Proceedings of International Structural Engineering and Construction, 9(1), 2022
State-of-the-art Materials and Techniques in Structural Engineering and Construction
Edited by Holschemacher, K., Quapp, U., Singh, A., and Yazdani, S.

ISSN: 2644-108X
www.doi.org/10.14455/ISEC.2022.9(1).MAT-27

CURING TEMPERATURES EFFECT ON EXPLOSIVE SPALLING IN ALUMINA CEMENT-BASED CONCRETES

ANDRIUS KUDŽMA[1], LINAS PLIOPLYS[2], VALENTIN ANTONOVIČ[1], RIMVYDAS STONYS[1], and VIKTOR GRIBNIAK[2]

[1]*Laboratory of Composite Materials, VILNIUS TECH, Vilnius, Lithuania*
[2]*Laboratory of Innovative Building Structures, VILNIUS TECH, Vilnius, Lithuania*

Alumina cement (AC) based refractory concretes are the primary building materials for steel, cement, glass, ceramics, and chemical industries. Those advanced materials are efficient at high operation temperatures (up to 1500 °C), conforming to thermal shock and mechanical and slag resistance requirements. For these purposes, fine-grade or ultra-fine powders partially replace the cement. However, that increases the material density and, depending on the first heating cycle regime, the evaporated steam pressure can cause cracking and even explosive spalling of the concrete. The coarse aggregates and temperature-melting fibers can regulate the water evaporation process—the melted fibers form micro-channels, allowing excessive water removal from the heated material. However, the concrete curing conditions also affect the hydration products' structure (density) and chemical composition, altering the water removal kinetics from the refractory material. This investigation focuses on the hardening conditions' effect on the hydration process and explosive spalling resistance of the AC refractory concretes. The research object is the refractory concrete with a 130 MPa target compressive strength and 7wt% of AC. The alternative mixture contains polypropylene fibers (0.1wt%). The cylinder samples were cured at different temperatures, representing "normal" (20 °C), "summer" (35 °C), and "winter" (10 °C) conditions. The test results demonstrate the fiber efficiency in preventing the spalling failure characteristic of the samples produced without fibers. On the other hand, the curing temperature was the essential parameter, affecting the water removal kinetics of the refractory material with fibers—the "winter" concrete samples tend to explosive spalling due to the formed hydrates.

Keywords: Refractory concrete, Tests, Fibers, Material, Compressive strength.

1 INTRODUCTION

Alumina cement (AC) based refractories are inorganic, non-metallic materials resistant to high temperatures without changing their mechanical performance (Bayoumi *et al*. 2021). These materials are typical for the steel, cement, glass, ceramic, and chemical industries (Fu *et al*. 2018). The refractory concretes are divided into the following groups depending on the AC percentage (Wöhrmeyer and Parr 2008): conventional concrete (CC, 15-30wt%), medium-cement concrete (MCC, 8-15wt%), low-cement concrete (LCC, 4-8wt%), and ultra-low cement concrete (ULCC, 1-3wt%). The latter three concrete types use fine-grade additives and plasticizers, which reduce permeability and porosity and increase the density of the material (Gitzen and Hart 1961). Besides, these refractories demonstrate higher thermomechanical properties and resistance to chemical corrosion regarding the CC concretes (Lee and Moore 1998). However, the refractories' dense structure restricts the internal water removal during the first concrete heating cycle, leading to explosive spalling (Innocentini *et al*. 2002a). This failure is a consequence of the excessive water vapor pressure resulting from the temperature gradient in the material during drying when the evaporated chemically bound water cannot escape through the dense refractory surface (Boris *et al*. 2015). The appropriately chosen first heating cycle that lasts up to a week, depending on the structure thickness, the concrete type and performance, and exploitation regime, can prevent the spalling failure (Mandecka-Kamień 2012). At the same time, the energy consumption unfavorable increases and technological process prolongs with increasing the heating duration (Mandecka-Kamień *et al*. 2014). Coarse aggregates and polypropylene fibers can reduce the explosive spalling risk and reduce the first heating duration, increasing the vapor permeability of the refractory material (Innocentini *et al*. 2002b, Collignon *et al*. 2011). The fibers begin to soften and shrink at relatively low temperatures (120-150 °C) and burn out completely when the temperature reaches 450 °C. The melting of fibers results in forming a network of interconnected microchannels, allowing easier evaporation of chemically and physically bound water from the deeper material layers (Mandecka-Kamień *et al*. 2014).

