

Calculation of critically supersaturated domains with respect to ettringite in the $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4\text{-H}_2\text{O}$ system at 20°C

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Abstract: The conditions of ettringite formation are very important factors to understand cement hydration but also sulfate attacks. The determination of the solubility of ettringite but also of the solubility of the phases usually found in a cement paste, made it possible to know, thanks to a thermodynamic approach, the stability domain of ettringite. However thermodynamics does not allow to know the rates of precipitation of ettringite. Thus a method has been developed to calculate the aqueous phase compositions, named critically supersaturated domains, leading to very fast nucleation rate, and thus quasi instantaneous precipitation of ettringite. From the knowledge of the aqueous phase at the boundary of the critically supersaturated domains, it is possible to assess the inhibiting or catalyzing effects of the ions on the rate of ettringite precipitation. Then typical kinetics equation can be used to simulate the precipitation rate of ettringite.

Introduction

From a general point of view, both dissolution and precipitation rates involved in cement hydration or chemical attacks of a cement paste, have to be assessed to simulate the kinetics. With respect to ettringite, the conditions of formation as well as the stability of this phase are very important factors to understand the role played by ettringite in internal or external sulfate attacks but also during early hydration of Portland cement. The determination of the solubility of ettringite but also of the solubility of the phases usually found in a cement paste, made it possible to know, thanks to a thermodynamic approach, the stability domain of ettringite as a function of the temperature and of the presence of ions such as alkali ions which generally remain in the aqueous phase contained in the porosity [1]. However thermodynamics does not allow to know the rates of dissolution or precipitation of ettringite which rely on kinetics. Precipitation is complex and the ratio between rates of nucleation and growth is very important with respect to the size of the ettringite crystals.

Aqueous phase compositions leading to very fast nucleation rate, and thus instantaneous precipitation, are often reported in various chemical systems [2] and will be defined thereafter as critically supersaturated domains. The dimension of these domains depends on the number of constituents of the hydrates in a similar manner as equilibrium conditions.

For example for an hydrate containing two constituents in addition to water which is considered to be in excess, the critically supersaturated domain is a surface delimited by a curve which is called critically supersaturated curve. In this case, the domain between the equilibrium curve and the critically supersaturated curve, leads to the precipitation of the hydrate after an induction period which duration mainly depends on the saturation index (SI). SI of a solid, represents the ratio of the equilibrium constant K calculated with the aqueous phase composition, over the same equilibrium constant that is calculated with the aqueous phase at equilibrium : the log value of the constant is often used thus $SI = \log K / \log K_{eq}$. For a solid that has an activity equal to 1, K corresponds to the ion activity product of the ions brought into solution by the dissolution of the solid.

A good example of critically supersaturated domains comes from C_2AH_8 ; the critically supersaturated curve of C_2AH_8 has been determined experimentally [3] and also calculated [4]. In this case, the knowledge of critically supersaturated curve is very important to understand the hydration mechanism of $C_{12}A_7$ and C_3A [5]. Indeed the critically supersaturated domains can restrict the dissolution of the hydraulic phases and inhibit the formation of other hydrates even if the aqueous phase is supersaturated with respect to them. This also explains that a critically supersaturated domain cannot be determined for all hydrates.

Several experimental facts lead us to postulate to the existence of a critically supersaturated domains of ettringite that is delimited by a surface (as the number of constituents of ettringite is 3 (Ca, Al and SO_4) instead of 2 for C_2AH_8 (Ca and Al), we have to consider a surface instead of a curve). It has to be pointed out that OH^- is not considered as a free variable of the system as its concentration can be obtained when keeping the electroneutrality of the aqueous phase. In all the following systems, CA +gypsum [6], $C_{12}A_7$ +gypsum [6] and C_3A +gypsum [7-8], C_2AH_8 is no longer the first hydrate formed and it is replaced by ettringite. Thus C_2AH_8 is not formed because the aqueous phase composition reaches critically supersaturated domains of ettringite before arriving to similar domains for C_2AH_8 . In consequence the critically supersaturated surface of ettringite, named "surface E", has to be determined if we want to be able to determine if ettringite precipitates in a given system and if yes at what rate this would occur.

