



## The di- and tricalcium silicate dissolutions



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### ABSTRACT

In this study, a specially designed reactor connected to an ICP spectrometer enabled the careful determination of the dissolution rates of C<sub>3</sub>S, C<sub>2</sub>S and CaO, respectively, over a broad range of concentration of calcium and silicates under conditions devoid of C–S–H. The kinetic laws, bridging the dissolution rates and the undersaturations, were obtained after extrapolation of rate zero allowing the estimation of the true experimental solubility products of C<sub>3</sub>S ( $K_{sp} = 9.6 \cdot 10^{-23}$ ), C<sub>2</sub>S ( $K_{sp} = 4.3 \cdot 10^{-18}$ ) and CaO ( $K_{sp} = 9.17 \cdot 10^{-6}$ ). The latter are then compared to the solubilities calculated from the enthalpies of formation. We propose that the observed deviations result from the protonation of the unsaturated oxygen atoms present at the surface of these minerals. Hydration rates measured in cement pastes or in C<sub>3</sub>S pastes are in excellent agreement with the kinetic law found in this study for C<sub>3</sub>S under conditions undersaturated with respect to C–S–H.

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### 1. Introduction

Tricalcium and dicalcium silicates (also known as C<sub>3</sub>S and C<sub>2</sub>S, respectively, in cement notation) represent about 75% of an ordinary Portland cement. They react with water through a dissolution–precipitation process, which leads to the precipitation, firstly, of calcium silicate hydrate, and secondly, of calcium hydroxide (Portlandite). Calcium silicate hydrate (so-called C–S–H) is the main hydrate responsible for the cohesion in cement binders [1] also investigations of the calcium silicates hydration in the last decades were of high importance in order to improve the properties of concrete. In general terms, we have to admit that the development of dissolution theories received significantly less attention in comparison with its counterpart, the crystal growth. In the field of cement, the nucleation and growth of C–S–H were comprehensively investigated whilst there are only few studies of the dissolution of C<sub>3</sub>S and none on C<sub>2</sub>S until today. Dissolution of calcium silicates was seldomly studied due to an experimental hurdle and also its quasi absence in nature. The experimental hurdle is connected to the much greater solubility of C<sub>3</sub>S compared to C–S–H. Indeed, only a very tiny quantity of dissolved tricalcium silicate is needed for the precipitation of C–S–H to occur, which impedes a measurement of the solubility of C<sub>3</sub>S under saturated conditions. This issue has therefore prevented the measurement of the solubilities of both these anhydrous calcium silicate phases until now. The lack of information about the dissolution behavior of C<sub>3</sub>S/C<sub>2</sub>S has consequently led to the proposition of various models describing their hydration based solely

on the growth of C–S–H [2–5]. Unsurprisingly, it was recently demonstrated that the dissolution should be taken into account for correctly modeling the hydration of tricalcium silicate [6].

Contrary to these two anhydrous cement phases, natural silicates have been the object of thorough investigations regarding their mode of dissolution in order to predict the evolution of complex geochemical systems. In this quest, one requirement is to quantitatively predict the dissolution kinetics of minerals, hence the need for bridging thermodynamics and kinetics. The driving force for dissolution is undersaturation, i.e. the deviation between the solubility and the ion activity of constituents of the mineral in solution. Crystal dissolution (like its counterpart crystal growth) proceeds through the transport of water and dissolution products to and from the crystal surface where reactions occur. The dissolution is then the resulting process of interfacial reactions and all transport phenomena but the overall rate is always limited by the slowest event, i.e. either the transport or one of the surface reactions. In the possible event of a limitation by a reaction, it makes sense to consider the corresponding chemical equilibrium:



and to calculate the deviation from equilibrium, i.e. the Gibbs free energy change

$$\Delta_{\text{diss}} G = \Delta_{\text{diss}} G^0 + RT \ln(A)^x (B)^y \quad (2)$$

where (A) and (B) are the activities of A and B in the solvent, R the gas constant and T the temperature.

The rate of dissolution should follow a general law such as:

$$\text{Rate} = k \cdot S_{\text{reac}}(t) \cdot f(\Delta G) \quad (3)$$

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with  $k$  being the rate constant,  $S_{\text{reac}}$  the reactive surface area and  $f$  a priori unknown function of the free enthalpy. The plot of the interfacial experimental dissolution rates against the free enthalpy change over a very broad range of undersaturation generally leads to such a sigmoidal graph as represented in Fig. 1 [7–11] showing three different kinetic domains.

First developments related to dissolution kinetics were derived from the transition state theory (T.S.T.) developed by Eyring. The system has to overcome an energy barrier due to the formation of an activated complex. Considering that the rate-law is limited by this formation, the overall interfacial rate law may be written as follows [12,13]:

$$\text{Rate}_{\text{interfacial}} = A \cdot \left( 1 - \exp\left(\alpha \frac{\Delta G_{\text{diss}}}{RT}\right) \right) \quad (4)$$

where  $A$  and  $\alpha$  are general constants,  $\Delta G$  is the Gibbs free energy associated with the dissolution reaction, and  $R$  the gas constant. However, a true T.S.T. model implies ignoring all crystal surface features and considering an amorphous-like surface which is rarely the case in natural systems. With the law expressed above (Eq. (4)), it is not possible to correctly fit such an S-curve presented in Fig. 1. Despite the fact that a unique theoretical description of  $f(\Delta G)$  over the entire range of  $\Delta G$  is still under debate, we will strive to describe the curve in Fig. 1, starting and deviating from the equilibrium, from a phenomenological point of view:

