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Effect of curing time on the properties of CAC bonded refractory castables

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Abstract

This work involved an investigation of the influence of the curing time on the properties of ultra-low cement high-alumina refractory castables cured at 10 °C. The hydration level of the composition was determined through thermogravimetric tests and then compared to theoretical estimations. The samples' mechanical strength and airflow permeability were strongly affected by the curing time, varying significantly in the period between 2 h and 30 days. The consequences of these changes on the drying behavior of castables are discussed.

Keywords: Al_2O_3; Castables; Drying; Mechanical properties; Refractories

1. Introduction

The first heat-up is a critical step in refractory castable processing. The steam generated by the vaporization of free water and the decomposition of cement hydrates may raise the pressure level inside the refractory, causing mechanical damage or even explosive spalling of the product. This situation is aggravated when the green structure displays low permeability and mechanical strength levels or if short heating schedules are applied.

The literature[1] has already established that castables bonded with calcium aluminate cement (CAC) require careful drying schedules to avoid explosive spalling, particularly when curing at low ambient temperatures (below 20 °C). Additionally, industrial practice has shown that these failures are more likely to occur during the dry-out of products cured for short time periods, even under controlled environmental conditions (relative humidity and temperature).

The reasons for the latter behavior, although not systematically investigated, are empirically related to the physical and chemical changes that take place in the castable structure during the curing process[2] (i.e. the time period after the molding step in which the cement reacts and develops the hydrated binding phases). In general, the stiffness taken on by the product in the early hours of curing (known as the *setting stage*) does not ensure that, after demolding, the maximum green strength provided by the hydration process (known as the *hardening stage*), has already been achieved.[2] Similarly, the permeability level of the castable structure, which determines the facility of steam release, may be differently affected during the setting and hardening stages.

Complete hydration of cement phases not only increases the castable's mechanical resistance but also decreases the content of free water retained in the pores, providing favorable conditions for safer drying.[3] Conversely, under partial hydration, the unreacted cement does not contribute to the development of green mechanical strength and leaves some fraction of free water readily available to promote steam pressurization. Therefore, knowledge of the appropriate curing time in which the main castable's properties are developed is important to help optimize the drying process of castables processed at low temperatures.

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Table 1
Characteristics of anhydrous phases present in CACs and their respective hydration and conversion reactions[a]

Anhydrous phase	Hydration rate	Low temperature (<20 °C) hydration (a,b,c) and Conversion (d,e,f) reactions
$C_{12}A_7$	Fast	$C_{12}A_7 + 60H \Rightarrow$(a) $2CAH_{10} + 5C_2AH_8 \Rightarrow$(d) $4C_3AH_6 + 3AH_3 + 27H$
CA	Slow	$6CA + 60H \Rightarrow$(b) $6CAH_{10} \Rightarrow$(e) $2C_3AH_6 + 4AH_3 + 36H$
CA_2	Very slow	$6CA_2 + 78H \Rightarrow^{(c)} 6CAH_{10} + 6AH_{x\ (gel)} \Rightarrow$(f) $2C_3AH_6 + 5AH_3 + 36H$

[a] Molar Mass [g/mol]: 1386 ($C_{12}A_7$); 158 (CA); 260 (CA_2); 18 (H). Hydration reactions (a,b,c) are mainly time dependent. Conversion reactions (d,e,f) are mainly temperature dependent.

2. Hydration/dehydration processes of calcium aluminate cements

Calcium aluminate cements (CAC) have been widely used as binder agents for refractory castables, providing relatively fast green mechanical resistance. Reactions between CAC and water lead to the formation of diverse hydrated phases. The type and content of the hydrates thus formed depend on the cement's mineralogical composition, the water-to-cement ratio and mainly on the curing temperature.[4–9] The hydraulic phases are responsible for reducing porosity and increasing mechanical strength until the sintering process initiates at temperatures around 900 °C for this composition.[10]

The relative amount of anhydrous phases ($C_{12}A_7$, CA and CA_2)[1] present in this type of cement varies considerably, depending on the raw materials and manufacturing process used.[4–6] The main practical differences among CAC phases are their hydraulic reactivity, hydration products and refractoriness. Moreover, depending on the proportion of each phase in the cement mix and the curing temperature applied, the setting time may change significantly.

