

TRANSIENT PROPERTIES OF REFRACTORY CASTABLE WITH HYDRAULIC BINDERS

Mohamed-Ali Maaroufi¹, Cécile Diliberto¹, André Lecomte¹, Olivier Francy², Pierre Le Brun³

¹Jean Lamour Institute, UMR/CNRS 7198, Lorraine University, Team “Materials for Civil Engineering”, 54600 Villers-les-Nancy, France

²Saint-Gobain CREE, Research Center, 550 Avenue Alphonse Jauffret, BP 20224, 84306 Cavaillon, France

³Constellium CRV, Research Center, 725 rue Aristide Bergès – CS 10027, 38341 Voreppe, France

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Abstract

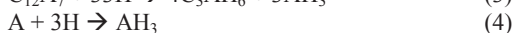
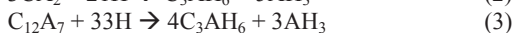
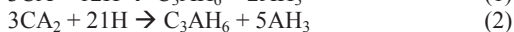
Refractory castables based on hydraulic binders have a widespread use in aluminium casthouses (furnaces, launders, etc.). Their selection is based on properties such as corrosion resistance to molten metal, mechanical behavior and insulation. Few studies concern the hydric exchanges between the refractory materials and the surrounding atmosphere, while this can affect their microstructure, durability or the quality of the produced metal, and may even have safety impacts. In this work, these exchanges have been studied in the case of refractory launders. A model has been built to describe the transient thermal behavior in the thickness of the launder material. The results have been compared to measurements obtained on an instrumented launder part. At the same time, an experimental approach has been developed to assess the transient hygrothermal behavior of refractory samples, through testing of moisture pick up in a climatic chamber at both ambient and at high temperature by thermogravimetric analysis. Observations have been correlated to hydration reactions at different temperatures.

Introduction

Generally speaking, water in the porous structure of the refractory can be chemically bound, adsorbed or free [1, 2, 3]. The chemically bound water is used for binder hydration. It cannot be eliminated under normal temperature conditions and is not involved in the moisture transport. The physically adsorbed water is constituted of several molecular layers (5 to 10 Å each) on the internal surface of the pores. This water is mobile and held to the walls by weak bonds. Free water is present as condensed liquid or steam in the larger capillary pores.

The physical adsorption mainly occurs at low temperatures and a temperature increase leads to desorption. It is a fully reversible phenomenon, mostly dependent on the relative humidity (RH) level. The chemical adsorption refers to the hydration of the cement compounds, it affects the microstructure and the mineralogy of the solid phase. It essentially depends on the temperature, and chemical desorption can only occur at high temperature, when hydrates are not stable any more [4].

In a CAC-containing castable (Calcium Aluminate Cement), the chemical adsorption mostly concerns CAC compounds, which are essentially A, CA, CA₂ and C₁₂A₇ [5, 6]. In cement chemist notation, C stands for CaO, A for Al₂O₃ and H for H₂O. The hydration reactions of these phases strongly depend on the temperature and on the material history. In the case of refractory concretes, temperatures higher than 35 °C are usually concerned. Thus, main reactions are [5]:



When temperature increases, hydrates can release their water and restore CA, CA₂, C₁₂A₇ anhydrous compounds, according to reverse reactions (1) to (4). Further, A can hydrate and form an amorphous compound referred to as AH_x.

Oppositely, after dehydration at high temperature, the calcium aluminate compounds can then rehydrate in the presence of water vapor in case of subsequent cooling down. For example, C₃AH₆ is likely to appear as soon as the temperature gets below 305 °C.

In this work a refractory based on an aluminous binder has been studied from the viewpoint of heat transfer and moisture pick up and release. To study these exchanges, the temperature profile of a refractory launder in use has been modeled at the different stages of its operation, using the finite element code COMSOL-Multiphysics®. This model has been calibrated on experimental temperature measurements obtained on a pilot line. At the same time, humidity pick up tests have been performed in a climatic chamber and by thermogravimetric analysis under different atmospheric conditions (temperatures and RH).

Tests show that the hardened binder phase of the castable is the main contributor to the hydric exchanges (bauxite aggregates are almost inert). Therefore, research has been focused on the binder phase in which several porous structures have been studied by varying the water / cement ratio (W/C).

