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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"

Patrick Juilland [a,*], Emmanuel Gallucci [a], Robert J. Flatt [b], Karen L. Scrivener [c]

[a] Sika Technology AG, Tüffenwies 16, CH-8048 Zurich, Switzerland
[b] ETHZ-IfB, Laboratory of Physical Chemistry of Building Materials, Schafmattstrasse 6, CH-8093 Zurich, Switzerland
[c] EPFL-STI-IMX ,Laboratory of Construction Materials, Station 12, CH-1015 Lausanne, Switzerland

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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

* Corresponding author. Tel.: +41 58 436 42 83.
E-mail address: juilland.patrick@ch.sika.com (P. Juilland).

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