

# EFFECT OF CURING CONDITIONS ON THE PROPERTIES OF ULTRA-LOW CEMENT REFRACTORY CASTABLES

Fábio A. Cardoso, Murilo D. M. Innocentini, Mario M. Akiyoshi and Victor C. Pandolfelli

Department of Materials Engineering, UFSCar – Federal University of São Carlos

Via Washington Luiz - km 235, 13565-905, São Carlos - SP, Brazil

This paper reports the effect of curing conditions on the properties of CAC bonded refractory castables. The hydration level of specimens cured at different temperatures (10° and 50°C) for time periods varying from two hours to 30 days was determined through thermogravimetric tests. The samples' mechanical strength and air-flow permeability were evaluated as a function of the curing time and temperature, and the presence of hydrated phases was assessed via XRD analyses. The changes observed in the castables' properties were associated with the diverse binding phases resulting from the various hydration conditions. It is also shown that the control of the curing process can be very effective in helping to optimize the use of the CAC content and to avoid problems in the subsequent steps of monolithic processing (i.e., demolding, drying, heat-up, etc.) by enhancing product uniformity and production routine predictability.

## 1. INTRODUCTION

High-purity calcium aluminate cement (CAC) is widely used as a hydraulic refractory binder mainly due to its high refractoriness and rapid development of strength [1-4]. The design of particle size distribution (PSD) and the cement hydrated phases generated during curing are the main factors responsible for the green properties of castables. The development of enhanced PSD methods and the use of reactive fillers, such as calcined alumina and fume silica, have increased the strength of monolithic bodies, allowing for the reduction of cement contents [5,6]. However, even in ultra-low cement compositions, CAC still exerts a major influence on the properties of green refractory castables [7].

CAC technology is based on the hydration ability of CA\*, CA<sub>2</sub> and C<sub>12</sub>A<sub>7</sub> to gradually yield a variety of calcium aluminate hydrated phases (CAH<sub>10</sub>, C<sub>2</sub>AH<sub>8</sub> and C<sub>3</sub>AH<sub>6</sub>) and alumina hydrates (gibbsite and gel) [1-4] when in contact with water. The hydrated phases formed depend mainly on the curing temperature, as shown in Table 1. These phases possess particular characteristics, such as density, crystal structure and number of combined water molecules, which affect the physical properties and the dehydration behavior of castables subjected to different curing temperatures. Some features of the diverse hydrated phases are shown in Table 2. In addition, the metastable hydrates, CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub>, undergo the conversion process into C<sub>3</sub>AH<sub>6</sub> and AH<sub>3</sub> with increasing time and temperature (and in the presence of water). Conversion can be very fast at temperatures of 80°-100°C in a highly humid environment and is completed after 1 day [1,3].

\*Cement notation: C = CaO, A = Al<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O.

The most relevant difference among CAC phases is the hydraulic reactivity, which is based on the CaO/Al<sub>2</sub>O<sub>3</sub> ratio. The amount of anhydrous phases (CA, CA<sub>2</sub> and C<sub>12</sub>A<sub>7</sub>) present in the cement, in association with the curing temperature, determines the hydration rate of the binder. In this context, curing conditions are of great importance regarding the control and optimization of refractory castables processing, since they determine not only the type of hydrated phases that confer strength on the structure, but also the formation rate of these binding phases. Therefore, the time required to take full advantage of the added cement (in terms of the development of green properties) varies considerably and may even lead to undesirable results during monolithic production.

In industrial contexts, various logistical and environmental problems may dictate the length of curing time, depending on production schedules and customer demands. This variability in such a crucial step of refractory castable processing gives rise to nonuniform production routines, higher rejection indices and lower efficiency of the entire process, since the subsequent stages of demolding, drying, transportation (for pre-cast parts) and first heat-up may

**Table 1. Most common binding phases resulting from the hydration of CAC at different temperatures [1-4].**

Anhydrous Cement	Curing Temperature	Hydrated Phases
CAC	T < 15°C	CAH <sub>10</sub> + alumina gel
	15° < T < 40°C	C <sub>2</sub> AH <sub>8</sub> + C <sub>3</sub> AH <sub>6</sub> + AH <sub>3</sub>
	T > 40°C	C <sub>3</sub> AH <sub>6</sub> + AH <sub>3</sub> (gibbsite)