Da Luz *et al*. (2015) reported that AC hydrates' shape, composition, density, and structure varies depending on the curing temperatures. For instance, a refractory material with a binder consisting of CA ($CaO_2 \cdot Al_2O_3$) and CA_2 ($CaO_2 \cdot 2Al_2O_3$) minerals produces hydrates of CAH_{10} ($CaO_2 \cdot Al_2O_3 \cdot 10H_2O$), hardening at temperature reaching 10 °C; it forms C_2AH_8 ($2CaO_2 \cdot Al_2O_3 \cdot 8H_2O$), hardening at 10-35 °C, and C_3AH_6 ($3CaO_2 \cdot Al_2O_3 \cdot 6H_2O$) forms at temperatures exceeding 35 °C. Garsel (1996) determined 1720 kg/m^3 density of CAH_{10} having the shape of hexagonal prisms; C_2AH_8 hydrates had 1950 kg/m^3 density in the form of plates, and C_3AH_6 hydrates demonstrated 2520 kg/m^3 density in a cubic shape. At the same time, the curing temperatures affect the chemical composition of the hydrates, changing the chemically bound water content. Cardoso *et al*. (2004) reported the following dehydration temperatures of AC: the amorphous AH_3 ($Al_2O_3 \cdot 3H_2O$) gel loses weakly bound water at 100 °C; CAH_{10} and C_2AH_8 dehydrate up to 120 °C and in the 170-195 °C temperature range, respectively; gibbsite (AH_3) and C_3AH_6 dehydrate at 210-300 °C and 240-370 °C temperatures.

This study focuses on the curing temperature's effect on the dehydration process and spalling resistance of the AC-based refractory material. The research object is concrete with the target 130 MPa compressive strength and 7wt% cement content; a comparative mixture contained polypropylene fibers (0.1wt%). The cylinder samples were cured at different temperatures, representing "normal" (20 °C), "summer" (35 °C), and "winter" (10 °C) conditions. The heating test results demonstrate the fiber efficiency in preventing the spalling failure characteristic of the samples produced without fibers. At the same time, the curing temperature was the essential parameter affecting the water removal kinetics of the fiber-reinforced material—the "winter" concrete tends to fail due to explosive spalling.

2 MATERIALS AND METHODS

This study considers two refractory mixtures. The reference conventional concrete (CC00), with 25wt% AC content, was designed to resist 30 MPa compression under 1000 °C. The alternative LCC (7wt% of AC) had a 130 MPa compressive strength at 1000 °C. One alternative mixture was produced without fibers (LC00); another was modified with polypropylene fibers (LC10). The fibers had length = 6±1 mm, diameter = 20±1 mm, and a 910 kg/m^3 density. Table 1 describes the mix proportions, where MS, RA, and QS are the microsilica, reactive alumina, and quarz sand; ST is the sodium tripolyphosphate; W is the water. The dry components were mixed with deflocculants for 5 minutes in the Hobart mixer when water was added and mixed for another 5 minutes.

Table 1. Mix proportions of the refractory concrete (wt%).

Mix	**AC**		**Chamotte BOS145**		**MS**	**RA**	**QS**	**Fiber***	**Deflocculant***			**W***
	Istra 40	**Gorkal 70**	**Crushed**	**Milled**					**Castament FS30**	**Castament FS20**	**ST**	
CC00	-	25	60	10	2.5	-	2.5	-	0.1	-	-	7.5
LC00	7	-	60.5	-	5	25	2.5	-	-	0.1	0.1	6.5
LC10	7	-	60.5	-	5	25	2.5	0.1	-	0.1	0.1	6.5

*Content exceeding the 100% dry concrete weight.

This study employs three ∅80 × 80 mm cylinder series produced from the mixtures listed in Table 1; each series consisted of six specimens hardened at 10 °C, 20 °C, and 35 °C in the environmental chamber for 120 h (24 h in forms) at 100% humidity. Two identical specimens were hardened at each temperature. After the 120 h curing, one of the twin samples was used to determine the weight loss (drying tests); another was applied for the explosive spalling tests.

An 11 kW electric furnace with balance (Nabertherm GmbH, Germany) was used for the drying test. The maximum test temperature reached 900 °C under 10 °C/min velocity. The normalized parameter W_d estimates the weight loss during the drying test. Ranging from zero to 100%, it determines the removed water amount regarding the initial water content originated in the sample (Eq.1):

$$W_d = 100\% \times \left(\frac{m_0 - m_i}{m_0 - m_g}\right) \tag{1}$$

where m_i is the instantaneous mass recorded at the time t_i; m_0 and m_g are the initial and final masses of the test sample. The time derivative defines the sample mass (Eq. 1) alteration rate:

$$\frac{dW_d}{dt} = \frac{W_{d,i+1} - W_{d,i}}{t_{i+1} - t_i} \tag{2}$$

Figure 1 shows a schematic mass loss rate (Eq. 2) curve of the refractory concrete sample. It indicates characteristic parameters, determining the dehydration process.

