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Chemical equilibria between C–S–H and ettringite, at 20 and 85 °C

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Abstract

Mixes of C–S–H and ettringite were synthesized in suspension systems and their equilibria were studied at 20 and 85 °C. Concentrations in solution (calcium, sulfate, aluminium) were measured and the mineralogical state of the systems was studied by means of X-ray diffraction. The equilibria between C–S–H and ettringite are described. The relative importance of sulfate bound to the C–S–H is evaluated. The kinetics of ettringite reprecipitation from a "C–S–H–ettringite" system at 85 °C placed at 20 °C are also evaluated.

Keywords: Calcium silicate hydrates; Ettringite; Temperature; Sulfate sorption

1. Introduction

The conditions under which a concrete can suffer Delayed Ettringite Formation (DEF) are still not fully understood. The steam cure, cement composition, fineness of the cement and water/cement ratio are important parameters in influencing DEF but no general relationship has yet been found between the risk of DEF and these parameters [1,2]. It is thus of prime importance to understand the mechanisms leading to DEF.

These mechanisms might include many aspects such as hydrated cement phases chemistry (equilibrium and kinetics) [2,3], microstructural phenomenons [4,5], diffusion at the local scale (sulfate diffusion to the place of ettringite precipitation, for instance [2]) and at the scale of the concrete element (water ingress or alkali leaching are considered as determining phenomena [5]) and finally mechanical considerations [6–9].

The present work focuses on the chemical mechanism usually proposed for DEF, in which ettringite forms after steam curing perhaps from a sulfoaluminate phase (such as calcium monosulfoaluminate) and from sulfate bound to the C–S–H [2,3,10–13].

Sulfate binding to C–S–H was studied and quantified in a preliminary study [13], on synthesized C–S–H in equilibrium with Na_2SO_4 solutions. The conclusions of the study were in accordance with results already published in literature: sulfate binding to C–S–H increases with sulfate concentration in solution, and the higher the Ca/Si ratio of the C–S–H, the higher the quantity of sulfate bound to the C–S–H.

In order to model a cement paste in a more realistic way, suspensions of C–S–H and ettringite were synthesized and studied. The equilibria between C–S–H and ettringite were determined at 20 and 85 °C. Particular attention was paid to the quantity of sulfate bound to the C–S–H, which is usually considered as the sink for sulfate during steam curing. The reversibility (from 85 to 20 °C) and the kinetics of the reactions were also evaluated, since it might explain the fact that DEF expansions are observed after a relatively long induction period.

2. Experimentals

C–S–H and ettringite were synthesized separately before being mixed together and put at the desired temperature. The synthesis protocols are described below.

2.1. Synthesis of C–S–H

Twenty C–S–H samples were synthesized by mixing 0.900 g of SiO_2 (silica fume Aerosil 200, ignition loss 4%) with 1.320 g of CaO in 100 mL of deionized, decarbonated water, in order to

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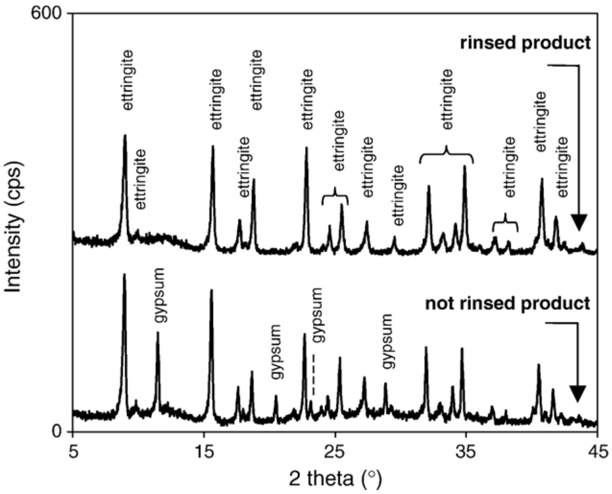

Fig. 1. X-ray diffraction diagram of synthesized ettringite, before and after rinsing with water.

obtain a Ca/Si ratio of 1.5 in the solid. All manipulations were performed in a CO_2-free glove-box. Samples were agitated daily during a three-week reaction period, after which equilibrium was believed to be reached.