**Table 2. Physical features and dehydration temperatures of the cement binding phases [1-4, 7].**

Phase	Crystal System	Density (g/cm <sup>3</sup> )	Dehydration Temperature (°C)
CAH <sub>10</sub>	Hexagonal	1.72	120
C <sub>2</sub> AH <sub>8</sub>	Hexagonal	1.95	170-195
C <sub>3</sub> AH <sub>6</sub>	Cubic	2.52	240-370
AH <sub>3</sub>	Hexagonal	2.42	210-300
Alumina gel	amorphous	-	≈ 100

be adversely affected if curing is not carried out properly. An adequate knowledge of hydration behavior can give refractory manufacturers good control over the curing procedure, enabling them to adjust it according to environmental conditions or to their own production requirements.

Based on these considerations, the main purpose of this work was to evaluate the effects of curing time and temperature on the hydration level and physical properties of a high-alumina, ultra-low cement refractory castable. To this end, thermogravimetric analyses (TG), airflow permeability and mechanical strength tests were conducted on refractory samples cured at 10° and 50°C for time periods varying from two hours to 30 days. The development of the hydrated binding phases resulting from the various curing conditions was investigated through XRD analyses in a cement / alumina paste.

## 2. EXPERIMENTAL PROCEDURE

The castable composition selected for this study consisted of a mixture of 98 mass% alumina and 2 mass% calcium aluminate cement [CA-14, (39 wt% CA<sub>2</sub>, 59% CA, 1% C<sub>12</sub>A<sub>7</sub>, 1% Al<sub>2</sub>O<sub>3</sub>) Alcoa – U.S.]. 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, U.S. and Brazil respectively. 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 [8]. The casting water content was 4.52 wt% (based on the dry weight of the composition) and the dispersing agent employed was citric acid (LabSynth – Brazil).

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. Samples were cured at 10° or 50°C in a saturated condition (≈100%RH) for periods ranging from two hours to 30 days.

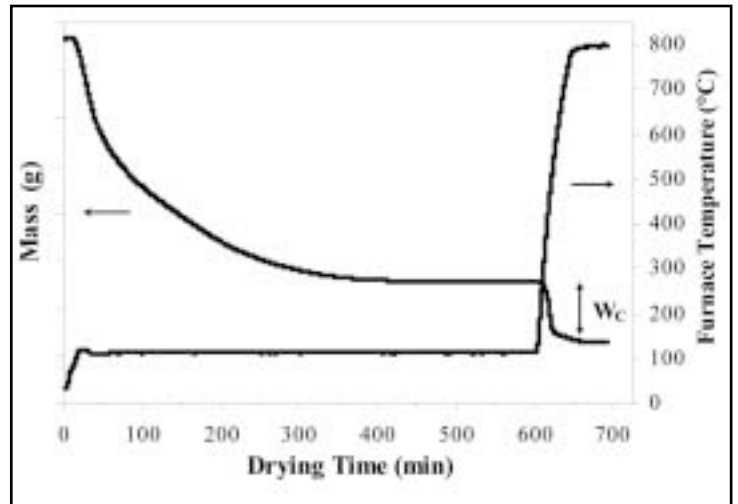
TG tests were conducted in an electric furnace coupled to a scale. The furnace temperature and mass data were computer-recorded at 5s intervals throughout the tests. The heating schedule applied consisted of a two-step procedure: (i) the sample was heated from room temperature to 110°C at a rate of 5°C/min and kept at this temperature until constant mass was reached (dwell time ranging from 250 to 700 minutes); (ii) the temperature was then increased at a heating rate of 18°C/min and held at 800°C until the mass loss was completed, as shown in Figure 1.

Based on the TG analyses, the fraction of chemical water contained in the structures (regardless of the curing temperature) was calculated as:

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

where M<sub>110</sub> is the constant mass after drying at 110°C and M<sub>F</sub> is the final mass after the test.

