

## Investigation of the early dissolution behavior of $C_3S$

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**Abstract:** The hydration of  $C_3S$  in water or in electrolytes proceeds through a dissolution-precipitation process that has been extensively studied by several techniques. More recently, the nucleation and growth of the hydrates, principally of C-S-H, has been investigated. However, less attention has been devoted to the dissolution of  $C_3S$  as the dissolution mechanism is difficult to study in normal static conditions because of the very rapid precipitation of hydrates. Thus a specific device has been developed to examine the early hydration of  $C_3S$  in dynamic conditions. Results indicate that the initial dissolution rate of  $C_3S$  is quite high, about  $15\mu\text{mol/s/m}^2$  in pure water, but varies considerably with pH and calcium ions concentration. This behavior can be simulated numerically using simplified kinetics equations.

### 1 – Introduction

The hydration of tricalcium silicate ( $C_3S$ ) proceeds through a the 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  $C_3S$  that dissolves and the hydrates, calcium silicate hydrate (C-S-H) and portlandite (CH) that precipitate : the solubility of  $C_3S$  is higher than the one of the hydrates. Thus the kinetics of the hydration of  $C_3S$ , is the consequence of a competition between the dissolution of  $C_3S$  and the precipitation of the hydrates. As a consequence the different hypothesis developed in order to explain the specific kinetics of  $C_3S$  hydration that presents two kinetic steps [2-3] have been focused either on dissolution or on precipitation.

Hypothesis originated from observation of the  $C_3S$  surface at different ages with several techniques are based on the observation of the formation of an hydration product on the surface of  $C_3S$  [4-6]. Thus some authors have considered that this primary hydration product completely covers the surface of the  $C_3S$  and determines the continuation of the hydration by its permeability that can be correlated to its later transformation or progressive destruction [7-9].

Other authors have focused their work on precipitation that can be described from nucleation and growth classical theories. The precipitation of C-S-H has been largely investigated compared to CH precipitation.

Aqueous phase compositions that induce an immediate precipitation of C-S-H compared to aqueous phase that present an induction period before precipitation have been determined experimentally : the boundary between these two domains has been named by Barret, maximum supersaturation curve of C-S-H [10]. From these experiments, Barret just considered kinetic features in order to explain the induction period, the end of which, depends on a conventional autocatalytic process induced by a seeding effect of more and more numerous nuclei formed [10-11]. Using this hypothesis, Gauffinet and Nonat [12-13] were able to simulate accurately the kinetics of  $C_3S$  hydration in different conditions by using just three parameters : the first one is the initial number of nuclei (formed during the early precipitation of C-S-H) and the two last describe the growth mode of C-S-H which is different for each of the two kinetic steps. The two processes that were taken into account to simulate the growth are, first, the rate of growth of clusters on the surface (named parallel growth) and second, the rate of the increase of the cluster thickness (named perpendicular growth). The good agreement obtained between simulated and experimental curves, seems to support an induction period governed by the nucleation and growth of clusters of C-S-H on the surface with a dissolution rate tuned accordingly.

On the other hand less attention has been devoted to the dissolution and it seems yet difficult to know if the rate of  $C_3S$  dissolution can be slow in the hydration conditions (and thus follows a slow precipitation rate of C-S-H during the induction period) or if it slows down by an alternative mechanism such as the precipitation of a layer at its surface.

First of all, dissolution of solids is a complex mechanism that deals with the surface that can be considered as a crystal with defects. Moreover in aqueous phase, the surface of mineral is subjected to protonation and adsorption or more or less complex aqueous species that can now be approached by different theories in relation with sorption mechanisms [14-16]. Dissolution is often more intense in some defects and sometimes some tips can be observed [17-18]. From a macroscopic approach, Barret described the dissolution process of  $C_3S$  as an interfacial reaction of  $C_3S$  with water molecules and called it superficial hydroxylation [19-20] : dissolution is a repeating sequence of interfacial steps as it is the case for some other minerals ; first an irreversible attack of superficial sites of  $C_3S$  by water molecules, then a reversible step resulting in the passage of the formed species from  $C_3S$  surface into solution.

