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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, “C_3S”) 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 $10^{-5}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ [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 $10^{-8}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}$, [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 $10^{-7}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ in the absence of chemical accelerators, and never above $10^{-6}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ even with strong chemical acceleration (e.g. in solutions of salts such as $CaCl_2$). 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 $10^{-8}\ \mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ [2,3]), and simple 1:1 ionic salts such as NaCl, which can have solubility rates as high as 0.1 $\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ [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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Table 1
Summary of reported experimental solubility rate data for four minerals (from [2]).

Mineral	Assumed formula	T,°C	pH	Maximum rate,[a]	ΔG_{soln} at inflection
				$mol\text{-}O\cdot m^{-2}\cdot s^{-1}$	point, kJ/mol-O
Smectite	$NaAl_3Si_3O_{10}(OH)_2$	80	3	1.0×10^{-10}	−7
Albite	$NaAlSi_3O_8$	80	8.8	2.8×10^{-10}	−4
Labradorite	(mol with 8O)[b]	25	3	1.6×10^{-10}	−4
Gibbsite	$Al(OH)_3$	80	3	1.5×10^{-9}	−0.3

[a] This is the maximum rate shown in the graphs in Fig. 5 of [2]; higher rates might be obtained under different conditions, but this value is useful for comparison.

[b] Labradorite refers to solid solutions (1:1 to 3:7) between albite and anorthite ($Ca_2Al_2Si_2O_8$) and I have assumed here that the formula used in [2] had eight oxygen atoms per molecule.

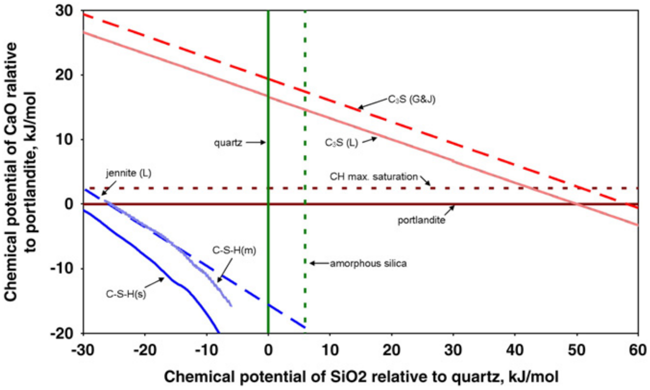

Fig. 1. Chemical potential diagram showing key phases relevant to C_3S hydration at 25 °C. The chemical potentials of CaO and SiO_2 are shown relative to portlandite and quartz, respectively, while the chemical potential of water is held constant at the value of pure liquid water at 25 °C, (i.e. the graph can be considered to be a projection onto the water plane), which is a reasonable approximation for alite hydration. The dashed line above the horizontal portlandite saturation line represents the typical maximum saturation level of calcium hydroxide observed in ordinary cement or alite pastes. Two lines are shown for C_3S; one using the data from [8] (G and J) and the other using data from [9] (L). Three curves are shown for different forms of "C-S-H"; the two curves from [8], C–S–H(m) and C–S–H(s), plus the line for jennite from [9] (L). All data from [9] were positioned relative to portlandite and amorphous silica data as also given in that paper, although it is not certain that the amorphous silicas cited in Refs. [8,9] are identical, which may lead to slight positioning errors. Typical error ranges for data are estimated to be about ± 2 kJ/mol for each axis.

minerals are usually fairly constant, whereas the "molecular weight" is somewhat arbitrary. The level of undersaturation at which the solubility rate increases rapidly (the "inflexion point") is expressed in terms of the free energy of solution (ΔG_{soln}) per gram-atom of oxide (mol-O). It is about −7 kJ/mol-O for smectite and −4 kJ/mol-O for both feldspars, but only about −0.3 kJ/mol-O for gibbsite. The maximum solubility rates measured at high undersaturations for the smectite and both feldspars are very close (especially if one considers the temperature and pH differences of the experiments) at about 10^{-10} $mol\text{-}O\cdot m^{-2}\cdot s^{-1}$, but the maximum measured rate for gibbsite is about an order of magnitude higher, perhaps because it is a hydroxide rather than an oxide. There is of course no minimum rate, as the rate must inevitably tend to zero as ΔG_{soln} approaches zero.