Experimental determination and calculation of the critically supersaturated domain with respect to ettringite : surface E

The concentrations are given in mmol/kg of solution and equilibrium constants used in the calculation are the same as in previous papers [1,4]. If we plot a projection of the equilibrium surface of ettringite on the $[Ca]$ -

[Al] plan at a given [SO₄] concentration, it appears that the part of the curve at moderate to high aluminate concentrations is quasi-linear (Fig. 1). The slope remains constant but the position of this straight part is shifted to higher lime concentrations at higher sulfate concentrations. From several experiments in calcium aluminate and calcium sulfate systems, which lead to important aluminate concentrations during the hydration beginning, Fentiman et al. [9] always found the precipitation of ettringite at the hydration beginning and concluded to the presence of what they called an « experimental plan » having the following equation :

$$[\text{Ca}] \text{ mmol/kg} = 1,415 + (0,526 * [\text{Al}] \text{ mmol/kg}) + (0,905 * [\text{SO}_4] \text{ mmol/kg})$$

This experimental plan corresponds to aqueous phase compositions that cannot be over-passed experimentally and thus represents a kind of experimental boundary. Reported to the previous graph showing the projection of the equilibrium surface of ettringite on the [Ca]-[Al] plan, the experimental plan corresponds to a straight line which belongs to supersaturated domains with respect to ettringite (Fig. 1).

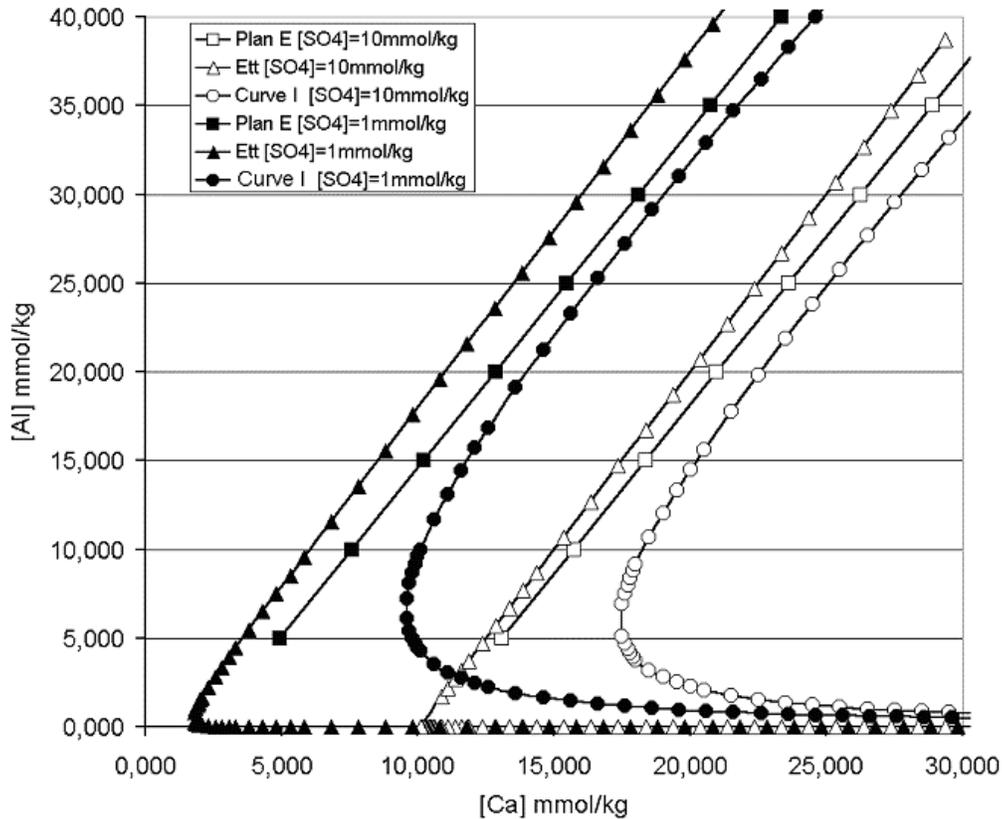


Figure 1 – Position of the equilibrium surface of ettringite, curve I and plan E on the [Ca]-[Al] plan for fixed sulfate concentrations, 1 and 10 mmol/kg, at 20°C

Moreover if we plot, curve I (critically supersaturated curve of C_2AH_8) on the same graph (Fig. 1), it can be seemed that the experimental plan is located before curve I and thus is reached before this curve if we consider the dissolution of calcium aluminate in the presence of gypsum. As a consequence the experimental plan defined by Fentiman et al [9]. is a part of surface E corresponding to the critically supersaturated surface of ettringite.

Lower parts of surface E corresponding to lower aluminate concentrations, and thus higher pH, can be obtained experimentally by recording the aqueous phase composition corresponding to the highest aluminate concentration at the hydration beginning of the C_3A +gypsum system hydrated in water or lime solutions and also for the C_3A +CH+gypsum system. We can also easily calculate these parts of surface E using a similar method as for curve I as it will be demonstrated thereafter. Nevertheless, it can be already observed that the position of the projection of the equilibrium surface of ettringite on the $[Ca]$ - $[Al]$ plan at a given $[SO_4]$ concentration and curve I are very close. This indicates that surface E should be located between these two curves, and that lower supersaturation levels are able to induce an immediate ettringite precipitation at higher pH.

