmbH" (SiO_2 – 96.1%): 410 kg/m^3.
- Deflocculant (NT) sodium tripolyphosphate $Na_5P_3O_{10}$.

Table 1. Chemical composition of cements, wt. %.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	L.O.I.
PC	54.90	20.50	5.41	4.41	3.62	0.12	0.89	0.98	2.73
AC	37–40	≤ 6	38–42	13–17	< 1.5	-	-	< 0.4	-

The temperature of exothermic reaction (EXO) during the hydration and hardening of concretes was determined according to the "Alcoa Industrial Chemicals" method [13]. The samples were prepared by mechanical mixing (2 min) of dry compositions (Table 2) with water and were cast in the moulds (100×100×100 mm) under light vibration (10 sec). The cast sample (EXO specimen) weighted about 1.5 kg. The filled mould was put into the insulating box and thermocouple was stuck into a freshly mixed composition. The temperature variation inside the mix was recorded along with the time of measurement with the help of a data logger connected with thermocouple and PC.

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 110±5 ºC for 48 h. Next, they were kept for 5 h under the investigated temperatures of 800 ºC and 1000 ºC in an electronic controller furnace and cooled. The shrinkage of samples was measured after heating at each temperature (105 ºC, 800 ºC and 1000 ºC).

Thermal shock resistance of the investigated concretes has been evaluated by heating-cooling test, where a concrete sample (70×70×70 mm) is heated for 60 min at 800 °C and then cooled for 20 min in air current. Such cycles are repeated until the samples break or lose 20% of their mass and if it does not break, residual strength value is measured.

3. Results and discussion

The experimental concrete compositions have been created on the basis of conventional composition (B0) of lightweight refractory concrete containing 40% of alumina cement, 50% of lightweight coarse aggregates (vermiculite and expanded clay) and 10% of dispersive filler (see Table 2). In experimental compositions (B1, B2 and B3), Portland cement has completely replaced alumina cement and dispersive expanded clay has been partially replaced with 1.5% and 2.5% of MS (B2 and B3 respectively). Deflocculant NT was used to decrease water consumption in MS-containing compositions (B2, B3).

Table 2. Concretes compositions, wt. %.

	B0	**B1**	**B2**	**B3**
MS	0	0	1.5	2.5
Expanded clay	40	40	40	40
Dispersive expanded clay	10	10	8.5	7.5
Vermiculite	10	10	10	10
CAC	40	0	0	0
PC	0	40	40	40
NT	0	0	0.35	0.35
Water *	32	33	31	31

* - over 100 % of dry components

The kinetics of binder hydration process is mainly determined by the mineralogical phases present in the cement. PC minerals, according to their reactivity, may be ordered as $C_3A > C_3S > C_4AF > C_2S$ [14]. For CAC minerals, this order is $C_{12}A_7 > CA > CA_2 > CA_6$ [15]. Thus, the presence of very reactive C_3A causes early beginning of hydration in B1 composition: PC-based concrete hydration processes occurred after ~60–80 minutes (figure 1). In CAC-based concrete, less reactive CA phase dominates and hydration starts later – after ~150 minutes with significant increasing of the heat release rate after ~4 hours. Exoterm profiles presented in figure 1 show that the hydration process for both CAC-based (B0) and PC-based concrete without MS additive (B1) develops during the first 6–7 hours with the main exopeaks occurring after ~360 minutes for B0 and after ~460 minutes for B1. Hydration of B0 is accompanied by more intensive heat release with maximum process temperature reaching 70 °C after ~6 hours, while for B1 much less main exothermic effect was obtained with the temperature reaching 37–40 °C. Very similar curves were obtained for PC-based compositions (B2 and B3) containing MS and deflocculated with NT. The combination of MS additive with NT deflocculant in denoted proportions (Table 2) has led to the decrease in the main exothermic effect temperature and to significant hydration process delay: main exothermic effect duration has increased about two times and the exothermic peak has appeared after ~16–17 hours.
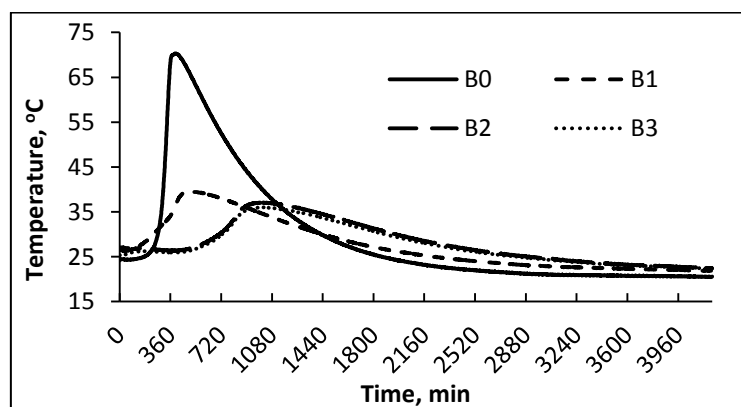
Figure 1. Development of EXO reaction in concretes.

