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Controlling the rate of hydration of calcium sulfoaluminate cements: the case of lithium and borate ions

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Abstract

Calcium sulfoaluminate (CSA) cements that require less energy and that produce less CO₂ than Portland cement during their manufacture are receiving increasing attention in the context of sustainable development. Moreover, by increasing their gypsum content, a wide series of materials can be designed, ranging from rapid-hardening to shrinkage compensating, and eventually to self-stressing. CSA cements have been used in China in a wide range of general construction. Besides, due to the structural flexibility and sorption properties of some of the hydrates precipitated during their hydration, CSA cements are of interest to stabilize hazardous wastes. Their setting time depends on their ye'elimite content, the kind and content of minor phases, and the amount and reactivity of the added calcium sulfate. In addition, admixtures may be useful to control the rate of hydration and fulfill the application requirements. This presentation is focused on the chemistry underlying the acceleration effect of lithium ions and the retardation effect of borate ions.

A panel of techniques was used to investigate the early age hydration of a belite CSA cement with a high ye'elimite content as a function of the lithium and borate concentrations in the mixing solution. The evolution of electrical conductivity and heat flow of the cement pastes were monitored with ongoing hydration. The pore solution was also extracted and analyzed by ICP-AES. In addition, the phase assemblage was characterized after fixed periods of time by X-ray diffraction, thermogravimetry and MAS-NMR (¹¹B, ²⁷Al).

Lithium salts (LiOH, LiNO₃) were shown to accelerate CSA hydration by decreasing the duration of the period of low thermal activity. This acceleration was even noticed with very small additions of lithium (2.5 μmol Li/g of cement). It increased with the lithium concentration up to 20 μmol Li/g of cement, and then reached a plateau. As for calcium aluminate cements, the postulated mechanism was a faster precipitation of aluminum hydroxide containing lithium ions, which accelerated the whole hydration process.

On the contrary, borate ions caused the precipitation of poorly crystallized ulexite at early age. As long as ulexite was present, dissolution of ye'elimite was strongly slowed down. The duration of the period of low thermal activity increased with the amount of ulexite precipitated, and the acceleration of cement hydration occurred only when this phase was destabilized.

When borate and lithium ions were simultaneously introduced in the mixing solution, these two mechanisms were superimposed.

Originality

Calcium sulfoaluminate cements (CSA) are regarded as a possible low-CO₂ alternative to Portland cements (PC). However, the mechanism of CSA hydration is complex and not as well understood as for PC. This work brings new insights into the influence of two admixtures (a retarder and an accelerator) on the hydration rate of a belite CSA cement. Thanks to a robust methodology combining experimental characterizations of the solid and liquid phases using a large panel of techniques, some mechanisms are proposed for the first time to explain the retardation caused by borate ions, which can be counterbalanced by the acceleration effect of lithium ions.

Keywords: calcium sulfoaluminate cement; hydration rate; retardation; acceleration; mineralogy

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1. Introduction

Due to the release of carbon dioxide from the raw materials and the large quantities of fuel used during manufacture, cement clinker production contributes to about 4% of the global CO₂ emissions from fuel use and industrial activities. Low energy cements producing less CO₂ than Portland cement during their manufacture are thus receiving increasing attention nowadays (Gartner, E. 2004; Chen, I.A. and C.G. Juenger, M. 2011). In this context, calcium sulfoaluminate (CSA) cements offer several advantages (Sharp, J.H. *et al.* 1999). (i) The lower lime content of the raw meal reduces the energy demand for limestone decarbonation (Popescu, C.D. *et al.* 2003), as well as the CO₂ emissions (Sharp, J.H. *et al.* 1999; Feraille, A. *et al.* 2007). (ii) The firing temperature of the clinker being 100 to 200°C lower than that required for Portland cement, the energy consumption of the kiln is reduced (Popescu, C.D. *et al.* 2003) and the emissions of NO_x gases are limited (Quilin, K. 2001; Takuma, Y. *et al.* 1994). (iii) The clinker is relatively easy to grind, giving a further saving in energy consumption (Janotka, I. *et al.* 1999). Finally, substitution of some natural raw materials by suitable industrial by-products or waste materials also leads to reduce the energy demand, as well as the cost of the raw meal (Sahu, S. *et al.* 1993; Majling, J. *et al.* 1999; Sherman, N. *et al.* 1995; Beretka, J. *et al.* 1993; Arjunan, P. *et al.* 1999).

CSA cements can have highly variable compositions, but all of them contain ye'elimite, also called Klein's compound C₄A₃Š², in their clinker (Klein, A. *et al.* 1958; Mehta, P.K. *et al.* 1965). In this article, we will consider only a sulfoaluminate belite cement in which ye'elimite predominates over belite (C₂S) (Andac, O. *et al.* 1995). A wide range of gypsum or anhydrite contents (typically from 10 to 25% for gypsum) can be ground with CSA clinker to produce different CSA cements, ranging from rapid-hardening (at low gypsum content) to shrinkage-compensating, and eventually to self-stressing (at high gypsum content) (Glasser, F.P. *et al.* 2001).