Similarly to curve I for C_2AH_8 , it is observed that SI ettringite is not constant along surface E : critically supersaturated domains do not correspond to iso-supersaturated domains. In order to be able to calculate the exact location of critically supersaturated domains using classical speciation code such as PHREEQE [10], an apparent solubility constant of the corresponding solid is used but the constant varies with the aqueous phase composition :

$$\ln K_{\text{critically supersaturated solid(parameters)}} = \ln K_{\text{solid}} + \ln \beta \text{ (parameters)}$$

with $\ln \beta$ corresponding to the saturation index.

This method was successfully applied to describe the critically supersaturated curve of C_2AH_8 at 20°C by using the following equation [4]:

$$\ln K_I(Al) = \ln K_{C_2AH_8} + \ln \beta_2([Al])$$

with $K_I(Al) = (Ca^{2+})^2(Al^{3+})^2(H^+)^{-10}(H_2O)^{13}$
and $\beta_2([Al]) = 2.934156 \cdot 10^{0.05235 \cdot [Al]}$ and $[Al]$ in mmol/kg

For surface E a similar approach can be used except that K_E as to be function of both aluminate and sulfate concentrations :

$$\ln K_E([Al], [SO_4]) = \ln K_{\text{ettringite}} + \ln \beta_E([Al], [SO_4])$$

If we consider the part of surface E that corresponds to the experimental plan, we can obtain the relation linking β_E with $[Al]$ and $[SO_4]$. Figure 2 presents the evolution of β_E with $[Al]$ at fixed $[SO_4]$ concentrations. The evolution is similar for both ions as an increase of β_E is observed for both $[Al]$ and $[SO_4]$ concentrations. The curve corresponding to $[SO_4]=1$ mmol/kg can be approximated by the following equation :

$$\ln \beta_E([Al], 1) = 6.92816 + 4.331082 \ln([Al])$$

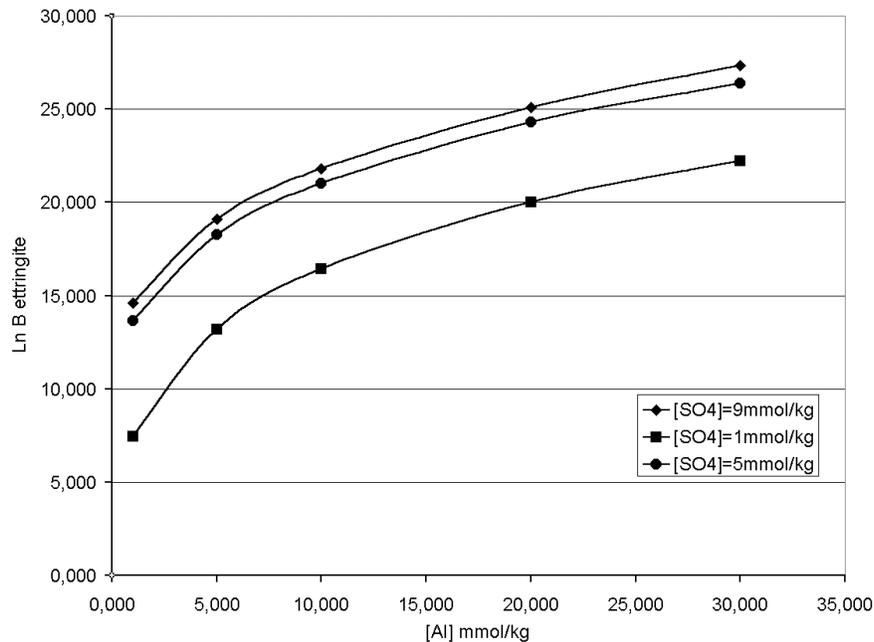


Figure 2 – Variation of saturation index of ettringite along the experimental plan as a function of aluminate concentration

A similar increase of β_E is observed if β_E is calculated as a function of $[SO_4]$ at fixed $[Al]$ concentrations. In this case we can normalize the results in order to obtain the relative increase of β_E as a function of $[SO_4]$ which is almost identical whatever the value of $[Al]$ (Fig. 3). This curve can be fitted by the following equation :

$$\Delta \ln \beta_E([SO_4]) = 0.8181946 + 2.205813 \ln ([SO_4]) \text{ for all } [Al]$$

Thus the function corresponding to $\ln \beta_E([Al], [SO_4])$ can be obtained by adding the two previous equations ;

$$\ln \beta_E([Al], [SO_4]) = 7.74635 + 4.331082 \ln([Al]) + 2.205813 \ln ([SO_4])$$

Note that for concentrations lower than 0.01 mmol/kg , the value of $\ln \beta_E([Al], [SO_4])$ can become negative due to the logarithmic regression used. This is not possible as surface E has to be supersaturated with respect to ettringite. If this case occurs in the calculation, the value of $\ln \beta_E([Al], [SO_4])$ is arbitrary fixed to 1 to maintain a small supersaturation.