The quantity of C–S–H in the system is approximated by the quantity of SiO_2 since the quantity of silicon in solution is very low. More details about this synthesis protocol can be found in Ref. [13].

2.2. Synthesis of ettringite

Ettringite was synthesized according the following protocol: a CaO slurry was kept at 5 °C before adding $Al_2(SO_4)_3{:}18H_2O$ in stoichiometric quantity. The mix was kept for 24 h at 5 °C and then at 20 °C for two weeks.

The solid suspension was separated from its equilibrium solution by filtration (0.22 μm filters), and part of it was vacuum-dried. X-ray diffraction (XRD) showed that the main phase was ettringite, but traces of gypsum were also detected. This gypsum could be eliminated by rinsing the solid phase with deionized, decarbonated water, as shown by X-ray diffraction (Fig. 1). From the concentrations in solution, and by difference with what was introduced, the composition of the solid phase was calculated: Ca:Al:S = 6:2:3, which is the stoichiometry of ettringite. The solid was vacuum-dried for two weeks. The mass lost by a sample of the dried solid after 4 h at 1100 °C showed that the dried solid contained ≈ 32 moles of water per mole of ettringite, which is the correct stoichiometry of ettringite. The synthesized solid could thus be considered as pure and dry ettringite.

Table 1
Quantities of CaO, SiO_2, ettringite and water introduced for syntheses at 20 °C

Synthesis	CaO (mmol)	SiO_2 (mmol)	Ettringite (mmol)	Water (g)
*101	23.7	15.0	0.010	100.2
*102	23.6	15.0	0.016	100.0
*103	23.7	15.1	0.040	100.0
*104	23.5	15.0	0.081	100.0
*105	23.6	15.1	0.200	100.0
*201	23.6	15.0	0.220	100.1
*202	23.5	15.0	0.435	100.0
*203	23.6	15.1	0.655	100.0
*204	23.6	15.0	1.090	100.1
*205	23.6	15.1	2.183	100.0

Table 2
Quantities of CaO, SiO_2, ettringite and water introduced for syntheses at 85 °C

Synthesis	CaO (mmol)	SiO_2 (mmol)	Ettringite (mmol)	Water (g)
C–S–H *106	23.6	15.1	0.009	100.0
C–S–H *107	23.6	15.0	0.016	100.0
C–S–H *108	23.5	15.1	0.041	100.0
C–S–H *109	23.6	15.0	0.080	100.0
C–S–H *110	23.6	15.0	0.201	100.0
C–S–H *206	23.6	15.0	0.217	100.0
C–S–H *501	235.8	150.9	3.206	1000.3
C–S–H *207	23.7	15.1	0.438	100.0
C–S–H *208	23.5	15.1	0.658	100.0
C–S–H *209	23.6	15.0	1.091	100.0
C–S–H *210	23.5	15.1	2.176	100.1

2.3. Mix of C–S–H and ettringite

Ettringite was added to the C–S–H suspensions in measured amounts, from 10 mg to 2.75 g. The mixes were then put at 20 or 85 °C and kept in sealed bottles for two weeks. The suspensions were agitated daily.

2.4. Solid and solution analysis

The solid suspension was separated from its solution by centrifugation, and the equilibrium solution was filtered (0.22 μm filters) for analysis.

The solid phase was lyophilized prior to X-ray diffraction. The liquid phase was investigated for calcium and sulfate by ionic chromatography and aluminium by atomic absorption.

