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Hydration modelling of an ettringite-based binder

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ABSTRACT

Aluminous cement, when mixed with calcium sulfate and water, produces a binder called an ettringite binder. A model of the hydration of an ettringite binder that accounts for the reactive surface of the solid phases in a solute was proposed. Mechanisms of precipitation and dissolution were considered. Calibration was performed based on the kinetics of the conductivity of the solute. Experimental pH kinetics are in accordance with the model prediction. Based on this good agreement, the final part of this article discusses the model predictions of the hydration of an ettringite-based binder.

1. Introduction

Compositions based on mixtures of calcium aluminate cement and calcium sulfate are used extensively in the field of building chemistry as repair mortars, tile adhesives, grouts and self-levelling floor screeds [1,2]. In these formulations, products dry and harden rapidly. The development of material microstructure is associated with many factors [3–7], such as temperature, humidity, cement content, various additives and the ratios of mixture compositions. Aluminous cement, when mixed with calcium sulfate and water, produces a binder called an ettringite binder because the main hydrate formed is ettringite ($C_6A\$_3H_{32}$). The formation of an ettringite binder is mainly based on the reaction between calcium aluminate cement (CAC) and calcium sulfate (C$), which leads to the formation of ettringite ($C_6A\$_3H_{32}$), aluminium hydroxide ($AH_3$) and calcium monosulfoaluminate ($C_4A\$H_{12}$). The formation of these hydrates depends on the mineralogy and crystallochemistry of the CAC, which varies greatly. Three different mineral phases are generally present in various amounts as a function of the following CAC components: calcium mono-aluminate (CA), calcium di-aluminate (CA_2) and mayenite ($C_{12}A_7$). The hydration reactions are indicated by chemical Eqs. (1), (2) and (3).

$$3CA + 3C\$H_x + (38-3x)H \rightarrow C_6A\$_3H_{32} + 2AH_3 \quad (1)$$

$$3CA_2 + 3C\$H_x + (47-3x)H \rightarrow C_6A\$_3H_{32} + 5AH_3 \quad (2)$$

$$C_{12}A_7 + 12C\$H_x + (137-12x)H \rightarrow 4C_6A\$_3H_{32} + 3AH_3 \quad (3)$$

When the calcium sulfate in the system is exhausted, ettringite dissolves and calcium monosulfoaluminate precipitates. In practice, mixture compositions can be more complex because they are often based on several other components, such as Portland cement, slag, pozzolan or calcite. Additionally, the aforementioned reaction scheme can be more complex as well, as shown in [8] and [9]. As example, when limestone is introduced into the mixture, carbonates react with aluminate phases promoting the formation of carboaluminate phases. Therefore the extra aluminates do not participate to the formation of monosulfoaluminate. Indeed, it was observed in [10] that calcium monosulfoaluminate does not form in cements containing limestone. Instead, monocarboaluminate (Mc) and hemicarboaluminate (Hc) phases form and more ettringite remains.

The mechanical performance and durability of this type of material depend on the features of the matrix microstructure and its kinetic development at an early age. The different characteristics as solubility or chemical stability of the hydrates formed at an early age govern the sensitivity of the mineral matrix sustainability toward carbonation and cracking. Improving knowledge about the early-age behaviour of these cement-matrix-based materials is a major objective in the development of new binders. The binders can show significant volume variations at an early age because of the shrinkage or swelling imposed by the hydration conditions and the hydric and thermic environment. Many studies have already been performed on the subject by researchers examining the calcium aluminate based binders. Particularly in the case of sulphoaluminate cement [11,12], a modelling approach was proposed in the aforementioned studies to describe the chemo-hydric-mechanical behaviour of the cement-based material at an early age. In this study, the behaviour of CAC cement was investigated. A model of ettringite binder hydration in a solute that accounts for the reactive surface compound of both the anhydrous and hydrate phases

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Table 1
Chemical composition of the anhydrous materials.

Raw materials	Main oxides/%wt									
	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	K_2O	Na_2O	SO_3	MnO
CAC	69.68	29.78	0.26	0.16	0,15	0.04	–	0.23	0.27	0.01
α-Plaster	–	38.70	0.27	0.03	0.1	0.003	–	–	52.40	–

was also developed. The hydration process is based on the dissolution–precipitation mechanism that occurs in solution. The model was calibrated by experimental conductimetry data, and its efficiency was confirmed by comparing calculated and measured pH kinetics. The results improve the understanding of the hydration of an ettringite binder at an early age.

2. Anhydrous materials

The anhydrous materials used in this study were a CAC and a plaster (α-plaster). The CAC was supplied by Kerneos Aluminates Technologies[1] (France) and was mainly composed of mayenite ($12CaO \cdot 7Al_2O_3$, denoted as $C_{12}A_7$) and ferrite ($Al_2O_3 \cdot Fe_2O_3 \cdot 4CaO$, denoted as C_4AF) and small amounts of calcium aluminate ($CaO \cdot Al_2O_3$, denoted as CA) and calcium di-aluminate ($CaO \cdot 2Al_2O_3$, denoted as CA_2). The second anhydrous material was an α-plaster with the trade name Prestia supplied by Lafarge.[2] The plaster contained a small amount of calcium carbonate (approximately 3%wt). The fact that this impurity is not taken into account in modelling of plaster is justified by the work of Martias et al. [13], which shows that a small amount of calcium carbonate has no effect on the hydration of the plaster. In the mixture with CAC, the presence of calcium carbonate can lead to Mc and Hc formation and to the stabilization of ettringite [10]. However, due to the CAC/α-plaster ratio, calcium carbonate represents only 0.75%wt, which is then negligible. The chemical composition in terms of oxide content for each anhydrous material is presented in Table 1.