The initial density of concretes after normal curing at 20 °C ranged from 1630 to 1680 kg/m^3 (see figure 2) with the lower value corresponding to PC-based composition without MS additive (B1) and with the upper value obtained on experimental compositions containing MS (B2 and B3). The reference sample (B0) showed medium value of 1660 kg/m^3. After drying (110 °C) accompanied by the evaporation of weakly bound water, the samples lost ~14–17 % of their density and the most significant decrease in density was obtained on B1 composition having the biggest water consumption. After firing (800 and 1000 °C), where destruction of hydraulic bonds and evaporation of chemically combined hydraulic phases take place, concretes gain their final density. Thus, after firing at 800 °C as well as at 1000 °C, the density of B0 and MS-unmodified B1 is 1270 kg/m^3, while for B2 and B3 containing MS additive final density increased by 4% and has a value of 1320 kg/m^3. Thus, PC-based cement with MS ultrafine filler tends to form slightly denser structure compared with CAC-based reference and PC-based cement without MS, what may be attributed to the MS ability to provide better structure compaction due to its morphology.

Heating of the samples is followed by dehydration, when, firstly, free water is removed and then dissociation of hydrates takes place along with some possible polymorphic transitions and formation of the new phases. It all causes local volume changes – expansion and/or shrinkage, determining the total deformation of the sample. Here, the gradual shrinkage has been determined on CAC-based concrete with the increase of heating temperature (figure 3, B0). The deformation after drying does not differ significantly for all the samples and is in the range between -0.15 (for B1) and -0.24 (B2). More noticeable shrinkage was determined on PC-based samples after firing at 800 °C with the increased values for the samples modified with MS. However, maximum deformation did not exceed ~1.1% and further heating (at 1000 °C) did not increase the shrinkage of PC-based samples: on the contrary, the deformation slightly reduced, most likely due to expansion of new formed phases.

Developing of structural discontinuity during heating caused by dehydration and differences in thermal deformation between the aggregates and the binder lead to the loss in strength with increasing temperature. For CAC concrete (B0), gradual wane in cold crushing strength (CCS) from 15 MPa to 9 MPa is established when the sample is exposed to temperature between 20 and 1000 °C (see figure 4). For PC-based samples (B1, B2 and B3), the nature of the curve is different and increasing strength is obtained after drying. It has been shown already in [16] that "*when temperature is lower than 350 °C (for ordinary Portland cement concrete)…, the strength of the concrete is increased due to accelerated hydration and strengthening effect caused by drying*". Further increasing temperature lead to the noticeable loss in CCS, largely caused by different expansion of the aggregates and the binder along with possible rehydration. The residual CCS for B1 composition after firing at 800 °C was 9.3 MPa and dramatic drop to 4.5 MPa has been established after firing at 1000 °C; such values yield significantly to CAC concrete.
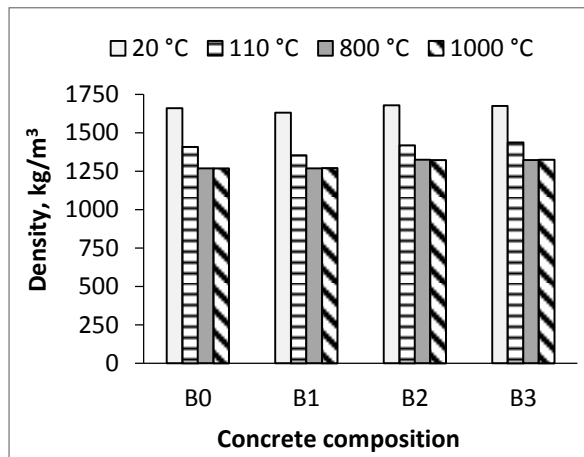
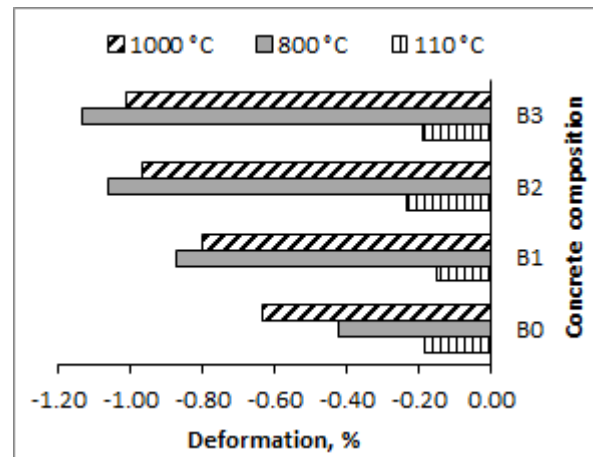**Figure 2.** Density changes in concretes after curing (20 °C), drying (110 °C) and firing (800 °C, 1000 °C).

