

Nanoscale Observations of Tricalcium Aluminate Dissolution in Water by Digital Holographic Microscopy

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INTRODUCTION

Mineral dissolution is a key process in geochemical reactions and environmentally relevant processes[1]. In recent years, the dissolution behaviors of cement clinkers have been obtaining increasing attention [2-6]. Portland cement is a low-cost material with multi-minerals, including alite, belite, tricalcium aluminate (C₃A), gypsum, etc. The hydration of cement, which is a complex reaction that combines mineral dissolution and product precipitation, is the origin of strength and determines other properties of cement paste. According to Julliard et al.[2], dissolution plays an important role in alite hydration, and the change of alite dissolution mechanism is responsible for the onset of the induction period. Similarly, Nicoleau et al.[5] proposed that the dissolution of C₃S is the rate-controlling step in the early hydration based on the change of saturation index of C₃S.

Besides alite, C₃A is also a key component of Portland cement. Though its content is much lower than alite, it has an important effect on the early properties of cement paste, especially for the workability[7]. Because C₃A has much higher reactivity than alite, it reacts much faster with water than C₃S, which makes it an even bigger challenge to measure its dissolution rate in water. To slow down the dissolution rate of C₃A, Brand and Bullard[8] lowered the water activity by incorporating ethanol in water and measured the dissolution rate in solutions with a high content of ethanol. However, the presence of ethanol is likely to change the dissolution mechanism of C₃A due to its adsorption to the C₃A surface[9-10]. Thus how the dissolution rate of C₃A in the mixture solutions is related to that in water still remains unresolved.

For the purpose of measuring the net dissolution rate of C₃A in water, this paper provides a new technique, the Digital Holographic Microscopy (DHM), to monitor the surface height change of polished C₃A samples on nano-scale. Because of the unique capability of fast image collection of DHM, the real-time observation of fast dissolution is realized.

RESULTS

• Flow rate effects

A flow-through liquid cell, like the cell used in [6], was built to provide water to flowing across the surface of tricalcium aluminate with specific flow rates. Figure. 1 shows the dependence on the flow rate of the overall dissolution rate in the first few seconds. It can be seen that with the increase of flow rate, the measured dissolution rates firstly reach a maximum value at a flow rate of 34 ml·min⁻¹, and then drops a little when the flow rate continuously increasing. It indicates that when the flow rate is lower than 34 ml·min⁻¹, ionic diffusion may play a more important role than

the surface reaction in controlling dissolution, and when the flow rate is higher, the flow becomes turbulent, resulting in the actual flow rate lower than the target value. Therefore, 34 ml·min⁻¹ is adopted as the flow rate for the following study.

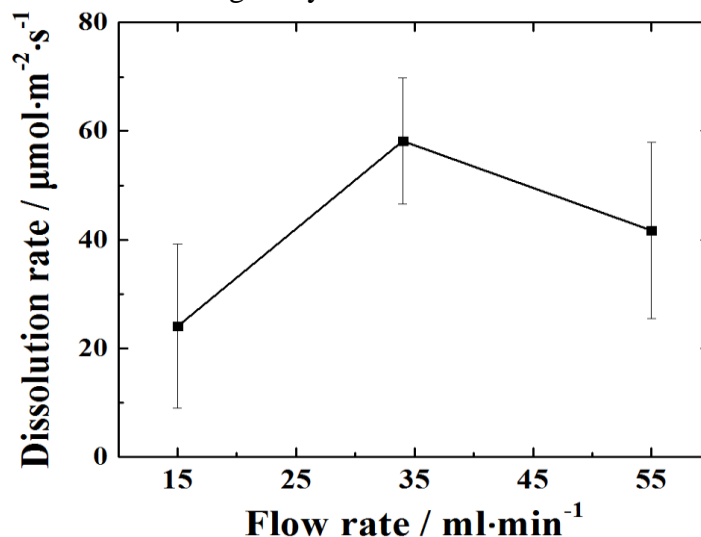


Figure 1. Overall dissolution rate as a function of water flow rate. Error bars are one standard deviation of the average overall dissolution rate for at least three samples at each flow rate.

Surface morphology after initial dissolution

The surface morphology of C₃A after the contact with water for about 2 s can be seen in Figure 2(a), in which the right bottom of Figure 2(a) is the reference surface, and it remains smooth during the measurement, though a small amount of hydration products appear in some local areas. This is due to the incomplete coverage of inert platinum in the reference surface, especially at the regions with deep scratches. Different from the reference surface, the surface not covered with a chemically-inert layer becomes very rough and a layer of hydration product with crumpled foil shape can be clearly seen, as shown in Figure 2(b). The thickness of this hydrates layer is measured from the side view of the specimen based on the brightness contrast with the bulk material, as shown in Figure 2(c). The thickness is about 300 nm.