Another difficulty arises from the fact that  $C_3S$  solubility cannot be reached experimentally as the hydrates precipitates before its attainment because their maximum supersaturation domains are reached. However  $C_3S$  solubility can be estimated from its Gibbs' free enthalpy of dissolution, and it appears to be very high : between 1.4 and 2.9 mol/kg depending on the

data used to calculate the Gibbs' free energy of reaction and the model used for the activity correction.

As a consequence, we have designed a specific device to assess the initial dissolution rate of  $C_3S$  in specific aqueous phase. Indeed the electrolyte composition can have a very intense effect such as it had been observed for the dissolution of glass [21].

## 2 - Materials and experimentation

The basic idea was first to be able to maintain at the  $C_3S$  surface a constant and defined aqueous phase composition such as in Lecoq [22] or Gauffinet [12] experiments. Second, the aim was to slow down as far as possible the formation of hydrates on the surface by heterogeneous nucleation, especially C-S-H, by adding a rapid flushing of the surface of the grains by a fast convective flow of the aqueous phase using a bed of  $C_3S$  on a filter linked to vacuum such as in Ménétrier's experiments [23-24]. Thus a specific device has been designed to perform  $C_3S$  hydration in an open system : the aqueous phase of a given and known concentration flows through a layer of  $C_3S$  spread on a filter (Figure 1).

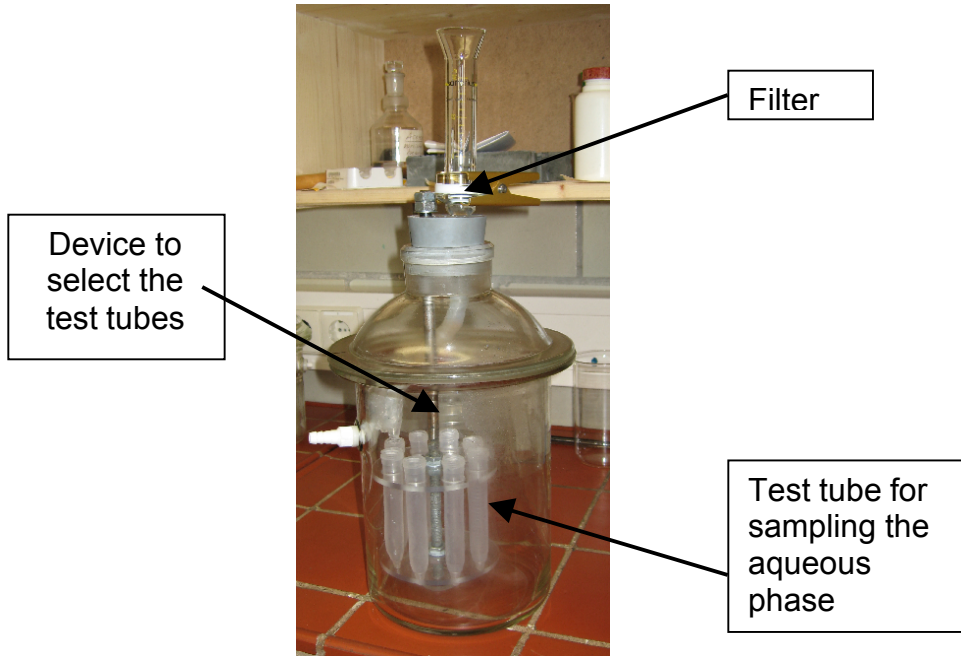


Figure 1 - experimental device designed for performing  $C_3S$  hydration in an open system with the sampling of the aqueous phase

All the experiments were carried out with 0.5gr of  $C_3S$  spread on a filter of 1 cm of radius having a mesh size of  $0.45\mu m$ .  $C_3S$  is just laid on the filter

and slightly compacted by the vacuum before adding the aqueous phase : the height of  $C_3S$  on the filter is close to 2 mm.

The flow of aqueous phase through the filter is in average 2.5ml per second that corresponds to  $7.96 \text{ l.s}^{-1}.\text{m}^{-2}$  instead of  $0.21 \text{ l.s}^{-1}.\text{m}^{-2}$  in Ménétrier's experiments. Thus the duration of the contact between the aqueous phase passing through the 2 mm layer of  $C_3S$  is equal to 0.25 s which is extremely rapid. As a consequence the device should enable a rapid flushing of the ions released by the dissolution of  $C_3S$ .