Samples for permeability and mechanical measurements, after being cured for the pre-set time, were dried in desiccant silica gel (blue type) prior further evaluation. The specimens were placed in plastic bags full of silica gel and held at this condition for about ten



**Figure 1. Heating schedule applied during the TG tests and mass loss response used to determine the W<sub>C</sub> of the samples cured for various periods of time at 10° and 50°C.**

days (curing temperature: 10° or 50°C). After each couple of days of drying, the desiccant material was renewed in order to keep the environment with a relative humidity around 5%. The purpose was that at the end of the treatment, around 95% of the physically absorbed water of the castable samples could be removed. No shrinkage or superficial defects were verified after this drying procedure, which was conducted primarily to prevent any influence of free water on the measurements and also to inhibit further hydration of the cement.

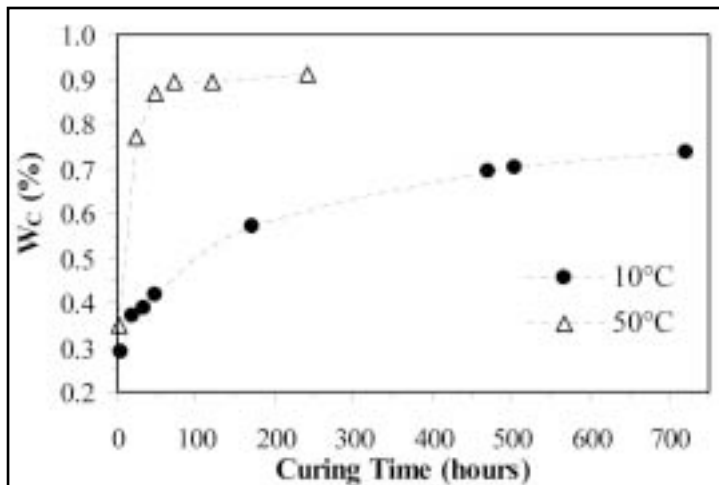
Permeability tests were carried out on two samples for each curing time. The experiments consisted of evaluating the easiness of airflow through the sample's thickness by measuring the exit air velocity in response to the variations of the inflow pressure applied. The permeability constants k<sub>1</sub> and k<sub>2</sub> were obtained by fitting the experimental data using Forchheimer's equation (2) [5]:

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

where P<sub>i</sub> and P<sub>o</sub> are the absolute inflow and outflow air pressures, respectively; v<sub>s</sub> is the fluid velocity; L the sample thickness; μ the fluid viscosity; and ρ the fluid density. The parameters k<sub>1</sub> and k<sub>2</sub> are, respectively, the Darcian and non-Darcian permeability constants.

The mechanical strength was evaluated according to the ASTM C496-90 standard (Splitting Tensile Strength of Cylindrical Concrete Specimens) in an MTS device (MTS Systems, Model 810, Minneapolis, MN). Six dried samples from each curing condition were mechanically tested.

XRD analyses were conducted on a mixture of 70 wt% CA-14, 30 wt% of calcined alumina, citric acid and water, using the same water / cement ratio as that employed in the castable composition. The matrix mixture was cast into 3.0 cm diameter by 1.0 cm high disks and cured at different temperatures. When the preestablished curing time was reached, the hydration was stopped by drying the samples in silica gel at the curing temperature. The unhydrated sample prepared for XRD was dry-pressed into the same geometry previously described. The equipment used for the analyses was a



**Figure 2. Experimental  $W_C$  for different curing times at 10° and 50°C. The connecting lines serve to guide the eyes.**

Siemens D5005 and the tests were carried out with the following features:  $2\theta$  range 5°-75°, step size of 0.033°, speed 1.98°/min and  $\text{CuK}\alpha$  radiation.