The explosive spalling tests of the refractory concrete samples were carried out following ISO 16334: 2013. After 120 h curing in the climate chamber, the cylinder samples were placed in a 3.4kW oven (Umega Group, Lithuania) already heated to 700 °C. A metal cage protected the heating equipment from the sample explosion. The open porosity of refractory concrete samples was measured following the LST EN ISO 10545-3: 2000 using a vacuum device.

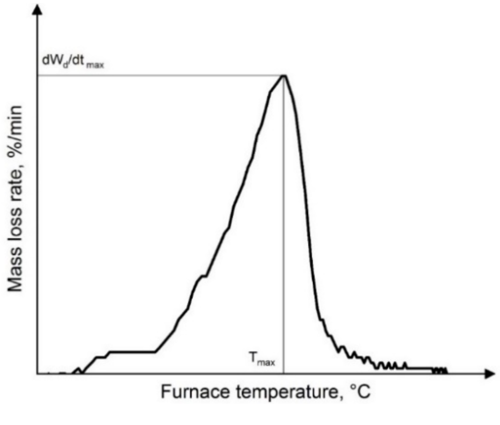

Figure 1. A schematic of the mass loss rate curve of the refractory concrete.

The AC hardening paste (W/AC = 1) microstructure was examined using a scanning electron microscopy microscope of JSM-7600F (JEOL, Japan) to evaluate the curing temperature effect on hydrate formation. The analysis was carried out after curing samples in the environmental chamber for 72 h at three different temperatures (i.e., 10 °C, 20 °C, and 35 °C).

3 RESULTS AND DISCUSSION

Figure 2 shows the split surface morphology of AC paste samples hardened at different temperatures. The SEM microphotograph of the specimen cured in the "winter" conditions (Fig. 2a) demonstrates the abundantly formed CAH_{10} hydrates with the shape of long hexagonal prisms. The "normal" curing conditions (20 °C) caused forming the C_2AH_8 hydrates in the form of plates and prismatic CAH_{10}, as shown in Fig. 2b. The C_3AH_6 hydrates of a cuboid shape are predominate in the sample cured the "summer" conditions (Fig. 2c); in some places, fine AH_3 (gibbsite) crystals coat the cuboid C_3AH_6 hydrates.

The microstructure and different hydrate properties affect the explosive spalling of refractory concrete. The spalling risk of the conventional refractory concrete is low and results from a sufficient open porosity (Innocentini *et al.* 2002a). For instance, the reference concrete CC00 porosity exceeded 23% in this study. The explosive spalling tests support this observation—the reference specimens did not face the explosion failure regardless of the curing temperature. The alternative concrete LC00 with increased fine-grade components' percentage and open porosity below 19% demonstrated the opposite result—all cylinder specimens exploded into small fragments independently on the curing conditions. Figure 3a shows the typical failure case.

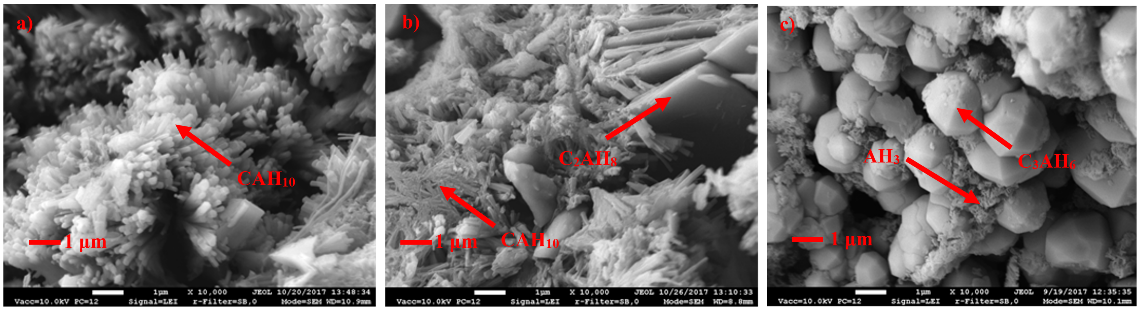

Figure 2. Microstructure of AC paste hardened at different temperatures: a) 10 °C; b) 20 °C; c) 35 °C.

