



# Influence of the reactivity of the amorphous part of mechanically activated alite on its hydration kinetics



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## ABSTRACT

The hydration of one mechanically activated alite passing through different drying procedures is examined by heat flow calorimetry and quantitative in-situ XRD analysis. The reactivity of the alite powders is strongly affected by the drying technique. It is shown that the reactivity of the amorphous part of the activated alite sample is particularly affected. Due to the fast initial dissolution of the amorphous “alite” part, the hydration progression is speeded up significantly. However, if the hydration is not speeded up by the amorphous “alite” dissolution, as in the case of surface passivation, the heat released until the transition to the deceleration period will increase. It is discussed that a crystalline alite dissolution by etch pit opening could increase the reactive alite surface and therefore increase the reaction degree at the transition to the deceleration period.

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## 1. Introduction

The intensive mechanical activation of alite has been shown to result in partial amorphous alite powders and a significant enhancement of their hydration process [1]. It was found that the amorphous part of the alite powder reacted before the crystalline alite and that the initial and main hydration period merged with a high amount of amorphous “alite”. The main hydration period could be attributed to the decrease of crystalline alite content as analysed by in-situ XRD. A considerable amount of XRD amorphous C-S-H was indicated as being formed during hydration of the mechanically activated alites. The XRD detectable “long-range ordered” C-S-H (C-S-H<sub>lro</sub>) was always detected when the dissolution of crystalline alite accelerated [1]. The deceleration of the main hydration period was found to be caused by the diminution of small alite particles as the mean CSD size of crystalline alite increased during acceleration and decreased during deceleration of the hydration reaction [1].

In our previous study on alite hydration [1], differently intensive mechanically activated alites were examined. In this study we present results for one alite powder, mechanically activated by a wet grinding process, which afterwards underwent different drying procedures. The reactivity of the variably-dried alites is significantly altered. The impact of this alteration on the hydration process of the activated alite will be

shown by means of heat flow calorimetry and quantitative in-situ XRD analysis and discussed.

Sprung examined the ageing of cements during storage in silos and found that the cements were showing retardation during hydration [2]. Effects on the aluminate reaction due to the precipitation of aluminate hydrates were found but no influence on silicate phases was described [2]. Winnefeld also described the delaying of hydration and reduction of the hydration rate and turnover of aged cement due to prehydration of aluminate phases [3]. Seifert et al. [4] showed for storage of cement at 70% RH that the reactivity of the cement and the turnover during the main period was lower with longer storage. The start of the main hydration period was found to be comparably delayed for cement that was stored for different lengths of time in comparison to fresh cement [4]. Stoian et al. [5] found it unlikely that the reduced heat of hydration found in calorimetric experiments could derive from the already released heat of hydration during the prehydration process, as the required degree of reaction would be very high (21% during prehydration of the sample that was stored for the longest time) [5].

Dubina et al. [6] stated that the adsorption of water vapor on C<sub>3</sub>S surface would only start at 75% RH and only a minor amount of water would be adsorbed. Nevertheless, Dubina et al. showed earlier that water was adsorbed on C<sub>3</sub>S surfaces during storage with a higher amount of adsorbed water for higher relative humidities (up to 0.29 and 0.54 wt.% for 60 and 85% RH) and non-linearly more for a longer storage [7,8]. The prehydration would cause the formation of C-S-H and portlandite on the surface of C<sub>3</sub>S. Due to the thin product layer, water took longer to reach the bulk C<sub>3</sub>S than in fresh pastes [7,8]. They showed in calorimetric experiments that the main hydration reaction

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for C<sub>3</sub>S shifted to later times with a prolonged induction period for a longer storage or a higher relative humidity [7,8].

Black et al. showed the formation of CaCO<sub>3</sub> and a silicon-rich outer surface layer on stored C-S-H samples with Ca/Si ratios >0.75 [9]. This could explain a passivation process of previously formed small amounts of C-S-H on the alite surface during storage. Stoian et al. assumed that C-S-H that precipitates during prehydration would differ from C-S-H formed in a normal hydration process [5]. This C-S-H would not be able to accelerate the hydration reaction but would form a layer of hydrated/carbonated solids on cement particles [5]. This layer would act as a mass transport barrier and therefore complicate the hydration reaction. They stated that surface relaxation/reconstruction could take place too [5]. Fierens and Verhaegen noted a significant loss in reactivity due to storage of C<sub>3</sub>S in “careful anhydrous conditions” which was accompanied by the decrease or disappearance of previously intensive thermoluminescence peaks [10]. It was suggested that the energy of trapped electrons could accelerate the hydration reaction [11]. The chemisorption of water on the excited surface centres of C<sub>3</sub>S grains with consecutive formation of C-S-H nuclei on those sites would be enhanced due to this energy [11].

## 2. Materials and methods

### 2.1. Materials

Monoclinic alite (M3 modification) was synthesized with a composition of 71.7 wt.% CaO, 25.9 wt.% SiO<sub>2</sub>, 1.8 wt.% MgO and 0.6 wt.% Al<sub>2</sub>O<sub>3</sub> as described elsewhere [1]. This alite was mechanically activated by intense grinding for 3 × 1 h (with an intermission of 0.5 h) in agate jars in a planetary ball mill from RETSCH at 250 rpm. 10 g of alite were milled in 40 ml ethanol with 175 g of 1.25 mm Y:ZrO<sub>2</sub> grinding balls. After the milling process, the alite-ethanol suspension was centrifuged at 3500 rpm and detached.