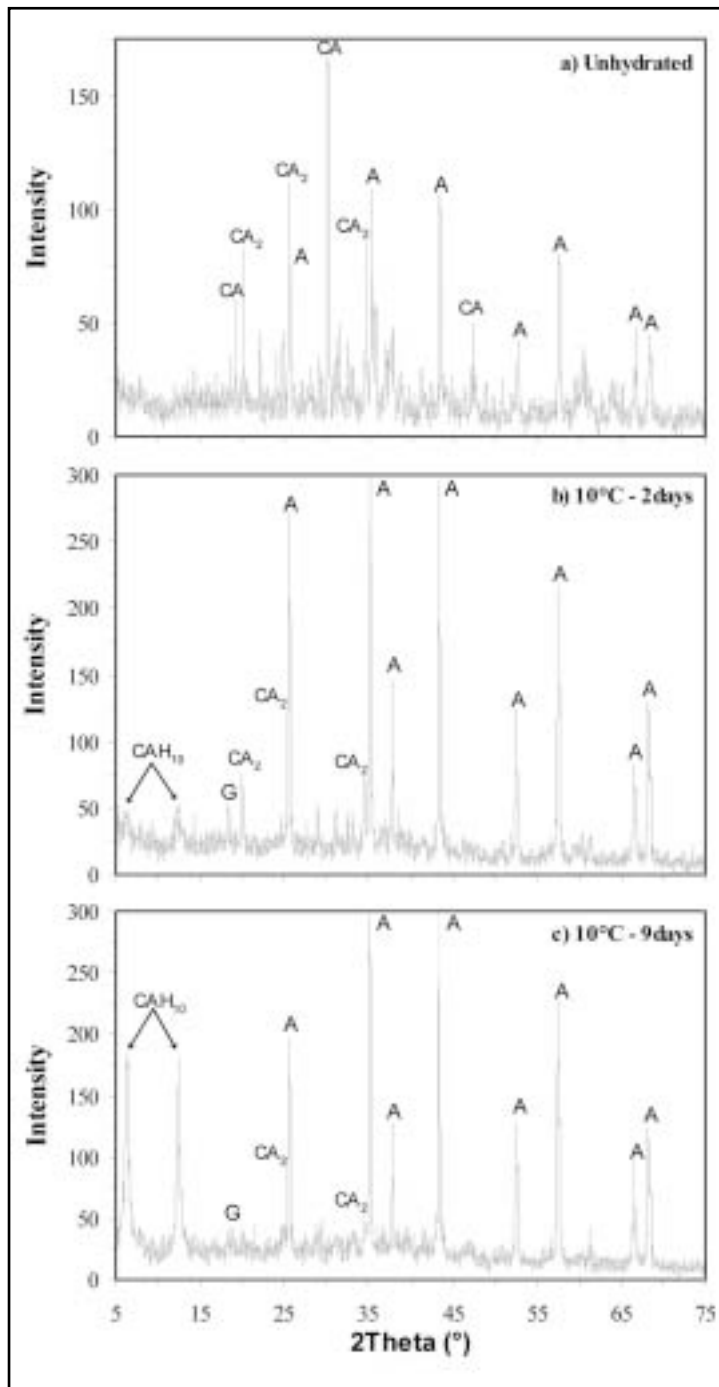
### 3. RESULTS AND DISCUSSION

In the TG evaluations of the samples cured at low temperature (10°C), the conversion of the metastable hydrate  $\text{CAH}_{10}$  is likely to have occurred during the dwell time at 110°C, since free water was present in the body for at least the first four hours of heat treatment at this temperature (Figure 1). The water content was reduced simultaneously because of the drying out of water from the bulk of the solid by evaporation. Subsequently, when the temperature rose to 800°C, additional water loss occurred due to the release of chemical water ( $W_C$ ), which is present mainly in the  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  hydrates formed by the conversion of  $\text{CAH}_{10}$  [7]. Conversely, the hydrates primarily formed in the specimens cured at 50°C were  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  (gibbsite), which do not undergo conversion at 110°C. Therefore, during the heat treatment at this temperature, no change except the removal of free water occurred in the hydrated phases.

The hydration level of the cement content in a castable can be measured, regardless of the curing temperature, through the quantification of its chemically combined water ( $W_C$  – equation 1). The TG results in Figure 2 show that  $W_C$  increased at different rates in the samples cured at distinct temperatures. The specimens cured at 50°C reached their maximum hydration after 3 days and remained at the same  $W_C$  level until the 10th day ( $\approx 250$  hours), indicating that hydration had already been concluded.