Table 3
Concentrations of calcium, sulfate and aluminum in solution, Ca/Si, S/Si and Al/Si ratios of the solid phase and phases detected by XRD at 20 °C

Synthesis	[Ca] (mmol/L)	$[SO_4]$ (mmol/L)	[Al] (mmol/L)	Ca/Si	S/Si	Al/Si	XRD
*101	21.5	0.11	0.0006	1.50	0.0014	0.0014	C–S–H, CH
*102	21.2	0.13	0.0006	1.49	0.0025	0.0023	C–S–H, CH
*103	21.5	0.21	0.0010	1.50	0.0068	0.0055	C–S–H, CH
*104	21.8	0.30	0.0010	1.51	0.0148	0.0112	C–S–H, CH
*105	21.7	0.38	0.0005	1.56	0.0387	0.0275	C–S–H, CH, ett.
*201	21.7	0.44	0.0012	1.58	0.0428	0.0305	C–S–H, CH, ett.
*202	21.2	0.44	0.0006	1.66	0.0873	0.0602	C–S–H, CH, ett.
*203	21.3	0.46	0.0028	1.75	0.1319	0.0900	C–S–H, CH, ett.
*204	21.0	0.28	0.0033	1.94	0.2248	0.1512	C–S–H, CH, ett.
*205	21.1	0.24	0.0012	2.39	0.4500	0.3011	C–S–H, CH, ett.

Table 4
Concentrations of calcium, sulfate and aluminum in solution, Ca/Si, S/Si and Al/Si ratios in the solid phase and phases detected by XRD at 85 °C

Synthesis	[Ca] (mmol/L)	[SO_4] (mmol/L)	[Al] (mmol/L)	Ca/Si	S/Si	Al/Si	XRD
*106	11.6	0.06	0.0008	1.55	0.0013	0.0012	C–S–H
*107	12.2	0.13	0.0004	1.56	0.0025	0.0023	C–S–H
*108	11.4	0.37	0.0006	1.56	0.0060	0.0057	C–S–H
*109	11.6	0.78	0.0003	1.59	0.0112	0.0111	C–S–H
*110	13.6	2.36	0.0005	1.62	0.0254	0.0278	C–S–H
*206	14.1	2.46	0.0005	1.63	0.0281	0.0301	C–S–H
*501	17.9	4.31	–	1.63	0.0366	–	C–S–H
*207	17.0	5.14	0.0003	1.70	0.0552	0.0604	C–S–H, ett.
*208	17.0	4.99	0.0006	1.78	0.1016	0.0907	C–S–H, ett.
*209	17.1	5.71	0.0004	1.96	0.1867	0.151	C–S–H, ett.
*210	16.7	5.36	0.0004	2.40	0.4123	0.299	C–S–H, ett.

The ratios Ca/Si, S/Si, Al/Si were calculated from the difference between the elemental quantities introduced in the system and the concentrations of the different ions in solution.

A summary of syntheses (quantities of constituents introduced) and results (concentrations in solution, molar ratios in the solid phase and XRD results) are given in Tables 1–4.

3. Results and discussion

Much information can be extracted from the results of these experiments. Three main results will be developed to answer three questions :

- What is the effect of temperature on the equilibrium between C–S–H and ettringite ?
- What is the relative importance of the sulfate fixed by the C–S–H as compared to the sulfate bound to sulfoaluminate phases ?
- Is the reaction reversible (from 85 to 20 °C), and if so, what is the rate of the return to the 20 °C equilibrium ?

The results will be presented essentially as the quantity of sulfate bound to the solid phase (S/Si ratio of the solid phase) as a function of the total sulfate concentration [SO_4^{2-}] measured in the equilibrium solution.

3.1. Equilibrium between C–S–H and ettringite — effect of temperature

The equilibria between C–S–H and ettringite are presented in Fig. 2. At 20 and 85 °C, the isotherms can be divided in two segments: first an increase of the sulfate concentration in solution, and second, an increase of the S/Si ratio as the sulfate concentration in solution remains constant.