The "vacancy island" theory of Dove et al. [3] is capable of explaining larger dissolution rate increases than Lasaga and Luttge's theory, as observed for certain minerals, (e.g. quartz dissolving in hot salt water). For reasons not fully explained, fairly modest salt concentrations (e.g. 0.05 M NaCl) lead to major increases in the maximum solubility rate of quartz, increasing from about 10^{-8} $mol\text{-}O\cdot m^{-2}\cdot s^{-1}$ to as much as 10^{-6} $mol\text{-}O\cdot m^{-2}\cdot s^{-1}$ (but note that this is at 200 °C). The range of undersaturations (σ) over which these rate increases manifest themselves is from −0.2 to about −3. Since, by definition, $\Delta G_{soln} = RT\sigma$, this range runs from about −0.4 to −6 kJ/mol-O at 200 °C.

The maximum solubility rates measured for C_3S or alite samples at ambient temperatures, converted to an oxygen atom basis for comparison with the data in Table 1, are at least 3×10^{-5} $mol\text{-}O\cdot m^{-2}\cdot s^{-1}$, i.e. about four orders of magnitude higher than the maximum rate shown for gibbsite in Ref. [2]; indeed, even the lowest rate of dissolution of alite during the induction period is an order of magnitude higher than the maximum rate reported for gibbsite. In order to determine the degree of alite undersaturation during the various stages of hydration, I prefer to use a chemical potential diagram, as first shown in Ref. [8], rather than the "solubility product" approach used by Juilland et al. [1] I believe it to be more accurate because all of the data are directly related to the free energies of formation of the compounds. Fig. 1 shows a revised version of the original diagram from Ref. [8] with additional data from Ref. [9] for another C_3S sample plus jennite (shown as C–S–H(J)). The aqueous phase at the end of the induction period is typically slightly supersaturated ($\sigma\approx+1$) with respect to portlandite. This is shown as a dashed horizontal line just above the portlandite abscissa. The free energy of dissolution of C_3S in such a solution can be found by measuring the distance parallel to the abscissa between the point where the C_3S curve crosses the portlandite supersaturation line to the point where the same line crosses the solubility curve for the form of C–S–H (referred to as "C–S–H(m)") thought to be in equilibrium with the aqueous phase at early ages, [8], and which, at high calcium hydroxide concentrations, also seems to coincide closely with the line for jennite ($C_{1.67}SH_{2.1}$) from Ref. [9]. By this approach, the free energy of solution calculated is more negative than −70 kJ/mol-C_3S (i.e. -14 kJ/mol-O), implying an undersaturation of the liquid phase with respect to C_3S of over 12 orders of magnitude ($-\sigma>28$). (But note that this is significantly less negative than the range of σ (−38 to −43) estimated by Juilland et al. [1] using a "solubility product" approach). In order to explain such high critical undersaturation values for alite, Juilland et al. [1] were obliged to assume a value of about 1 J/m² for the interfacial energy for step creation, α, which dictates the onset of the increase in dissolution rate either due to dislocations or to vacancy islands. This is in contrast with α values well below 0.1 J/m² for several typical silicate minerals calculated by Dove and Han [10]. But it is not only the high critical undersaturation value that is surprising in Juilland et al.'s explanation; it is also the fact that, during the acceleratory period, the rate of dissolution of alite increases typically by more than one order of magnitude, while the solution composition apparently changes very little (portlandite supersaturation decreases significantly, but the solution composition remains on the "C–S–H(m)" curve, [8], so this has little effect on the value σ with respect to alite, as can be seen clearly in Fig. 1, taking into account that one mol of alite contains one mol of SiO_2). The hypothesis of Juilland et al. thus implies that, by pure chance, the critical undersaturation for the onset of rapid alite dissolution happens to coincide with the point where the solution is close to equilibrium with portlandite and "C–S–H(m)". To me, this seems to be too much of a coincidence to be likely. Clearly, both the magnitude of the rate change and the very high degree of undersaturation at which it is proposed to occur are far outside the range for which either the theory of Lasaga and Luttge or the theory of Dove et al. has been experimentally validated, and I am aware of no theoretical reason to expect such dramatic changes in solubility rate at such high undersaturations. Moreover, it appears that alite dissolution, even during the induction period, is always far more rapid (at close to ambient temperatures) than the dissolution rates of any of the minerals analyzed by Lasaga and Luttge [2] or Dove et al. [3,10], which is another reason to doubt the applicability of that theory in this case.