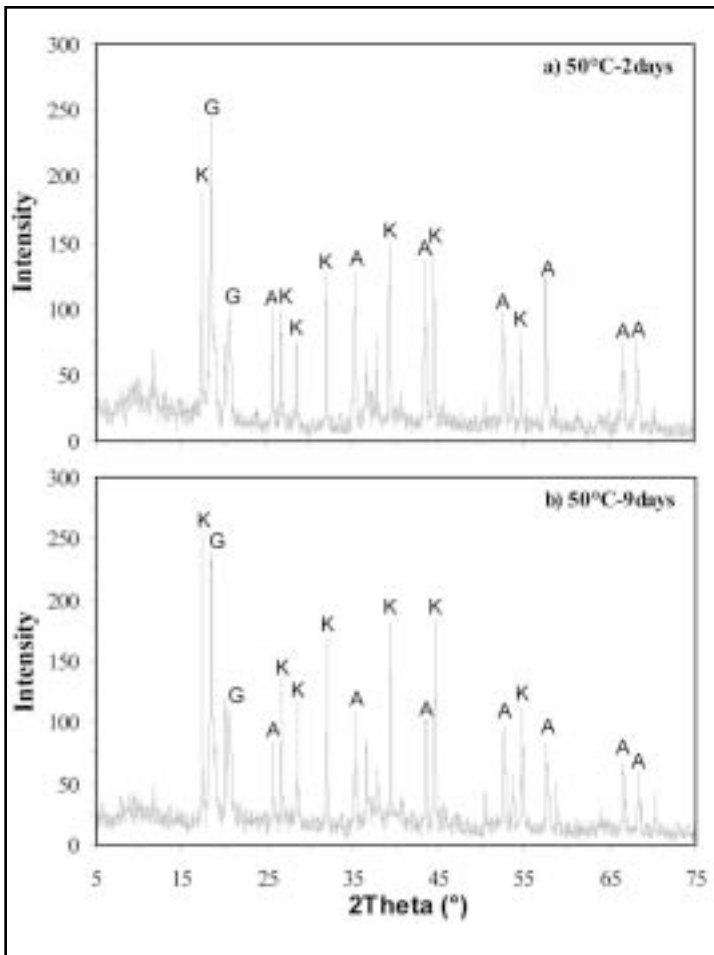
On the other hand, the castable cured at 10°C took longer to cure due to the effect of temperature on the hydration kinetics and to the high  $\text{CA}_2$  content of the cement. As a result, hydration was still in progress even after 30 days of curing. It was also noted that, during the first 50-100 hours, hydration developed faster than in the subsequent curing period (100-720 hours). This behavior was attributed to the hydration kinetics of the major cement phases CA and  $\text{CA}_2$ , which display moderate to slow rates at this temperature.

These observations were confirmed through the XRD analyses shown in Figures 3a, 3b and 3c, which correspond to the diffraction patterns of the unhydrated sample and the pastes cured at 10°C for two and nine days, respectively. The unhydrated specimen (Figure



**Figure 3. X-ray diffraction patterns of: (a) unhydrated sample, (b) cement / alumina paste cured at 10°C for two days, and (c) paste cured at 10°C for nine days. Phases: A (Alumina) –  $\text{Al}_2\text{O}_3$ ; CA –  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ;  $\text{CA}_2$  –  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ ;  $\text{CAH}_{10}$  –  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ ; G (Gibbsite) –  $\text{AH}_3$ .**

3a) displayed alumina (added to the paste) and the cement constituents CA and  $\text{CA}_2$  as the main crystalline phases. Figure 3b shows that, after the first two days of curing at 10°C, a large part of the  $\text{CA}_2$  remained anhydrous, while the CA phase was undetectable, supporting the hypothesis that it reacted first.  $\text{CAH}_{10}$  was barely visible in short broad peaks, indicating a poorly crystallized  $\text{CAH}_{10}$  or that a small amount of this phase was formed after two days. On the other hand, the sample cured for nine days displayed intense peaks of hexagonal  $\text{CAH}_{10}$  crystals, and the main position