In the first part of the curves, at 20 and 85 °C, the sulfate concentration in solution increases as ettringite is added in the system: ettringite is fully dissolved. The S/Si ratio of the solid increases only slightly, showing that almost all sulfate passes into solution. X-ray diffraction measurements showed no crystalline phase. The sulfate not in solution could be bound to the C–S–H (up to S/Si ≈ 0.04 at 85 °C), and this will be discussed in Section 3.2.

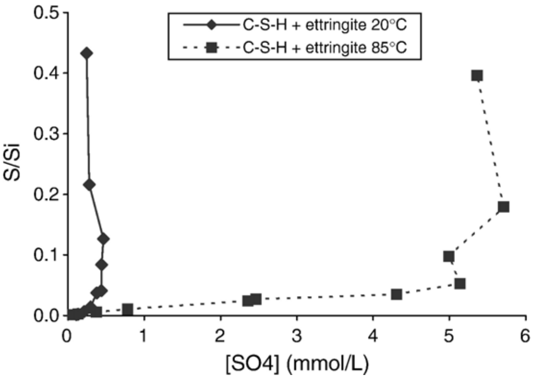

Fig. 2. Sulfate bound to the solid phase (S/Si ratio) as a function of sulfate concentration in the solution and temperature (20 and 85 °C).

At about [SO_4^{2-}] = 0.4 mmol/L at 20 °C and [SO_4^{2-}] = 5 mmol/L at 85 °C, the S/Si ratio of the solid increases abruptly and the sulfate concentration remains constant as more ettringite is added. As confirmed by XRD analysis, this increase of sulfate in the solid corresponds to ettringite precipitation (Tables 3 and 4). Aluminium concentration in solution confirms this result since the Al/S ratio in the solid phase (calculated from the meaured aluminium concentration in solution) increases with a 2/3 slope (Fig. 3), which corresponds to the ettringite stoichiometry. At 85 °C, calcium monosulfoaluminate, which is often observed at high temperature in hydrated cement systems, was expected but could not be detected by XRD measurements. No other phase (apart from C–S–H, portlandite and ettringite) was detected by XRD.

The effect of temperature is to increase the sulfate (and aluminium) concentrations in solution. This is no surprise since the ettringite solubility increases with temperature [14,15].

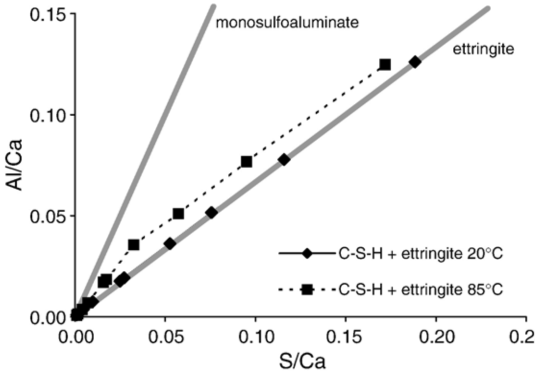

Fig. 3. Aluminium bound to the solid phase (Al/Si ratio) as a function of sulfate bound to the solid phase (S/Si ratio) at 20 and 85 °C. A 2/3 slope correspond to ettringite precipitation, a 2 slope correspond to calcium monosulfoaluminate precipitation.

3.2. Comparison with results obtained in a "C–S–H–Na_2SO_4" system

Sulfate adsorption on the C–S–H is now considered by many authors as the probable source for sulfate release after steam curing leading to Delayed Ettringite Formation [2,3,5]. Sulfate binding on C–S–H has been studied in detail [3,10,12,13]. Besides, the thermodynamics of the CaO–Al_2O_3–SO_3–(Na_2O)–H_2O system have been the object of much experimental and modeling work [14,15]. However, to the authors' knowledge, no data obtained on synthetic systems on sulfate binding is available in the more complex system C–S–H – calcium sulfoaluminate.

