Cement and Concrete Research 41 (2011) 568–569

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Discussion

Reply to the discussion by J. Makar, J.J. Beaudoin, T. Sato, R. Alizadeh and L. Raki of "Dissolution theory applied to the induction period in alite hydration"

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ARTICLE INFO

Article history:
Received 24 January 2011
Accepted 25 January 2011

We thank Dr. Makar et al. for their contribution to the discussion [1] of the early age hydration mechanisms proposed in our paper [2]. The main argument in their discussion seems to be that some of the aspects of dissolution by pit formation are more complex than we described in the original paper. This may indeed be true, but we see no justification for then claiming that early hydration must therefore be controlled by the formation of a barrier layer, especially as their own images show absolutely no evidence of such a layer, in spite of their very high resolution.

The main arguments in the discussion are:

1. Etch pits are only seen at the end of the induction period
2. The density of dislocations in alite is too low for the pits to originate at dislocations
3. Later when the pits enlarge, this occurs at the sides rather than the base as might be expected if they form at dislocations.
4. Rather than pit formation in the mineral alite, the objects seen are holes in a barrier membrane

1. Etch pits are only seen at the end of the induction period.

In pastes with a low water to cement ratio, the period in which the solution is undersaturated is much shorter compared to more dilute systems, therefore any etch pits formed in pastes will be very small, much smaller than in dilute solutions where they have more time to develop. Such very small pits can indeed be identified on the right hand side of the grain of the picture 5 provided by Makar and co-workers [1]. In addition to that, experiments performed by Ménétrier and co-workers show dissolution features after 5 minutes of hydration for paste having a water to cement ratio of 1.

2. The density of dislocations in alite is too low for the pits to originate only at dislocations.

Hudson and Groves [3] were not able to determine the dislocation density by TEM which normally implies a low dislocation density, but densities as high as 10^{11} cm/cm^3 have been achieved in minerals such as shocked loaded rutile [4] and strained calcite specimen [5], so similar densities might be expected for ground alite. Nevertheless, we agree that the dislocation density in alite will be much lower than in cold worked metal. However dislocations are not the only crystalline possible defaults and it is very likely that other types of structural defects such as vacancies, stacking faults, impurities, twinning and grain boundaries constitute reactive sites that could contribute to the formation of pits.

3. The inverse pyramidal structure typical of an etch pit was not identified and the surface appears more resistant than the interior of the material.

There are other examples showing flat bottom pits in minerals, which are well known to follow the defect related dissolution mechanisms ascribed to alite in our paper. Fig. 1 shows dissolution pits for dolomite [6] having also a very irregular morphology. The pits dissolve most at the edges where dissolution is facilitated due to a higher kink density.

It is also not possible to say from SEM images of different samples at different times that the surface is less dissolved. Once pit formation becomes limited, step retreat dominates dissolution. Step retreat leaves a smooth, apparently unattacked surface and may also remove small pits [7].

4. Rather than pit formation in the mineral alite, the objects seen are holes in a barrier membrane

Makar and co-workers claim elsewhere that the objects we call pits are in fact pores forming in a protective membrane [8]. We disagree with this interpretation for three reasons:

a) The similarity of the features to pit formation in other minerals, where it is known that a protective membrane does not form.
b) The similarity of these features in alite hydrating in paste or in dilute suspension and the ones of Sakurai and co-workers which were treated in a special etchant composed of 0.4% HF with 0.6% HNO_3 in ethyl alcohol [9]. In the later case, no hydration is taking place but the surface still exhibits the same type of pitted area. It is

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doi:10.1016/j.cemconres.2011.01.021

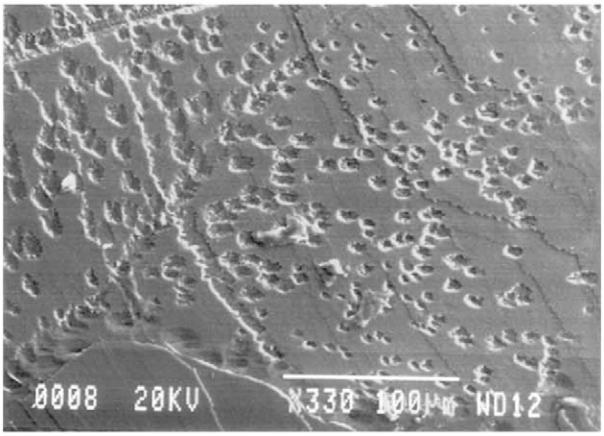

Fig. 1. SEM microphotograph of etch pits on dolomite surfaces [6].

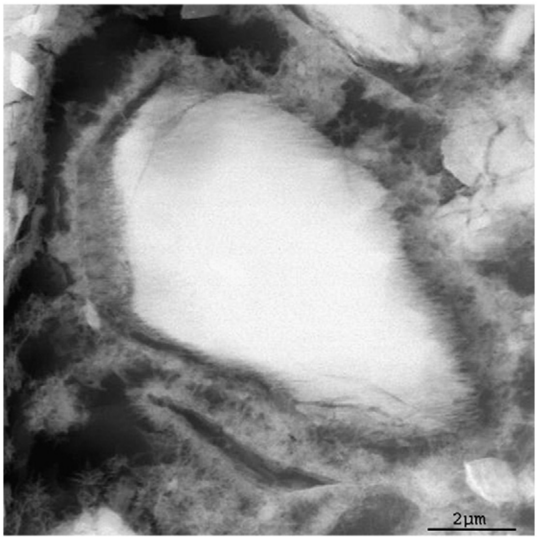

Fig. 2. TEM images of alite grains hydrating in cement paste for 18 hours [10].

therefore a particular feature of the crystal to produce such a morphology of pits and it is not likely to be related to a pore structure of some early hydration product.

c) TEM images of alite hydrated for several hours [10] show also a clear crystallographic orientation of alite consumption, which shows again the importance of the crystal structure and of the defects therein (see Fig. 2).

Furthermore the images of Makar and co-workers and of many other researchers clearly show the presence of a spiky, fibrous C-S-H from very early ages, it would seems unlikely that two C-S-H type products with very different morphologies (one spiky and one a continuous membrane) would form under the same conditions.

To conclude our hypothesis proposes

1. Upon initial exposure to water a process of dissolution of the alite surface starts at vacancies, stacking faults, dislocations, grain boundaries or other types of structural defects, which may lead to the formation of etch pits. Since the period of high undersaturation conditions is very short, the pits do not have enough time to grow. They remain very small and soon shut off due to the build up of concentration in solution. Small pits may even disappear due to step retreat.
2. Primary hydrates precipitate but not as a continuous layer. Due to the drop in undersaturation, the dissolution slows down and proceeds by step retreat until the end of the induction period.
3. At the end of the induction period, rapid growth of C-S-H and calcium hydroxide starts, which lowers the local saturation level in solution due to the build up of concentration gradients and so the growth of pits restarts. The reasons for this onset of rapid growth remains unclear, but may be related to the polymerisation of silicate monomers and formation of a stable form of C-S-H.

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