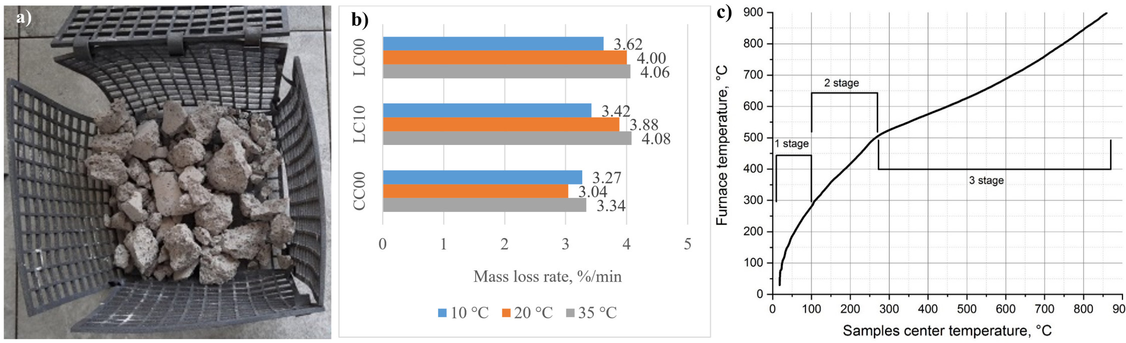

Figure 3. Heating test results: a) typical spalling failure; b) weight loss rate; c) drying stages of LC sample.

Figure 3b shows the drying test results of the 10 °C/min heating velocity. Test results indicate the maximum 3.27 %/min mass-loss rate of the reference CC00 samples; this corresponds to 513 °C. On the other hand, the mass-loss rate of the LC00 concrete was higher regarding the reference material, exceeding 3.62 %/min and the corresponding temperature reached 536 °C.

Ismael *et al*. (2007) defined three stages of refractory dehydration. The first stage involves free water evaporation (up to 100°C). The second stage lasts to 250-300°C. At this stage, hydrates begin to decompose, increasing the vapor amount escaping from the sample. The third stage initiation corresponds to the maximum mass-loss rate (above 300°C). During this stage, the hydrates' decomposition slows down, reducing the chemically bound water removal drastically. Figure 3c correlates these stages with the mass-loss rate resulting from AC hydrates decomposition.

Polypropylene fibers improved the concrete spalling resistance, forming micro-channels when the fiber melts at a temperature of about 150°C, and water vapor can escape freely from the material. Figure 3b shows a slight difference between the mass-loss rates of LC10 and LC00 concrete samples. The maximum rate temperatures are also different—this boundary was reached in LC10 at 12-37 °C lower temperature regarding concrete without fibers (LC00).

All refractory specimens demonstrated the same tendency when the temperature corresponding to the maximum mass-loss rate of samples cured at 35 °C exceeded the 10 °C temperature curing results. The dehydration of 35 °C temperature cured samples' predominant C_3AH_6 hydrate and gibbsite (AH_3) (Fig. 2c) explains the abovementioned difference. Cardoso *et al*. (2004) found that the C_3AH_6 and AH_3 dehydration requires the highest temperatures (240-370 °C and 210-300 °C) regarding other AC hydrates. Figure 3c relates the furnace and sample center temperatures. It demonstrates that the sample surface 480-520 °C temperature corresponds to 250-320°C temperature inside the specimen, which could be insufficient to dehydrate C_3AH_6 completely.

The LCC specimens cured at 10°C demonstrated the most significant average total mass loss (6.92%) than concretes stored at 20 °C (6.80%) and 35°C (6.59%). Therefore, an additional study with reduced polypropylene fiber content was carried to analyze the LCC explosive spalling risks. Thus, the fiber reduction from 0.1wt% to 0.075wt% caused the spalling failure of the cylinders cured at 10°C and 20°C temperatures. The CAH_{10} hydrate formation at relatively low temperatures (Fig. 2) can explain the observed tendency. The drying test results (Fig. 3b) support the above insight. Furthermore, the CAH_{10} domination in the samples curried at 10°C (Fig. 2a) makes such refractory concretes potentially vulnerable to the explosive spalling that should be the focus of further research.

4 CONCLUSION REMARKS

Polypropylene fibers can protect high-performance, low-cement concretes from explosive spalling. The addition of 0.1w% fibers prevented the spalling because a micro-channel network of melt polypropylene during the heating process has increased the material's open porosity and allowed water evaporation. However, the curing temperature affects the hydrates' decomposition and increases the explosive spalling risk during the first heating cycle of low-cement refractory concretes. Refractory material cured at "winter" conditions (i.e., 10 °C) tends to fail due to CAH_{10} hydrates, which forms in alumina cement-based concretes at relatively low temperatures (below 20 °C). Furthermore, these specimens had the highest amount of chemically bound water and corresponding mass loss, regarding the samples, cured at temperatures exceeding 20 °C.