CA, which is the main component of high-alumina cements, has a relatively slow setting kinetics. Nevertheless, when hydration begins, strength develops rapidly. $C_{12}A_7$ has a very short setting time and can even undergo flash setting (i.e., an abrupt stiffness development that occurs almost simultaneously with the end of water addition to the solid mix). For this reason, most cements usually contain only small amounts of this phase to accelerate CA hydration.[4–6] On the other hand, lower $CaO{:}Al_2O_3$ ratio phases, such as CA_2, are notably less reactive and more refractory (decomposition temperature = 1750–1765 °C).[4,5] CA_2 is usually present as the minor phase in commercial CACs, although more recent formulations include larger contents of this phase (up to 50%) in order to yield products with superior refractoriness.[4] The hydration kinetics of all these cement phases can be severely diminished if low curing temperatures are used, requiring longer setting periods to provide full hydration.

After cement hydration at low temperatures ($T < 20$ °C), CAH_{10} and alumina gel are the main hydrated products in the castable structure, as shown in Table 1 (reactions a, b and c). Actually, the hydrated phases CAH_{10} and C_2AH_8 are metastable, thus undergoing conversion to C_3AH_6 and AH_3 with increasing time and temperature (reactions d, e and f), if moisture is available for the dissolution and re-precipitation processes to take place. Conversion to C_3AH_6 can occur extremely fast at temperatures of 80–100 °C in a high humidity environment, and is completed after 1 day.[4,6,11] On the other hand, in the absence of sufficient water, these phases do not convert but dehydrate, releasing their combined water. Table 2 lists the decomposition temperatures of the diverse hydrated phases. CAH_{10} decomposition occurs at around 120 °C,[4,5] whereas C_2AH_8 decomposes between 170 and 195 °C. Crystalline AH_3 loses its molecules in the form of water vapor between 210 and 300 °C, although the peak of mass loss is mainly detected at 230 °C.[5] C_3AH_6 decomposes between 240 and 370 °C.[5,7,8] Some authors[6,7] have observed crystallization of alumina gel to AH_3 (gibbsite) in the temperature range of 27–40 °C, whereas others[4,5] suggest that this amorphous phase decomposes at around 100 °C.

Due to their importance for the development of monolithic refractory technology, CAC-related phenomena (such as the hydration, conversion and dehydration processes) have been investigated thoroughly in the last few decades. However, the consequences of cement hydration on the properties of refractory castables have been insufficiently explored. For this reason, the effect of the curing time on the properties of a high-alumina ultra-low cement composition was

Table 2
Decomposition temperatures of the diverse hydrated phases resulted from the reaction between the calcium aluminate cement and water[4–8]

Hydrated phase	Decomposition temperature (°C)
CAH_{10}	120
C_2AH_8	170–195
C_3AH_6	240–370
AH_3–gibbsite	210–300
Alumina gel	100

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[1] Cement notation: C(CaO), A(Al_2O_3), H(H_2O).

investigated. The changes observed in permeability and mechanical strength parameters were quantified and related to the hydration process of the different mineralogical phases contained in the refractory cement. The consequences of the variations in properties on the explosive spalling behavior were also determined.

3. Experimental procedure

The castable composition chosen for this study consisted of a mixture of 98 wt.% alumina and 2 wt.% calcium aluminate cement [CA-14, (39 wt.% CA_2, 59% CA, 1% $C_{12}A_7$, 1% Al_2O_3) Alcoa. USA], as shown in Table 3. The matrix powders (calcined A1000 SG and A3000 FL aluminas) and the aggregate grains (white fused aluminas, grades 4/10, 8/20, 10/36, 20/40 and 200F) were supplied by Alcoa, Brazil and USA. The particle size distribution of this composition was adjusted to a theoretical curve based on Andreasen's packing model, with a coefficient of distribution (q) of 0.21 to obtain a potentially self-flowable castable[12] and the casting water content was 4.52 wt.% (based on the dry weight of the composition).The dispersing agent employed was citric acid (LabSynth, Brazil, 0.039 wt.% in a dry basis), although the literature[13] reports that this additive may also retard the setting of castables.

