Discussion

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

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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 Fig. 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] Fig. 7 and an earlier work by Ménétrier et al. [6], and in the presence of synthetic C−S−Hs (Fig. 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 Fig. 7 and the images in Makar, Esseghaier and Chan [2] is difficult to make due to potential differences in the C_3S 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 (Fig. 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 (Fig. 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. Fig. 8 in Makar and Chan [3], repeated here with additional annotation as Fig. 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_3S [2] and OPC [3]. Classical C–S–H, of the type shown in Fig. 21b in Juillard et al. [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 (Fig. 6b in Ref. [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