Acknowledgments

The authors acknowledged financial support received from European Regional Development Fund (Project No 01.2.2-LMT-K-718-03-0010) under grant agreement with the Research Council of Lithuania (LMTLT).

References

Bayoumi, I. M. I., Ewais, E. M. M., and El-Amir, A. A. M., *Rheology of Refractory Concrete: An Article Review*, Boletín de la Sociedad Española de Cerámica y Vidrio. doi: 10.1016/j.bsecv.2021.03.003. March, 2021.

Boris, R., Kerienė, J. R., Antonovič, V., and Madej, D., *Characterization of Microstructural Evolution and Mechanical Properties of Refractory Composite*, Composite Structures, 134, 811-819. doi: 10.1016/j.compstruct.2015.08.059. December, 2015.

Cardoso, F. A., Innocentini, M. D. M., Miranda, M. F. S., Valenzuela, F. A. O., and Pandolfelli, V. C., *Drying Behavior of Hydratable Alumina-Bonded Refractory Castables*, Journal of the European Ceramic Society, 24(5), 797-802. doi: 10.1016/S0955-2219(03)00326-1. May, 2004.

Collignon, B., Moyne, C., Guichard, J.-L., Perrot, C., and Jannot, Y., *Modelling the Pressure Dependence and the Influence of Added Polymeric Fibers on the Permeability of Refractory Concretes*, Ceramics International, 37(2), 627-634. doi: 10.1016/j.ceramint.2010.09.030. March, 2011.

Da Luz, A. P., Braulio, M. A. L., and Pandolfelli, V. C., *Refractory Castable Engineering*, F.I.R.E. Compendium Series, Göller Verlag GmbH, Baden-Baden, 2015.

Fu, L., Gu, H., Huang, A., and Ni, H., *Correlations Among Processing Parameters and Porosity of a Lightweight Alumina,* Ceramics International, 44(12), 14076-14081. doi: 10.1016/j.ceramint.2018.05.005. August, 2018.

Garsel, F., *High Alumina Cements and Chemical Binders. Refractories Technology – An Introduction Update*, IRE, South Africa, 1996.

Gitzen, W. H., and Hart, L. D., *Explosive Spalling of Refractory Castables Bonded with Calcium Aluminate Cement*, American Ceramic Society Bulletin, 40(8), 503-510, 1961.

Innocentini, M. D. M., Pardo, A. R. F., Menegazzo, B. A., Rettore, R. P., Bittencourt, L. R. M., and Pandolfelli, V. C., *Permeability of High-Alumina Refractory Castables Based on Various Hydraulic Binders*, Journal of the American Ceramic Society, 85(6), 1517-1521. doi: 10.1111/J.1151-2916.2002.TB00306.X. June, 2002a.

Innocentini, M. D. M., Salomeo, R., Ribeiro, C., Cardoso, F. A., Pandolfelli, V. C., Retton, R. P., and Bittencourt, L. R. M., *Permeability of Fiber Containing Refractory Castables*, American Ceramic Society Bulletin, 81(7), 34-38, July, 2002b.

Ismael, M. R., Salomão, R., and Pandolfelli, V. C., *Refractory Castables Based on Colloidal Silica and Hydratable Alumina*, American Ceramic Society Bulletin, 86(9), 58-62, 2007.

Lee, W. E., and Moore, R. E., *Evolution of in Situ Refractories in the 20th Century*, Journal of the American Ceramic Society, 81(6), 1385-1410. doi: 10.1111/j.1151-2916.1998.tb02497.x. June, 1998.

Mandecka-Kamień, L., *Low Cement High-Aluminate Concrete*, Patent Application P.399695, AGH University of Science and Technology, 2012.

Mandecka-Kamień, L., Rapacz-Kmita, A., and Wójcik, Ł., *The Effect of the Addition of Polypropylene Fibres on the Properties of Corundum Refractory Concretes with a Low Cement Content and an Addition of Aluminium Phosphate*, Ceramics International, 40(10A), 15663-15668. doi: 10.1016/j.ceramint.2014.07.087. December, 2014.

Wöhrmeyer, C., and Parr, C., *MCC and HCC: Deflocculated High-Performance Castables Rich in Calcium Aluminate Binder*, Refractories Manual, 57-60, 2008.