To define the equilibrium hydric state of the material, the water vapor adsorption isotherms *WVAIs* quantifying the moisture adsorption capacity of the material have been determined for various hygrothermal conditions. They may be provided by several methods [7, 8]. In our study, the gravimetric method was preferred [9, 10]. For the physically adsorbed moisture the weight increase over time has been recorded for different samples of a castable or the binder phase only (hardened cement paste *HCP* at different ratios W/C). The equilibrium water content reached for different humidity rates, at the same temperature allows constructing the *WVAIs* [11, 12]. Since the hygrothermal equilibrium may require a long time before it is reached, an analytical method has been developed to extrapolate measurements and forecast the equilibrium water content.

Finally, the hydric behavior at different temperatures has been correlated to the hydration reactions of this matrix. Hydrates formed by chemical adsorption at high temperatures have been identified.

Experimental conditions

Materials of the study

The refractory castable used in this study contains bauxite aggregates bonded by a matrix based on CAC and various admixtures (including silica fume, reactive alumina, dispersing aid...). The matrix used in this study has the following composition (table 1):

| % | Al ₂ O ₃ | SiO ₂ | CaO | Others |
|--------|--------------------------------|------------------|------|--------|
| Binder | 46.7 | 23.5 | 24.1 | 7,2 |

Table 1. Chemical composition of the matrix.

The castable and its main components (matrix and aggregates) were studied separately, since the matrix was expected to be responsible of the main moisture exchanges. The matrix was studied through hardened cement paste samples (HCP) prepared with various water/cement ratios or W/C (0.15, 0.25 and 0.35).

Some thermal analyses were performed on a HCP sample with a W/C ratio = 0.25, in order to make a preliminary validation of chemical adsorption mechanisms and hydration/dehydration reactions (Fig. 1). Mixing water was added at 80 °C thus only higher temperature reactions are considered in the following. Endothermic peaks at 120, 280 and 305 °C correspond to the dehydration of respectively AH_x (①), C₃AH₆ (②) and AH₃ (③). They are consistent with the dehydration temperatures found in the literature [6].

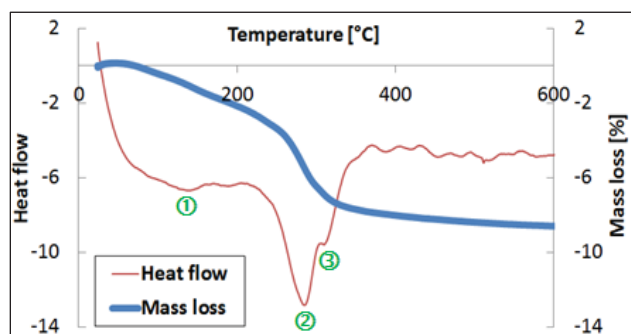


Figure 1. TDA/TGA analysis of HCP with W/C = 0.25.

Experimental procedure

All samples were prepared according to the following procedure: mixing with water 10 min, pouring into cylindrical molds maintained into slow rotation, to avoid bleeding and segregation during hardening. Samples were then maintained at ambient temperature in sealed conditions for 3 days to allow proper setting and hardening. Then all the samples were heated up to a maximum temperature of 750 °C, following a five-days sintering schedule with ramps and levels.

Moisture pick-up experiments were performed on castable samples and their components (aggregates, HCP) initially dried at 105 °C.

A first set of experiments consisted of weight follow-up of 5x5x5 cm³ cubic samples in a climatic chamber at various temperature-humidity conditions kept constant. This method is the most common and probably the most accurate to determine materials WVAIs, but it is also limited to temperatures lower than 100 °C. So it provides key information about physisorption, condensation and kinetics of moisture transfers through the porous network. However it does not give any access to moisture pickup above 100 °C, which is probably the most relevant temperature range with regard to field operating conditions.

