MODELING OF THE EFFECT OF ELECTROLYTES ON THE RATE OF EARLY HYDRATION OF TRICALCIUM SILICATE

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Abstract

The hydration of the phases contained in hydraulic binders such as tricalcium silicate (C₃S) in Portland cement proceeds through a dissolution-precipitation process as explained a long time ago by H. Le Chatelier [1]. The global kinetics of hydration of C₃S in water or in electrolytes has been extensively studied by numerous experimental techniques. However less attention has been devoted to study the dissolution of C₃S as periods, where only dissolution occurs, are difficult to study due to the very rapid precipitation of hydrates. Thus a specific device has been developed to measure the average dissolution rate of C₃S paste in several electrolytes. From these experimental data, it was possible to define the parameter of Lasaga’s equation and to model the dissolution rate of C₃S in different electrolytes. The simulation was quite accurate at the exception of saturated lime solution. For this later case an additional mechanism is expected to restrict the dissolution rate.

1. INTRODUCTION

The hydration of the phases contained in hydraulic binders such as tricalcium silicate (C₃S) in Portland cement proceeds through a dissolution-precipitation process as explained a long time ago by H. Le Chatelier [1]. The driving force of hydration is the difference in solubility between the solid that dissolves and the hydrates that precipitate; the solubility of the dissolving solid is higher than the one of the hydrates. Thus the kinetics of the cement hydration is the consequence of a competition between the dissolution of the cement phases and the precipitation of the hydrates.

The mechanisms involved in the dissolution of a mineral at the nanoscopic scale are quite complex nevertheless from a practical point of view, dissolution can be defined at the macroscopic scale through the dissolution rate. Experimentally the dissolution rate is generally measured from batch experiments using crushed particles or rotating disk
experiments using polished mineral surfaces. From these experiments, the dissolution rate can be estimated by the following general equation determined by Lasaga et al. [2]:

\[
Rate = k_0, A_{\text{min}} e^{-Ea/kT} a_i^{n_i} \prod a_{H^+}^{n_{H^+}} g(I).f(\Delta G_r)
\]

(1)

with:
- \(k_0\) is the rate constant (Average or instantaneous at \(t=0\)),
- \(A_{\text{min}}\) is the reactive surface area of the mineral,
- \(e^{-Ea/kT}\) is a term related to the temperature dependence,
- \(a_i^{n_i} \prod a_{H^+}^{n_{H^+}}\) with \(a_i\) and \(a_{H^+}\) are the activities in solution of species \(i\) and \(H^+\), respectively, \(n_i\) and \(n_{H^+}\) are the orders of the reaction with respect to these species. This represents pH dependence of the dissolution reactions and other possible catalytic effects on the overall rate,
- \(g(I)\) is a function of the ionic strength. The \(g(I)\) term indicates a possible dependence of the rate on the ionic strength (I),
- \(f(\Delta G_r)\) is a function of the Gibbs free energy. It accounts for the important variation of the rate with deviation from equilibrium.

The commonly used experimental techniques to measure dissolution rate cannot be directly used for the phases contained in Portland cement due to the very rapid hydrates precipitation. One possibility is to slow down the rate of increase of concentrations in the aqueous phase by using very high water to solid weight (W/S) ratios in batch experiments. This method was applied by Nicoleau [3] on C\(_3\)S in water and different lime concentrations with or without superplasticizers. Nevertheless huge W/S ratios (>100000) can induce major uncertainties on the calculation of the rate. Moreover catalyzing or inhibiting effects by electrolytes like OH\(^-\) or by adsorption of superplasticizers may be of very different intensities when using W/S ratios close to 0.5 that are representative of a conventional use of hydraulic binders.

The aim of this work was to determine the dissolution rate of the phases contained in hydraulic binder in the presence of different electrolytes thanks to a specific device that operates with W/S ratios close to 0.5. The second objective was to test if Lasaga’s equation could be used to simulate these dissolution rates. This paper summarizes the results obtained on tricalcium silicate.

2. EXPERIMENTAL SETUP

The basic idea of the device was to have the shortest possible contact time between the dissolving solid and a defined electrolyte in order to dissolve the slightest quantities of the dissolving phase and thus to avoid the attainment of maximum supersaturation domains with respect to the hydrates that induce an immediate precipitation. As one of the key parameter was to keep a W/S ratio close to 0.5, a bed of solid was led on a filter linked to vacuum to enable a very rapid convective flow of the electrolytes. Another innovative part of the device was to sample the aqueous phase passing through at different times instead of analyzing the bulk solution at the end of the experiment. During an experiment, 8 test tubes having a volume of 15 ml could be selected and filled when desired. If the experiment runs well, the concentration in the different samplings should be the same. If not some parameters have
varied too much such as the reduction of surface area of the dissolving solid, formation of holes in the solid layer inducing change in the velocity of the flow or precipitation of solids.