Fig. 4 compares the sulfate bound to the solid phase (S/Si ratio) in the system "C–S–H–Na_2SO_4" (data from a previous study [13]) and in the system "C–S–H–ettringite".

For systems in which ettringite is detected, the S/Si ratio of the solid increases mainly because of the sulfate participating in ettringite formation. Before ettringite precipitation, no other crystalline sulfate-bearing phase could be detected by XRD (within the limits of the technic, which can detect crystalline phases only, and only above a given detection limit). This result, in addition to the fact that the quantities of sulfate in the solid phase are similar in the "C–S–H–Na_2SO_4" and in the "C–S–H–ettringite" systems (Fig. 4 at 85 °C), is a good indication that below ettringite equilibrium, sulfate present in the solid phase is bound to the C–S–H only.

This allows estimation of the proportion of sulfate bound to the C–S–H (as compared to the sulfate in sulfate-bearing phases such as monosulfoaluminate or ettringite) in a model system of cement hydrates.

An additional observation is that the sulfate concentration in solution, which is imposed by the sulfoaluminate phases present at equilibrium and their solubility with temperature, determines the quantity of sulfate bound to the C–S–H, as can be seen Fig. 4. For instance, at 20 °C, the sulfate concentration in solution is so low that the quantity of sulfate bound to the C–S–H is negligible. On the contrary, at 85 °C, the sulfate concentration in equilibrium with ettringite is much higher, leading to higher quantities of sulfate bound to the C–S–H. Whether the aluminium is incorporated in the C–S–H structure (which is not proven by the present experimental data) or in the form of a calcium-aluminate phase, its presence does not seem to modify the sulfate binding of C–S–H.

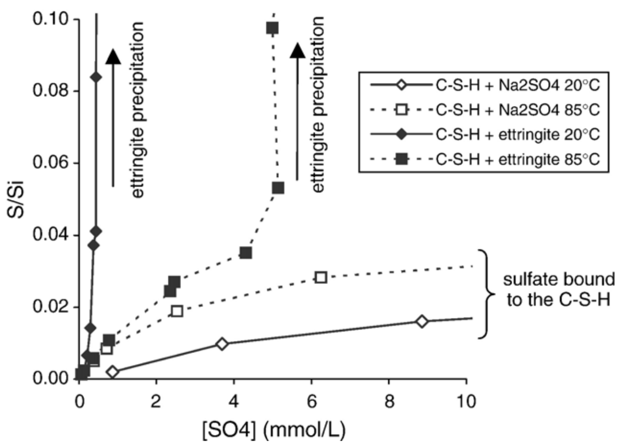

Fig. 4. Comparison between the sulfate bound to the solid phase (S/Si ratio) in the "C–S–H–ettringite" system (present work) and the sulfate fixed on the C–S–H in the "C–S–H–Na_2SO_4" system (Ca/Si = 1.50 at 20 °C, Ca/Si = 1.58 at 85 °C, data from a previous study [13]).

3.3. Effect of temperature on sulfate distribution

C–S–H synthesized in the present study are different from C–S–H in a cement paste (lower Ca/Si ratio, no Al incorporated initially to the structure and C–S–H precipitated in a high liquid/solid ratio suspension). They can however be considered as a model for the behavior of C–S–H in a cement paste, since the trends in chemical equilibria will be similar. The aim of the following paragraph is to evaluate the significance of the previous results extrapolated to a cement paste if the cement paste would behave as the synthetic system.

These results were obtained from synthetic systems in which the relative importance of C–S–H and ettringite differs from that encountered in a cement paste. For an average Portland cement, $Al/Si \approx 0.44$, and $S/Si \approx 0.15$ (cement type 10 cited in [16]). The maximum quantity of sulfate fixed by a $Ca/Si = 1.5$ C–S–H is $S/Si \approx 0.02$ at 20 °C (and $S/Si \approx 0.04$ at 85 °C) [13]. If the C–S–H were saturated with sulfate, the S/Si ratio remaining for the formation of a sulfoaluminate phase such as ettringite would only be $S/Si \approx 0.13$ ($S/Si \approx 0.11$ at 85 °C). Thus, at 20 °C, 13% of the total sulfate initially present in the cement would be fixed by the C–S–H. This value would reach 26% at 85 °C.

