



# Use of micro-reactors to obtain new insights into the factors influencing tricalcium silicate dissolution



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## ABSTRACT

A micro-reactor approach, developed previously, is used to study the early dissolution of tricalcium silicate. This approach uses micron-sized gaps mimicking particles in close contact to understand dissolution, nucleation, and growth processes. The main factors influencing the dissolution kinetics of tricalcium silicate are presented. We show that the presence of defects caused by polishing does not affect the extent of dissolution. A strong effect of aluminum in solution reducing the extent of dissolution is however identified. This effect is highly dependent on the pH, and is much lower above pH 13. We show also that superplasticizers reduce the extent of dissolution; however, the exact reason for this effect is not clear.

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## 1. Introduction

The hydration of ordinary Portland cement (OPC) is extremely complicated; therefore, the hydration of alite (an impure, defected form of tricalcium silicate,  $3\text{CaO}\cdot\text{SiO}_2$ ), its main volumetric phase, is used as a model system to understand OPC hydration. The hydration reactions of alite and tricalcium silicate ( $\text{C}_3\text{S}$  in cement notation) are similar, and are as follows: immediately after mixing with water, there is a short initial period of high reaction rate that slows down quite rapidly, leading to a period where the rate is low and almost constant [1]. This period is usually called the induction period. After 1 to 2 h, the induction period finishes, and the reaction begins to accelerate, continuing at an increasing rate for about 10 h and then, it subsequently decelerates. Later hydration occurs at much lower rates. The causes of these different reaction stages are not totally clear and currently there are several theories that attempt to explain them [2, 3]. The high early reaction rate is usually thought to be due to rapid dissolution [2, 3], and according to recent studies [4], the rate and mechanism of dissolution depend on the solution undersaturation. With water, the dissolution is fast and proceeds via the formation of etch pits and vacancy islands, whereas in calcium containing solutions, the driving force for the dissolution is lower, and dissolution occurs through step retreat from pre-existing etch pits [4].

Although this theory explains the induction period quite well, some questions remain; for example, the role that defects play in determining dissolution kinetics. Using isothermal calorimetry and electron microscopy, it has been shown that annealed material, with a lower defect

density than untreated material, has a longer induction period and a lower amount of hydrate growth on the surfaces of grains [4, 5]. However, other researchers [6, 7], working in more dilute systems postulate that defects do not significantly affect dissolution kinetics, but instead affect the nucleation and growth of hydrates on the grain surface.

Although the hydration behaviors of  $\text{C}_3\text{S}$  and alite are similar, the former usually reacts faster, even when using material with similar specific surface area. This has been attributed to the presence of aluminum in alite, and there is quite some evidence showing that aluminum slows down  $\text{C}_3\text{S}$  hydration [8–13]. Explanations for this behavior include the formation of C—S—H containing aluminum, which acts as a poor nucleating site for additional C—S—H [8, 9, 12], or to aluminum stabilizing alite [11], or, to aluminum slowing down initial dissolution [10, 12] via the formation of Al—Si species interacting with the  $\text{C}_3\text{S}$  surfaces [10]. The latter view is supported by experimental data showing that aluminum slows down dissolution of amorphous silica [14].

Another big open question in cement hydration concerns the effect of chemical admixtures. These are used to modify concrete properties, and may have complex effects on alite (and  $\text{C}_3\text{S}$ ) hydration. For example, superplasticizers, which are used to fluidify concrete, usually have the side effect of retarding cement hydration [15–18]. This is explained by several hypotheses such as inhibition of dissolution, inhibition of nucleation and growth, deactivation of active sites, and complex formation between the admixture and calcium that would modify diffusion rates [16, 17]. Sometimes superplasticizers are added after a small delay, from 5 to 30 min after the addition of water, and this can cause drastic differences in the performance of the superplasticizer, for complex reasons [18–22].

The present study extends work published earlier using micro-reactors [23–26]. In those studies, micron-sized gaps were milled into

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alite grains using a focused ion beam and subsequently filled with solution to mimic hydration between grains in close contact. These gaps were imaged at various ages after hydration was stopped to gain insights into aspects of dissolution, nucleation and growth and how solution composition and chemical admixtures affect them. Results showed a strong support for the initial reaction being dissolution controlled, and that selected superplasticizers and retarders likely acted by slowing down dissolution. It was also shown that nucleation seeding with C—S—H works primarily by increasing growth, but does not affect dissolution significantly [24].

In this work, the micro-reactor approach is used to study the dissolution of  $C_3S$ , and to clarify the roles of aluminum, superplasticizers, and defects on the dissolution kinetics. As compared to the previous study, more elaborate experiments that subtly manipulate dissolution kinetics are presented.

## 2. Materials and methods

### 2.1. Materials

Tricalcium silicate was prepared as follows:  $SiO_2$  and  $CaCO_3$  (>99% pure; Sigma-Aldrich CO, St. Louis, MO) in the ratio of 1:3 were mixed and homogenized in a turbula (Turbula® T2F; Glen Mills, Clifton, NJ) for 24 h and then pressed into pellets 1 cm in diameter, weighing about 0.5 g, using a manual press (VLP-Series; Enerpac, Menomonee Falls, WI) under a load of 25 kN. These pellets were then placed in a platinum crucible and heated at 1600 °C for 8 h in a furnace (Nabertherm LHT 08/16; Nabertherm GmbH, Lilienthal, Germany) and then rapidly cooled by quenching under compressed air. Using XRD Rietveld (D8 ADVANCE; Bruker CO, Billerica, MA), the resulting material was identified as tricalcium silicate (triclinic polymorph), with less than 1% impurities.

