

THE DRYING BEHAVIOR OF HIGH-ALUMINA ULTRA-LOW CEMENT REFRACTORY CASTABLES UNDER DIFFERENT HEATING RATES

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In this work, a thermogravimetric study of the dewatering process of high-alumina ultra-low cement refractory castables was carried out. Samples containing 2 wt% of calcium aluminate cement cured at 8°C were tested at heating rates varying from 0.5 to 25°C/min. Results showed that the water loss in a homogeneously heated castable occurs in stages that progressively change in intensity as the heating rate increases. No substantial reduction in the time of drying was observed for rates above 10°C/min while explosive spalling was evidenced in bodies heated at a rate above 20°C/min.

I. INTRODUCTION

Explosive spalling is a serious concern during the first heating of refractory castables. If steam becomes trapped within the structure, the pressure developed may exceed the ultimate strength of the hydraulic bond, causing mechanical failures and even the explosion of the product [1-7].

The usual test to determine the tendency of a castable composition to steam explosion consists of abruptly thrusting an undried sample into a furnace at a specific test temperature. If explosion does not occur within a stipulated time (~30 min), then the specimen is considered to have survived the test and is removed from the furnace. The whole procedure is repeated with other specimens at increasingly higher temperatures until an explosion event occurs. The steam spalling temperature is given by the average of the highest temperature at which the sample does not spall and the lowest temperature of failure [3].

Despite the useful information – the higher the furnace temperature at which explo-

sion occurs, the greater the castable resistance to spalling – this test is very simplistic, especially considering that: 1) no detail is given about the kinetics of water loss during the heat-up; 2) samples are subjected to unrealistic heating rates, much higher than those applied in the industry; 3) the thermal shock due to the sudden heating can damage the specimen prior to the steam pressure buildup, changing the explosion temperature.

Due to such restraints, this empirical procedure is not reliable to attain feasible dry-out schedules or even to guide producers in the development of spalling-free compositions. In this respect, the present work investigates the influence of the heating rate on the drying/spalling behavior of high-alumina ultra-low cement refractory castables. A thermogravimetric apparatus was used in order to provide a continuous assessment of the loss of weight in a sample during the heat-up, allowing not only the evaluation of the steam spalling temperature for a given heating schedule but also the study of the kinetics of drying.

II. EXPERIMENTAL PROCEDURE

(1) The thermogravimetric apparatus

The apparatus employed for the thermogravimetric tests comprises a 1500W electric furnace controlled by a proportional-integral-derivative (PID) system of 4 sequential programs, with heating rates varying from 0.1 to 25°C/min to a maximum temperature of 1100°C. The furnace chamber (10x10x20 cm³) is protected against explosion by a stainless steel cage. The mass loss is measured by an electronic scale (Gehaka, Brazil, 400 g ± 0.002 g), fixed above the furnace. Samples with dif-

ferent shapes may be tested, with a mass limit of 400 g. The test sample is suspended at the center of the furnace through a metallic wire connected to the bottom of the scale, so that heat can simultaneously reach all faces of the body. The temperature within the furnace is measured near the sample with a K-type thermocouple. Data on both sample mass and furnace temperature are recorded each 5 seconds during the whole experiment.

(2) Castable composition

The composition chosen for this study consisted of a mixture of 98 wt% alumina and 2 wt% calcium aluminate cement (CA-270, Alcoa – U.S.). The matrix powders (calcined aluminas A1000 SG and A3000 FL, 24 wt%, dp < 100 μm) and the aggregate grains (white fused aluminas, grades 4/10, 8/20, 10/36, 20/40, 8F, 60F and 200F, 76 wt%, dp < 5.6 mm) were supplied by Alcoa, Brazil and U.S. A citric acid content of 0.40 mg/m² (Labsynth, Brazil) was used to promote the dispersion of fine particles. The particle size distribution of this composition was adjusted to a theoretical curve based on Andreasen's packing model. A coefficient of distribution, q = 0.21, was chosen in order to obtain potentially self-flowable castables.

The castable suspension was prepared by mixing cold water (8°C, 4.47 wt% dry basis) to the raw materials in a paddle mixer for approximately 5 minutes. Samples were cast as 4 cm diameter by 4 cm thick cylinders (mass ≈ 180 g) and cured at 8°C/100% relative humidity for 24 hours. This curing condition was chosen to provide bodies with greater tendency to explosive spalling [3].