The more innovative part of the device is that it is possible 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 can be selected and filled each in less than 5 seconds (the tube is filled with 12 ml of aqueous phase). As the study was focused on the very early hydration, the sampling rate was equal to 1 sample per 15 seconds with a total duration of the experiment less than 2 minutes (figure 2). The first sampling started after 1 second. The reservoir on the top of the filter is continuously filled but always contains less than 10 ml of aqueous phase in order to avoid diffusion to the reservoir.

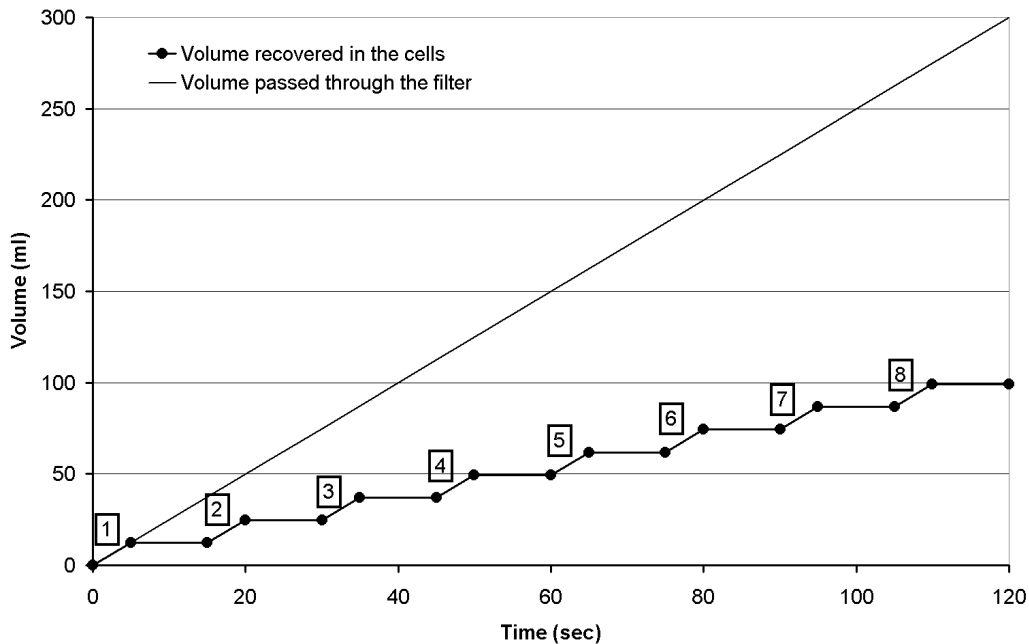


Figure 2 - Sampling rate versus the volume passed through and the recovered volume

At the end of the experiment, a small fraction of the remaining solid on the filter is generally observed as quickly as possible (less than 5 minutes), in its wet state and thus without coating, under an environmental scanning microscope (Philips ESEM XL 30). The remaining solid is dried with

isopropanol for further analysis and the aqueous phase is analyzed by ICP-OES (Optima 3000 Perkin Elmer).

### 3 - Results

Experiments have been carried out in the following aqueous phase compositions in order to check the influence cations ( $H^+$ ,  $Na^+$ ,  $Ca^{2+}$ ) and anions ( $OH^-$ ,  $Cl^-$ ,  $H_2SiO_4^{2-}$ ) on the rate of  $C_3S$  dissolution comparatively to pure water :

- $Ca(OH)_2$  at 6 (noted  $Ca(OH)_2$  (6)) and 22 mmol/l (noted  $Ca(OH)_2$  (22))
- $CaCl_2$  at 20 mmol/l (noted  $CaCl_2$ )
- NaOH at 30 mmol/l
- HCl at 32mmol/l
- Silicate ions at 1.5mmol/l (noted silicate)
- Solution obtained during early hydration of  $C_3S$  that contains 2.65 mmol/l of calcium and 0.86 mmol/l of silicate ions (noted  $C_3S$  1)

The cumulated amounts of calcium and silicate ions recovered as a function of the time are reported on figures 3 and 4. These amounts are calculated with the approximation that the aqueous phase composition over the 15 seconds between each sampling is equal to the aqueous phase composition analyzed in the sample (5 seconds of sampling time).

