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Castable matrix, additives and their role on hydraulic binder hydration

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Abstract

The influence of alumina-based castable matrices, dispersants and Li_2CO_3 on the hydration process of different hydraulic binders was evaluated. The experiments were followed by temperature measurements with the time, the oscillatory rheometry technique and the normal force during the penetration of a blade through the material's surface. By doing these tests, the chemical features of binder hydration, working and demolding time of suspensions could be assessed. The experiments have shown that the alumina-based matrix presented an accelerating effect which is related to its sodium content. Citric acid and ammonium citrate were the dispersants with the highest delaying effect and could be effectively associated with the accelerator (Li_2CO_3) in order to adjust the setting time of the suspensions. Nonetheless, their accelerating and retarding effect varied according to the hydraulic binder.

Keywords: A. Suspensions; D. Al_2O_3; E. Refractories

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1. Introduction

Hydraulic binders generally consist of anhydrous oxides that in the presence of water form hydrated phases that impart cohesion to a shaped body. The rheological behavior and strength evolution during the hydration of castables is strongly influenced by the type of hydraulic binder and its hydration kinetics, defining their workability and demolding time, respectively.

Calcium aluminate cements (CAC) may be appointed as the most widely used refractory hydraulic binders [1]. The hydration process of their particles starts when water comes into contact with their surfaces. This step is described by the following chemical equation [2,3]:

$$Ca(AlO_2)_2 + 4H_2O \Leftrightarrow Ca^{2+} + 2Al(OH)_4{}^{-} \tag{1}$$

The $Al(OH)_4{}^{-}$ ions formed impart a basic character to the suspension, as a small quantity of them dissociate into Al^{3+} and OH^{-} ions, setting an equilibrium given by the basic constant K_b. As a result, the pH increases, according to Eq. (2) [4]:

$$Al(OH)_4{}^{-} \Leftrightarrow Al^{3+} + 4OH^{-} \tag{2a}$$

$$K_b = \frac{[Al^{3+}][OH^{-}]^4}{[Al(OH)_4^{-}]} = 1.8 \times 10^{-2} \tag{2b}$$

The dissolution of cement anhydrous phases increases the concentrations of the Ca^{2+} and $Al(OH)_4{}^{-}$ ions in solution. After a while, the concentration of these ions in water reaches the solubility limit, which is followed by the precipitation of a hydrated calcium aluminate phase, allowing further dissolution of the anhydrous phases. As a result, a cyclic process of ion dissolution–precipitation proceeds until most (or all) of the anhydrous cement particles exposed to water are consumed [4,5]. The cement hydration kinetics decreases at lower temperatures, resulting in longer setting times [5].

A slow nucleation process precedes the precipitation of hydrated phases. This period, which is known as the ''induction period'', remains until the first crystalline hydrate nuclei are formed [5]. After the induction period, precipitation is carried out quickly, as a result of crystal growth. Because heterogeneous nucleation on the particle surface is favored, the precipitated hydrated phases tend to form strong connections

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among neighboring particles, which result in the so-called setting phenomenon.

Commercial calcium aluminate cements mainly consist of anhydrous phases: CA ($CaO{\cdot}Al_2O_3$, 40–70 wt%), CA_2 ($CaO{\cdot}2Al_2O_3$, <25 wt%) and $C_{12}A_7$ ($12CaO{\cdot}7Al_2O_3$, less than 3 wt%). The CA_2 phase is the most refractory and requires a long time to hydrate completely. Conversely, the $C_{12}A_7$ phase presents low refractoriness and needs a short time for hydration, and can speed up the setting time of the CA [3]. As a consequence, the higher the $C_{12}A_7$ content in the cement, the faster the saturation and precipitation of hydrates is.

The differences in the hydration process of each anhydrous phase is related to the amounts of Ca^{2+} and $Al(OH)_4^-$ they can release in a solution, which defines the hydrated phases that are generated. At 25 °C, if the concentrations of CaO and Al_2O_3 are close, the formation of the CAH_{10} ($CaO{\cdot}Al_2O_3{\cdot}10H_2O$) is favored. The C_2AH_8 ($2CaO{\cdot}Al_2O_3{\cdot}8H_2O$) is induced in solutions with a higher Ca^{2+} concentration, whereas for a higher content of $Al(OH)_4^-$, the formation of AH_3 prevails. However, for temperatures above 35 °C, the precipitation of C_3AH_6 is predominant. These hydrates present the following order of solubility: $C_3AH_6 < C_2AH_8 < CAH_{10} < AH_3$. The formation of less soluble hydrates will imply in an increase of the precipitation, reducing the cement setting time. In contrast, the most soluble hydrate (AH_3) requires a higher induction period [2].

