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Discussion of "Dissolution theory applied to the induction period in alite hydration"

J.M. Makar, J.J. Beaudoin, T. Sato, R. Alizadeh, L. Raki

Institute for Research in Construction National Research Council Canada 1200 Montreal Road, Ottawa, Ontario K1A 0R6 \*corresponding author: jon.makar@nrc-cnrc.gc.ca

Juilland et al.[1] present a very interesting and significant discussion of the importance of dissolution in the initial stages of alite hydration. Their drawing together of results from a number of sources highlights the significance of the dissolution process, while the theoretical discussion in part 5 will be very beneficial to scientists interested in investigating and understanding dissolution. Their proposed model for the induction period described in part 6, however, does not correspond with recently published and forthcoming experimental evidence.

The model can be summarized as follows:

- Initial exposure to water starts a process of dissolution of the surface of the alite at dislocations, forming etch pits;
- Some C-S-H forms on the surface, as indicated by the heat generated in the first stage of the hydration process (phase I in the author's Figure 1);
- Dissolution continues slowly, limiting further growth of C-S-H; and
- At the end of the induction period dissolution speeds up again and C-S-H resumes.

The model specifically excludes the formation of a barrier layer on the surface of the alite at the start of the hydration process.

There are a number of points where the experimental evidence does not support the model. Extensive studies of the induction period in both  $C_3S$  [2] and ordinary Portland cement (OPC) [3] showed that at water/cement ratios typical of concrete construction significant pitting only forms in the alite surfaces at the end of the induction period, not at its beginning as suggested in Juillard et al.[1] Even when the hydration process is accelerated by the presence of nanostructures such as single walled carbon nanotubes [4] or nanometric calcium carbonate [5], formation of pits was not seen until at or after the end of the induction period as determined by isothermal conduction calorimetry. The high resolution of the images (5 nm or better) makes it unlikely that any pits were missed.

There are two special cases where the pits do appear to form before the onset of the main hydration reactions: where alite is exposed to excessive water as in Juilland et al.'s[1] Figure 7 and earlier work by Ménétrier, et al. [6], and in the presence of synthetic C-S-Hs (Figure 1), which have extremely high surface areas [7]. The early formation of pits in the former cases suggests that ion concentration in the mix water does indeed limit the dissolution of alite surfaces, but in the latter case the effect is likely due to initial reactions on the high surface area synthetic C-S-H itself during the first few minutes of exposure to water. A direct comparison between the image presented by Juillard et al.[1] in their Figure 7 and the images in Makar, Esseghaier and Chan [2] is difficult to make due to potential differences in

the C<sub>3</sub>S material used in each case. However, the results with and without synthetic C-S-H in Alizadeh, et al. [7] are directly comparable to each other and it is apparent that a much higher degree of pitting was present in the samples with synthetic C-S-H throughout the hydration process. This would also argue against dislocation driven dissolution, as increased dissolution activity under that mechanism should be expected to primarily produce deeper pits, not a higher number of surface pits.

A careful examination of the pits formed during dissolution at 0.5 w/c ratio shows that in many cases the bottom of the pit can be seen (Figure 2). Where this is the case, the images tend to show a relatively flat bottom in each pore at early stages of hydration. Upon closer examination of the pits (Figure 3), it is apparent that the pits have approximately the same depth in different parts of the same surface. The inverse pyramidal structure that is typical of an etch pit was not identified in any of the images that were examined [2,3]. Instead, pits resemble those seen in corrosion pitting in metal [8], suggesting that step retreat may be a predominant mechanism. The sample size was very large, with well over 1000 different alite surfaces examined and the SEM technique used [2,3] was capable of resolving structures with dimensions as low as 5 nm, so it is very unlikely that the characteristic etch pit shape would have been missed.

Deeper and more complex networks of pits do, of course, form in the alite as it hydrates. Figure 8 in Makar and Chan [3], repeated here with additional annotation as Figure 4, shows an example of such a pit network. Examining the figure shows that while parts of the surface remain intact (indicated by an \*), there is a complex network of small pits that appear to connect below the surface of the alite. The widening and deepening of a smaller number of pores that would be expected of etch pits was not apparent, but the image does suggest that the surface of the alite is more resistant to dissolution than the interior material.