The residuum was treated in two different ways: one activated alite was dried as described before [1]. The centrifuge tubes were put in a vacuum drying chamber at 50 °C, operating at 20 mbar of N<sub>2</sub> atmosphere. The vacuum drying chamber was flushed with N<sub>2</sub> in 6 flushing and evacuation cycles during the 2 days of drying. This sample will be referred to as alite VDC. In the second case, the centrifuge tubes were put in a drying chamber at 50 °C in air. In the drying chamber, the humidity was reduced by silica gel to 44% RH during drying times of 21, 63 and 112 h (samples DC 1–3). After drying, all the samples were ground carefully in an agate mortar and sieved for better deagglomeration.

### 2.2. Methods

The BET surface areas of the resulting samples were measured with a GEMINI Model 236 from MICROMERITICS in liquid N<sub>2</sub> by adsorption of N<sub>2</sub> gas. The surfaces of the samples were conditioned by heating the samples to 150 °C and 350 °C under He flow for 3 h. The loss of ignition (LOI) of the dried powders was determined at 1000 °C ± 30 °C in Pt-crucibles in air.

The dried samples were analysed by powder XRD using a D8 Advance from BRUKER-AXS equipped with a LynxEye detector at 40 kV and 40 mA. Measurements were recorded from 7° to 80° 2θ with a step size of 0.0223° 2θ and a counting time of 0.5 s. The samples were measured with and without Kapton® polyimide film. The diffractograms were refined with the help of the program TOPAS 4.2 from BRUKER-AXS with consecutive calculation of the absolute phase contents in the samples by the external standard method [12–14]. NIST Silicon SRM 640d was used for calibration of the factor G. Two alite structures (both based on the same structural proposal [15]) were refined with different crystallite sizes and strains, both with Lorentzian functions. The lattice parameters were refined in very narrow constraints. The recordings with and without Kapton film were

refined by coupling parameters over all samples under the assumption that the powders should consist of the same relative amounts of crystalline alite and amorphous inorganic material. In addition, factors for the determined LOI, the respective mass attenuation coefficients and for the presence of the Kapton film were introduced in the refinement. As all samples were measured on the same day, one constant G-factor was used for all samples with Kapton film and for all samples without Kapton film. This way, lattice parameters, crystallite size, strain and scale factors were refined coupled over all 4 samples in a threefold analysis.

The results presented in Section 3 were normalized to the mass of reactive solid, which is the sum of crystalline and amorphous alite. The amount of amorphous “alite” was determined to be the difference to 100 wt.% after subtracting the amount of crystalline alite and LOI. However, for the results of the in-situ XRD analysis, the phase content in paste will be given.

The hydration kinetic of the variously-dried activated alite samples was examined by heat flow calorimetry (TAM AIR, TA Instruments) in combination with the InMixEr that allows the equilibration, injection of water to the powder, and mixing of both to a paste within the calorimeter cell. The kinetics can thus be determined directly from the start of the hydration process. The measurements were performed at 23 °C ± 0.2 °C at a water/solid (w/s) ratio of 1 due to the high water demand of the activated alite powders. The InMixEr holding the samples was previously equilibrated for at least 2 h within the calorimeter cell. At the start of the measurements, the water was injected and the sample was mixed at 860 rpm for 1 min. The heat flow curves were corrected for the calorimeter time constant, the baseline shift, and the calibration constant of the InMixEr [1].

The phase development within the hydrating activated alite pastes was determined by in-situ XRD measurements at the above-described D8 advance. A custom-made heating and cooling device ensured the constant temperature of 23 °C ± 0.2 °C of the samples. Additionally, the housing of the diffractometer was air-conditioned to 23 °C ± 2 °C. The measurements were recorded from 7° to 55° 2θ with a step size of 0.0236° 2θ with a counting time of 0.27 s (one diffractogram every 10 min). The samples were equilibrated before the measurements at 23 °C ± 0.2 °C. After injection of water (w/s = 1), the samples were mixed manually with a spatula to a paste for 1 min and prepared in the PVC sample carrier. The samples were covered by a Kapton polyimide film to minimize water loss or CO<sub>2</sub> uptake during the experiment.

For the refinement of the in-situ experiments, the lattice parameters, crystallite sizes and strains of the two alite structures were fixed to the values determined in the dry refinement. All diffractograms of one experiment were refined together. This allowed the refinement of, e.g., the scale factor of the Kapton film model or the lattice parameters of portlandite coupled over all diffractograms of one measurement. The structure proposal of Busing & Levy was used for portlandite [16]. The C-S-H<sub>1r0</sub> phase model of [17] was used in combination with “hkl” models for Kapton film and free water and a Chebychev polynomial of 1st order to model the background of the diffractogram [17]. The resulting phase contents were fitted with one to three 5 parameter logistic functions [18] with the program Fityk [19].

The phase content of XRD amorphous C-S-H in the paste was calculated. For this, the phase development of portlandite was scaled to the expected content of total C-S-H in paste following Eq. (1). For practical reasons it was assumed that also the amorphous part of the samples would react in the same manner as the crystalline alite and a stoichiometry of C<sub>1.7</sub>SH<sub>2.6</sub> for both XRD amorphous C-S-H and C-S-H<sub>1r0</sub>. To get to the phase development of XRD amorphous C-S-H, the measured C-S-H<sub>1r0</sub> content was subtracted from the derived expected total C-S-H content. The significant differences of 162 J/g in ΔH between the hydration reaction of the crystalline alite and the amorphous “alite” to C-S-H and CH represents the decrease in standard enthalpy of formation due

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