Hydratable alumina is another sort of hydraulic binder, which can be used to substitute CAC cements in calcium-free castables. Such alumina-based binders are produced by the fast calcination of gibbsite, resulting in mainly ρ-alumina, among other alumina transition phases. This reactive alumina presents a high specific surface area, low crystallinity and, in the presence of water, it hydrates according to Eq. (3), setting the castable [6]:

$$\rho\text{-}Al_2O_3 + H_2O \rightarrow Al_2O_3{\cdot}3H_2O + Al_2O_3{\cdot}(1{-}2)H_2O \qquad (3)$$

In the early stages of hydration, a thick layer of alumina gel is formed, which is partly converted to bohemite ($Al_2O_3{\cdot}(1{-}2)H_2O$) and mainly to bayerite ($Al_2O_3{\cdot}3H_2O$). The interlinked crystals of bayerite and the gel result in a pre-firing mechanical strength to the castables by filling pores and reducing surface defects. Such crystallization also favors the formation of crystal structures in the surface of aggregates, connecting adjacent grains to the surrounding matrix [7].

The kinetics of a binder's hydration can be significantly affected by the type of hydraulic binder, matrix and additives typically used in castables. Although many papers [8–11] have shown the influence of additives on the binder hydration process, their impact on castable processing, including setting behavior (working time) and demolding time needs to be evaluated.

In this context, the aim of this work was to study the kinetics of the hydration process of different binders in the presence of additives and predict the consequences of the rheological properties and strength evolution of castables, which defines their workability range and demolding time, respectively. Temperature and normal force measurements were associated to oscillatory rheometry in order to investigate these properties in suspensions containing usual castable matrix refractory raw materials.

Table 1
Chemical compositions and physical properties of the binders studied.

Phases (%)	Alphabond 300	CA 270	Secar 71	Secar Plenium
Al_2O_3	88	73	68	82
CaO	0.1	26	31	18
SiO_2	0.3	0.3	0.8	0.3
Na_2O	0.6	0.3	0.5	0.7
25–250 °C[a]	4.5	–	–	–
250–1100 °C[a]	6.5	–	–	–
Density (g/cm^3)	3.20	3.15	2.98	3.25
BET surface area (m^2/g)	194	1.9	1.2	5.8
d_{50} (μm)	3.3	7.8	13	10

[a] Mass loss in the temperature range.

2. Materials and methods

The hydraulic binders evaluated in this work include the hydratable alumina, Alphabond 300 (Almatis, US) and calcium aluminate cements of two different suppliers: CA 270 (Almatis, US), Secar 71 and Secar Plenium (Kerneos, France). The characteristics of these binders are presented in Table 1. Different types of calcined alumina (Esy Pump 1000, A17-NE and A-1000SG, Almatis, US) were also evaluated (Table 2). These aluminas are commonly used in the matrix of refractory castables and were tested either separately (Esy Pump or A17-NE) or combined (A17-NE:A-1000SG = 93:7 wt% ratio). Lithium carbonate, Li_2CO_3 (Labsynth, Brazil) was selected as an accelerator. Different compounds were evaluated as dispersing agents: sodium polymetacrylate (Darvan-7S, Vanderbilt, 2500 g/mol), citric acid anhydrous (Labsynth, 192 g/mol), diammonium citrate (Sigma Aldrich, 226 g/mol), sodium hexametaphosphate (HMPNa, Labsynth, 612 g/mol) and the family of polyglycol polymers developed by Basf, Germany (FS20, FS30, FS40 and FS60).

A standard laboratory mixer (Ética, Brazil) was used to prepare the suspensions for all experiments. The suspensions were prepared in water heated at 50 °C and mixed for 5 min prior to each measurement.

Table 2
Chemical compositions and physical properties of the aluminas used.

Phases (%)	Esy Pump 1000	A17-NE[a]	A-1000SG[a]
Al_2O_3	99.4	99.8	99.8
CaO	–	0.02	0.02
SiO_2	0.10	0.03	0.03
Na_2O	0.30	0.10	0.07
Density (g/cm^3)	3.99	3.94	3.95
BET surface area (m^2/g)	3.3	2.9	8.4
d_{50} (μm)	2.6	4.0	0.57

[a] The A17-NE:A-1000SG (93:7 wt% ratio) matrix presents surface area of 3.28 m^2/g and Na_2O content of 0.098% (calculated).