

Dissolution kinetics of cubic tricalcium aluminate: effect of magnesium sulfate

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INTRODUCTION

Quantifying the dissolution kinetics of cementitious minerals has been identified as a significant research need [1,2], as these data have been demonstrated to be critical in understanding hydration mechanisms [3–5] and developing cement hydration models [6,7]. Recently, surface topography measurements have proven to be useful in monitoring the dissolution kinetics at the microscale, such as with vertical scanning interferometry [8,9], and recent applications of digital holographic microscopy (DHM) have been utilized to quantify the *in situ* dissolution rates of calcite [10], gypsum [11], cubic tricalcium aluminate (C_3A) [12], and β -dicalcium silicate (β - C_2S) [13]. These studies have demonstrated that dissolution is spatially and temporally heterogeneous, owing to the distribution of defects and other reactive surface sites [14–16].

The previous DHM study of C_3A dissolution only considered the effects of water and variable water activity [12]. However, it is well-established that sulfate affects the hydration rate of C_3A [17], although the mechanism is still poorly defined. The literature suggest that C_3A reactivity is influenced through sulfate ion adsorption at C_3A defect sites [1,4,18–21] or through sulfate and calcium ion adsorption on an aluminum-rich surface layer [22–25]. This DHM study will evaluate how C_3A dissolution rates are affected by magnesium sulfate ($MgSO_4$) in low activity solutions. While the effect on the dissolution rate has not been explicitly studied before, one study showed that, relative to $CaSO_4$, $MgSO_4$ may increase the C_3A hydration rate [26].

EXPERIMENTAL METHODOLOGY

The synthesized C_3A was found to consist of 89.7% cubic C_3A , 2.2% free CaO , 4.3% mayenite ($C_{12}A_7$), and 3.8% amorphous content [12]. Only smooth, flat surfaces can be evaluated by DHM. To achieve this, a pressed pellet of C_3A powder was sintered and polished [12], resulting in polycrystals at the surface. Once polished and cleaned, a mask of chromium was applied to part of the surface to serve as an inert reference plane. The sample was placed in an inert flow-through reaction cell [10–13,27]. A flow rate of 33 mL min^{-1} was found to be sufficient to obtain flow rate-independent measurements [12]. Since C_3A reacts so rapidly in water, a reduced water activity was needed, which was produced using a binary mixture of deionized water ($> 0.18 \text{ M}\Omega \text{ m}$) and absolute ethanol at a mole fraction of 0.317 [12], which is 40% water and 60% ethanol by volume.

The DHM is able to measure full-frame surface topography (*e.g.*, three-dimensional surface) at tens of frames per second. Figure 1 shows an example of surface topography evolution (*e.g.*, etch pit formation) during C_3A dissolution. Therefore, the dissolution rate was quantified by tracking the surface normal velocity, v_s , per pixel, which is the height change per time interval, $\Delta h/\Delta t$. The surface normal dissolution rate, J_s , is then $J_s = (\Delta h/\Delta t)/V_m = v_s/V_m$ [28], where V_m is the molar volume of C_3A . Full-frame surface topography data was collected at a rate of 12.5 s^{-1} , and a set of 15 to 20 frames were collected every 10 to 30 s and averaged to reduce noise effects. Experiments were performed in solutions of 40% water and 60% ethanol by volume with $MgSO_4$ concentrations of 0, 1, 2.5, 5, 10, and 15 mmol L^{-1} .

