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Sulphate crystallization modelling and surface reactivity in solution

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HIGHLIGHTS

- Hydratation modelling of plaster in solution.
- Crystallization pressure is considered in precipitation mechanism.
- Concept of chemical activity versus particles size is raised.
- Reactive surface is taking into account in the solid/liquid chemical reaction.

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ABSTRACT

The hydration of mineral phases corresponds to dissolution – precipitation mechanisms. A model considering crystallization pressure and particle size distribution of both anhydrous and precipitate sulphate is proposed. The model is applied in the case of β-plaster hydration in a solute. Numerical results demonstrate that the hydration process can be viewed as the sequence of nucleation, high growth regime and decreasing growth regime. Modifications in the particle size distribution and reactivity surface are characteristic of each phase.

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1. Introduction

This work is part of a larger goal addressing the behaviour at an early age of cement based materials. The mechanical performance and durability of these materials depend on the features of the matrix microstructure and its kinetic development at an early age. Mixtures of calcium aluminate cement (CAC) and calcium sulphate (C$) are widely present 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 components.

In a previous article [8], a modelling approach was proposed to describe the hydration mechanisms of calcium aluminate cement and calcium sulphate mixtures in a solute. The numerical results are in good agreement with the measured pH and conductivity. The modelling is based on the hypothesis that the granular medium can be represented by a set of spherical grains. We assume that the amount of dissolved or precipitated solid is located on the periphery of the beads and corresponds to a constant thickness e. For the anhydrous phase, this assumption is sufficient to evaluate the kinetics of dissolution on the base of particle size distribution. In the case of the precipitated solids, we need to consider another assumption otherwise the number of particles and their respective radius are two degrees of freedom. A strong hypothesis was also introduced considering a polynomial relationship between the cumulated number of particles and their size. Nevertheless, this point is unsupported by scientific evidence. Then, the new modelling approach proposed in this article is enhanced and expanded by the consideration that the crystal growth is dependent on both the supersaturation of the solution and the crystal curvature [9–12]. Crystallization takes place when the radius of the crystal is more than a critical radius.

We focus on plaster dissolution and gypsum precipitation in order to highlight the ability of this approach to describe hydration kinetics in a solute. A considerable amount of research on the

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mechanism of calcium sulphate dehydration exists in the scientific literature [13–17]. Hemihydrate occurs in two different forms: an α-form is produced by wet methods and a β-form is produced by dry methods from calcium sulphate dehydrate. The scanning electron microscopic technique (Fig. 1) has shown that the α-hemihydrate consists of well-formed needles with sharp crystal edges whereas β-hemihydrate consists of flaky particles made up of small crystals [12]. The assumption of perfect spherical grains to describe the anhydrous plaster phase appears to be more consistent for β-hemihydrate than for α-hemihydrate. It is commonly accepted that the gypsum phase develops needle morphology. The authors are aware of the simplification introduced in the proposed modelling by the assumed spherical morphology of the crystals. Apart from an integral involving a more complex surface, nothing prevents consideration of crystal particles with cylindrical or other forms.

Different modelling approaches exist in the literature to describe plaster hydration [12,18,19]. Most of these approaches rely on empirical relationships that fit well with conductivity measurements. The simulation obtained with the Avrami equation, which is generally applied for nucleation or autocatalytic phenomena, reproduces the typical S—shape kinetics well. The disadvantage of this approach is the lack of information regarding the mechanisms involved. Other more complex models [18,16] are built on clear scientific evidence, such as crystal growth laws and the typical development of gypsum needles. Their efforts are essentially focused on the geometrical development of gypsum hydrate and its morphology. In this article, we considers the dependence of dissolution-precipitation kinetics on a crystallization process defined by factors such as ionic force (chemical potential), surface area, and crystal curvature. Dissolution precipitation modelling takes into account chemical activity at the scale of the particles or more specifically considering the particle size distribution. Literature has not yet disclosed this kind of approach.

2. Experimental techniques and plaster characterization

The anhydrous material used in this study is a β-plaster with the trade name Selecta supplied by Lafarge. This plaster contains 95.45%$_{wt}$ bassanite, 2.00%$_{wt}$ anhydrite, 2.01%$_{wt}$ calcite and 0.54%$_{wt}$ quartz. These measurements have been obtained thanks to the Bruker D8 Advance X-ray Diffraction diffractometer measuring between $2\theta = 6°$ and $2\theta = 80°$ in 15 min with a 0.0197° pitch (Cu K-alpha 1: 0.154056 nm). The quantification was realized thanks to the Rietveld method using the software TOPAS R3 (the quantification of anhydrite is less reliable than the others due to preferential orientations).