The castable mixture was molded into 4.0 cm diameter by 4.0 cm high cylinders for the thermogravimetric (TG) and mechanical tests, and into 7.5 cm diameter by 2.2 cm thick disks for permeability measurements. All the samples were cured at 10 °C in a saturated condition (≈100%RH) for times varying from 2 h to 30 days.

TG tests were conducted in an electric furnace coupled to a scale. The furnace temperature and mass data were computer-recorded at 5-s intervals throughout the tests. A detailed description of the equipment can be found elsewhere.[14] The heating schedule applied consisted of a two-step procedure: (1) the sample was heated from room temperature to 110 °C at a heating rate of 5 °C/min and kept at this temperature until constant mass was reached (dwell time ranging from 250 to 700 min); (2) the temperature was then increased at a heating rate of 18 °C/min and kept at 800 °C until the mass loss was concluded.

Table 3
Maximum particle size of the raw materials and their respective content used in the castable formulation

Raw materials	Maximum particle size (mm)	Content (wt.%)
Matrix powders (calcined aluminas)	0.1	22
Aggregate grains (white fused aluminas)	4.5	76
Refractory cement (calcium aluminate)	0.1	2

The conversion process probably occurs[4] in the first part of the heating schedule, since free water is present in the body for at least the first 4 h of heat treatment at 110 °C. The water content is simultaneously reduced because of the drying out of water from the bulk of the solid by evaporation and ebullition. Subsequently, when the temperature rises to 800 °C, an additional water loss occurs due to the release of chemical water (W_C), which is present mainly in the hydrates C_3AH_6 and AH_3 formed by the conversion of CAH_{10}. The fraction of chemical water contained in the structure was calculated as:

$$W_C[\%] = \frac{(M_{110} - M_F)}{M_F} \times 100 \tag{1}$$

where M_{110} is the constant mass after drying at 110 °C and M_F is the final mass after the test.

Explosion tests were conducted using the same equipment previously described,[14] but an aggressive heating rate of 20 °C/min was continuously applied from room temperature to 800 °C. Explosion temperatures were evaluated in terms of actual furnace temperature. The curing times chosen for the tests were 1 day and 16 days, and seven samples were evaluated for each condition. An additional sample cured for 16 days was heated from room temperature to 800 °C, at a heating rate of 10 °C/min, to verify if the water content added during the castable's preparation remained constant during the curing process.

Samples for permeability and mechanical tests were dried in silica gel at the curing temperature. This removal of moisture was conducted primarily to prevent any influence of free water on the measurements and avoid further hydration of the cement.

Permeability tests were carried out on two samples for each curing time. The experiments evaluated the ease of airflow through the sample's thickness by measuring the exit air velocity in response to the variations of the inlet pressure applied. The permeability constants k_1 and k_2 were obtained by fitting the experimental data using Forchheimer's Eq. (2)[10]

$$\frac{P_i^2 - P_o^2}{2PL} = \left(\frac{\mu}{k_1}\right) v_s + \left(\frac{\rho}{k_2}\right) v_s^2 \tag{2}$$

where P_i and P_o are the absolute inlet and outlet air pressures, respectively; v_s is the fluid velocity; L the sample thickness; μ the fluid viscosity; and ρ the fluid density. The parameters k_1 and k_2 are, respectively, the Darcian and non-Darcian permeability constants.

Mechanical tests were conducted according to the ASTM C496-90 (Splitting Tensile Strength of Cylindrical Concrete Specimens) in an MTS device (MTS Systems, Model 810, Minneapolis, MN) on six dried samples of each curing time to ensure reliable results.

4. Results and discussion

The increase in the amount of combined water (W_C) during the curing stage is a good indication of the cement's hydration level and the maximum value for W_C is reached when complete hydration occurs. The TG results in Fig. 1 show that the measured W_C increased with curing time in response to the development of hydration.