**Domain III:** In this part, a slow evolution of the dissolution rate with the free enthalpy is usually observed. At the solubility equilibrium,  $\Delta G=0$ , the rate is zero. The rate increases with the decrease of  $\Delta G$ . When the free enthalpy is sufficiently low, smaller than  $\Delta G_{\text{crit}}$  (see below), another mechanism occurs. Lasaga et al. [14] proposed that the dissolution occurs by step-waves emanating from surface defects. Train of steps originating at the outskirts of etch pits causes the retreat of the overall crystal surface layer by layer. This theory was developed as the counterpart of the B.C.F. (Burton–Cabrerá–Frank) theory for the crystal growth. The defects outcropping at the surface, source of these stepwaves and thus of mass removal are preferential sites of dissolution if the free energy  $\Delta G_{\text{nucleation}}(r)$  for the nucleation of a dissolution hole of radius  $r$  is reached:

$$\Delta G_{\text{nucleation}}(r) = \frac{\pi r^2 \cdot h}{V_m} \left[ \Delta G_{\text{diss}}^{\frac{1}{2}} \right] + 2\pi r \cdot h \cdot \sigma. \quad (5)$$

With  $h$  the depth of the hole,  $\sigma$  the surface free energy,  $V_m$  the molecular volume, and  $v$  the number of molecules per formula unit of the dissolving phase. Similarly, as for the crystal nucleation,

a hole of dissolution is only initiated if the critical size  $r^*$  is reached, or in other words if  $\Delta G_{\text{diss}} \leq \Delta G_{\text{crit}}$ :

$$r^* \approx - \frac{\sigma \cdot V_m}{\left[ \Delta G_{\text{diss}}^{\frac{1}{2}} \right]}. \quad (6)$$

The critical size is proportional to the surface energy. Moreover, the closer the system is from equilibrium, the larger the value of  $r^*$  is for the initiation of a dissolution hole.

**Domain II:** Domain II is placed between domains I and III and is usually difficult to characterize since it lies between two steady-state mechanisms and does not represent a steady-state itself [15]. In this part, the distance from equilibrium is superior to the critical energy barrier ( $\Delta G_{\text{diss}} < \Delta G_{\text{crit}}$ ) to surmount for the opening of “hollow cores”. For instance, screw dislocation pits will open up. A kinetic theory embodying the linear dependence with the undersaturation and the opening of crystal defects has been proposed by Lasaga et al. [14]. The model describes the bivalent role of etch pits being (1) themselves major sites of dissolution and (2) the source of dissolution steps. As it is depicted in Fig. 1, the switch between the two mechanisms can lead to a difference in the dissolution rate up to 1–2 orders of magnitude [16].

**Domain I:** (called dissolution plateau). The system is extremely far from equilibrium and the rate is quasi-independent of the undersaturation; it is often referred to the “distilled water” case. The scope of studies has been limited in this case to variables such as the ionic strength and the temperature. In this domain, the surface reaction is very fast and maybe faster than the molecular diffusion. In this case, the dissolved species would be depleted close to the surface, and the dissolution rate may be influenced by the transport of these species from the interface to the bulk.

The few previous studies seem to indicate that the dissolution of tricalcium silicate behaves similar to other natural silicates [17,18]. These ones are praiseworthy for shedding light on the dissolution of this phase with the usual concepts developed in geochemistry. First indications showing a strong dependence of the dissolution rate of tricalcium silicate on the undersaturation have been revealed. Moreover, as seen also in many other natural systems, the dissolution of tricalcium silicate is accompanied by the formation of etch pits, often identified by microscopy (see Fig. 2 for examples).

The present paper is mainly centered on pursuing the bridging between the dissolution kinetics and the solution chemistry as well as assessing more quantitatively the relevance of the undersaturation in dissolution kinetics of calcium silicates. From the kinetic point of view, the problem of the C–S–H precipitation is tackled in this work through the use of a specially designed reactor linked to an ICP spectrometer enabling the investigations of ultra-diluted suspensions. By doing so, the suspensions of calcium silicates are never supersaturated with respect to C–S–H during the time of experiment and the true dissolution rates are determined. From the thermodynamic point of view, the solubilities of  $C_3S/C_2S$  have never been experimentally determined but only calculated from thermodynamical data. Due to a difference of many orders of magnitude between the alite dissolution rate in pure water and in typical cement pore solutions, some recent controversial debates arose about the apparent solubilities and the calculated ones [18–20]. Provided with this new experimental set-up, it is possible to extrapolate a rate law at rate zero, i.e. when equilibrium should be matched and then to determine experimentally the standard free enthalpy of dissolution. The original discrepancy between the apparent and calculated solubilities will be discussed under the light of our experiments. Finally, we will discuss the open questions about the kinetics of early hydration of tricalcium silicate.

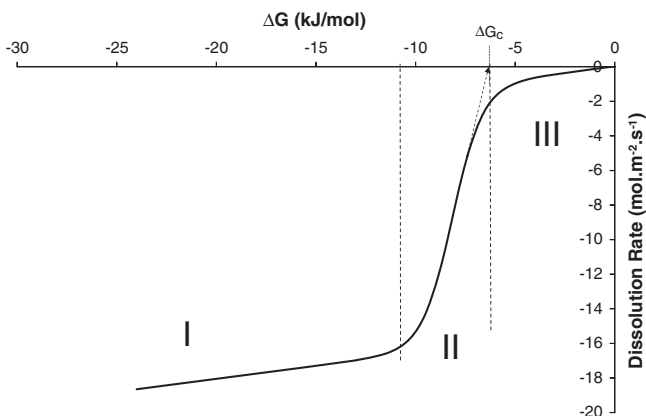


Fig. 1. Typical evolution of the dissolution rate of a mineral according to the Gibbs free energy of dissolution. Three domains can be usually recognized (see text).

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