Thus a second set of experiments were made specifically on smaller HCP samples (W/C ratios resp. 0.15, 0.25 and 0.35) with a TGA unit, coupled with a steam generator that can deliver wet air at fixed RH. This paper is mostly focused on these TGA experiments. Samples (about 100 mg in weight) were first heated up to 350 °C (above the temperature of the main signal detected

by the preliminary TGA analysis on Fig. 1) at a 10 °C/min increase rate. Temperature was held constant at 350 °C for 12 hours to ensure stability of anhydrous compounds. Moisture pick-up was then studied at respectively 300, 200, 100 and 40 °C. At each temperature, four relative humidity levels were successively delivered by the steam generator: 20, 40, 60 and 80%. Between each experiment, samples were re-dried at 350 °C (Fig. 2).

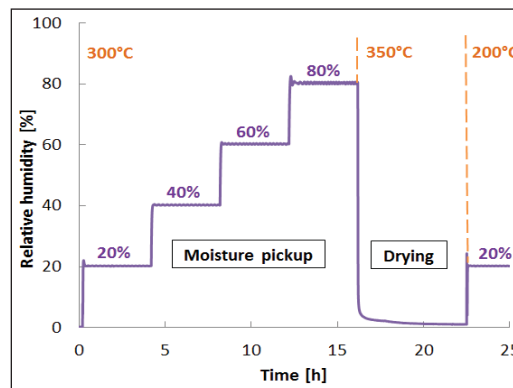


Figure 2. Hygrothermal conditions for TGA tests on hardened cement pastes.

However, this second kind of experiment also has some limitations, since the actual RH seen by the samples is not precisely known. In fact, the steam generator operates at 23 °C, and the TGA cell is approximately at atmospheric pressure. As a result, although the generated steam is injected directly onto the sample, there is probably a significant drop in RH between the generator and the sample itself. Such experiment is then more representative of a hot refractory in contact with a wet ambient atmosphere, which is definitely in accordance with real conditions. On the other hand, the results cannot be interpreted as a true WVAIs, contrarily to results obtained with a climatic chamber.

Beyond the mere quantification of moisture pickup, our primary objective is to obtain equilibrium water contents as functions of the relative humidity. However, this equilibrium can take some time before being reached, even on small TGA samples. This is even more critical for the large cubic samples used in our climatic chambers. An analytical equation was systematically fitted on the experimental data (collected over a limited period of time) to forecast equilibrium water content by extrapolation, and ultimately build the WVAIs of the material. A hyperbolic equation was chosen (Rel. 5):

$$X = \frac{a(t-t_0)}{1+b(t-t_0)} \quad \text{and} \quad X_{eq} = \frac{a}{b} \quad (5)$$

In this equation, X is the water content, t the time. a, b and t₀ are fitting parameters. X_{eq} is the equilibrium water content.

Thermal profile in the refractory material

Instrumentation of an experimental launder

A launder section of refractory castable based on hydraulic aluminous binder is shown in Fig. 3. This type of refractory material has been widely used in aluminium casthouses, due to its good resistance to high temperatures and abrasion [13, 14].

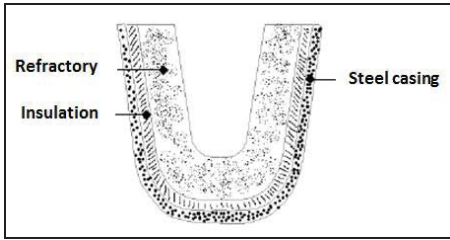


Figure 3. Structure of a refractory casting launder. The insulation layer may be made of one or several sub-layers.

In the experimental study, four K-type thermocouples were placed in a launder in use, respectively at 10, 20, 30 and 45mm from the inner wall of the launder, below the liquid aluminium / air interface and far enough from this interface, so that the thermal profiles obtained at this position may be considered as not influenced by the interface and thus mainly unidirectional (Fig. 4). In the lower portion of this launder a boundary condition at the inner wall is the coefficient of heat exchange by forced convection with the liquid metal. The temperature evolution over time in these four points will enable to record the propagation of the thermal shock imposed on the inner wall of the launder.

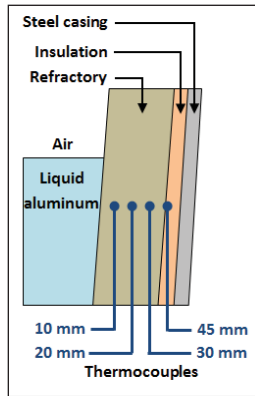


Figure 4. Position of the thermocouples in the launder.