Evidence for reaction product formation during the early stages of hydration was also examined for C<sub>3</sub>S [2] and OPC [3]. Classical C-S-H, of the type shown in Figure 21b in Juillard et al.'s [1], was not seen in any of the images until the end of the induction period. The C-S-H formed initially on the alite surface has a characteristic spear point shape (Figure 6b in reference[2]) and is easily recognized. It appeared to be as likely to form on a relatively flat surface as on a rough grain end. The imaging examined ends of grains, flat surfaces and stepped surfaces formed by broken alite grain boundaries and found no difference in the extent or timing of hydration product formation (Figure 5).

In addition, unpublished work [9] has examined the effect of various solvents used to stop hydration on the surface of hydrating alite. All of the solvents increased the size and number of pits visible on the surface as compared to freeze-dried samples. This result suggests that the sides of the pits are more vulnerable to dissolution than the bottoms of the pits, which again argues against pit formation on dislocations.

A final point is based on the dislocation density required to produce the number of pits seen in the images. Makar and Sato [9] also examined the density of pits on the surfaces of alite as part of their study. The average pit number densities for the freeze dried samples was 26 / $\mu$ m<sup>2</sup>. If this number represents the dislocation density, the number of dislocations present in the commercially produced

OPC that was investigated approached the values seen in cold worked metals [10]. This value is much higher than that reported for alite [11] and for  $\beta$ -C<sub>2</sub>S [12]. In both of the latter cases the dislocations were seen at grain boundaries, not in the body of the grains. Hudson and Groves [11] specifically state that the dislocation density was too low to be calculated. The scale of their images is such that a dislocation density sufficient to create the observed pitting should have been readily apparent.

Taken together, these points suggest that the model of the induction period being solely dependent on dissolution mechanics at dislocation sites is not well supported by the experimental evidence. Instead, the evidence suggests that a barrier layer of some form does indeed exist. This barrier layer likely inhibits both dissolution and the formation of C-S-H. Dissolution then initiates at defects or dislocations in the barrier layer, not in the alite itself. Once the pit has initiated, the relatively flat shape of the pits suggest step retreat dissolution is the predominant dissolution mechanism, rather than etch pit formation.

While there are strong arguments against the specific model proposed by Juillard et al.[1], both their model and the one briefly proposed here have the advantage of being directly testable. Comparisons of dislocation density and pore density, specific studies of the numbers of pores formed at different w/c ratios and investigation of the effect of additional calcium and silicon on the pit formation may all provide useful evidence to support either model. It is also possible that the pits may be directly imaged through transmission electron microscopy. Work on some of these possibilities is currently underway in our laboratory.

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#### Figures



Figure 1 – Dissolution pit formation in  $C_3S$  seeded by synthetic C-S-H with a C/S ratio of 0.8. Imaging conditions and experimental details are given in [7].



Figure 2 – Example of surface with many pores with visible bottoms and the same apparent depth, St. Lawrence (now Holcim Canada) General Use OPC, 0.5 w/c, 4 hours of hydration. Imaging conditions and sample preparation are given in [3].



Figure 3 – High magnification image showing details of pore structure. Pit bottoms are concave and no evidence of etch pits are seen. St. Lawrence (now Holcim Canada) General Use OPC, 0.5 w/c, 3 hours of hydration. Imaging conditions and sample preparation are given in [3].



Figure 4 – Surface of OPC showing areas of intact surface (asterisks) and pore structures that appear to connect below the surfaces. Lafarge General Use OPC, 0.5 w/c, 6 hours of hydration. Imaging conditions and sample preparation are given in [3].



Figure 5 – Different alite surface structures during the induction period. Ettringite prisms can be observed, but no evidence of C-S-H formation is present on the rough surfaces. St. Lawrence (now Holcim Canada) General Use OPC, 0.5 w/c, 1.5 hours of hydration. Imaging conditions and sample preparation are given in [3].