The dewatering tests were performed in the range of 25 to 800°C with constant

heating rates between 0.5 and 25°C/min. Mass loss on drying was evaluated through the normalized parameter W , which measures the cumulative fraction of water expelled during the heat-up per total amount of water initially present in the body. W was defined in this work as:

$$W(\%) = 100 \times \left(\frac{M_0 - M}{M_0 - M_f} \right) \quad (1)$$

where: M is the instantaneous mass recorded at time t_i during the heating stage, M_0 is the initial mass and M_f is the final mass of the tested sample. For spalled samples, M_f was estimated based on the initial mass M_0 and the average water content of equivalent undried bodies.

The derivative dW/dt , which expresses the drying rate during the heat-up, was obtained at each time t_i by:

$$\left(\frac{dW}{dt} \right) = \frac{W_{i+1} - W_{i-1}}{t_{i+1} - t_{i-1}} \quad (2)$$

The comparison of the drying behavior for different heating rates was made through the parameters $T_{50\%}$ and $t_{50\%}$, which represent, respectively, the furnace temperature and the elapsed time when half of the water content was removed ($W = 50\%$).

III. RESULTS AND DISCUSSION

Figure 1 compares the thermogravimetric patterns of 4 similar bodies heated at different rates. Results show that the dewatering kinetics is strongly affected by the heating rate applied.

For the specimen heated at 0.5°C/min (Figure 1a), water was expelled in three main stages, as suggested by the peaks in the derivative curve at 81°, 130° and 275°C. Figures 1(b-d) show that the increase in the heating rate not only shifted these peaks to higher furnace temperatures, but also changed the fraction of water removed in each stage. In general, as the heating rate increases, less water is removed in the first stage and more in the second stage. For instance, in the test at 0.5°C/min, the first and second stages were responsible, respectively, for the removal of 62% and 25% of the total water content. This situation inverted in the test conducted at 10°C/min, where 26% and 67% water content were eliminated in the first and second stages, respectively. The most drastic behavior was observed in the test conduct-

ed at 25°C/min, during which explosive spalling occurred in the second stage at a furnace temperature of 433°C.

Concerning the causes of this behavior, the literature has shown that the type of hydrate formed during the castable cure has a decisive effect on the occurrence of spalling [3]. Below 20°C, the hydration of calcium aluminate cement generates mostly CAH_{10} ($CaO \cdot Al_2O_3 \cdot 10H_2O$), whose decomposition imparts undesirable properties to the heated castable, particularly decreasing the mechanical strength and releasing water into the castable's pores at a similar temperature in which free water starts boiling [3, 8].

The hypothesis that dehydration affected the dewatering stages observed in Figure 1 was investigated with two different samples heated at 5°C/min. The first sample was tested after curing for 24 h at 8°C, while the second sample, also cured at 8°C for 24 h, was pre-fired for 6 h at 900°C (rate of 1°C/min) for the elimination of all the hydrates and then saturated with water for the TG test.

The similar profiles observed for both cured and fired samples in Figure 2 reveal that cement dehydration was not the cause of any of the peaks in the drying rate curves. This result indicates that probably CAH_{10} dehydration directly affects the explosive spalling by reducing the castable strength rather than by disturbing the steam release profile. Furthermore, it strengthens the hypothesis that the stages of drying are in fact related to different mechanisms by which free water is removed from the structure during heating.

The first stage of drying is most likely related to the evaporation of free water, caused by a difference in the vapor pressure of the liquid in the castable and the ambient vapor pressure. In this stage, water is evaporated at the castable surface while the capillary pressure gradient transfers the inner liquid to the surface through the porous network. Since evaporation is enhanced by the temperature increase [9], the drying rate is proportionally increased during the early stages of the heating process. However, as the water is rapidly removed at the surface, the liquid/vapor interface recedes into the pores of the body where the evaporation rate is lower [9]. The temporary equilibrium between these two effects corresponds to the first peak observed in the derivative curves of Figures 1 and 2.