Thermal cycling – Experimental measurements

Experimental measurements are related to a typical casting cycle. This cycle comprises a preheating phase, a waiting phase, then the cast itself and finally a cooling down before a new cycle is started. The measurements obtained during a typical cycle are shown in Fig. 5.

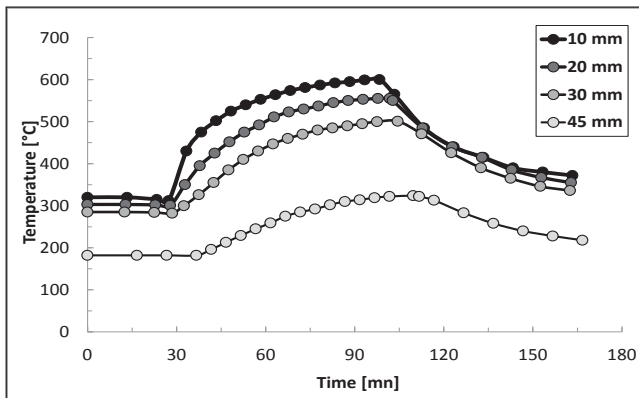


Figure 5. Temperature measured in the experimental launder.

Thermal cycling - Modeling

Numerical simulations of heat transfer were performed by the finite element code COMSOL-Multiphysics®. The model describing the transient thermal behavior in the thickness of the material is governed by the heat equation. It is calibrated using experimental data. It allows simulating the thermal changes within a launder during the transient states of the cast.

The transfer modes on the inner surface of the launder are respectively forced convection and radiation with hot air (preheat, waiting phase), forced convection with the liquid aluminium (casting phase), and natural convection and radiation (cooling phase).

For the geometrical model, the longitudinal metal conduction in the third dimension (Z axis) was neglected and the wall of the launder section was simply approached by a rectangle of thickness dX (Fig. 6). Since the launder has an axial symmetry, only half of the section is considered. The properties used for the modeling work are given in table 2.

| | Density (kg/m ³) | Thermal conductivity (W/m.K) |
|------------------|------------------------------|------------------------------|
| Dense refractory | 2700 | 2 |
| Insulation layer | 160 | 0.1 |
| Steel casing | 7800 | 40 |

Table 2. Properties used for the thermal modeling.

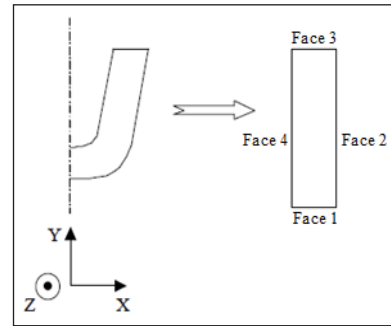


Figure 6. Geometric model considered for heat transfer.

The nature of heat exchange on the four sides of the model was considered as follows:

- Face 1: by symmetry, the exchanged flow is zero.
- Face 2: natural convection ($h=5W/m^2.K$) and radiation (emissivity coefficient = 0.8), with ambient air temperature at 25 °C.
- Face 3: natural convection and radiation, with ambient air temperature of 25 °C.
- Face 4: exchange by forced convection with the molten metal or hot air ($h=100W/m^2.K$), or natural convection with ambient air and by radiation according to the phases of the cast.

Calculations have been performed using the simplified model. They show that the thermal gradient over the thickness of the refractory layer (45 mm) is about 410 °C, while the gradient reaches about 190 °C vertically on the same distance (Fig. 7).

Fig. 8 shows the results of the calculations applied to the cycles described in Fig. 5. Although the model is a simplification of the real geometry of the launder the results are in good accordance with the measured data. Most inaccuracies are seen with the thermocouple located at 45 mm from the metal surface. This can be due to several reasons, including:

- An imperfect contact of the thermocouple with the refractory,
- Higher air circulation at this interface.
- Measurement inaccuracies due to a high temperature gradient at this place in the refractory structure.
- A variation of only 1 mm of refractory thickness can explain the discrepancy between calculation and measurement in this high temperature gradient area.