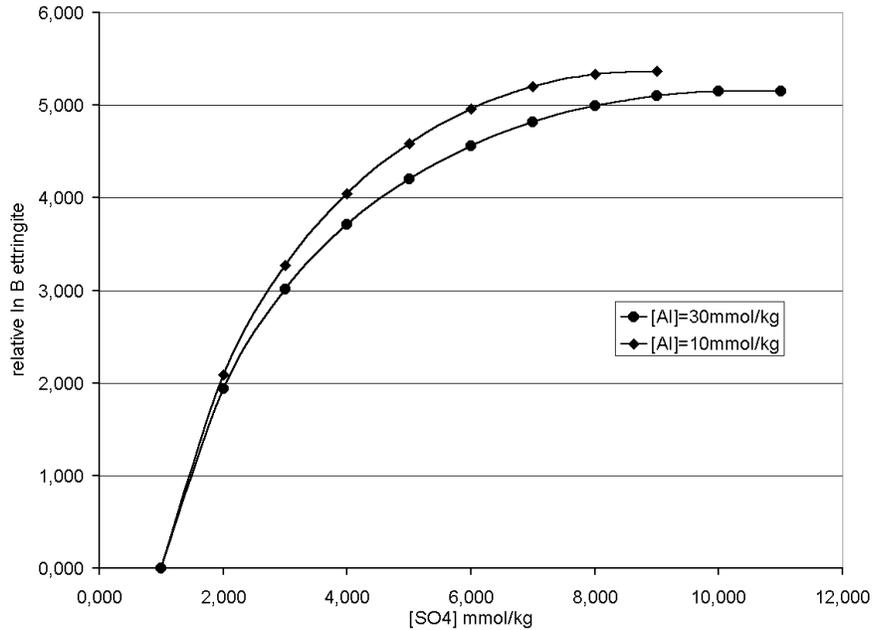


Figure 3 – Variation of the relative saturation index of ettringite along the experimental plan as a function of sulfate concentration

Discussion

The results of the calculation can be checked by drawing the of surface E but also curve I on the CaO-Al₂O₃-SO₄-H₂O system at 20°C presented on the [Ca]-[Al] axis when the sulfate concentration is fixed.

Two sulfate concentrations, 1 and 10 mmol/kg, are given (Fig. 4 and 5). The calculation enables to extent the knowledge of the position of surface E at low aluminat concentration without using experimental data. In the case of the dissolution of solids releasing calcium, aluminat and sulfate ions, the projection of surface E is always reached before curve I as expected ; at the beginning of hydration, ettringite is precipitated very rapidly and C₂AH₈ is not formed. Moreover the position of the projection of surface E is found before the equilibrium curve of C₂AH₈ for aluminat concentrations lower than 10mmol/kg ; in this case C₂AH₈ will never form even at longer ages as the aqueous phase is always undersaturated with respect to this solid.

The fact that β_E increases with $[Al]$ indicates that at high aluminate concentrations, the values of β_E inducing an instantaneous precipitation (nucleation favored with respect to growth) are more difficult to reach. Thus in these systems ettringite crystals are expected to be bigger and the precipitation rate to be slower, even if the supersaturation value may be high but this value has to be considered relatively to β_E .

