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Discussion

Reply to the discussion by E. Gartner of the paper "Dissolution theory applied to the induction period in alite hydration"

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We thank Dr. Gartner for his comments [1] on our paper [2]. Our answers are grouped below in 4 main parts:

1) In his discussion, Dr. Gartner reports that alite should lie in the category of moderately soluble salts. We agree with him and the report of the most recent K_{SP} value of $1.14 \cdot 10^{-4}$ by Damidot et al. [3] which actually places alite in the range of materials which might have a dissolution rate either controlled by transport (diffusion) or by surface reactions [4].

In our recently submitted article [5] which investigated the influence of mixing on the early hydration of cementitious systems, we report that the alite hydration rate is sensitive to mixing when deionized water is used, whereas this is not the case if the starting solution is already saturated with lime.

These differences enable us to refine our model by proposing a transition from transport to surface reactions limited kinetics before the onset of the acceleratory period. However, these new insights do not change our position regarding the role of dissolution as a controlling parameter during the very early hydration but only show that during the fast dissolution regime (taking place by pitting at crystallographic defects) the kinetics are limited by the diffusion of the dissolved ions from the surface to the bulk solution. As the undersaturation decreases, the concentration gradient between the surface and the bulk solution diminishes and diffusion does not limit the rate of dissolution anymore. The rate then becomes limited by surface reactions, taking place by step retreat at pre-existing roughnesses.

It therefore appears that the rates of dissolution using deionized water reported in the literature would be strongly dependent on the experimental conditions. Consequently, it is not surprising that the rate of dissolution measured in highly agitated dilute suspensions with pure water would be much higher than for low alite to water ratios. In the first case ions can quickly move away from the dissolving surface; whereas in pastes there is a fast build up of ions throughout the solution, limiting the dissolution rate.

Dr. Gartner also reports in his discussion that the rate stays at a relatively low value for only a short time (the induction period) except in cement pastes that are chemically retarded. This is not true in the case of the annealed experiments presented in Fig. 12 of [2] where the induction period lasts for several hours without being chemically retarded. This evidence of the role of the crystallographic defect density on the kinetics of hydration is not considered by Gartner and is difficult to interpret with the protective membrane theory.

2) The high undersaturation of −43 calculated in [2] is strongly dependent of the K_{SP} value used. In this calculation, we used the value of 3 proposed almost 40 years ago by Stein [6]. However, if the more recently reported value of $1.14 \cdot 10^{-4}$ is used, this undersaturation drops to the range of −33 to −29 which is relatively close to the value calculated by Gartner using a free energy approach (−28) [7]. Dr Gartner also reports that the free energy of solution of −70 kJ/mol-C_3S leads to an undersaturation of the liquid phase with respect to C_3S over 12 orders of magnitude. This is comparable to that for smectite, for which the undersaturation of the liquid phase at which the dissolution drastically decreases is on the order of 14 by following the same free energy approach (−7 kJ/mol-O [1] and accounting for 12 O atoms). A very wide range of values are found for natural mineral: including 14

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for smectite; 5 for feldspars and 0 for gibbsite, so the values for alite are by no means anomalous.

The solid–liquid interfacial energy value of 1 J m^{-2} back-calculated from an undersaturation of -43 using Eq. (5) in [2] reduces to 0.92 and 0.87 J m^{-2} with the new range of undersaturation of -33 to -29. These new values of liquid–solid interfacial energies nevertheless remain relatively high (by a factor of about 8) compared to natural minerals. These high values could be related to the fact that alite is a mineral synthesized at, and only stable at, high temperatures.

In any case these values are only estimates as they are calculated with parameters such as the Burger vector and the shear modulus taken from albite as no experimental values are available for alite. Furthermore, this approximation only holds for pit nucleating at dislocations since the energetic contribution of the strain field around the dislocation is estimated by $\alpha G\vec{b}^2$ [8]. Better values of alite-pore solution interfacial energy could maybe be obtained using molecular dynamic simulation.

Dr. Gartner also remarks that the rate of dissolution increases during the acceleration period while the pore solution concentration remains more or less unchanged. After the end of the induction period the rate of reaction is no longer controlled by the solution concentration, but by the growth of hydrates which removes ions from solution immediately after they are provided by alite dissolution.

3) Another aspect brought up by Dr. Gartner concerns the normalization of the dissolution rates in terms of oxygen atoms. While as we recognize that normalizing dissolution rates by the molecular weight as originally proposed is not ideal, it is the most commonly approach still adopted in the literature.

4) Finally, our dissolution theory was proposed based on experimental evidence showing morphological features as well as the dependence of the alite dissolution rate on the solution undersaturation in a similar way to the one observed for natural minerals. This theory should of course be refined and there is still a need for further understanding to elucidate the details of the different processes. We have done our best to introduce semi-quantitative arguments to help the discussion, but we re-emphasize that in doing so, many parameters could only be estimated. We hope that research advances in this area will bring better data on these parameters to help advance the debate on the subject of cement hydration.

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