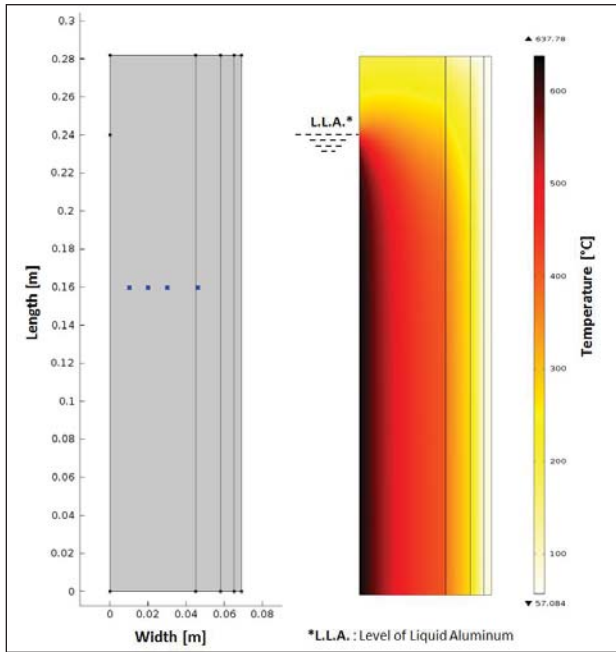


Figure 7. Simulation of the thermal behavior of the launder: geometrical model and thermal gradient at the end of the cast.

With this simple model it is possible to estimate the temperature at any position in the refractory at any time into the life of a launder. Moisture pick up data are needed to allow the quantification of the thermohydric coupling in the material.

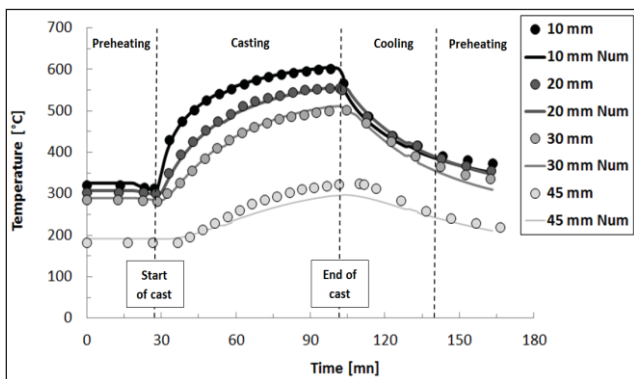


Figure 8. Temperature profile: numerical vs. experimental.

Moisture pickup and hydric exchanges

Results and discussion

The table 3 and Fig. 9 give some equilibrium water contents obtained in climatic chambers on castable, aggregates and HCP samples at 25 °C. They confirm that the matrix is the main

contributor to moisture pickup and that aggregates play a negligible role, due to their low porosity and reactivity. Similar results were obtained at 80 °C. These data also emphasizes that there is a good correlation between the castable and HCP respective VWAs, accounting for the volume fraction of matrix in the castable (about 25%). Therefore it proves relevant to focus investigations on HCP.

| Sample | Eq. water content (wt%) |
|-----------------------------|-------------------------|
| Castable W/C 0.2 | 0.32 |
| Aggregates 1-3 mm fraction | 0.00 |
| Aggregates 0-80 μm fraction | 0.02 |
| HCP W/C 0.15 | 1,2 |

Table 3. Moisture pickup of castable, aggregates and HCP at 25 °C, 85 %RH in a climatic chamber.

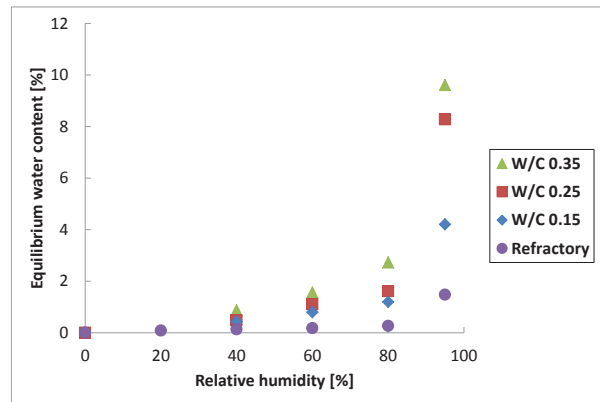


Figure 9. VWAs of castable and HCP with varying W/C.