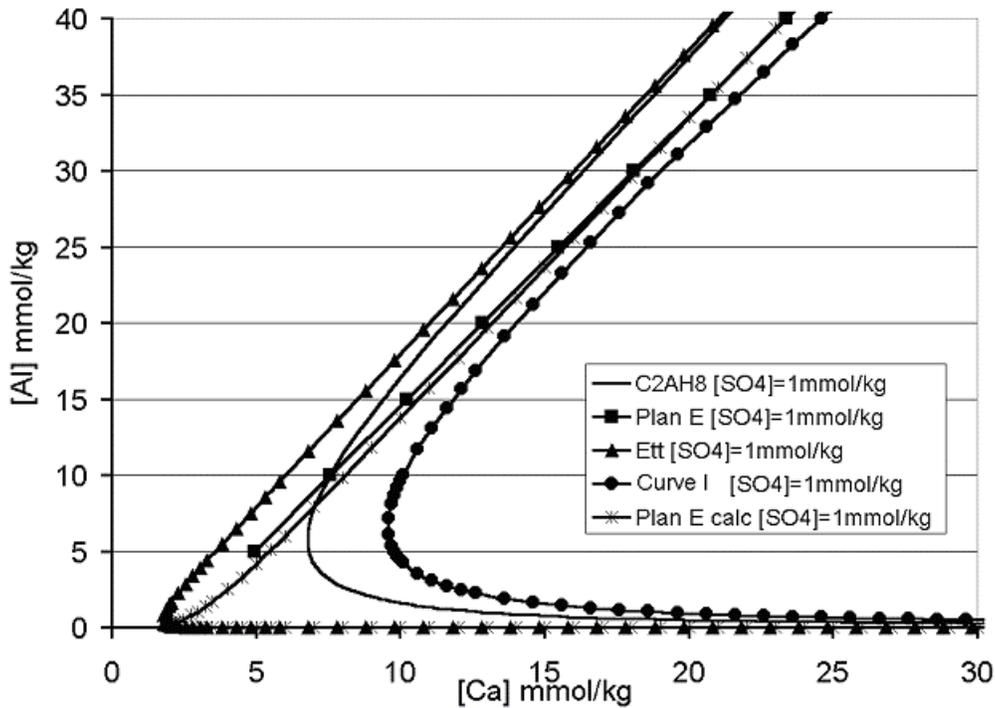


Figure 4 - Position of the equilibrium surface of ettringite, equilibrium curve of C_2AH_8 , curve I and plan E on the $[Ca]$ - $[Al]$ plan for $[SO_4] = 1$ mmol/kg

This can be demonstrated by CA +gypsum [6] and C_3A +gypsum [11] systems which both form ettringite at the hydration beginning but in higher amounts and with smaller crystals in the case of C_3A +gypsum.

The results tend to indicate a kind of inhibiting effect induced by aluminate and sulfate ions that has to be linked with the corresponding decrease in pH. These information enabled us to use a simplified equation to simulate the kinetics of ettringite precipitation that takes into account supersaturation level ($SI-1$), the catalyzing effect of pH and of the inhibition effects of sulfate and aluminate ions :

$$\frac{d \text{ ettringite}}{dt} = A.K_0.(SI - 1).[H^+]^{-0.05}[SO_4^{2-}]^{0.2}[Al(OH)_4^-]^{0.3} \text{ (Eq. 1)}$$

Concentrations correspond to the ionic species and not the total concentration of a chemical element. The rate constant of the reaction is denoted by K_0 and estimated to be $20 \mu\text{mol}/\text{sec}/\text{m}^2$. A (m^2/m^3) is a constant that represents the volumic surface area of ettringite linked with the nucleus size. The power constants applied to the concentrations have been set using an average value calculated from different precipitation experiments. Equation 1 refers to homogenous nucleation of ettringite from ions in the aqueous phase.