Solutions were prepared on a mass basis; details are presented elsewhere [24]. Aluminum was incorporated into solution using water-soluble sodium aluminate (>95% pure, VWR International, Radnor, PA). In experiments with aluminum in solution, the solution pH was controlled by using KOH (>85% pure, Riedel-de Haen GmbH, Seelze, Germany); the pH was approximately 12.5 for 35 mM KOH, 13 for 150 mM KOH, and 13.5 for 600 mM KOH. DI water (ultrapure Millipore water with resistivity >18 MΩ cm at 25 °C (Milli-Q; Millipore, Billerica, MA)) was used to prepare all solutions.

The effect of superplasticizers was studied by using a commercial superplasticizer (ACE 30; BASF SE, Ludwigshafen, Germany) and a synthesized, grafted, pure comb-type polycarboxylate superplasticizer (3PMA1000S, molecular weight 26,600 g/mol, side chain molecular weight 1000 g/mol, and carboxylic to ester groups ratio 3.2); the superplasticizer was synthesized by copolymerization of methoxy polyethylene glycol methacrylates and methacrylic acid (Sigma-Aldrich CO, St. Louis, MO), additional details of the characterization are presented elsewhere [24].

### 2.2. Preparation of the gaps, hydration, and imaging

Preparation of the gaps, hydration, and imaging was done in a similar manner as explained in detail earlier, and the method is summarized here [24].  $C_3S$  pellets were lightly ground using a mortar and pestle to obtain pieces about 0.1–0.5 mm in size, then a piece was placed on a flat rubber surface and a drop of liquid epoxy (EPO-TEK 301, Epoxy Technology, Inc., Billerica, MA) was dropped on it and left to harden overnight. After the piece was embedded in the epoxy, the side of the sample close to the piece was polished for about 4 min manually to expose a flat surface of the  $C_3S$ . The polished sample was gold coated (MED010; Oerlikon Balzers, Balzers, Liechtenstein), then placed in a dual beam SEM-FIB (Quanta 200 3D; FEI CO, Eindhoven, Netherlands), and gaps were milled in the  $C_3S$  with the Ga-FIB using a current of 50 pA and a voltage of 30 kV.

The samples were then taken out of the microscope, and immersed in solutions. The volume of solution used was around 1 ml; this is fifteen orders of magnitude higher than the gap volume ( $5 \mu m^3$ ), therefore, reactions take place in infinitely dilute conditions, nevertheless hydrates do form, possibly due to high local concentrations [24]. Low vacuum (150 mbar) was applied for about a minute to better enable impregnation of the solution into the gap. The hydrating gaps in solutions are what we term *micro-reactors*. The gold coating is generally waterproof and protects the rest of the sample from solution ingress.

The samples were then stored, fully submerged, and allowed to hydrate for the required reaction time. When the hydration had to be stopped, the samples were immersed in reagent grade isopropanol for 2 h at  $-18$  °C, and then dried at 60 °C for 2 h. The samples were then gold coated (SCD050; Oerlikon Balzers, Balzers, Liechtenstein) and the gaps were then imaged using a high-resolution SEM (Leo 1530 Gemini; Carl Zeiss AG, Oberkochen, Germany) using an in-lens secondary electron detector. For results from every gap presented here, at least three gaps were imaged, and usually all three were qualitatively similar in terms of the dissolution behavior.

## 3. Micro-reactors background

In this section, a short summary of the results obtained in our previous study with alite is presented [24]. Readers who are familiar with the work may skip this section. All initial gaps had initial dimensions of  $5 \mu m$  in length,  $1 \mu m$  in width and  $1 \mu m$  in depth. Before dissolution, all gaps had very smooth and regular surfaces. The dissolution behavior of the gaps strongly depends on the solution composition. With water, dissolution is immediate, with samples at 2 min already showing evidence of dissolution. At 30 min, the extent of dissolution is already large, and the dissolution continues further with time. The dissolution continues and the extent is quite large at 4 h and 2 days. The walls and the bottom of the gaps cave in, with the dissolution occurring in three dimensions. Typical results at 4 h with water are shown in Fig. 1. The results shown in the figure are qualitatively similar to results published earlier at different hydration times [24].

When using solutions containing calcium (2 mM and 20 mM calcium hydroxide solutions), there is a low extent of dissolution (compared with water) till 30 min. From 4 h onwards, the behavior changes as follows: for the 20 mM CH solution, at 4 h and 2 days, the surface of the gap is completely covered with hydration products with significant porosity between them. The dissolution extent is always relatively low, with deep holes in the gap almost never being observed. With the 2 mM CH solution, the dissolution extent increases at 4 h and 2 days and the gaps look much more similar to

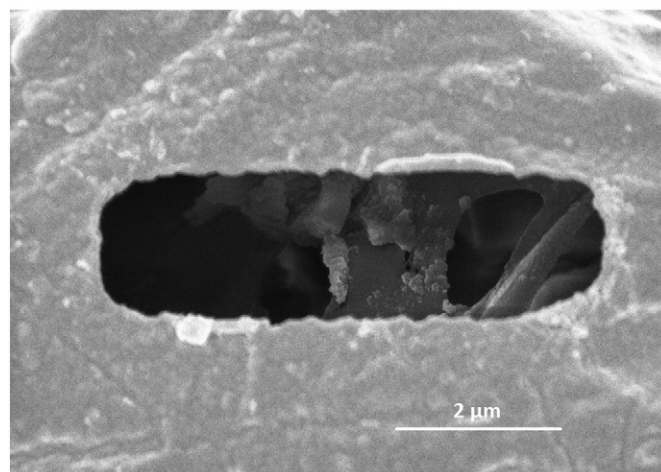


Fig. 1. Gaps in alite after 4 h hydration in pure water using the same batch of material as in [24]. The extent of dissolution is large and the walls and base of the gap have dissolved.

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