3. Experimental techniques

Particle size distribution curves and mean diameters were obtained by laser granulometry using a dry process (Mastersizer 2000, Malvern Ltd). The air pressure was 0.5 bar, and the vibration rate of the hopper used to introduce the powder was 20%. Particle diameters were determined to range from 0.3 to 300 μm.

Conductivity and pH value measurements were performed using a suspension containing demineralized water and CAC and/or α-plaster on a SevenExcellence device (Mettler Toledo). The ratio between the demineralized water and solid (w/s) in solution was 20. This ratio allowed for the formation of a homogeneous suspension during the experiment without precipitation around the probe or on the wall of the beaker. Data acquisition began with the demineralized water (200 g). After the stabilization of the pH value and conductivity, the anhydrous material powder was added (10 g) using magnetic stirring. The pH value and conductivity were recorded every 5 s for 24 h using the software LabX direct pH (Mettler Toledo). The plaster was investigated first to account for its rate of dissolution and precipitation. A mixture composed of 75%wt CAC and 25%wt α-plaster, which led to the formation of ettringite, was then investigated.

Measurements by in situ infrared spectroscopy were performed using a ThermoFisher Scientific IS50 device in the attenuated total reflectance (ATR) mode [14]. To study the structuralization of the cement paste, a mixture of powder and water with a w/s ratio of 0.3 was studied by simply placing the mixture into a cylinder which is fixed around the diamond crystal with a seal at the bottom (Fig. 1). To conduct representative measurements of the material's behaviour, the cylinder was filled to the top (12 cm^3). A cover was placed on the surface to minimise water evaporation. The material was then studied under endogenous conditions. Spectra were recorded every minute for 6 h. Measurements were performed from 4000 cm^{-1} to 450 cm^{-1} (number of scans: 32, resolution 4.0). The software Omnic Series (Nicolet instrument) was used to record and process the data. To eliminate the contribution of carbon dioxide to the spectra, the spectra were corrected with a straight line between 2400 and 2000 cm^{-1}. The spectra were then corrected with an automatic baseline. The result of these tests was the temporal evolution of the spectra. This follow-up could show, for example, the formation of gypsum, ettringite and aluminium hydroxide due to the absorbance variation of the bands at 1110 cm^{-1} and 1020 cm^{-1} [15–18]. By monitoring the band absorbance over time, the competition between species formation and consumption in a paste could be observed.

4. Conductivity results

To understand the basic hydration mechanisms of gypsum and the ettringite binder mixture (75%wt CAC and 25%wt α-plaster), the species' behaviour in solution was investigated by measuring the electrical conductivity and pH. Experiments were performed on the suspension of powder and water (w/s = 20) to monitor the dissolution/precipitation process. Although the dissolution kinetics of these anhydrous materials are documented in the literature [19], experiments were required to calibrate the model to the materials actually used. The kinetics are highly dependent on the crystal habit and lattice order, which vary with the origin of the anhydrous materials [20,21]. The results were collected over a period of 24 h after mixing with water but they are presented on shorter period (6–10 h) (Fig. 2). This short interval was chosen because of the rapid setting of the ettringite binder, which under normal conditions can occur in less than 1 h [22].

4.1. α-Plaster

The conversion of hemihydrate to dihydrate appears to be a simple process but has nevertheless fuelled much research. The hydration of hemihydrate occurs through a solution mechanism leading to the formation of calcium sulfate dihydrate [22–24]. The evolution of the conductivity and that of the pH value of the α-plaster suspension (w/s = 20) over time are reported in Fig. 2(A). First, as soon as the hemihydrate comes into contact with water, the hemihydrate partially dissolves, which makes the solution saturated with Ca^{2+} and SO_4^{2-} ions, and the suspension reaches its maximum conductivity (5940 $\mu S.cm^{-1}$). This step is very quick and takes only 4 min. The conductivity then remains quite stable for 10 min, which corresponds to the induction period. According to Singh and Middendorf [22,13], during the induction period, clustering of hydrated Ca^{2+} and SO_4^{2-} occurs, leading to the formation of calcium sulfate dihydrate nuclei. Then, the nuclei grow, and the gypsum begins to crystallize. During this stage, the conductivity suddenly decreases after 14 min of reaction due to the germination and crystallization of $CaSO \cdot 2H_2O$. As the dihydrate crystallizes in the solution, the conductivity decreases. Finally, the suspension conductivity stabilizes at a value of approximately 2090 $\mu S.cm^{-1}$ after 80 min, which corresponds to the solubility of gypsum [25]. The variation of the pH value is similar, with a rapid increase followed by a decrease due to the dissolution of the plaster and its precipitation as gypsum. After 6 h, the pH value stabilized near a value of 7.9, which is similar to that of gypsum, which naturally occurs at a pH value level of 7. Despite the

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[2] Lafarge, 61 rue des Belles Feuilles, 75116 Paris, France.