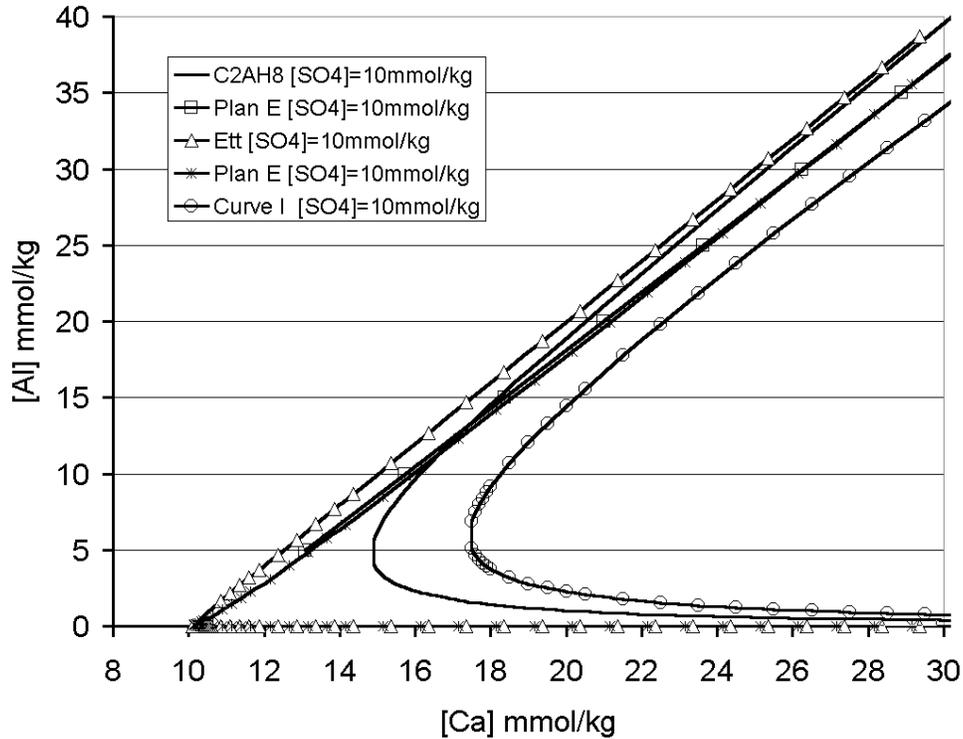


Figure 5 - Position of the equilibrium surface of ettringite, equilibrium curve of C_2AH_8 , curve I and plan E on the $[\text{Ca}]-[\text{Al}]$ plan for $[\text{SO}_4] = 10 \text{ mmol}/\text{kg}$

If both calcium and sulfate concentrations are fixed and thus aluminate concentration progressively increased, the saturation index of ettringite that passes through a maximum (Fig. 6). Thus we have used two sets of aqueous phase composition in equation 1 in order to simulate the duration of the induction period as a function of the evolution of SI ettringite : we should observe a decrease of the induction period before ettringite precipitation up to an instantaneous precipitation and then go back to an induction period.

The first set of compositions had fixed sulfate and calcium concentrations, 1 and 5 mmol/kg respectively and variable aluminate concentrations. For the second set of experiments, aluminate concentrations was also variable

and sulfate concentration was set to 10 mmol/kg and the calcium one to 12 mmol/kg.

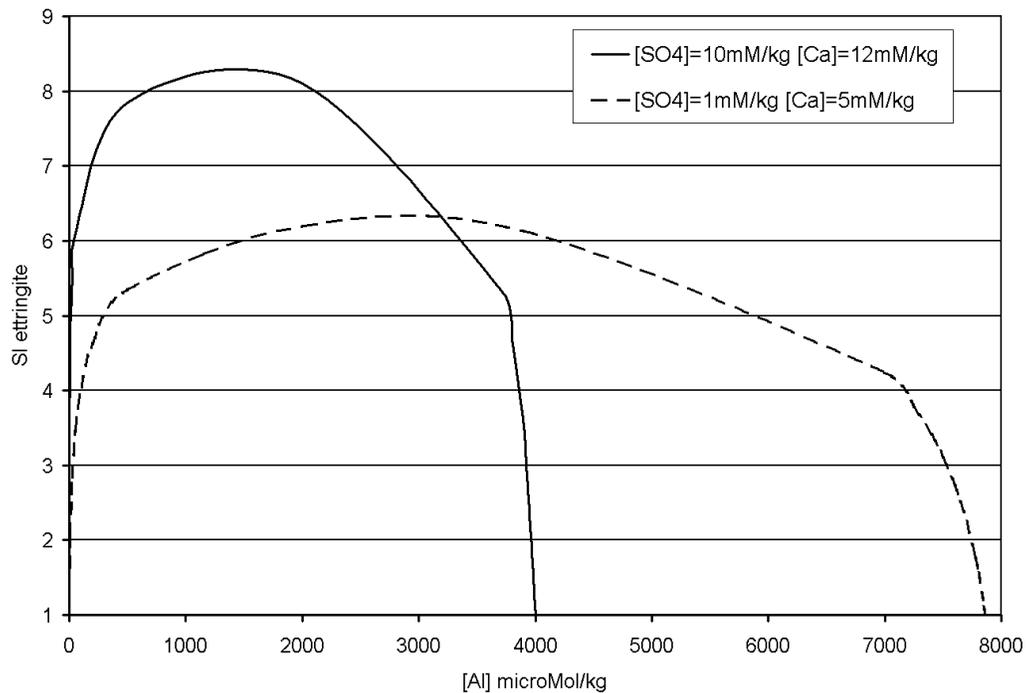


Figure 6 – SI of ettringite for the two sets of aqueous phase compositions :
 set 1 : [Ca] = 5 mmol/kg; [SO₄] = 1 mmol/kg and variable [Al],
 set 2 : [Ca] = 12 mmol/kg; [SO₄] = 10 mmol/kg and variable [Al].

Figure 7 presents ettringite amounts formed as a function of time with 1 liter of a starting aqueous phase having the following composition : [Ca] = 5mmol/kg; [SO₄] = 1mmol/kg and [Al] = 20μmol/kg. This kind of aqueous phase displays an induction period before the massive ettringite precipitation that will be considered at the inflexion point observed during the precipitation (Fig. 7).