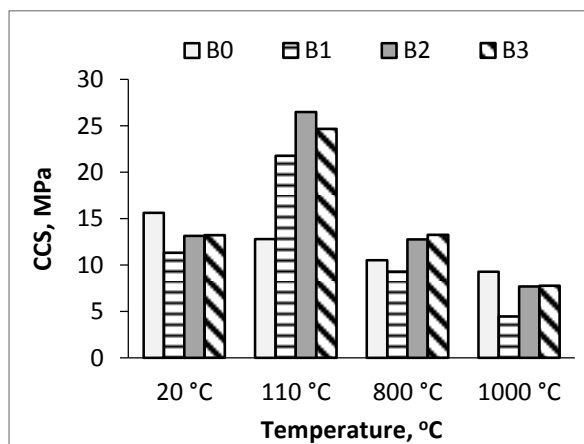**Figure 3.** Concrete shrinkage after drying (110 °C) and firing (800 °C, 1000 °C).

Figure 4. CCS of concrete after curing (20 °C), drying (110 °C) and firing (800 °C, 1000 °C).
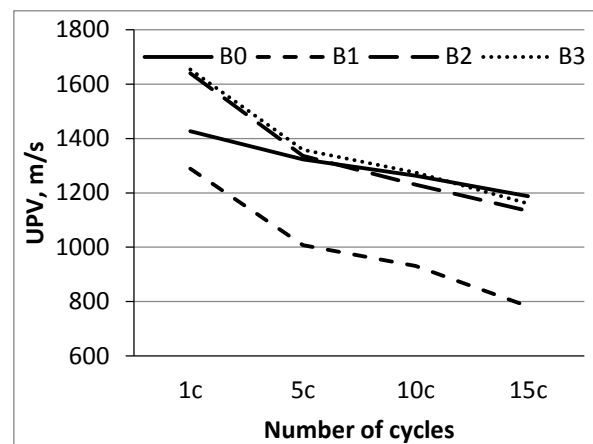

Figure 5. Ultrasonic pulse velocity variation after heating-cooling cycles.

Compressive strength of PC concrete has been notably improved with MS additives. Thus, the following increase in CCS values has been obtained on B2 and B3 compositions compared with B1: 17% (for both) – after normal curing; 22% and 15% (respectively) – after drying; 38% and 43% – after firing at 800 °C; 71% and 73% – after firing at 1000 °C. The obtained results show that positive impact of MS additive on compressive strength of PC concrete is expressed more significantly when concrete is exposed to high temperatures (800 and 1000 °C). It must be also noted that better CCS values here correspond to the higher MS content in the composition. Moreover, CAC concrete yields to MS-containing PC concrete in strength after firing at 800 °C: 22% (B2) and 27% (B3) better CCS values have been obtained on PC concrete with MS additives compared with CAC composition.

Heating-cooling procedure and measuring of ultrasonic pulse velocity (UPV) after 1, 5, 10 and 15 heating-cooling cycles have been employed to evaluate thermal shock resistance of experimental

compositions. The results of UPV measurements are presented in figure 5. Ultrasonic wave flows faster in materials with better compaction; the structural damages disturb ultrasonic wave propagation and decrease its velocity. Here, sloping UPV curves illustrate clearly decreasing UPV related to developing of microstructure discontinuity occurring during heating of all the investigated samples. The arrangement of UPV values after the first stage of thermal shock test is in a good correlation with CCS values obtained after firing at 800 °C, being B0 between B1 (lower value) and B2, B3 (upper values). The UPV in B1 decreases critically with further thermal cycles. The loss of the UPV in MS-modified compositions (B2 and B3) has the same nature: first they showed more rapid decrease in UPV compared with B0 and after 5 cycles their results became equal to UPV, exhibited by B0. Finally, B1 showed much less UP velocities while very similar UPV values have been obtained on B0, B2 and B3.

Table 3. The residual CCS of concrete after 15 heating-cooling cycles, %.

Concrete composition	Residual CCS, %
B0	66
B1	66
B2	78
B3	73

Moreover, after 15 cycles, the CCS test showed less loss in compressive strength for MS-modified PC concrete compared with CAC-based composition: residual CCS of 78% and 73% (from CCS after firing at 800 °C) has been obtained for B2 and B3 respectively (see Table 3). Thus, it all testifies good suitability of MS additives in improving of thermal resistance of PC concretes.

4. Summary
1. Compressive strength and thermal shock resistance of the concrete with Portland cement have been significantly improved by addition of microsilica.
2. The properties of the created PC-based insulating refractory concretes containing expanded clay aggregates and modified with microsilica additives have been obtained similar to those of insulating refractory concrete with calcium aluminate cement.

5. References
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