The evolutions of water content (in weight%) on various HCP during TGA experiments are shown on Fig. 10. It is interesting to note that moisture pickup can be detected even for temperature as high as 300 °C, even if the corresponding pickup is limited to 0.1%. In addition, the 5-hours soaks at 350 °C prove sufficient to achieve complete drying of the samples.

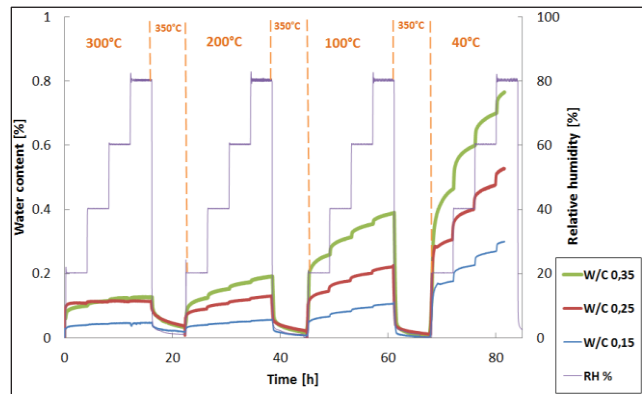


Figure 10. Water content evolution for various HCPs during TGA experiments.

Fig. 11 shows a detailed section of a TGA experiment (HCP with W/C=0.35 at 200 °C), including the fitted theoretical curves for equilibrium water content extrapolation.

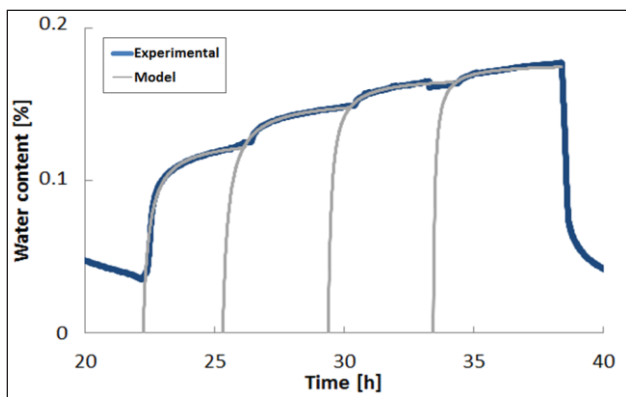


Figure 11. Comparison of the analytical model (thin curve) and the TGA results (thick line).

The resulting curves, obtained after calculation of equilibrium values, are plotted on Fig. 12. The general shapes of the curves [4] tend to show that chemisorption is predominant at high temperature (200-300 °C), the major moisture pickup occurring at low RH, and then remaining almost constant when RH increases. On the contrary at lower temperature (i.e. 40 °C), physisorption and presence of free water become much more significant, as the moisture content clearly increases with humidity.

We must however consider the analysis cautiously since the RH values in abscissa correspond to the RH delivered by the steam generator at 23 °C and not the one actually seen by the sample, which must be somehow lower at high temperature. Thus it is likely that curves given on Fig. 12 are not “true” WVAs and should be shifted towards the left in proportion of temperature increase. One of the main consequences is that physisorption is probably underestimated at high temperature.

Moisture pickup also appears to be strongly related to W/C (and hence to the porosity), even at high temperature. The water content values for the HCP prepared with W/C=0.35 are about twice as high as the ones obtained for the HCP with W/C=0.15, for given RH and temperature. XRD analyses performed on fired HCP samples demonstrated that mineralogy was basically independent on W/C, except for slight variations of CA₂ which remains a minor constituent and a minor contributor to chemisorption compared to A and CA [15]. Therefore, the dependence of the equilibrium water content on the porosity can be mostly related to the porous network and the pore surface area. A higher pore surface area brings both more sites for physisorption and more reactive surface for hydration. So it is likely to state positively that both mechanisms are impacted by the W/C ratio.