Hydration of CSA cements strongly depends on the amount and reactivity of the added calcium sulphate. The main crystallized hydrates are calcium monosulfoaluminate hydrate and ettringite, the former being progressively replaced by the latter with increasing gypsum content (Glasser, F.P. *et al.* 2001; Winnefeld, F. *et al.* 2010). Both of them are precipitated together with amorphous aluminum hydroxide. Depending on the composition of the minor phases, other hydration products may also be observed, such as C-S-H (Glasser, F.P. *et al.* 2001; Zhang, L. and Glasser, F.P. 2002), strätlingite (Takuma, Y. *et al.* 1994; Andac, M. and Glasser, F.P. 1999), siliceous hydrogarnet (Takuma, Y. *et al.* 1994) and / or calcium hemi- or monocarboaluminate hydrate (Zhang, L. and Glasser, F.P. 2005). The hydration progress of CSA cement pastes occurs by the initial precipitation of ettringite and aluminum hydroxide, followed by the precipitation of calcium monosulfoaluminate hydrate once calcium sulphate has been depleted (Zhang, L. and Glasser, F.P. 2002, Sherman, N. *et al.* 1995). Belite has a slower hydration rate (Kasselouri, V. *et al.* 1995).

Accelerators and retarders may be useful to adjust the rate of hydration of CSA cements, depending on the intended application. Lithium salts (Li₂CO₃, LiCl) are known as powerful accelerators (Pera J. and Ambroise J., 2004). On the contrary, borate ions are strong retarders (Champenois, J.B. *et al.* 2013). This article aims at giving new insight in the processes involved in both cases. It also investigates the combined effect of borate and lithium ions on CSA cement hydration.

2. Experimental

2.1. Materials and preparation of the specimens

The CSA cement was prepared by mixing a ground industrial clinker (d₅₀ = 15.1 μm, specific surface area = 4.8 m²/g – measured by adsorption of N₂ using BET isotherm) with analytical grade gypsum (10% by weight of cement, d₅₀ = 18.7 μm, specific surface area ~ 0.5 m²/g) for 15 min using a Turbula mixer. The composition of the CSA clinker is reported in Table 1. In the clinker, ye'elimite (C₄A₃Š) predominated over belite (C₂S) and mayenite (C₁₂A₇). The other minor constituents, mainly phases containing titanium and iron, could be regarded as hydraulically inactive.

² Shorthand cement notations are used : C= CaO, S = SiO₂, A= Al₂O₃, F = Fe₂O₃, H = H₂O, Š = SO₃

Cement pastes were prepared using a water-to-cement (w/c) weight ratio of 0.6. Three kinds of mixing solutions were investigated: (i) a lithium hydroxide solution (0 to 0.1 mmol Li/g of cement), (ii) a 1.0 mol/L sodium borate solution prepared by titrating a solution of boric acid with sodium hydroxide up to pH 11.0, and (iii) a solution containing borate and lithium ions ($[B]_{\text{tot}} = 1 \text{ mol/L} - B$ introduced as $B(OH)_3$, variable lithium concentration – Li introduced as LiOH) at pH 11.0 adjusted with sodium hydroxide.

Mixing was performed for 5 min using a laboratory mixer equipped with a U-shaped stirrer blade rotating at 100 rpm. Cement pastes were cast into airtight polypropylene boxes (20 mL of paste per box) and cured at 25°C.

Experiments were also performed on cement suspensions (w/c ratio = 10) to study the hydration kinetics of rapidly-reacting systems. The mixing solutions were either pure water (reference) or solutions of lithium hydroxide, lithium nitrate or sodium hydroxide with concentrations ranging from 1 to 10 mmol/L.

Table 1 Mineralogical composition of the CSA clinker (KTS 100 provided by Belitex)

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	P ₂ O ₅	Cr ₂ O ₃	SrO	Na ₂ O	K ₂ O	SO ₃	ZnO	Cl ⁻	LOI
Wt%	5.44	38.53	1.19	41.98	1.47	1.64	0.01	0.17	0.03	0.09	0.03	0.14	8.83	0.01	0.03	0.41
Minerals	C ₄ A ₃ S̄		C ₂ S	C ₁₂ A ₇		CT	Periclase		C ₃ S̄	Quartz		Others ^a				
wt%	68.5		15.9	9.5		2.9	1.5		0.5	0.5		2.4				

2.2. Characterization methods

Hydration of cement pastes was followed using a highly sensitive Setaram C80-type microcalorimeter under isothermal conditions at 25.0 ± 0.5°C. The evolution of the heat flow of the fresh cement pastes was compared to the heat flow recorded for a sample aged of 6 months minimum with a stable temperature of 25°C.