The change in the curve's slope in Fig. 1 indicates that hydration occurred at different rates throughout the curing period. This behavior is likely related to the balance between the moderate hydration of CA (accelerated by the small content of $C_{12}A_7$) in the first 50–70 h of curing, followed by the slow hydration of CA_2 throughout the rest of the curing period. Because the majority of CA is reacted, the hydration rate in the later stage is determined mostly by CA_2, which presents very slow hydration kinetics at 10 °C, thus substantially extending the entire hydration period.

This feature was confirmed not only by the literature[15] but also by X-ray diffraction (XRD) analysis (Siemens D5005, 2θ range 5–75°, step size of 0.033°, speed 1.98°/min, CuKα radiation) conducted on a mixture of 70 wt.% CA-14, 30 wt.% of calcined alumina and water (using the same W/C ratio as that employed in the castable composition). The XRD results indicated that CA was undetectable after 2 days of curing at 10 °C, while the presence of CA_2 was verified along with large quantities of CAH_{10} and traces of crystalline AH_3, reinforcing the aforementioned hypothesis that the transition of the predominant hydrating phase from CA to CA_2 took place between 50 and 70 h of curing.

In addition, theoretical calculations of the fraction of water present in the hydrated products after total conversion were obtained based on the data given in Table 1. The line in the upper part of Fig. 1 represents the maximum W_C value ($W_{Cmax}=0.924\%$) that can be reached when complete hydration of the cement phases occurs. Based on these results one can assume that, even after 30 days of curing, the hydration process was still incomplete.

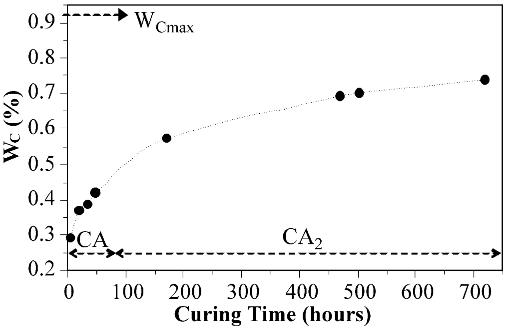

Fig. 1. Experimental W_C for different curing times at 10 °C and maximum W_C value theoretically predicted. The main hydration periods of the cement phases are indicated by arrows. The connecting line is present just to guide the eyes.

Although some authors[4] have suggested that, after partial curing, the unreacted cement particles might become hydrated during the drying stage, this feature was not verified in the present study. Because W_C increases continuously as the curing time progresses, as depicted in Fig. 1, it can be assumed that the unreacted cement fraction remained anhydrous. Otherwise, all the castable samples would have presented very similar levels of chemically bonded water.

Fig. 2a and b show the plotted permeability parameters k_1 and k_2 versus curing time. Both permeability constants decreased dramatically during the formation of hydrated phases. The low curing temperature of CA led to the formation of low-density CAH_{10} (1.72 g/cm^3). As the amount of hydrated phases increased with time, a more densely packed structure of interlocking crystals was created, reducing porosity and blocking the airflow through the castable. Therefore, as hydration occurred relatively fast during the first 2 days, the permeability drop in this period was very intense (50.1% and 80.6% for k_1 and k_2 respectively). The permeability continued