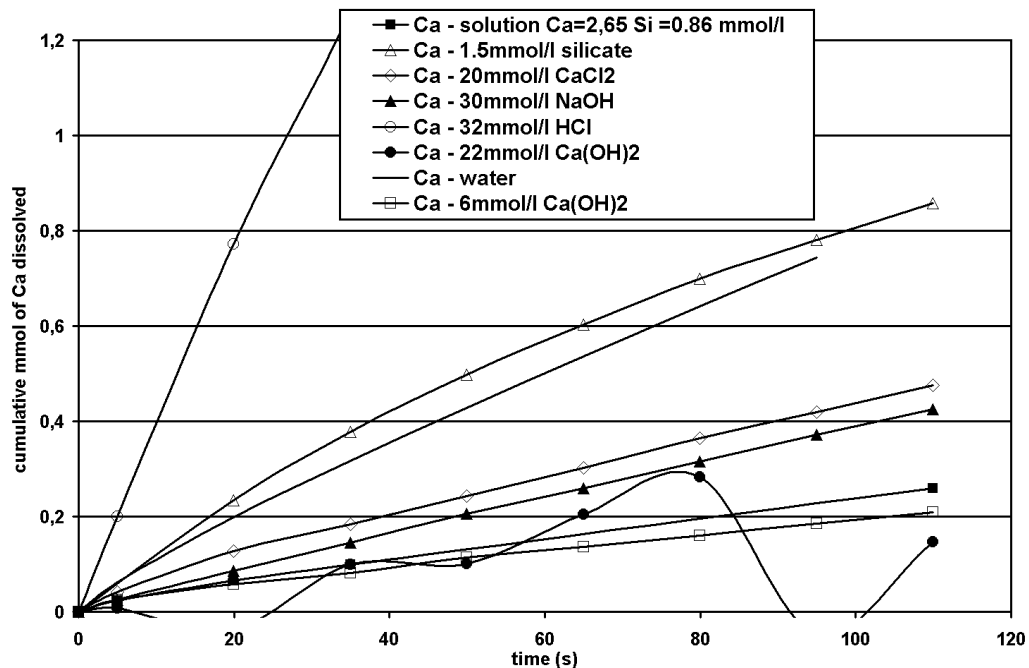


Figure 3- Cumulated amount of calcium ions as a function of the time

For pure water, the cumulated amounts of both calcium and silicate almost correspond to a straight line. Thus it exists a quasi steady state between

the dissolution rate and the flow of water through  $C_3S$  layer on the filter. In these conditions, the dissolution rate does not appear to become restricted and more than 10% of  $C_3S$  has been dissolved during the experiment that lasts less than 2 minutes.