If the time at which the inflexion point occurs is plotted for all compositions of the two sets of aqueous phase composition (Fig. 8), it is indeed observed that an increase of the aluminate concentration at fixed calcium and sulfate ones, reduces the duration of the induction period to reach an immediate precipitation and then presents an increasing induction period when the aqueous phase composition becomes close to the upper part of ettringite equilibrium curve. As expected with the relative position of the equilibrium curve of ettringite with respect to surface E, most of the aqueous phase compositions induce an immediate precipitation, especially for low aluminate concentrations, corresponding to high pH, where a variation of a few micromoles is enough to make the system passing from a quite long induction period to an immediate precipitation.

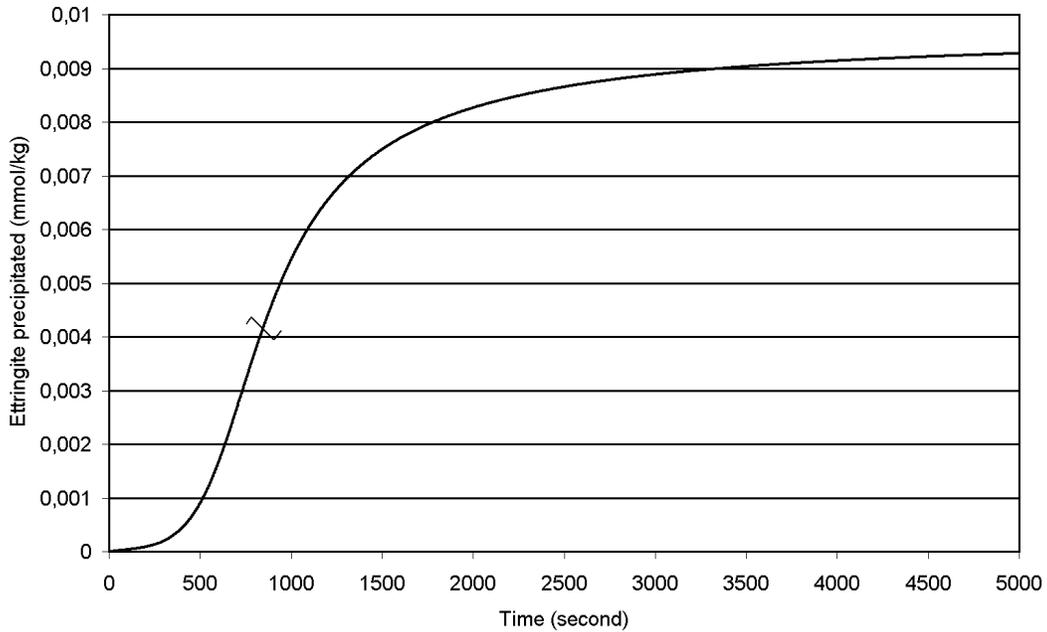


Figure 7 – Simulated rate of ettringite precipitation from an aqueous phase containing : [Ca] = 5mmol/kg; [SO₄] = 1mmol/kg and [Al] = 20μmol/kg.

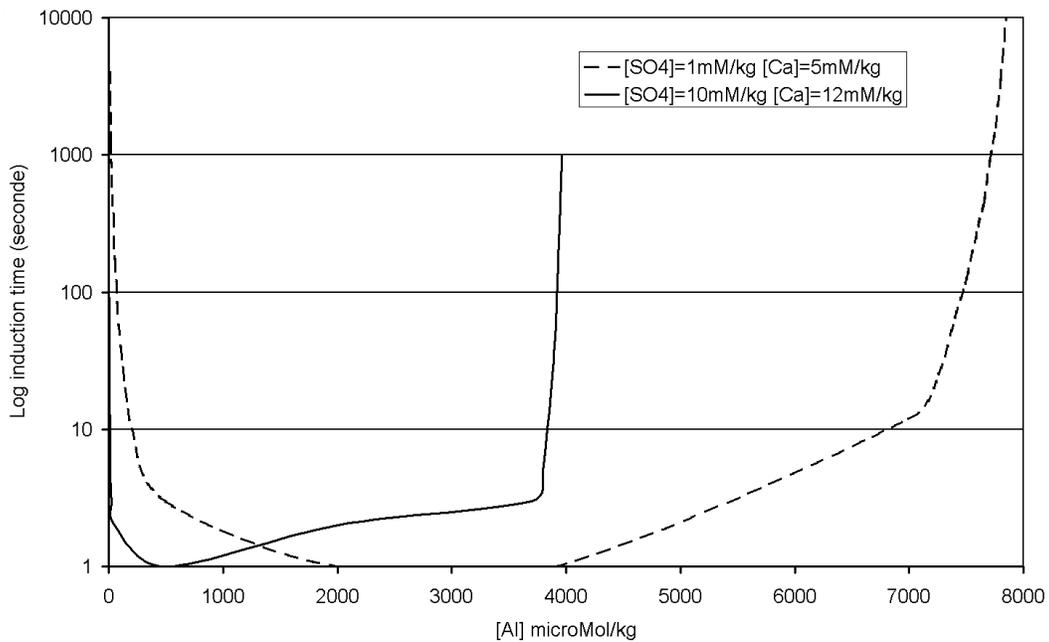


Figure 8 – Induction time before ettringite precipitation for the two sets of aqueous phase compositions :

- set 1 : [Ca] = 5 mmol/kg; [SO₄] = 1 mmol/kg and variable [Al],
- set 2 : [Ca] = 12 mmol/kg; [SO₄] = 10 mmol/kg and variable [Al].