This is the *maximum* quantity of sulfate that can be bound on C–S–H of $Ca/Si = 1.5$, i.e. if C–S–H were saturated with respect to sulfate. This is not the case in a cement system since the quantity of sulfate bound to the C–S–H strongly depends on the sulfate concentration in solution. The equilibrium curve (Fig. 4) shows that at 20 °C, the sulfate concentration in solution is very low (the maximum concentration is at equilibrium with ettringite, that is about $[SO_4^{2-}] \approx 0.4$ mmol/L), leading to a very low quantity of sulfate bound to the C–S–H ($S/Si \approx 0.002$). On the contrary, the sulfate concentration is much higher at 85 °C: $[SO_4^{2-}] \approx 5$ mmol/L, thus the quantity of sulfate fixed by the C–S–H is much higher ($S/Si \approx 0.027$). Thus, the difference between the quantity of sulfate bound to the C–S–H at 85 and 20 °C can represent about 15% of the total sulfate initially present in a cement, which is not negligible.

Temperature increases the solubility of ettringite (increasing the sulfate concentration in solution), thus increasing the quantity of sulfate bound to the C–S–H. This can be considered as a good mechanism explaining ettringite dissolution (or non-formation during hydration) at high temperature.

3.4. System reversibility between 85 and 20 °C

The first sections described the equilibria between C–S–H and ettringite at 20 and 85 °C. No kinetics were considered. In

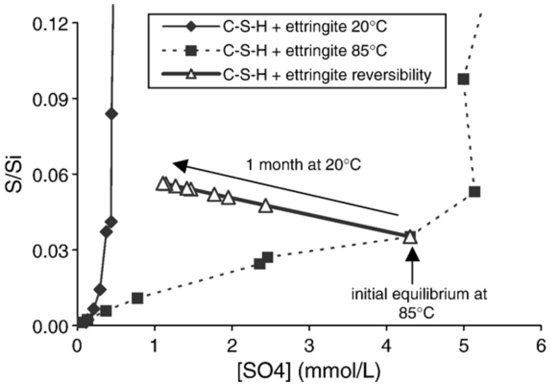

Fig. 5. Reversibility of the system equilibrated at 85 °C and put at 20 °C. The isotherms (20 and 85 °C) represent the sulfate bound to the solid phase (S/Si ratio) as a function of sulfate concentration in the solution. The points between the isotherms represent the state of the system which was at equilibrium at 85 °C slowly heading to a new equilibrium after being put at 20 °C.

the case of delayed ettringite formation, the expansion is believed to be related to the formation of ettringite from an aluminium-bearing phase (usually calcium monosulfoaluminate) and the sulfate released from the C–S–H [2,3,10,12]. The kinetics of the overall reaction (release of sulfate, monosulfoaluminate dissolution, ettringite precipitation) are unknown, but could partly explain why the ettringite formation is *delayed*.

In order to evaluate the reversibility and the kinetics of the return to the 20 °C equilibrium for a system equilibrated at 85 °C, a one-month experiment was performed. As described initially, a suspension consisting in C–S–H and ettringite was proportioned so that at 85 °C no ettringite was present in the system.[1] This system is a model for the chemistry of a cement paste during a steam curing, in which ettringite is absent due to sulfate sorption on the C–S–H and formation of another sulfoaluminate phase. This preparation, kept for two weeks at 85 °C, was returned to 20 °C and the sulfate in solution was monitored for one month. The S/Si ratio was calculated as explained before and the results are reported in Fig. 5. The solid phase was also analyzed by X-ray diffraction.