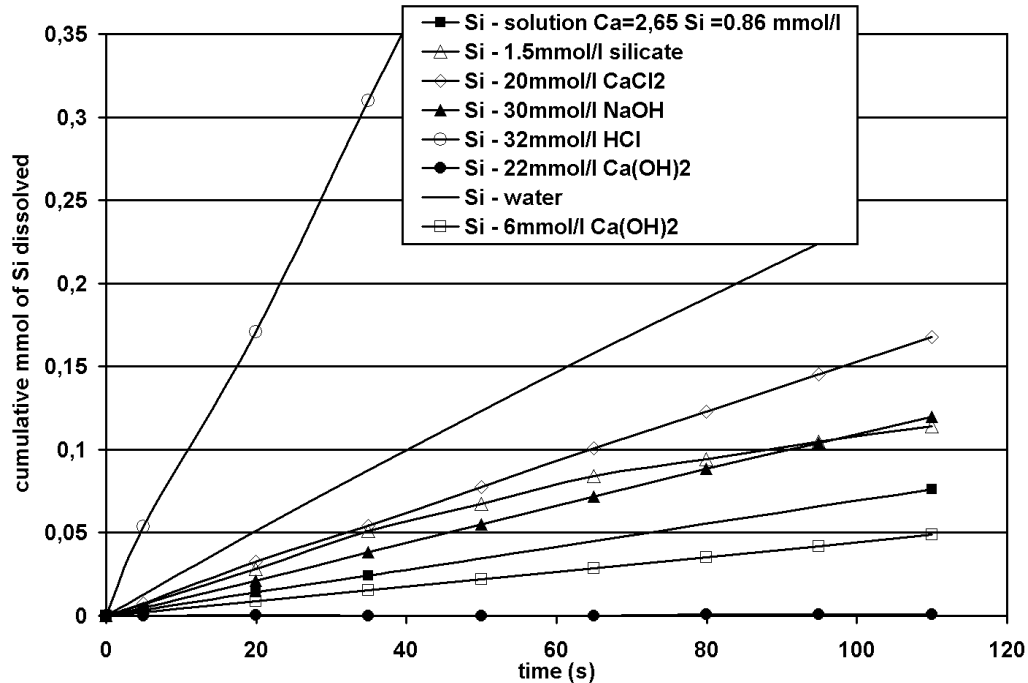


Figure 4 - Cumulated amount of silicate ions as a function of the time

If we consider the cumulated amounts of silicate ions, a similar evolution is observed with the different aqueous phase compositions studied but the slope of the curves differs significantly depending on the composition. All compositions, apart HCl, lead to a decrease of the cumulated amount of silicate ions compared to water in the following order :  $Ca(OH)_2$  (22) <  $Ca(OH)_2$  (6) <  $C_3S$  1 < NaOH = silicate <  $CaCl_2$  < water < HCl. For the cumulated amounts of calcium ions, a comparable order is found at the exception of  $Ca(OH)_2$  (22) that is not monotonous and also for the silicate solution that is higher than water :  $Ca(OH)_2$  (6) <  $C_3S$  1 < NaOH <  $CaCl_2$  < water < silicate < HCl.

If the C/S ratio (or  $\Delta C/\Delta S$  ratio if the starting solution is not pure water) of each sampling is considered (Figure 5), it can be noted that the value progressively decreases and stabilizes to values a little higher than 3 : average value equals 3.37 if the silicate experiment that behaves very differently is not taken into account. Similar results reported by Ménérier [23] had been explained by the fact that the local concentrations at the interfaces are higher than those of the bulk aqueous phase and as a consequence, some silicate ions are missing due to the precipitation of small amount of C-S-H. However ESEM observations did not reveal common pattern of C-S-H on the surface and no real observable deposit of hydrate.