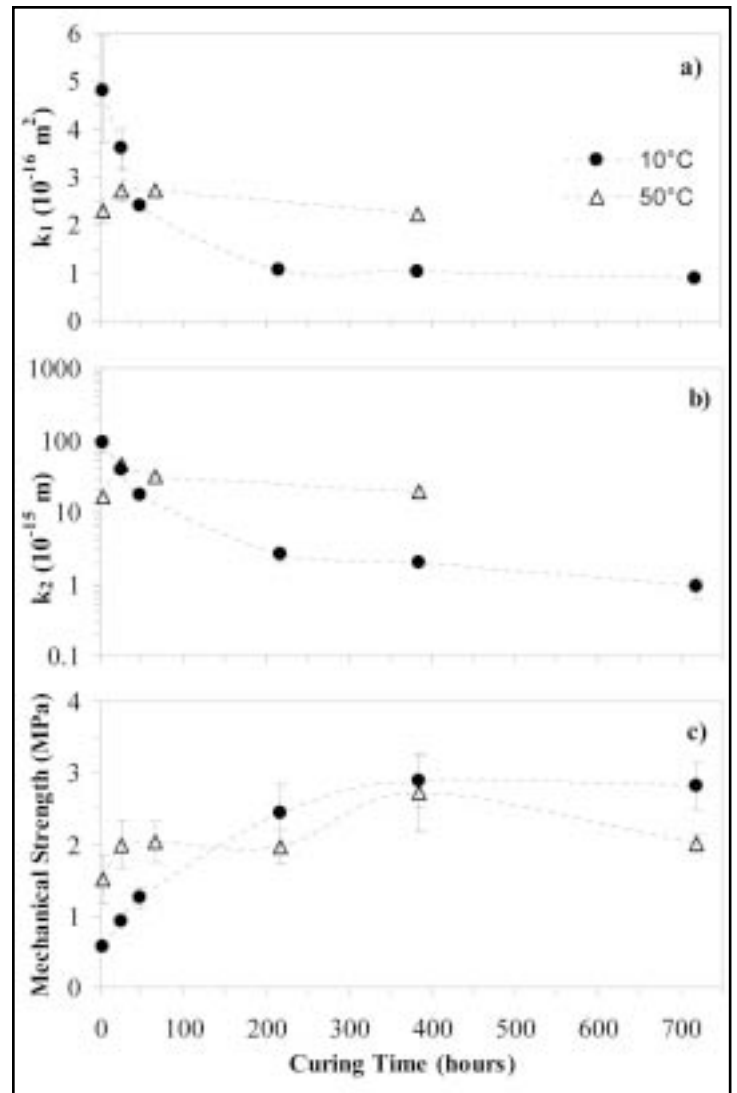


**Figure 4.** X-ray diffraction patterns of the paste cured at 50°C: (a) for two days, (b) for nine days. Phases: A (Alumina) –  $\text{Al}_2\text{O}_3$ ; K (Katoite) –  $\text{C}_3\text{AH}_6$  or  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ ; G (Gibbsite) –  $\text{AH}_3$  or  $\text{Al}(\text{OH})_3$ .

of the diffraction peak of the crystalline  $\text{AH}_3$  (G – Gibbsite) exhibited a short small band. This band may have corresponded to the hydration of a minor amount of reactive alumina present in the cement or to amorphous alumina gel, which is also formed at low curing temperatures. The  $\text{CA}_2$  peaks diminished significantly after nine days, although they were still detectable, evidencing the slow hydraulic reactivity of this phase when subjected to low hydration temperatures. Alumina (A –  $\text{Al}_2\text{O}_3$ ) was detected in every sample.

Figures 4a and 4b shows the XRD patterns of the paste specimens cured at 50°C for two and nine days. Unlike the pastes cured at low temperatures, the samples cured at 50°C presented no anhydrous cement phase. As expected, the hydrated phases formed were  $\text{C}_3\text{AH}_6$  (K – Katoite) and  $\text{AH}_3$  (G – Gibbsite), see Table 1. The only difference between the samples cured for two and nine days was the intensity of the  $\text{C}_3\text{AH}_6$  diffraction peaks, which were greater for the latter specimen due to its higher crystallinity, since the hydration level remained constant after the third curing day. Alumina was detected in both samples.