It has to be pointed out that if the calculation is made without the term related to the concentration in equation 1, the precipitation would have been immediate for very small supersaturation and thus the domains

between equilibrium curve and maximum supersaturation domains (that display an induction period) could not be simulated.

Conclusion

It is possible thanks to homogeneous or heterogeneous nucleation and growth experiments to determine domains called maximum supersaturation domains that induce an immediate precipitation. The location of the boundaries of these domains can be estimated from these experiments using an apparent solubility constant that varies with the aqueous phase composition :

$$\ln K_{\text{critically supersaturated solid}}(\text{parameters}) = \ln K_{\text{solid}} + \ln \beta (\text{parameters})$$

with $\ln \beta$ corresponding to the saturation index.

Once these boundaries are known, it is possible to know the evolution of the saturation index as a function of the aqueous phase composition at the boundaries, and thus define autocatalytic or inhibiting effects with respect to nucleation and growth of the solid. These effects can be used to define a simplified equation in order to estimate the precipitation rate.

The reported methodology has been successfully applied to ettringite precipitation in the CaO-Al₂O₃-CaSO₄-H₂O system at 20°C. Moreover additional terms related to other ions could be easily added to consider more complex systems and also to use some precipitation experiments of the literature such as the work done by Cody et al. [12].

References

- [1] D. Damidot, F. P Glasser, Thermodynamic investigation of the CaO-Al₂O₃-CaSO₄-H₂O system at 25°C and the influence of Na₂O, Cem. Concr. Res. 23 (1993), pp 221-238
- [2] V. Tantayakom, T. Sreethawong, H. Scott Fogler, F.F. de Moraes, S. Chavadej, Scale inhibition study by turbidity measurement, Journal of Colloid and Interface Science 284 (2005) pp 57-65
- [3] P. Barret, D. Bertrandie, Hydration of aluminat cements, Advances in Cement and Concrete, in Grutzeck and Sarkar (Eds), Proc of Engineering Foundation Conference, Durham, 1994, pp 132-145
- [4]. D. Damidot and P. Barret, Calculation of the maximum supersaturation curve of C₂AH₈ in the CaO-Al₂O₃-H₂O system at 20°C, in Justness (Ed.), Proc of 10th Int. Congress on the chemistry of cement, Goteborg, 1997, 2ii024

- [5] D. Damidot and F. Sorrentino, Modification of the hydration process from $C_{12}A_7$ to C_3A at 20°C , in Justness (Ed.), Proc of 10th Int. Symposium on the chemistry of cement, Goteborg, 1997, 2ii025
- [6] D. Damidot, A. Rettel, Effect of gypsum on CA and $C_{12}A_7$ hydration at room temperature, Grieve and Owens (Eds) in Proc of 11th Int. Congress on Cement Chemistry, Durban, 2003, pp 1855-1864
- [7] M. Collepardi, G. Baldini, M. Pauri, and M. Corradi, "Tricalcium aluminate hydration in the presence of lime, gypsum or sodium sulfate", Cem. Concr. Res. 8 (1978) pp.571-577
- [8] P.W. Brown, L.O. Libermann and G. Frohnsdorff, Kinetics of the early hydration of tricalcium aluminate in solutions containing calcium sulfate, J. Amer. Ceram. Soc., 67 (1984) pp.793-95
- [9] C.H. Fentiman, A. Bonin, M. Testud, Etude de compréhension du système $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$, Internal Report Lafarge, 1990
- [10] D.L. Parkhurst, D.C. Thorstenson, L.N. Plummer, PHREEQE - A computer program for geochemical calculations, U.S. Geological Survey, USGS-WRI-80-96, 1980
- [11] D. Damidot, F.P. Sorrentino, Observation of the hydration of cement paste by ESEM: care needed to study the early hydration, 18th Proc. Int. Cement Microscopy, Houston, 21-25 Avril, 1996, pp 342-355
- [12] A.M. Cody, H. Lee, R.D. Cody, P.G. Spry, The effects of chemical environment on the nucleation, growth and stability of ettringite $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$, Cem. Concr. Res. 34 (2004), pp 869-881