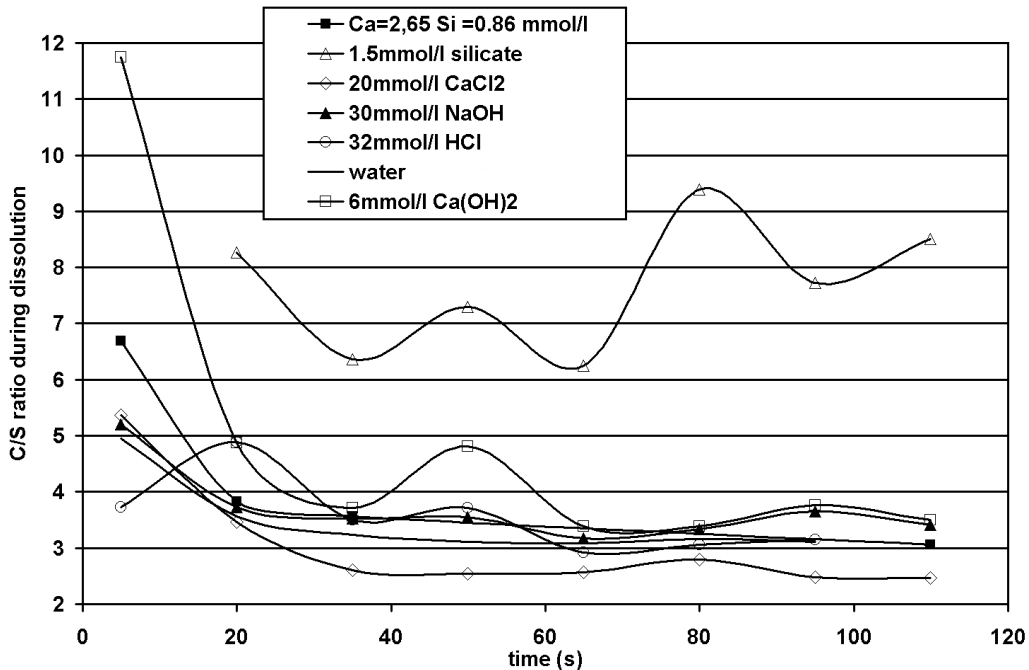


Figure 5 – Evolution of the C/S ratio of each sampling during the experiment

An additional explanation could be attempted in considering that the velocity of the flow is quite high and thus leads to an apparent incongruity of  $C_3S$  dissolution due to the difference of rate in the two steps of the superficial hydroxylation process. Traces of free lime are also expected to increase the C/S ratio but mainly during the two first samplings as observed.

The behavior of the silicate solution is quite different and the C/S ratio remains high. This behavior could be associated to the precipitation of a phase having a C/S ratio below 3 such as C-S-H. But also in this case, the typical honeycomb morphology of C-S-H was not observed by ESEM even at very high magnification. However some uncommon trapezoidal shape crystals can be observed. At first it was believed to be calcium carbonate, but EDS analysis did not reported the present of carbon.

The very variable calcium amounts and the associated very low silicate amounts recorded during the experiment using a  $Ca(OH)_2$  solution of 22 mmol/l (corresponding to the solubility of Portlandite) tend to indicate a very low dissolution rate with some possible portlandite and C-S-H precipitation. Nevertheless in this case also, no typical morphologies of known hydrates were observed.

On the other hand, the faster experiment, carried out in HCl, leads to a very corroded surface resulting from the high quantity of  $C_3S$  dissolved but

with higher intensities at the joint between the crystals of  $C_3S$  that are contained in the grains.

#### 4 - Discussion

The cumulated amounts of ions in the aqueous phase show a different behavior during the very initial dissolution of  $C_3S$  as a function of the aqueous phase composition. If we want to estimate the dissolution rate of  $C_3S$  from these data, we have to estimate if only dissolution of  $C_3S$  occurs or if some hydrates were also precipitated. A first approach can be made thanks to the calculation of the saturation index (SI) of the phases that may precipitate (amorphous silica, C-S-H and CH). In order to restrict as far as possible any precipitation, only the first sampling (5 s of hydration) has been used for the calculation of the saturation index (Fig 6). Nevertheless the recovered aqueous phase is always supersaturated with respect to C-S-H at the exception of the HCl solution that remains undersaturated with respect to C-S-H.