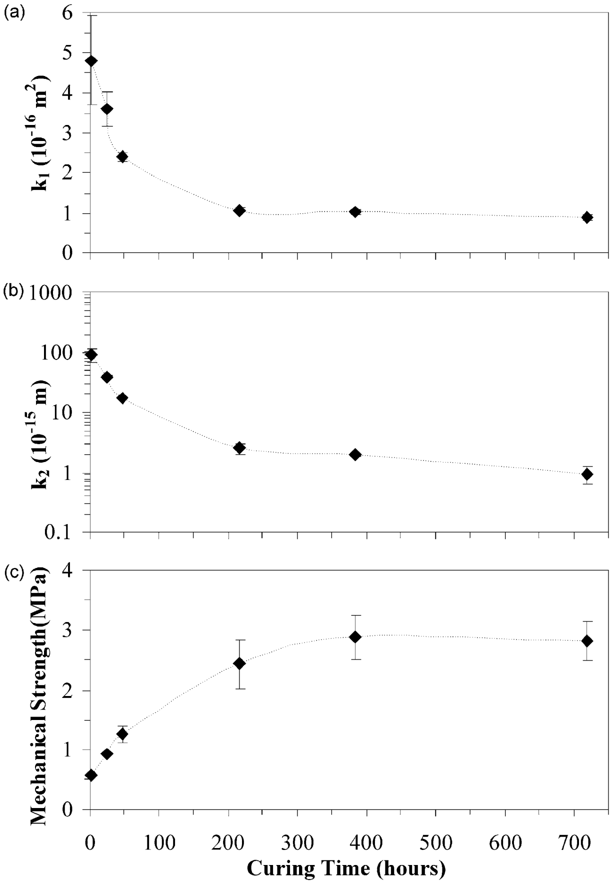

Fig. 2. Castable's properties variations along the curing period at 10 °C: (a) Darcian permeability constant k_1, (b) non-Darcian permeability constant k_2, (c) mechanical strength. The connecting lines are just to guide the eyes.

to decrease significantly (27.7% for k_1 and 16.6% for k_2) between the 2nd and 9th days, associated with the predominant hydration of CA_2, because alumina gel was formed in addition to CAH_{10}.[4,15] This gel phase contributed to further clog the structure owing to its gelatinous character and its ability to fill voids around and between hydrate crystals whatever their morphology, as reported in the literature.[16] Finally, permeability decreased slightly (3.9% for k_1 and 1.7% for k_2) from the 9th to the 30th day, mostly because the majority of hydrates had already been formed.

Fig. 2c illustrates the mechanical strength as a function of curing time. From 2 h up to 30 days of curing, there was an almost fivefold increase in mechanical resistance (0.57 to 2.81 MPa). This behavior was caused by the continuous rise in the quantity of hydrated phases (CAH_{10} and alumina gel) formed while hydration was in progress.

In face of the difficulty to systematically quantify the actual spalling resistance of refractory castables, several researchers[1,7,17] have proposed the explosion temperature as a ranking criterion. This parameter can be used to compare the spalling propensity of different castables compositions subjected to equal heating conditions and, according to this approach, the higher the explosion temperature the greater the spalling resistance of the body. Thus, in order to evaluate the importance of the development of hydration on the castable's spalling behavior, the number of explosion events and their temperatures were obtained for two curing times (1 and 16 days). After one day of curing, five out of seven tested samples failed by explosive spalling with a mean temperature of 416 $^{\circ}C \pm 9$. On the other hand, the seven samples cured for 16 days exploded with a higher average temperature, 440 $^{\circ}C \pm 7$. Fig. 3a and b illustrate the typical damage caused by the explosive spalling in these samples.

The increase in average explosion temperature results from the higher mechanical strength of bodies cured for longer periods. Damage occurs when the pressure developed inside the castable structure—caused by steam being generated more rapidly than it can be released from the bulk of the solid—reaches the body's maximum tensile strength. Therefore, more resistant pieces are able to withstand higher pressurization levels.

Reductions in permeability and increases in mechanical strength both depend on the castable's level of hydration, although they have opposite correlations with the curing time. Moreover, the cement hydration causes not only significant changes in the aforementioned properties of the castable but also reduces its free water content, since part of the casting water is consumed to form the hydrated phases.

Increases in mechanical strength and decreases in free water content obviously help to prevent the occurrence of spalling, although a considerable reduction in permeability may still contribute to pressure build up within the castable's pores during the drying stage. This fact can be better observed, when one compares the laboratory and the industrial curing procedures. In the present study, the initial water content (4.52 wt.%) of the specimens subjected to explosion tests was maintained constant, even after 16 days of curing, by use of plastic sealed storage. Under these circumstances, the drop in the permeability level was the main cause of the augment in the number of explosion events (5 after 1 day to 7 after 16 days), even though the explosive spalling resistance was enhanced (as seen by the higher average explosion temperature) due to the increase in the mechanical strength. On the other hand, in industrial practice the green bodies cured for longer periods