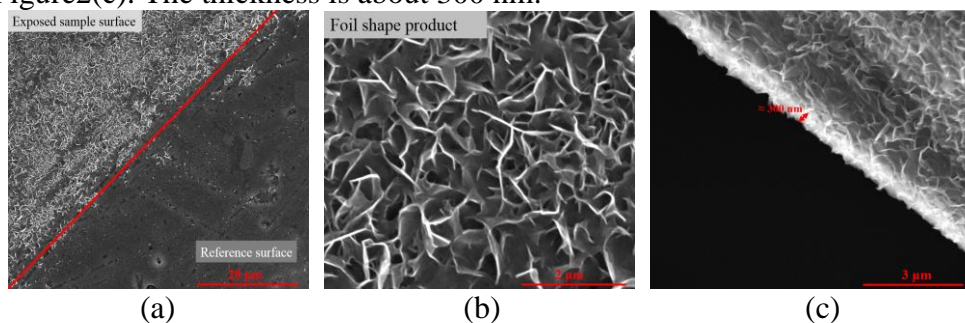


Figure 2. Surface morphology after initial dissolution (a) The front view of C₃A surface after dissolution. (b) Morphology of hydration product layer. (c) The side view of C₃A surface after dissolution.

- **Analysis of C₃A dissolution kinetics**

By tracing the average relative surface height change to the reference surface, it is clearly seen in Figure 3 that the surface height changing can be roughly divided into three periods, including the

initial fast height reducing, followed by the slow height increasing and the moderate height reducing. It suggests that after the rapid dissolution lasting for about half of a second in the first stage, the surface starts to be gradually covered by the hydration product in the second stage, in agreement with the results shown in Figure 2(a)-(c). Though covered by a layer of product, the dissolution continues because the product has foil shape and not able to stop dissolution completely. Nevertheless, combined with the decreasing effect of dissolution and increasing effect of hydration on surface height change, the average relative surface height decreases at a relatively constant rate which is much slower than the initial dissolution. The overall dissolution behavior is similar to the heat flow during C_3A powder hydration in water[11]. For C_3S and cement, it also can be found in the literature that the heat flow behaves similarly[12-13]. Although it is not completely the same with protective layer hypothesis which assumes a layer formed on the surface can control the hydration reaction for a much longer-term, often dozens or hundreds of minutes[14-15], according to the DHM measurements, this surface layer is able to decrease the dissolution rate dramatically within the time frame of a quarter of a second.

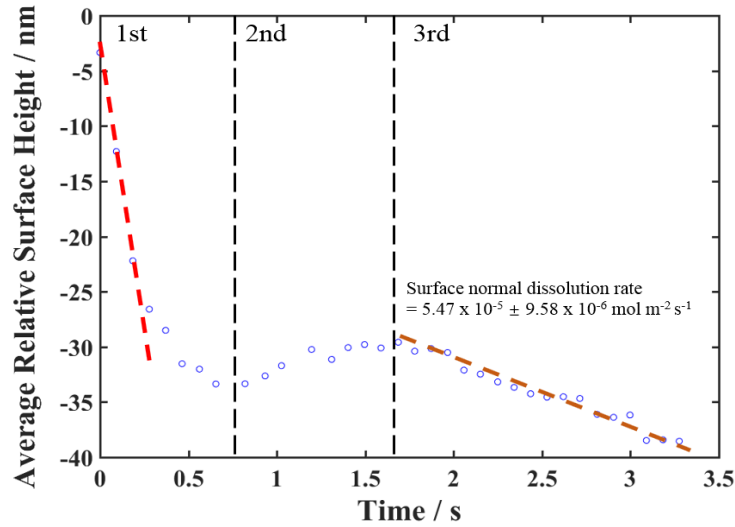


Figure 3. The average surface height change during dissolution.

Probable initial dissolution behavior (a timescale of a few seconds)

As mentioned above, precipitation happens even within the first second of contact with water. Therefore, any dissolution measurement longer than one second is actually a result of the combination of both dissolution and precipitation. By analyzing the data in Figure 3, it can be seen that the average pure dissolution rate of C_3A (in the first quarter of a second) is about 15 to 20 times larger than the rates obtained after two seconds. So according to equation (1), the surface height change, $\Delta h/\Delta t$, is about $73.6 \sim 97.6 \text{ nm} \cdot \text{s}^{-1}$. Given the uncertainty of the measurement results shown in Figure 1, $\Delta h/\Delta t$ can reach a maximum value at about $140 \text{ nm} \cdot \text{s}^{-1}$. If we assume that the pure dissolution rate of C_3A and the pure precipitation rate of hydration product remain constant during the first few seconds, so combined Figure 3 and the value calculated above, the absolute value of precipitation rate should be just slightly lower than that of dissolution rate. Within 2 seconds of contact with water, the product layer thickness is estimated to be able to reach 200 ~300 nm. This is close to the value measured under SEM (Figure 2(c)), which is actually slightly higher. This small difference can be attributed to the higher reactivity of the edge region of the sample measured under SEM than the flat regions measured by DHM^[17].

CONCLUSIONS

In-situ nanoscale measurement on C₃A dissolution was for the first time performed by DHM in flowing deionized water. At a flow rate of 34 ml·min⁻¹, C₃A can dissolve at an average rate of 0.5 ~ 1.5 mmol · m⁻² · s⁻¹ within the first a quarter of a second after contact with water. After then, a crumple foil-like hydration product starts to form, which dramatically reduces the dissolution rate of C₃A.

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