As the castable continues to be heated, the temperature at the liquid/vapor interface eventually rises above the boiling point of water and a second important drying stage starts with the conversion of water into steam. In this stage, associated with the second peak in the derivative curves, the rate of steam formation and the permeability of the body rule the drying rate. In this situation, the temperature increase causes an increase in the drying rate until most of the liquid water in the body is converted into steam. When the permeability of the castable is low (as is often the case), the increase in temperature may be followed by a proportional increase in the pressure of steam, since it is trapped within the pores and slowly driven toward the heated surfaces. Thus, the intensity of the peak in the second stage may also be an indication of the steam pressure developed within the castable. When the permeability of the body is sufficiently high or the heating rate is low, no significant pressure build-up is developed during the heat-up and the water loss can be considered mainly influenced by the rate of water converted to steam by boiling.

The cause of the third drying stage related to the small peak in the derivative curves is not yet clear, but one hypothesis is that the steam flow exiting the body during the second stage absorbs the incoming heat, reducing its conduction to the castable core. When the main bulk of steam is finally expelled, the structure is exposed to a large thermal gradient that leads to a rapid rise in the internal temperature which drives off the remaining water retained in the body [7].

The consequence of this behavior, not assessed by traditional explosion tests, is that the higher the heating rate applied, the faster the liquid/vapor interface recedes into the porous network and a lower content of liquid water is removed in the first stage by the capillary transport/evaporation mechanism. Therefore, increasingly larger amounts of water have to be eliminated in the second stage, increasing the likelihood of excessive steam pressurization and thus of the occurrence of explosive spalling, as observed in the test at 25°C/min.

Figure 3(a) shows a clear relationship between the heating rate applied and the temperature reached in the furnace for removal of 50% of the sample water content. Figure 3(b) shows that above a given heating rate (10°C/min in this work), no

substantial reduction in the time of drying was achieved. In fact, 15°C/min appeared to be the maximum safe rate to prevent the occurrence of explosive spalling.

Considering that an appropriate dewatering process should be slow enough to prevent any mechanical damage to the piece but fast enough to provide savings in the processing time, these results point toward the existence of an optimized heating schedule that guarantees a safe and economical drying process. In this sense, the proposed evaluation technique seems to be a more realistic tool to relate the susceptibility to explosion of castables to different processing variables, including the size/geometry of the piece and the curing conditions, guiding the optimization of refractory castables with respect to potential spalling-free compositions.

IV. CONCLUSIONS

The dewatering behavior of high-alumina castable samples containing 2wt% of calcium aluminate cement and cured at 8°C was assessed in this work at differing heating rates. The results revealed that, under the tested conditions, dewatering occurred in stages of different intensities, depending on the mechanism by which the free water is removed. Cement dehydration appeared to not affect the drying profile. No substantial reduction in the drying time was observed for rates above 10°C/min while explosive spalling occurred in bodies heated above 20°C/min.