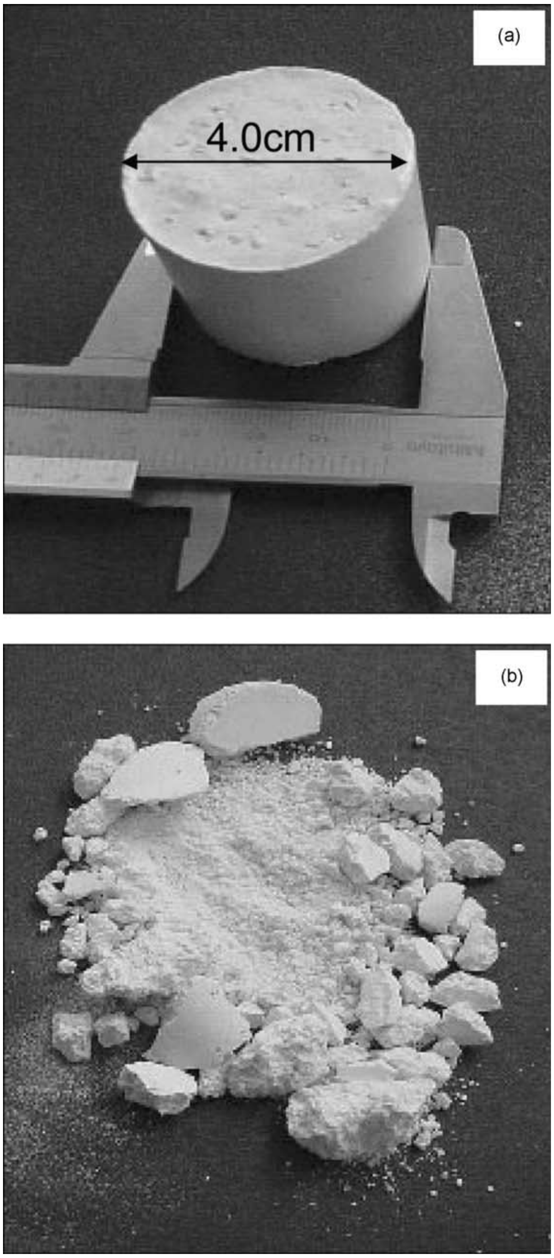

Fig. 3. Pictures of (a) an as-cured specimen before the test and (b) the remaining fragments after an explosion event.

are more likely to lose part of their physical water due to mass transfer between the pieces and the surrounding environment. In these cases, when the free water content of the pieces is diminished during the curing stage, the reduced permeability has no longer such a deleterious effect on the drying behavior, since steam pressurization becomes less severe and the required strength to withstand mechanical loads is lower. Consequently, the decrease of moisture content as well as the increase in the product's mechanical strength caused by hydration are the main reasons for the reduction in spalling tendency as a function of the curing time that is observed in the industrial field.

Considering the importance of moisture content to the spalling behavior of castables, drying schedules should be designed focusing on the free water removal, for instance, based on dwell times in the temperature range of 100–150 °C, which does not promote high pressures (0.1–0.47 MPa)[18] and ensures fast dewatering. Additionally, if this first drying step is well conducted, the absence of free water during the subsequent heatup (to temperatures above 150 °C) makes steam pressurization not likely to occur and a more aggressive heating rate may be applied without causing mechanical damage (for ultra-low cement compositions) while simultaneously reducing the overall drying times.

5. Conclusions

The present study revealed that curing time is a pertinent variable in the processing of refractory castables based on calcium aluminate cements, affecting the specimens' hydration level and, hence, their properties and characteristics. The association of low curing temperatures and high CA_2 compositions promoted long setting periods, causing a gradual drop in the permeability level and simultaneous gains in mechanical strength. This behavior was ascribed to characteristics of the hydrated products formed by the different mineralogical phases of the cement. The results indicated that, in an industrial environment, the gain in mechanical strength may be more important for a safe drying process than the reduction in the permeability level, since a smaller amount of free water becomes available for steam pressurization, either by the consumption of cast water for the hydration of cement phases or by the loss of moisture to the surrounding environment during the curing stage.

