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Thermo-hydrous behavior of hardened cement paste based on calcium aluminate cement

Mohamed-Ali Maaroufi [a], André Lecomte [a,*], Cécile Diliberto [a], Olivier Francy [b], Pierre Le Brun [c]

[a] Institute Jean Lamour, UMR/CNRS 7198, Lorraine University, Team "Materials for Civil Engineering", IUTNB, CS 90137, 54600 Villers-les-Nancy, France
[b] Saint-Gobain CREE, 550 Avenue Alphonse Jauffret, BP 20224, 84306 Cavaillon, France
[c] Constellium Technology Center, 725 rue Aristide Bergès, CS 10027, 38341 Voreppe, France

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Abstract

Refractory castables based on aluminous hydraulic binders are commonly used in aluminium casthouses (furnaces, ducts, etc.). Their selection is based on their good mechanical strength, thermal behavior and compatibility with molten aluminium. However, few studies focus on their hydrous evolution in operation, whereas this property can also have an influence on the produced metal quality. In this article, the internal moisture of twelve hardened cement pastes fired at high temperature, made with four aluminous hydraulic binders and three different Water/Binder ratios was registered under diverse thermo-hydrous conditions, including at high temperature. The water trapped by physisorption and chemisorption can be significant for some products, and it strongly depends on the mineralogy and porosity of the hardened cement paste. The more the binders contain alumina phase, the more the hardened cement pastes mobilize and render moisture.

Keywords: Calcium aluminate cement (CAC); Moisture; Physisorption; Chemisorption; Water vapor adsorption isotherms (WVAIs)

1. Introduction

1.1. Context

Refractory castables based on hydraulic binders or calcium aluminate cement (CAC) are widely used in aluminium casthouses.[1] Their selection is based on properties such as corrosion resistance to molten metal, mechanical behavior and insulation.[2–5] They also exhibit faster development of the mechanical strength and do not release lime during hydration.[6,7] However, these castables contain residual moisture which can affect the safety of the process or even the final quality of the metal produced. This moisture results from water exchange with the surrounding atmosphere, which is controlled by the porosity, the permeability, and the chemical and mineralogical composition of the materials.[8,9] The aim of this paper is to present a study of the exchanges in CAC materials as function of both the thermo-hydrous conditions and the temperature.[10]

1.2. Description of the study

Tests on refractory castables and their components taken separately[11] show that the hardened cement paste (HCP) is the main seat of water transfer while the refractory aggregates are quasi-inert in this respect. For this reason the experiments are focused on the cementitious matrix. Several porous structures were studied by varying the amount of added water (water/binder ratio W/B). Here, hydraulic binders are CAC, that also contain various mineral and organic additions in order to increase the paste compactness, to facilitate shaping, to control the curing time or to limit the reactions with the surrounding molten metal (refractory corrosion and inclusion entrainment in the melt).[12]

Hydration, setting, curing and mechanical behavior of the HCP have been extensively studied.[13–17] However, few studies focus on their hygrothermal behavior at different stages of their use while the form of water present in the porous structure of the HCP can evolve (free, adsorbed or chemically bound[18–20]):

(1) Free water is condensed liquid or steam in large capillaries.

* Corresponding author. Tel.: +33 0 383 682 575; fax: +33 0 383 682 532.
E-mail address: andre.lecomte@univ-lorraine.fr (A. Lecomte).

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Table 1
Density and chemical composition of binders.

	CAC	B1	B2	B3	B4
	Density (g/cm^3)	3.198	3.038	2.771	2.76
	Spectral particle size (μm)	0.3–250	0.2–250	0.3–250	0.4–250
	Median-diameter (μm)	6	4.3	7	9
	Specific surface (m^2/g)	8.7	9.3	7.4	8.4
% weight	Al_2O_3	81.1	46.7	49.1	32.1
	SiO_2	<0.01	23.5	14.2	26.6
	CaO	19.0	24.1	29.3	35.8
	Others (inert)	0.2	3.9	6.35	4.2
	Loss of ignition	0.3	2.4	2	2

(2) Physically adsorbed water covers the inner surface of the pores in several molecular layers which are weakly bound (5 to 10 Å thick) and have some mobility. Physical adsorption mainly occurs at low temperature and is a reversible phenomenon.
(3) Chemically bound water forms hydrates that are not involved in the transport of moisture. These hydrates can only decompose above their threshold stability temperature[21].

The usual approach to study the hydric behavior of porous materials is to determine their water vapor adsorption isotherms (WVAIs) from moisture pickup curves obtained in various thermodynamic conditions. These measurements also provide the moisture pickup kinetics, and the products storage capacity, depending on the test conditions (sample size, etc.). These data may be provided by several methods.[22,23] In the current study, the gravimetric method was preferred.[24,25] While most tests were made at 20 °C at different relative humidity RH, temperatures as high as 300 °C were also considered.

For low temperature tests (20 °C), after shaping, setting and hardening, samples were subjected to curing at high temperature (750 °C) typical for the industrial operation temperature in the aluminium industry. This treatment transforms the products in a totally anhydrous state. They were then weighed hot to determine their dry mass (reference). After cooling, they were immersed and saturated in water to determine their porosity by hydrostatic weighing. Finally, they were dried at 105 °C until a constant weight was reached to eliminate physical water,[21] and probably also a part of chemical water (see Rel. (5)). The moisture pick up test consisted to record the samples mass increase over time in a controlled climatic chamber at 20 °C and at different successive RH (drying at 105 °C between each RH level). The equilibrium water content reached for each condition enables to build WVAIs at 20 °C[26,27] (adsorption phase).

For high temperature tests ($T > 100$ °C), only the chemical adsorption can theoretically take place.[21] It is related to the high-temperature rehydration of some cementitious phases in presence of water vapor, and in relation to the temperature changes which occur within the castable during its use (for example between casting cycles). Tests were performed with a thermogravimetric analysis chamber (Setaram Setsys Evolution TGA) coupled to a steam generator (Setaram Wetsys) which delivers controlled humidity. The observed behavior is attributed to the cement hydration reactions, at high temperatures.

Finally, 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. Similarly, WVAIs were modeled.

2. Preliminary investigations on studied materials

2.1. Characterization of binders

Four binders based on calcium aluminate cement or CAC and various admixtures were used in this study. They were referenced B1, B2, B3 and B4. These binders are commonly used to manufacture various kinds of refractory castables based respectively on aggregates of tabular alumina, bauxite, fired clay and silica, respectively.

The density of the binders was measured with a DKD certified pycnometer (non-reactive liquid). The values are given in Table 1. Spectral particle size, median diameter and specific surface area are also given in Table 1.

Their chemical composition, expressed as weight percentage of oxides (X-ray fluorescence, Bruker S4 Explorer AXS apparatus), is given in Table 1. B1 is essentially constituted of alumina. B2 and B3 contain about 50% alumina and variable silica amounts. B4 contains less alumina, but more silica than B2 and B3. These binders also contain other inert elements in variable proportions.

The binder mineralogy was measured by XRD analysis (X-Pert Pro diffractometer, copper anticathode $K\alpha = 1.54506$ Å) and EVA-plus® software with the JCP2 database. Rietveld quantification was made with Topas®. Results are shown in Table 2.

Table 2
Quantification of aluminous anhydrous cement phases in the four binders (in mass percentage).

CAC	B1	B2	B3	B4
A	44	30	29	0
CA	40	14	22	30
CA_2	9	9	11	20
$C_{12}A_7$	7	0	0	0
Others (inert)	–	47	38	50