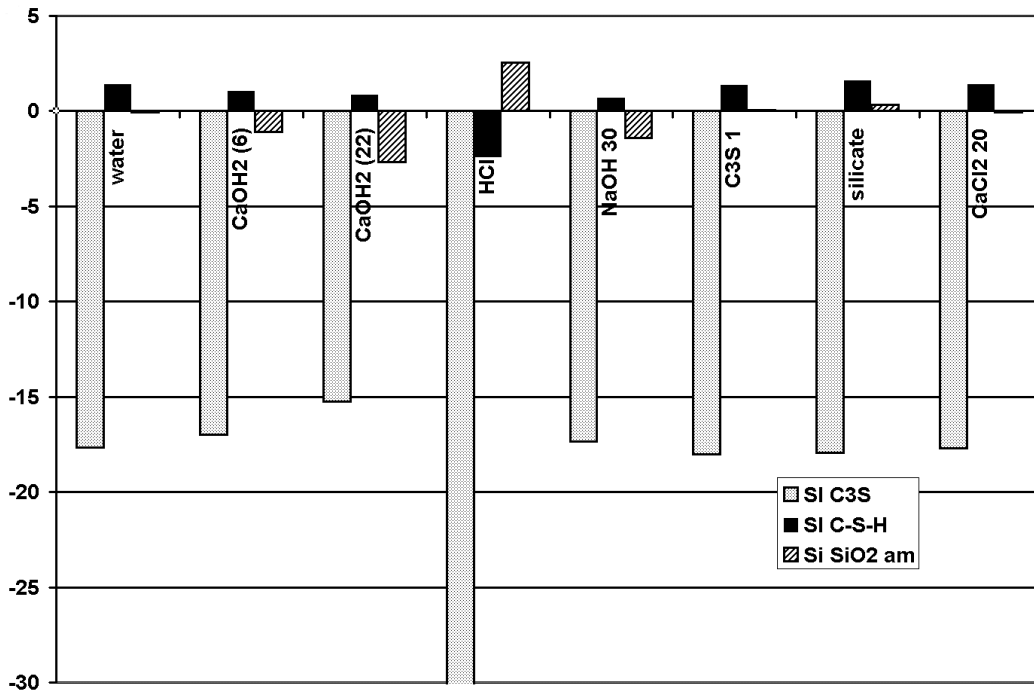


Figure 6 : Saturation index for  $C_3S$ , C-S-H and amorphous silica calculated from the aqueous phase composition corresponding to the first sampling of each experiment.

As the reaction time is very short, C-S-H has a chance to be formed only if the maximum supersaturation of C-S-H is attained otherwise the induction period before C-S-H precipitation would be too long. Considering the values of SI C-S-H, maximum supersaturation may be reached during



some experiments but the quantity of C-S-H formed is expected to be very low even at the end of the experiment (120 s), as C-S-H was not really observable by ESEM at very high magnifications (x100000). Small amounts of amorphous silica could also form in HCl and silicate solutions.

As a consequence, precipitation has been neglected in order to calculate  $C_3S$  initial dissolution rate from the cumulated amounts of silicate ions (Fig 7). The dissolution rate calculated after 5 seconds follows the order found for the cumulated amounts of silicate obtained after 120 s, except that silicate is closer to  $CaCl_2$  than to NaOH :  $Ca(OH)_2$  (22) <  $Ca(OH)_2$  (6) <  $C_3S$  1 < NaOH < silicate =  $CaCl_2$  < water < HCl.

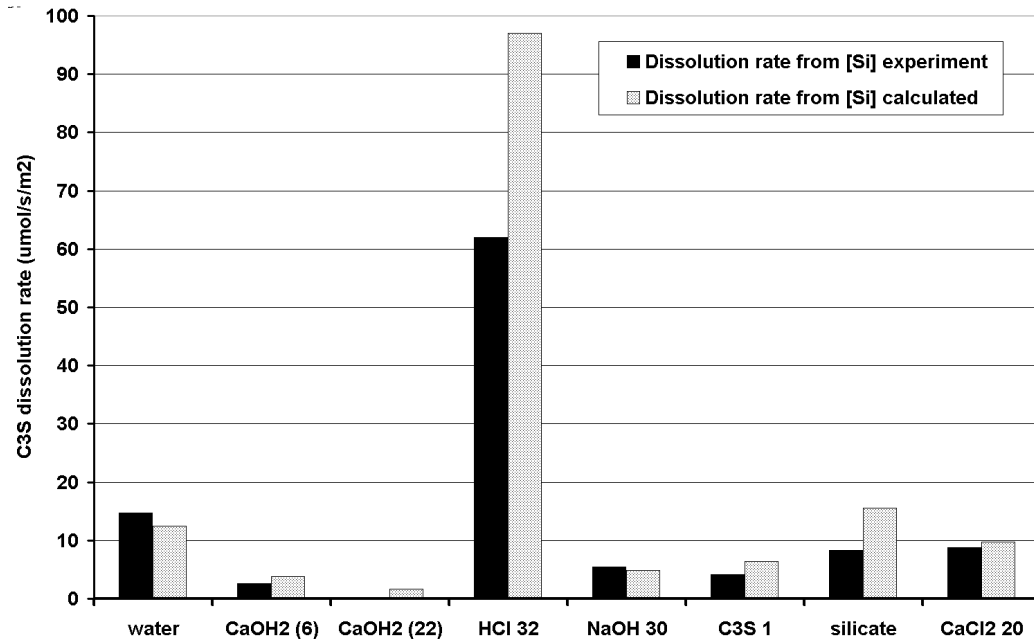


Figure 7 – Initial  $C_3S$  dissolution rate in different aqueous phase compositions calculated using [Si] given by experiment or simulation.