In order to calculate the dissolution rate, several parameters have to be known. First the velocity of the flow, V, has to be determined. This can be done by recording the mass of electrolyte passed through the filter over the time. From diameter of the filter (D) and the height of the packed solid on the filter (H), it is possible to estimate the volume of water that is in contact with the solid. In the reported experiments, 0.5g of C3S was packed on the filter having a mesh size of 0.45µm. H was measured to be 1.3mm, As D was equal to 1mm, the total volume was 0.41 cm³ with 0.16 cm³ for C3S and 0.25 cm³ of water. Thus the W/S mass ratio was equal to 0.5. As V was equal to 2.5 cm³.s⁻¹, the time of contact between the aqueous phase and C3S was 0.1 second.

The calculated rate is the average rate corresponding to the experimental parameters and if can be calculated from the following equations (Eq. 2):

\[
\text{Dissolution rate (mmol.m}^{-2}.s^{-1}) = \frac{\text{output concentration (mmol.L}^{-1}) - \text{input concentration (mmol.L}^{-1})}{\text{Time of contact (s) mass of solid for 1 kg solution passed (g.L}^{-1}) \cdot \text{SSA (m}^{2}.g^{-1})}
\]

and considering the water / solid mass ratio on the filter (W/S), it can written that:

\[
\text{Time of contact (s)} = \frac{\text{Volume water on filter (L)}}{\text{Velocity of flow (L.s}^{-1})} = \frac{\text{Mass of water on filter (g)}}{\text{Velocity of flow (L.s}^{-1})} = \frac{\text{W/S mass of solid on filter (g)}}{\text{Velocity of flow (L.s}^{-1})}
\]

and:

\[
\text{Mass of solid for 1kg solution (passed through)} (g) = \frac{1000}{\text{W/S}}
\]

then Eq. 2:

\[
\text{Dissolution rate (mmol.m}^{-2}.s^{-1}) = \frac{\text{output concentration (mmol.L}^{-1}) - \text{input concentration (mmol.L}^{-1})}{1000 \cdot (\text{mass of solid on filter (g)}) \cdot \text{SSA (m}^{2}.g^{-1})} \cdot \text{velocity of flow (L.s}^{-1})
\]

3. RESULTS

The Si concentrations measured during the dissolution of pure C3S in pure water with our device (0.5g of C3S on the filter, W/S=0.5 and time of contact of 0.1 second) are presented on figure 1. First of all, the concentration of Si is constant as expected and is close to 1mmol/L. Inhibiting or catalyzing effects from the ions released by C3S dissolution, calcium ions, silicates ions and hydroxide ions, if they exist, can be assessed by dissolving C3S in lime solutions of different concentrations. If there is no inhibiting or catalyzing effects, Si concentration should not be modified as the solubility of C3S is so high that starting from pure water or a lime solution would not change the undersaturation with respect to C3S. The results obtained with a 5.75 and a 22 mmol/L Ca(OH)₂ solutions (Figure 1) clearly indicate that the dissolution rate is very influenced by the lime concentration of the input flow. The average dissolution rates calculated from the average value of Si in the experiments (Table 1) indicate that the dissolution rate is 5 times lower starting in 5.75 mmol/L Ca(OH)₂ and more than 200 times lower in 22 mmol/L Ca(OH)₂. This demonstrates a strong inhibiting effect of calcium and/or hydroxide ions. The effect of hydroxides ions and thus of pH has been previously reported especially for some minerals but also for glass [4]. Thus to test if hydroxides or/and
calcium ions have an inhibiting effect, some complementary experiments have been performed in NaOH having a pH between the two Ca(OH)$_2$ solutions and in CaCl$_2$ solution having about the same calcium ions concentration as for the 22 mmol/L Ca(OH)$_2$ solution. Results (Figure 1 – Table 1) indicate that hydroxide ions have a marked inhibiting effect but nevertheless this effect is less the presence of sodium ions compared to calcium ions. The experiment in CaCl$_2$ tends to indicate that calcium ions have also an inhibiting effect but not as strong as hydroxide ions. Other experiments would be needed to assess if sodium and chloride ions would have an effect but nevertheless if it exists, it should be of a lesser intensity than hydroxide and calcium ions.