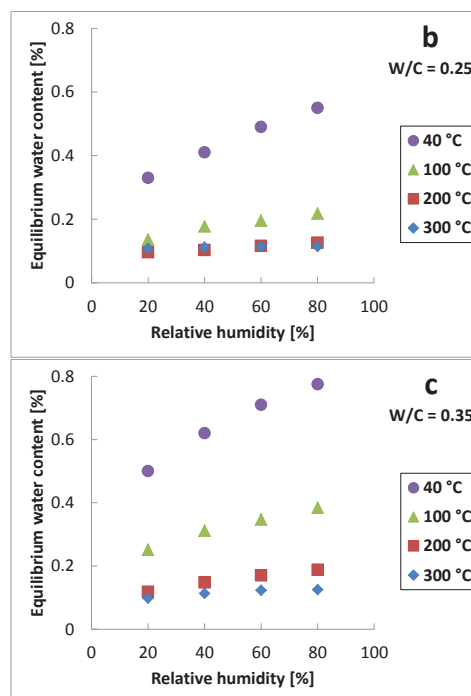
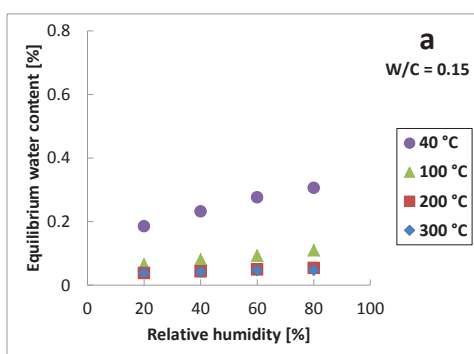


Figure 12. Eq. water contents VS injected RH, for HCPs having different W/C ratios (a: 0.15, b: 0.25, c: 0.35).

The low-RH parts of the curves, assumed to be indicators of chemisorption, should normally be related to the amount of stable hydrates at the corresponding temperature. As pointed out in the literature [5, 6], the chemisorption at 300°C is normally associated to alumina hydration to form gibbsite AH₃. Between 300 °C and 200 °C, anhydrous calcium aluminates are converted into C₃AH₆. And between 200°C and 100°C, it is likely that amorphous AH_x can appear. However this correlation does not fully appear. Based on preliminary results showed on Fig. 1, a more significant difference should be observed between 200 °C and 300 °C curves on Fig. 12. Indeed, most of the hydration/dehydration processes are supposed to occur in this particular temperature range (especially through the formation or decomposition of C₃AH₆). On the contrary curves at 40 °C and 100 °C are very different with regards to the behavior at low RH, although no hydrate is supposed to form or decompose between 40 and 100 °C, according to Fig. 1. Again, the uncertainty on the relative humidity actually seen by the sample, can partly explain these discrepancies.

These TGA experiments provide extremely useful quantitative data about moisture pickup of a refractory exposed to wet air during cooling down, which can be immediately transferred to field operations. But at this stage, further investigations are needed to fully correlate the results with chemical and physical phenomena. Tests in climatic chamber tests and more precise knowledge of the RH seen by samples during TGA shall bring complementary information.

Thermo-hydrical coupling

Knowing the potential and kinetics of adsorption (climatic chamber + TGA experiments) and the refractory temperature (thermal model), it becomes possible to forecast the actual moisture pickup in the launder section over the casting cycle. This work is in progress.

Conclusion

Hydric transfer quantification in refractory castables based aluminous hydraulic binder is a new approach in their characterization. Therefore it is needed to:

- Develop a thermal model which can predict the temperature and its evolution in the refractory castable, at any time and any position, and that can reproduce the cycles involved during a whole cast cycle (waiting time, preheating, cast, cooling);
- Quantify the water either physically or chemically available within the material, as function of the surrounding hygrothermal conditions.

These two steps have been approached in the work presented in this paper.

- A launder has been instrumented in order to provide data on the temperature history of the material during the whole cycle of a cast, at different positions in the thickness of the material.
- A finite element model has been developed and evaluated in comparison to the experimental data. Although the description of the model is a simplification of the real launder shape it has been shown to satisfactorily reproduce the measured thermal profiles.
- Moisture pick up tests have been performed in varying temperatures and RH conditions, including at high temperatures in TGA. The tests have been done on the aggregates and on the matrix of the refractory material and show that the hydric exchanges mainly take place in the hardened cement paste.
- A simple model has been used to extrapolate the equilibrium humidity content of the refractory material. Water vapor adsorption isotherms have been derived from these data.

These results will be used to quantify hydric exchanges during the hygrothermal solicitation of refractory castables based on aluminous hydraulic binder.

Acknowledgments

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