The mechanisms involved in kinetic dissolution are generally complex but can be macroscopically related to several parameters such as the saturation index : the higher the undersaturation of a mineral the faster its dissolution. The saturation index of  $C_3S$  do not vary much in the experiments apart for the experiment carried out in HCl that has a higher undersaturation and is clearly the faster experiment (Fig 7). Thus additional parameters, different from the specific surface area that is almost constant during the first seconds in our experiments, have to be considered in order to simulate the influence of the aqueous phase composition on the dissolution rate. It is known that the kinetics is very often strongly affected by the presence of ions or complex species in the aqueous phase that may be not directly involved in the reaction. They can have a catalyzing effect when the reaction rate increases, or an inhibiting effect when it is slowed down. For example  $H^+$  and thus pH has a great

influence on glass dissolution [21]. If the pH of the aqueous phase is taken into account and sorted accordingly to the dissolution rate of C<sub>3</sub>S, the following sequence is found ; 12.53 < 12.11 < 11.83 < 12.45 < 11.79 < 11.63 < 11.89 < 8.76. It seems that as a general trend, the dissolution rate is increased with a decrease of pH but nevertheless calcium ions appears to have an additional inhibiting effect if we compare NaOH and Ca(OH)<sub>2</sub>.

Experiments enabled us to define a simplified equation to simulate the kinetics of C<sub>3</sub>S dissolution that takes into account the effects of undersaturation (SI-1) and of the inhibition of pH and calcium ions :

$$\frac{dC_3S}{dt} (\text{mmol} / \text{s} / \text{m}^2) = A.K_0.(SI - 1).[H^+]^{0.29} [CaOH^+]^{-0.27}$$

The rate constant of the reaction is denoted by K<sub>0</sub> and estimated to be 40 μmol/s/m<sup>2</sup>. A (m<sup>2</sup>/m<sup>3</sup>) represents the volumic surface area of the C<sub>3</sub>S : initially 0.5g of C<sub>3</sub>S having a specific surface area of 0.35 m<sup>2</sup>/g. The power constants applied to [H<sup>+</sup>] and [CaOH<sup>+</sup>] have been set using the experiment in water as a reference. Calculations were made for a duration of 5 seconds considering that 0.5g of C<sub>3</sub>S dissolves in 12.5 ml of solution. The reaction rate has been calculated from the silicate concentration of the aqueous phase as precipitation is not allowed in the simulation.

The calculated dissolution rates follow the same trends than the experimental ones with a quite good estimation. The main differences are reported for HCl and silicate solutions where amorphous silica may form and thus lower the amounts of silicate in the aqueous phase. Also the calculated dissolution rate in the solution saturated with respect to portlandite (Ca(OH)<sub>2</sub> (22)) is higher than the experimental one. It is known that in these conditions, a very small amount of silicate ions is sufficient to immediately form C-S-H [12] and thus this could explain the very low silicate concentration but also the non monotonous cumulated amounts of calcium. If the calculation is made without the term related to the pH and calcium inhibiting effects, the dissolution rate is found to be the same for all experiments and its value is about 80 times higher compared to the rate found in water when the inhibiting effect are taken into account.

## 5 - Conclusion

A specific device has been developed in order to assess the initial dissolution rate of C<sub>3</sub>S, and if needed other minerals, on different aqueous phase compositions.

This enables us to give for the first time ever, a good approximation of C<sub>3</sub>S dissolution rate but also proves that pH and calcium ions have an inhibiting effect whereas Na<sup>+</sup>, Cl<sup>-</sup> and silicate ions have a less marked effects. A simplified equation can be defined in order to estimate the

dissolution rate. The proposed method could also be used for other ions such as sulfate but also organic molecules.

If we consider a paste of  $C_3S$  having quasi instantaneously a high pH, the dissolution rate become about 50 times lower than in pure water but is still quite high relatively to other minerals. The question now raised is to know if this effect is enough to induce an induction period governed by nucleation and growth of the C-S-H or if an additional mechanism, such a surface layer of C-S-H in temporarily in equilibrium with the aqueous phase, governs the dissolution rate as suggested by Jennings et al. [25].

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