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References

1. Gitzen, W. H. and Hart, L. D., Explosive spalling of refractory castables bonded with calcium aluminate cement. *Am. Ceram. Soc. Bull.*, 1961, **40**(8), 503–507,510.
2. Bier, T. A., Mathieu, A., Espinosa, B. and Bayoux, J. P., The use of conductimetry to characterize the reactivity of calcium aluminate cements. *Proceedings of the Unified International Technical Conference on Refractories*—UNITECR'1993, São Paulo, Brazil, 1993, pp. 705–716.
3. Innocentini, M. D. M., Ribeiro, C., Bittencourt, L. R. M. and Pandolfelli, V. C., Fluid dynamics and thermal aspects of the dewatering of high-alumina refractory castables: removal of physically absorbed water. *J. Am. Ceram. Soc.*, 2001, **84**(11), 2696–2698.
4. Parker, K. M. and Sharp, J. H., Refractory calcium aluminate cements. *Trans. J. British Ceram. Soc.*, 1982, **81**, 35–42.
5. Nishikawa, A., *Technology of monolithic refractories.* Plibrico Japan CO, Ltd, Tokyo, 1984.
6. George, C. M., Aspects of calcium aluminate cement (CAC) hydration. Presented at the *Refractories Symposium,* The American Ceramic Society, St. Louis Section, St. Louis, 1994.
7. Maczura, G., Hart, L. D. and Heilich, R. P., Refractory cements. *Ceramic Proceedings*. The American Ceramic Society, Inc., 1983, pp. 11.
8. Schmitt, N., Hernandez, J. F., Lamour, V., Berthaud, Y., Meunier, P. and Poirier, J., Coupling between kinetics of dehydration, physical and mechanical behaviour for high alumina castable. *Cement and Concrete Research*, 2000, **30**, 1597–1607.
9. Bentsen, S., Seltveit, A. & Sandberg, B., Effect of microsilica on conversion of HAC. Presented at the *Midgley Symposium on Calcium Aluminate Cement*, London, 1990.
10. Innocentini, M. D. M., Pardo, A. R. F., Menegazzo, B. A., Bittencourt, L. R. M., Rettore, R. P. and Pandolfelli, V. C., Permeability of high-alumina refractory castables based on various hydraulic binders. *J. Am. Ceram. Soc.*, 2002, **85**(6), 1517–1521.
11. Nilforoushan, M. R. and Sharp, J. H., The effect of time on the hydration reactions of a refractory calcium aluminate cement investigated by SEM. *Proceedings of the Unified International Technical Conference on Refractories*—UNITECR'2001 ALAFAR, Cancun, 2001, 1586–1597.
12. Studart, A. R., Pileggi, R. G. and Pandolfelli, V. C., High-Alumina Multifunctional Refractory Castables. *Am. Ceram. Soc. Bul.*, 2001, **80**(11), 34–39.
13. Studart, A. R., Oliveira, I. R., Valenzuela, F. A. O. and Pandolfelli, V. C., Setting behavior of ultra-low cement refractory castables in the presence of citrate and polymethacrylate salts. *J. Eur. Ceram. Soc.*, 2003, **23**, 2225–2235.
14. Innocentini, M. D. M., Cardoso, F. A., Akyioshi, M. M. and Pandolfelli, V. C., Drying stages during the heating of high-alumina, ultra-low cement refractory castables. *J. Am. Ceram. Soc.*, 2003, **86**(7), 1146–1148.
15. Chatterji, S. and Jeffery, J. W., Micro-structure of set high-alumina cement pastes. *Transactions of the British Ceramic Society*, 1968, **67**, 171–183.
16. Freitas, C. M. M., Brandão, P. R. G. and Rettore, R. P., Hydration conditions and microstructure development in calcium aluminate cements' pastes. *Proceedings of the Unified International Technical Conference on Refractories*—UNITECR'1993, São Paulo, Brazil, 1993, pp. 684–696.
17. Moore, R. E., Smith, J. D., Headrick, W. L. and Sander, T.P. Monolithic Dewatering Theory Testing and Practice: New Challenges. Presented at the *Refractories Symposium*, The American Ceramic Society, St. Louis Section, St. Louis, 1996.
18. Bell, D. A., First heat-up of ladle linings. *Proceedings of the Unified International Technical Conference on Refractories*—UNITECR '99, pp. 292–294 (Berlin, Germany, 1999). American Ceramic Society, Westerville, OH, 1999.