![Figure 1: Concentration of Si measured during the dissolution of pure C$_3$S in water, 30 mmol/L NaOH, in 20 mmol/L CaCl$_2$ and in 5.75 and a 22 mmol/L Ca(OH)$_2$ solutions : W/S=0.5 and time of contact of 0.1 second. Points on the drawing indicate the time at which the samplings have been made.](image)

![Table 1: Average dissolution rate for pure C$_3$S in different electrolyte after 0.1 second of dissolution with W/S=0.5 and SSA=4265 cm$^2$.g$^{-1}$](table)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Water</th>
<th>Ca(OH)$_2$ 5.75mmol/L</th>
<th>Ca(OH)$_2$ 22mmol/L</th>
<th>NaOH 30mmol/L</th>
<th>CaCl$_2$ 20mmol/L</th>
</tr>
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<tbody>
<tr>
<td>Average Rate $\mu$mol.s$^{-1}$.m$^2$</td>
<td>10.92</td>
<td>2.07</td>
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</tr>
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4. DISCUSSION

From the reported experiments, it appears that the average dissolution rate of C$_3$S measured in our experimental conditions (time of contact of 0.1 second, W/S=0.5 and SSA=4265 cm$^2$.g$^{-1}$) can be markedly modified with some relatively small variation of the
electrolyte in which C$_3$S dissolves. Thus the reported inhibiting effects of hydroxide and calcium ions are very strong and have to be taken into account to simulate the dissolution rate of C$_3$S.

As $K_0$ and the coefficients for hydroxides and calcium ions have to be found for Lasaga’s equation (Eq. 1), the experiments in water and 5.75 mmol/L Ca(OH)$_2$ have been used to find the best fit of these parameters. $K_0$ has been estimated to 70 mmol.m$^{-2}$s$^{-1}$ that is consistent with Nicoleau’s results [3] and the coefficient for H$^+$ and CaOH$^+$ have been set to 0.465 and –0.33 respectively giving the following equation (3):

$$\frac{dC_3S}{dt} (\text{mmol.L}^{-1}\cdot \text{s}^{-1}\cdot \text{m}^{-2}) = 70.A.(S-I-1)(\text{H}^+)^{0.465}(\text{CaOH}^+)^{-0.33}$$

(3)

A is the specific surface area in m$^2$.g$^{-1}$ and SI the saturation index with respect to C$_3$S. The solubility of C$_3$S was estimated from its Gibbs’ free enthalpy of dissolution, to be close to 1.3 mol.kg$^{-1}$. This equation has different coefficients than the one previously reported [5] because $K_0$ was not well estimated before.

Without these inhibiting effects, it would take less than 0.1 second to reach equilibrium of course if no precipitation would occur. This equation has been used to simulate the dissolution rate of C$_3$S with W/S ratios of 5 and 50 because such experiments have been often performed in stirred suspensions (Figure 2). As expected the increase of Si concentration is more rapid with lower W/S ratios. If we consider the time at which the maximum Si concentration is reached before C-S-H precipitation, the simulation gives slightly quicker rate than experiments in stirred suspensions. This can be partly explained by the fact that in experiments, the inhibiting effects are stronger because the stirring is not strong enough to avoid a concentration gradient at the surface whereas it does not exists in the simulation.

Figure 2: Simulation of batch experiments in water on C$_3$S having a specific surface area of 3200 cm$^2$.g$^{-1}$ and W/S ratios of 0.5, 5 and 50
Table 2 gives the calculated average rates compared to the experimental one. The calculated rates are in good agreement with the experimental ones except for the saturated lime solution for which the calculated rate for is 100 times higher. Such a difference tends to let us consider that an additional mechanism, like a very rapid precipitation of a surface layer, could restrict the dissolution rate of C₃S. This is consistent with very strong reductions of dissolution rate that have also been reported for some minerals. For example the precipitation of an otavite layer (CdCO₃) of less than 0.01 micron in thickness on calcite surfaces decreases its dissolution rate by about two orders of magnitude [6]. The existence of such a layer on C₃S and its nature, if it exists, still have to be proven.

Table 2: Calculated and simulated dissolution rate for pure C₃S in different electrolyte after 0.1 second of dissolution with W/S=0.5 and SSA=4265 cm².g⁻¹

<table>
<thead>
<tr>
<th>Electrolyte</th>
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<td>2.01</td>
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<td>2.89</td>
<td>8.14</td>
</tr>
</tbody>
</table>

7. CONCLUSIONS

A specific device has been developed in order to assess the dissolution rate of very reactive minerals such as C₃S in the presence of different electrolytes and with W/S ratios comparable to cement use.

The average rates calculated from the device enable us to find K₀ and if needed the coefficients of Lasaga’s equation in order to simulate the dissolution rate. K₀ for C₃S is close to 70 mmol.m².s⁻¹ and is about 50 times higher than for gypsum that is known to be a quite rapid dissolving solid.

For C₃S it appears that hydroxides and calcium ions have strong inhibiting effects that reduce rapidly the rate to a few µmol.m².s⁻¹ as experimentally observed. Without these inhibiting effects, C₃S solubility would be theoretically reached if no precipitation would occur in less than 0.1 second where that it would take 30 hours with theses inhibiting effects.

Nevertheless these effects do not seem to be strong enough to explain the very strong decrease of C₃S dissolution rate when the Ca(OH)₂ concentration is close or higher to Portlandite solubility. This strong reduction of the rate could be explained by the very rapid formation of a very thin surface layer whose nature still has to be determined.

REFERENCES