I therefore contend that the hypothesis of Gartner and Gaidis [4], that a hydrated phase on the surface of alite is responsible for controlling its solubility rate during the induction period, still seems a more plausible explanation. Although they used the terminology "C–S–H(m)" to describe this superficial phase, this was never meant to imply that it was necessarily structurally related to the ordinary stable C–S–H of hydrated cement systems. In fact, one can argue that it is likely to be very different from the normal C–S–H because, in order to bind reasonably strongly to the alite surface (as is necessary to explain its effectiveness as a retarding surface hydrate) it is likely that the phase has a structure much closer to that of C_3S itself. This seems possible if it is created by a mechanism such as simple proton–calcium exchange at the surface, i.e. by replacing some of the calcium ions with proton pairs, which could give, for example, a hydrate of composition $Ca_2(HSiO_4)(OH)$. Such proton–metal ion exchange processes are commonly believed to occur as important steps in the dissolution of many mineral phases, [11], and, in the event that one of the intermediate structures produced happened to be relatively stable when bonded to the surface of the anhydrous phase, it is not inconceivable that it could persist as a surface layer of sufficient thickness and stability to dominate the hydration kinetics and solution equilibria of the underlying anhydrous phase. This hypothesis is consistent with the observation of hydrated silicate monomers at early ages during the hydration of ultrafine C_3S [12], and could also help to explain why vapour-phase hydration of alite tends to retard its later hydration in liquid water, rather than to accelerate it (by producing C–S–H nuclei) as would seem likely if the hydrates formed by vapour-phase hydration were not strongly bound to the alite surface. Note also that a similar surface hydration process may help to explain why other highly basic oxide minerals, such as, for example, MgO, and even CaO, also dissolve relatively slowly in water. It seems to me that the study of the hydration mechanisms of these two simple oxides could well provide valuable insights that might help to confirm or refute the validity of the approach of Juilland et al.

References

[1] P. Juilland, E. Gallucci, R. Flatt, K. Scrivener, Dissolution theory applied to the induction period in alite hydration, Cem. Concr. Res. 40 (2010) 831–844.

[2] A.C. Lasaga, A. Lüttge, Variation of crystal dissolution rate based on a dissolution stepwave model, Science 291 (2001) 2400–2404.

[3] P.M. Dove, N. Han, J.J. De Yoreo, Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behaviour, PNAS 102 (43) (2005) 15357–15362.

[4] E.M. Gartner, J.M. Gaidis, Hydration mechanisms, I, in: J.P. Skalny (Ed.), The Materials Science of Concrete, I, American Ceramic Society, 1989, pp. 95–125.

[5] E.M. Gartner, J.F. Young, D.A. Damidot, I. Jawed, Hydration of Portland cement, Structure and Performance of Cements, 2nd edition, Spon Press, 2002.

[6] J. Colombani, J. Bert, Holographic interferometry study of the dissolution and diffusion of gypsum in water, Geochim. Cosmochim. Acta 71 (2007) 1913.

[7] M. Alkattan, E.H. Oelkers, J.-L. Dandurand, J. Schott, Experimental studies of halite dissolution kinetics. 1. The effect of saturation state and the presence of trace metals, Chem. Geol. 137 (1997) 201–219.

[8] E.M. Gartner, H.M. Jennings, Thermodynamics of calcium silicate hydrates and their solutions, J. Am. Ceram. Soc. 70 (1987) 743–749.

[9] B. Lothenbach, T. Matschei, G. Möschner, F.P. Glasser, Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement, Cem. Concr. Res. 38 (2008) 1–18.

[10] P.M. Dove, N. Han, Kinetics of mineral dissolution and growth as reciprocal microscopic surface processes across chemical driving force, AIP Conference Proceedings, 916, 2007, pp. 215–234.

[11] J. Schott, R.A. Berner, E.L. Sjoberg, Mechanism of pyroxene and amphibole weathering—I. Experimental studies of iron-free minerals, Geochim. Cosmochim. Acta 45 (1981) 2123–2135.

[12] F. Bellmann, D. Damidot, B. Möser, J. Skibsted, Improved evidence for the existence of an intermediate phase during hydration of tricalcium silicate, Cem. Concr. Res. 40 (2010) 875–884.