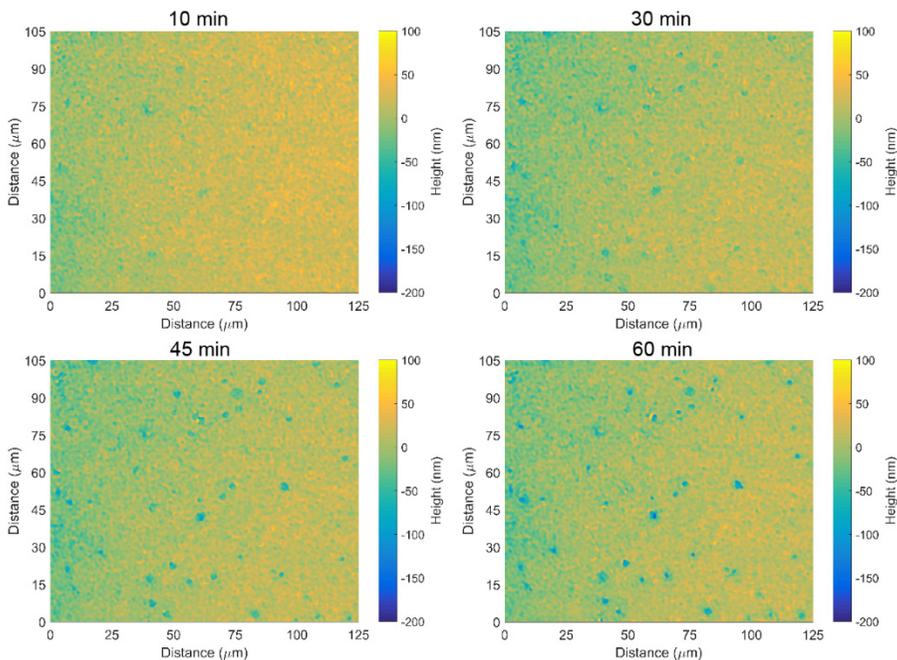


Figure 1. Surface topography evolution (etch pit formation) in C_3A exposed to a static solution with a 0.419 mole fraction of ethanol (30% deionized water and 70% ethanol by volume) [12].

RESULTS AND DISCUSSION

As expected based on previous experiments [10–13], the dissolution rate of C_3A follows a skewed distribution (Figure 2). Because of the heterogeneous distribution of defects and other reactive surface sites (Figure 1), dissolution rates from surface topography measurements are better described by probabilistic distributions, which have been termed “rate spectra” in the literature [14–16]. These distributions have been found to be described best as a generalized extreme value distribution [10,29].

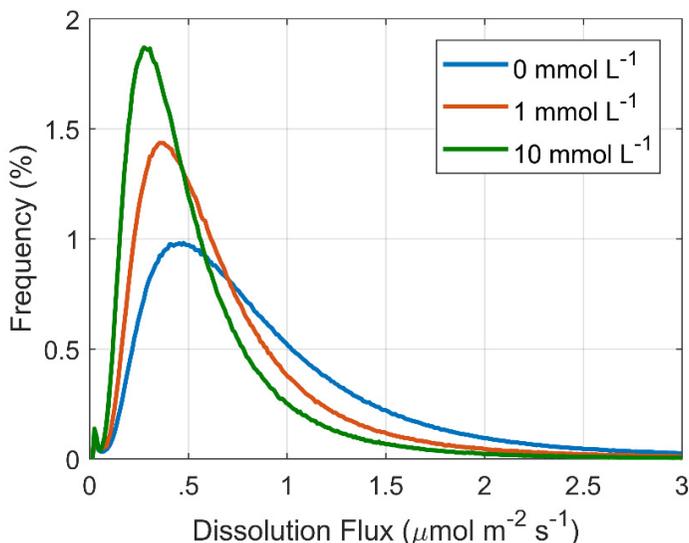


Figure 2. Dissolution rate distribution of C_3A exposed to flowing $MgSO_4$ solutions at concentrations of 0 mmol L^{-1} , 1 mmol L^{-1} , and 10 mmol L^{-1} .