Particle size distribution curve (Fig. 2.) and mean diameter of plaster were obtained by laser granulometry using a dry process

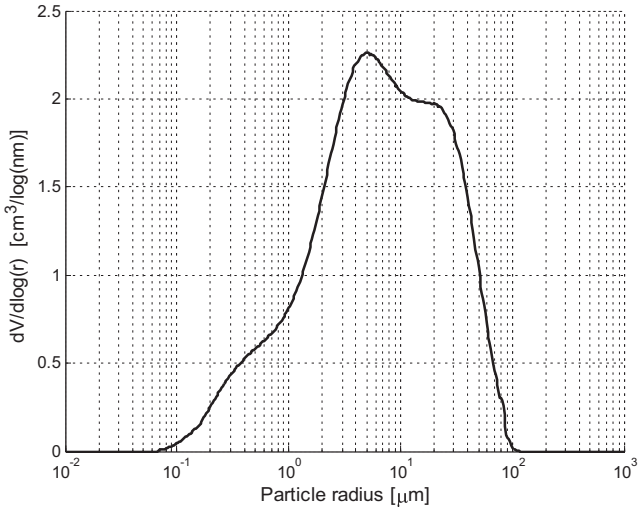
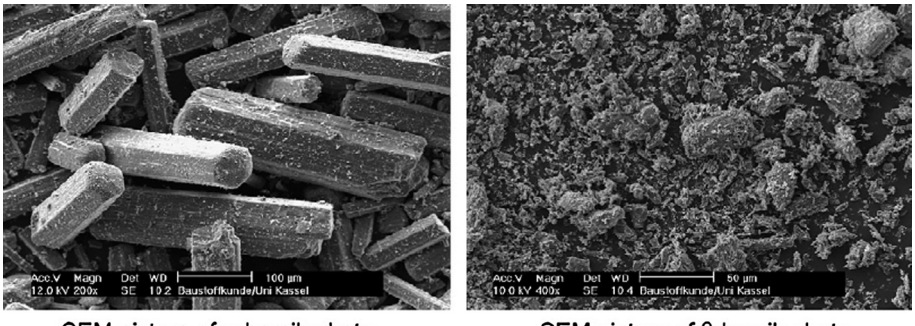


Fig. 2. Particle size distribution of the volume of plaster.

(Mastersizer 2000, Malvern Ltd). The air pressure was 1 bar for calcium sulphate. The vibration rate of the hopper used to introduce the powder was adjusted to obtain an obscuration rate between 0.5% and 6% in order to respect Mie conditions. Particle diameters were determined within the range from 0.2 to 2000 μm. The granulometer uses a He-Ne laser (633 nm) and a solid state light source (466 nm). The data were processed with a global distribution model (multimodal) and Mie scattering (for plaster, refractive index: 1.59 and absorption: 0.1). The volume-median-diameter D_{50} is 13 μm. The repartition in volume is composed of three families that can be distinguished: approximately 9 μm (5.5% of the volume), 10 μm (43% of the volume) and approximately 40 μm (77.8% of the volume). The specific surface area obtained from the laser diffraction analysis considering the measured particle size distribution and 2.7 of density is equal to 5740 cm^2/g.

The Blaine fineness criteria (cm^2/g), indicates that very fine particles with their larger surface area are in equilibrium with an aqueous solution. Indeed, the Prestia Selecta has a Blaine fineness of 7890 ± 50 cm^2/g. The Blaine fineness has been determined thanks to a Euromatest Sintco permeabilimeter respecting the norm NF EN196-6 and using 587E Rundfilter paper filters from Schleicher & Schuell (diameter = 12.7 mm).

Conductivity and pH measurements were performed on a suspension containing demineralized water and β-plaster with a pH meter/Conductimeter *SevenMulti* from *Mettler Toledo Ltd.* The conductivity probe used is from the range *InLab 731* (NTC 30 kΩ) from *Mettler Toledo Ltd.* The calibration is achieved at the experimental temperature with two standard solutions: 1413 μS/cm and



SEM picture of α-hemihydrate SEM picture of β-hemihydrate

Fig. 1. SEM picture of two forms of hemihydrates [12].