Considering the diversity of hydrated binding phases that can be formed and the difference in their generation rates, the development of the green castable's properties was carefully evaluated during the curing period at both temperatures (10° and 50°C), as shown in Figure 5.



**Figure 5.** Variations in castable properties over the curing time period at 10° and 50°C: (a) Darcian permeability constant  $k_1$ , (b) non-Darcian permeability constant  $k_2$ , (c) mechanical strength. The connecting lines serve to guide the eyes.

Figures 5a and 5b illustrate the permeability parameters  $k_1$  and  $k_2$  versus curing time for the two temperatures used (10° and 50°C). Both permeability constants decreased dramatically in the samples cured at 10°C during the formation of the low-density  $\text{CAH}_{10}$  crystals and alumina gel. As the amount of hydrated phases increased over time, a more densely packed structure of interlocking crystals was generated, reducing porosity and blocking the airflow through the castable. In addition, the amorphous alumina contributed to further clog the structure due to its gelatinous character and consequent ability to fill voids and interfacial defects. This resulted in a very sharp decline in permeability within the 30-day period studied, since  $k_2$  dropped by two orders of magnitude.

The samples cured at 50°C behaved quite differently from the ones cured at 10°C. Their permeability began at a lower level than at 10°C, but increased slightly from two hours on up to one day, after which both constants ( $k_1$  and  $k_2$ ) decreased slightly up to the 16th day, returning to their initial level. Comparing the final permeabilities of the specimens cured at both temperatures, it can be concluded that the samples cured at 50°C were considerably more permeable than those cured at the lower temperature. The samples

cured at 50°C presented a 2.5-fold higher constant  $k_1$  and a tenfold greater  $k_2$  than the values of these constants at 10°C. The use of Forchheimer's equation (eq. 2) allowed for a more precise and reliable assessment of the magnitude of permeability variation as a function of the cement hydration conditions. These findings regarding the dry-out of castables are important, since the permeability level is the key parameter that indicates how easily steam is released and, hence, what the tendency for explosive spalling is during the drying operation.

Lastly, Figure 5c indicates the mechanical strength developed over the curing time at both hydration temperatures. In the first 100 hours (four days), the mechanical strength of the samples cured at 50°C was twice that of the ones cured at 10°C. After this period, the maximum hydration level had already been reached in the samples cured at 50°C, whereas hydration in the samples cured at 10°C was still in progress, resulting in an increase of strength. After 30 days, the mechanical strength of the samples cured at 10°C was 50% higher than that of the samples cured at 50°C (3.0 MPa and 2.0 MPa respectively). This behavior resulted from the different hydration rates at the curing temperatures applied and from the physical features of the binding phases. Hydration at 50°C was completed during the first few days, and the total expected amount of hydrates was already formed, thus providing full binding capacity. In contrast, the samples cured at 10°C developed greater strength, albeit at a slower rate. In the samples cured at 10°C, the alumina gel, which is very efficient in filling voids, and the low density  $CAH_{10}$  crystals certainly contributed to improve the castables' mechanical strength.

#### 4. CONCLUSIONS

The present investigation demonstrated that curing conditions, time and temperature are key parameters in the processing of CAC bonded refractory castables, since they affect the specimens' hydration rate and the type of hydrated binding phases formed. The hydration level of the cement content in the refractory castable was assessed "in situ" through a modified TG heating schedule, revealing that hydration proceeded at different rates depending on the curing temperature. Therefore, the time required for complete development of the castables' green properties differed in the specimens cured at distinct temperatures (10° and 50°C). The samples cured at 10°C displayed a very sharp decline in permeability, reaching a significantly lower permeability level at the end of the curing period than the samples cured at 50°C. The mechanical strength of the samples cured at 10°C developed more slowly than in the ones

cured at 50°C, but reached a higher level. Although the results discussed here confirm information that is common knowledge and already applied in practice, the authors believe it is rare to find these data compiled and correctly evaluated in the literature, especially data concerning permeability.

Acknowledgements: The authors would like to thank the Brazilian research-funding institutions CAPES and FAPESP, and also ALCOA S.A. and MAGNESITA S.A. for supporting this work.

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