The first point of the reversibility curve, which was measured on the system at 85 °C, is on the S/Si isotherm determined at 85 °C. After being placed at 20 °C, the sulfate concentration slowly decreases, and at the same time the S/Si ratio in the solid increases. Ettringite could be detected by XRD after less than 15 days at 20 °C. Total reversibility was not reached after one month at 20 °C, but was almost completed.

From these results, it can be deduced that a system "C–S–H–ettringite" equilibrated at 85 °C can return to the 20 °C equilibrium when placed at 20 °C. However the kinetics of the overall reaction (sulfate desorption from the C–S–H and the reaction of sulfate with an Al-bearing phase to form ettringite) are quite slow, requiring more than one month. During one month, the sulfate concentration was supersaturated with respect to ettringite. This is a necessary condition in which crystallization pressures can be generated. If ettringite crystallization occurs in small pores and if supersaturation is important enough, this mechanism could lead to expansion.

These slow kinetics could explain (at least in part) the delay before any expansion can be observed on mortars suffering from DEF. Results of laboratory experiments show typical induction periods of three months after steam curing [5,8,16] before any expansion can be detected. Diffusion phenomena (much slower in a hardened mortar than in a suspension) and mechanical considerations (initiation of microcracking) could explain why expansions are even more delayed.

4. Conclusions

The present work aimed at determining the equilibria between C–S–H and ettringite in water at 20 and 85 °C. C–S–H and ettringite were synthesized separately before being mixed together in suspension and put at the desired temperature. This specific synthesis protocol and a precise measurement of the ionic concentrations in solution gave the isotherms of equilibrium between C–S–H and ettringite in water at 20 and 85 °C. The conclusions of this study are the following :

- The equilibrium between C–S–H and ettringite is a affected by temperature. At 20 °C, ettringite precipitates at around 0.4 mmol/L of sulfate in solution. At 85 °C, ettringite precipitation occurs at around 5 mmol/L of sulfate in solution. This is due to the increased solubility of ettringite at high temperature. The sulfate concentration range before ettringite precipitation at 20 °C was too narrow to be studied precisely. At 85 °C, before the ettringite equilibrium precipitation is reached, the ettringite introduced in the system is entirely dissolved, all the aluminium is in the solid phase and only part of the sulfate is bound to the solid phase (the remaining sulfate being in the solution).
- The sulfate present in the solid phase before ettringite precipitation seems to be bound to the C–S–H, since the measured S/Si ratios are similar whether aluminium is present (this work) or not (previous work, sulfate adsorption on the C–S–H only was studied) in the system. These results reveal that the quantity of sulfate bound to the C–S–H is not negligible in a cement paste, particularly at high temperature since the higher sulfate concentration increases the quantity of sulfate bound to the C–S–H.
- The kinetics of the return to the 20 °C equilibrium for a system synthesized at 85 °C and put at 20 °C were estimated. The reactions (sulfate release from the C–S–H and precipitation of ettringite) seem reversible but were not fully completed after one month at 20 °C, showing slow overall kinetics.

These conclusions can help understand the mechanism of Delayed Ettringite Formation. At high temperature (during steam curing for instance), ettringite becomes more soluble, the sulfate concentration in solution increases and the quantity of sulfate bound to the C–S–H increases accordingly. When the system is placed at room temperature, ettringite can precipitate,

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[1] The composition of the system was the following: C–S–H suspension made from 236 mmol of CaO, 151 mmol of SiO_2 and 1 L of water, to which was added 3.2 mmol of ettringite. The initial sulfate concentration was about 4.5 mmol/L at 85 °C.

but the kinetics are quite slow (not even considering diffusion or nucleation phenomena that make ettringite precipitation even slower). These slow kinetics might explain, on the one hand the delay before any expansion can be observed on steam-cured mortars, and on the other hand, crystallization pressures induced by the supersaturation of the solution with respect to ettringite that could lead to expansion of the material on a macroscopic scale.

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