Figure 2 demonstrates that, as the $MgSO_4$ concentration of the solution increases, the modal dissolution rate decreases, which suggests that sulfate in solution does affect the dissolution rate of C_3A . Table 1 shows the statistical analysis of the distributions from each experiment, including the mean, median, standard deviation, and interquartile range (IQR). Figure 3 shows the median and IQR of each distribution as a function of increasing $MgSO_4$ concentration, which shows a plateau in the median dissolution rate, suggesting that the median rate is independent of concentration above a concentration of about 2.5 mmol L^{-1} .

Table 1. Dependence of C_3A Dissolution Rate Statistics on $MgSO_4$ Concentration*

Solution [SO_4^{2-}] (mmol L^{-1})	Dissolution Flux ($\mu\text{mol m}^{-2} \text{ s}^{-1}$)				Number of Data Points
	Mean	Median	Standard Deviation n	IQR (P_{25}, P_{75})**	
0	1.121	0.754	1.57	0.741 (0.473,1.214)	$10^{6.91}$
1	0.736	0.553	0.752	0.494 (0.364,0.858)	$10^{6.68}$
2.5	0.559	0.446	0.451	0.367 (0.303,0.670)	$10^{6.45}$
5	0.627	0.471	0.628	0.464 (0.290,0.754)	$10^{6.55}$
10	0.548	0.429	0.453	0.383 (0.283,0.666)	$10^{6.64}$
15	0.621	0.508	0.430	0.466 (0.337,0.767)	$10^{6.51}$

* All solutions used a water-ethanol solvent with ethanol mole fraction of 0.317

**The 25th (P_{25}) and 75th (P_{75}) percentiles that correspond to the IQR

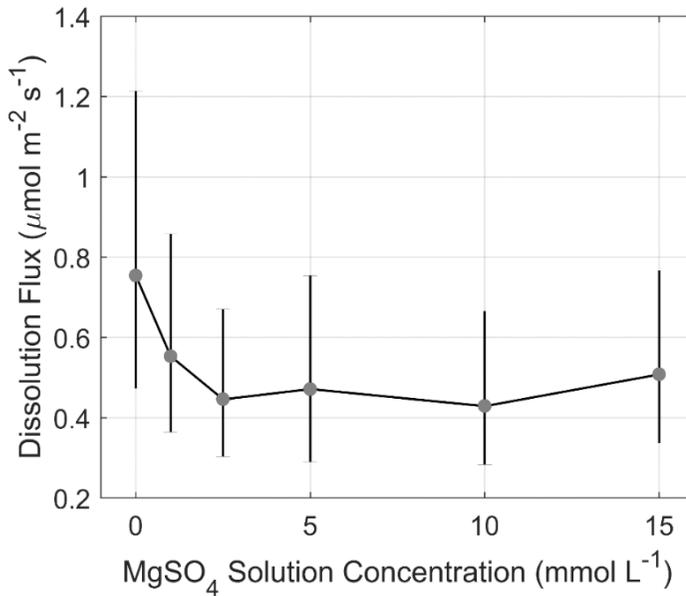


Figure 3. Median dissolution flux (red circles) as a function of MgSO_4 concentration. The bars indicate the IQRs given in Table 1.

The literature have suggested that sulfate affects C_3A hydration through sulfate adsorption to defect sites [1,4,18–21]. The plateau behavior in Figure 3 may suggest that there are a finite number of sites that the sulfate can adsorb to, which is why the dissolution rate does not continue to decrease after a certain sulfate concentration. However, it should be noted that sulfate is reducing, but not completely halting, C_3A dissolution, which may indicate that sulfate ions are only affecting certain reactive surface sites.

CONCLUSIONS

Using *in situ* digital holographic microscopy, the dissolution rate of cubic C_3A was quantified in the presence of MgSO_4 in solutions of low activity. The presence of sulfate in solution was found to diminish the median dissolution rate of cubic C_3A , although above a concentration of about 2.5 mmol L^{-1} the median rate was found to be approximately constant. These data may suggest that sulfate only affects certain reactive surface sites and that there are only a finite number of surface sites that sulfate can affect.

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