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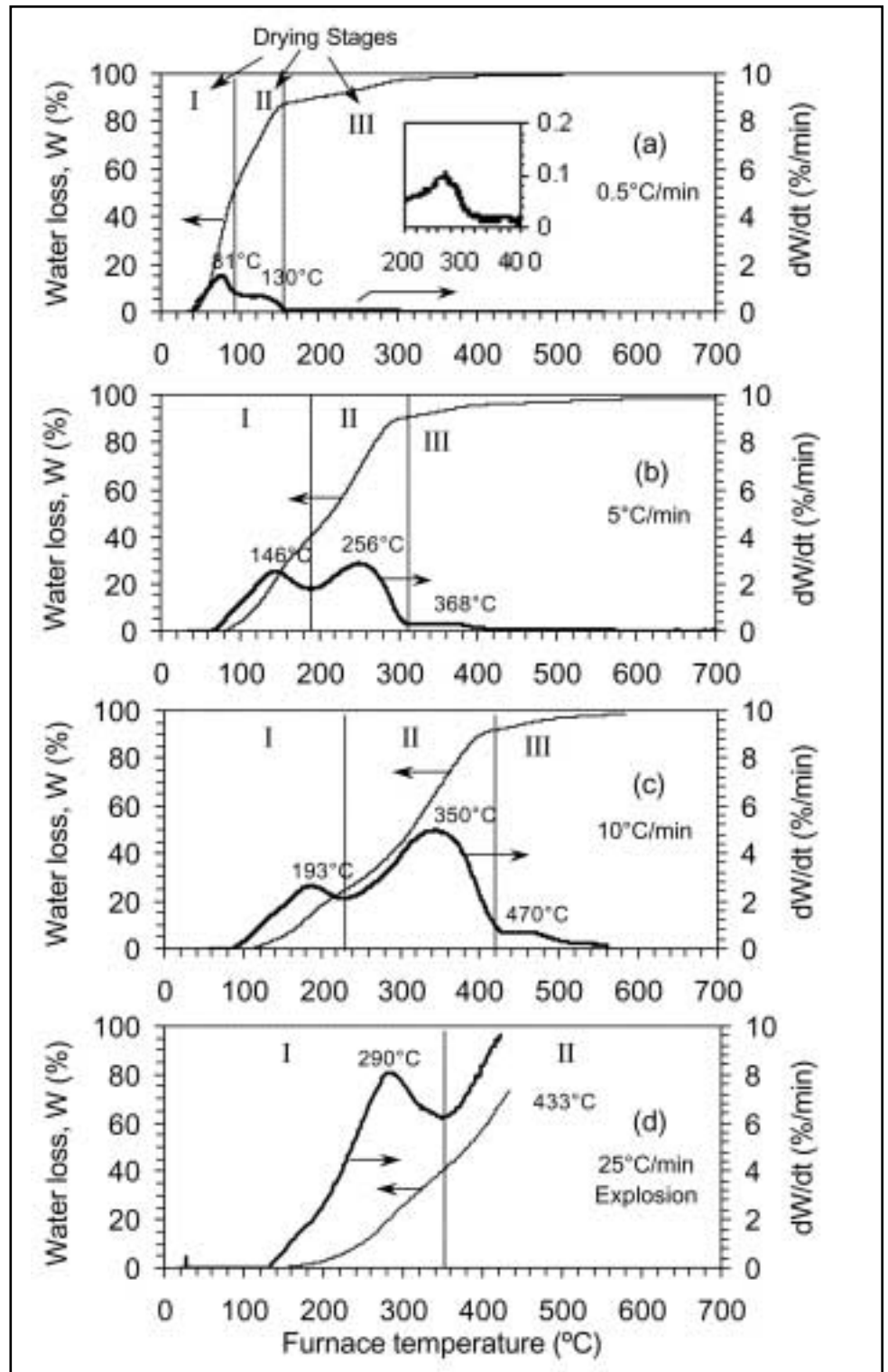


Figure 1. Dewatering curves of moistened castable samples cured at 8°C and heated at different heating rates.

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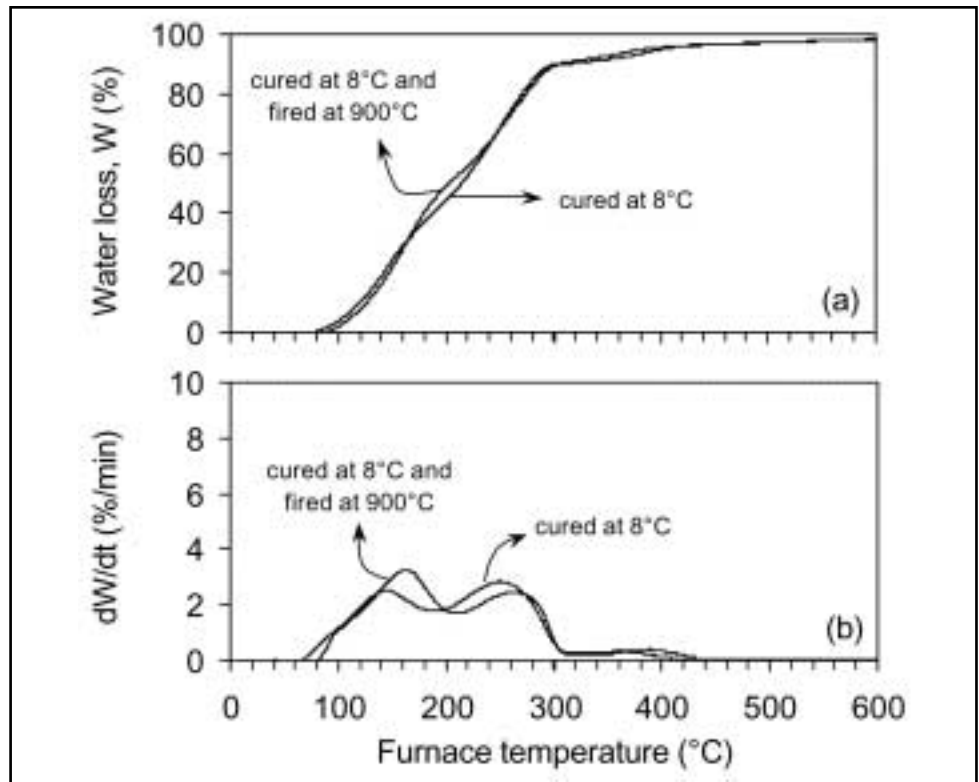


