Discussion

Discussion of the paper "Dissolution theory applied to the induction period in alite hydration" by P. Juilland et al., Cem. Concr. Res. 40 (2010) 831–844

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ABSTRACT

The new mechanism proposed by Juilland et al. [1] to explain the induction period in alite hydration is discussed with reference to the free energy of dissolution under typical hydration conditions calculated from published data. It is concluded that the proposed mechanism is theoretically possible but requires an unusually high interfacial energy for step formation, plus an unusually large increase in dissolution rate over small changes in the degree of solution undersaturation, compared to typical published values for silicate minerals. It is suggested that comparisons with the hydration rates of CaO and MgO might shed further light on the mechanism.

1. Introduction

In a recent paper, [1], Juilland et al. propose a new mechanism to explain the onset of the induction period in alite hydration. This mechanism is based on recent advances in the theory of dissolution kinetics applied to common (mainly silicate) minerals [2,3]. I congratulate Juilland et al. for drawing the attention of the cement research community to these advances, which are certainly of potential relevance to understanding the hydraulic reactivity of cement phases. However, I am not yet convinced by the specific mechanism that they propose to explain the induction period in alite hydration, for reasons detailed subsequently.

2. Discussion

As is well known, alite (impure tricalcium silicate, "C₃S") is the major phase in Portland cement and its reactions with water dictate most of the properties of such cements. Maximum measured alite solubility rates (e.g. in highly agitated dilute suspensions in pure water) are at least 10^{-5} mol·m^{-2}·s^{-1} [4,5]. However, at the low water/alite ratios typical of most cement applications, the rate is observed to fall very rapidly to values below 10^{-8} mol·m^{-2}·s^{-1}, [5], i.e. a decrease in rate by a factor of about 1000. The rate stays at this relatively low value for only a short time (the "induction" period) except in cement pastes that are chemically retarded, and then increases again during the acceleratory period, typically to values of the order of 10^{-7} mol·m^{-2}·s^{-1} in the absence of chemical accelerators, and never above 10^{-6} mol·m^{-2}·s^{-1} even with strong chemical acceleration (e.g. in solutions of salts such as CaCl₂). Thus, the rate remains at least an order of magnitude less than the maximum rates observed in very dilute systems.

The maximum solubility rate of alite is only about a factor of five less than that of gypsum, putting alite in the category of moderately soluble salts for which bulk diffusion and surface kinetics compete for overall rate control under typical experimental conditions [6]. It therefore lies in-between very poorly soluble minerals, (such as many silicate rocks, for which the recent rate theories were developed, and which typically display maximum solubility rates well below 10^{-8} mol·m^{-2}·s^{-1} [2,3]), and simple 1:1 ionic salts such as NaCl, which can have solubility rates as high as 0.1 mol·m^{-2}·s^{-1} [7]. (Note: this comparison refers to rates of dissolution in pure water at close to ambient temperatures).

Juilland et al. [1] propose that the large difference in alite solubility rate between the rapid initial dissolution and the induction period can be explained by the difference in the free energy of solution as the aqueous phase becomes closer to alite saturation. They make use of the theory of Lasaga and Luttge [2] to explain the rate increase due to step propagation away from existing defects at moderate solution undersaturation levels, and the "vacancy island" theory of Dove et al. [3] which allows for even higher rates at higher undersaturation levels. Lasaga and Luttge's theory had previously been applied to mineral phases of very low solubility and low dissolution rate, such as feldspars and clay minerals, where increases in rate from the slow regime to the rapid dislocation-dominated regime were typically about one order of magnitude, as shown in Fig. 5 of Ref. [2], (reproduced also as Fig. 6 in Ref. [1]). It is difficult to compare solubility rates on a molar basis for minerals of very different composition and molar volume, so I have instead used the oxygen atom content to compare them in Table 1. I believe that this should provide a better comparison than "molecular weight," since all are oxides or hydroxides, and oxygen atom packing densities in such

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