Figure 2. Comparison of the dewatering behavior of cured and pre-fired samples heated at 5°C/min.

Guest Review Continued from Page 12

CONCLUSION

Based on the preceding comments we would indicate as general tendencies for the refractories market in the near future:

- Specific consumption will remain stable or will have a slight decrease;
- “Tailor made” refractories will be the solution for the consumer’s different needs;
- Technical and commercial partnerships between supplier and client will be essential to achieve good results;
- Continuous modernization of facilities and controls will be extremely important to guarantee low cost and super-reliable products;
- Applied modern technology in the development and manufacturing of refractories will be essential to reach the high-quality level that will be required of the products;
- Purer high-quality raw materials will be increasingly used in the manufacture of refractories. RAA

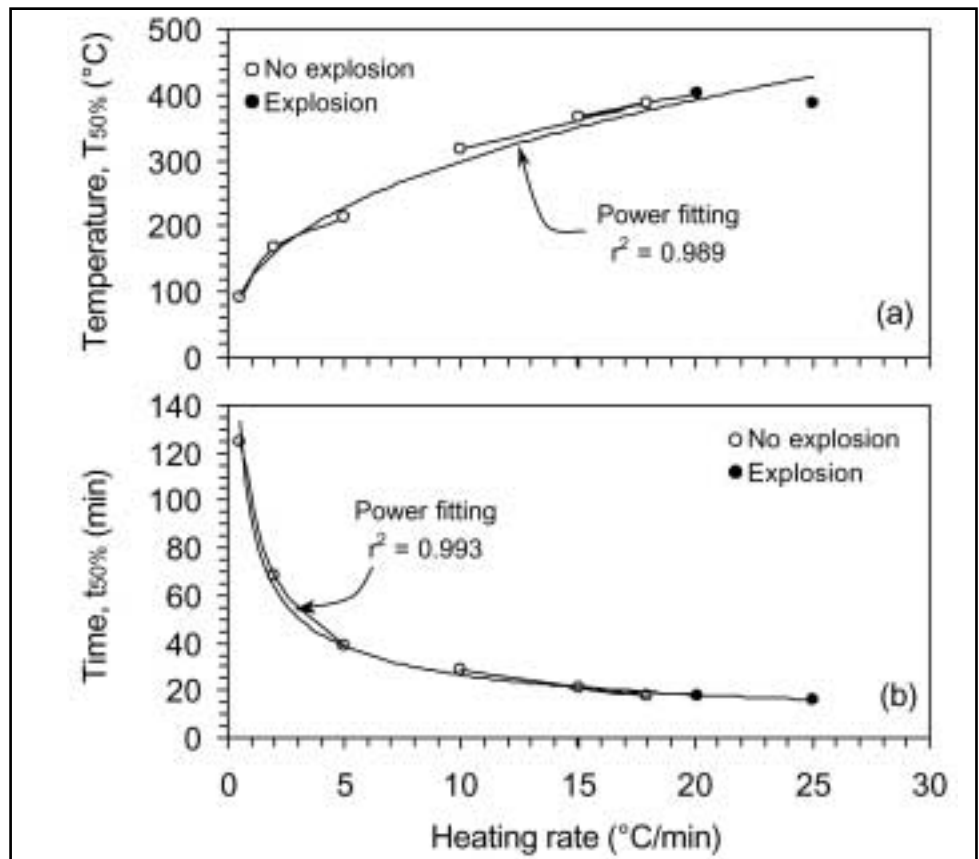


Figure 3. Temperature and time required for the removal of 50% of the water retained in castable samples heated at different rates.