Hydration of cement suspensions (w/c = 10) was investigated using a Multicad CDM 210 conductimeter. Experiments were performed in a thermo-regulated vessel (25°C) under magnetic stirring. The vessel was tightly closed to avoid carbonation. The conductivity cell was calibrated with a standard KCl solution (12.8 mS/cm) before every trial. At constant temperature, the electrical conductivity of the suspension depends on the concentration and type of ions in solution. Variations in the conductivity thus indicated changes in the chemical composition of the aqueous phase.

Cement hydration was stopped after fixed periods of time, depending on the samples, by successively immersing the crushed pastes into isopropanol and drying them in a controlled humidity chamber (with 20% relative humidity at 23 ± 2 °C). Crystallized phases were identified by X-ray diffraction (PANalytical X'Pert PRO MPD - copper anode $\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$ generated at 45 mA and 40 kV) on pastes ground to a particle size of less than 100 µm. Before analysis, silicon was added to the samples (10% by mass of sample, correction to take into account the amount of bound water increasing with ongoing hydration) and carefully mixed by grinding in a mortar to be used as an internal standard. Thermogravimetric analyses were carried out using a TGA/DSC Netzsch STA 409 PC instrument at 10°C/min up to 1000°C.

Some cement pastes samples were characterized using ¹¹B and ²⁷Al-MAS NMR. The spectra were recorded at a Larmor frequency of 256.7 MHz using a Bruker Avance III 800 MHz (18.8 T) spectrometer. The samples were spun at 20 kHz in a 2.5 mm probe. The ¹¹B spectra were made up of 64 free induction decays with a pulse length of 1µs ($\pi/10$) and a relaxation delay of 5s. The ²⁷Al spectra were made up of 2048 free induction decays with a pulse length of 1µs ($\pi/10$) and a relaxation delay of 1s to ensure quantitative reliability of the intensities observed for the ²⁷Al central transition for sites experiencing different quadrupole coupling. The chemical shifts were referenced to NaBH₄ and Al(NO₃)₃ respectively. Spectral decomposition was performed using DMFit software (Massiot D. *et al.*, 2002).

During the early age hydration (up to 60 hours), the pore solution of the cement pastes was also extracted by pressing (~5 kN) using a specific device. The pH of the recovered liquid was immediately measured with a high-alkalinity electrode (Mettler Toledo InLab Expert Pt1000 pH 0-14 T 0-100°C) calibrated using two IUPAC pH buffers at 10.012 ± 0.010 (25°C) and 12.45 ± 0.05 (25°C). Therefore the chemical composition was determined using ICP-AES (Vista Pro Varian). The analytical error was $\pm 5\%$.

2.3. Synthesis of aluminum and lithium hydroxides

Aluminum hydroxide precipitating in CSA cement at early age is poorly crystallized. To investigate the influence of lithium on its precipitation, synthetic amorphous $\text{Al}(\text{OH})_3$ was prepared by mixing aluminum nitrate and lithium nitrate in demineralized water at a Li/Al molar ratio comprised between 0 and 0.5. The pH was then set to 5.5 with a 30 wt % ammonia solution. A white gel-like compound precipitated instantaneously. The suspension was filtered and the compound washed several times with demineralized water, then with isopropanol. The solid was dried at 50°C.

A well-crystallized hydrated lithium aluminate, $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$, is known to precipitate when high contents of lithium are added to an aluminate solution (Matusinovic, T. *et al.* 1994). Such phase was synthesized by slowly neutralizing a 1 mol/L nitrate aluminum solution with a 30 wt % ammonia solution. Then, the pH was raised to 12 by adding a 1 mol/L lithium hydroxide solution. The suspension was left at room temperature for 12 hours. It was then filtered and the solid was successively washed several times with demineralized water and isopropanol. The precipitate was then dried under slight vacuum at room temperature. Drying at higher temperature was avoided because the loosely bound water was easily lost near 100°C.

The solids were characterized using X-ray diffraction and ^{27}Al -MAS NMR according to the protocols described in Section 2.2. The filtrates were analyzed using ICP-AES. The lithium and aluminum contents in the solid were assessed from the composition of the liquid phase by mass balance.

2.4. Ulexite synthesis

Ulexite is a mixed borate mineral containing sodium and calcium ($\text{NC}_2\text{B}_5\text{H}_{16}$) (Kemp, P.H. *et al.* 1956). This phase was synthesized as a reference by mixing calcium hydroxide and boric acid in demineralized water with a B/Ca molar ratio of 9 (Casabonne Masonnave J.M., 1987). The pH was then set to 10.5 by addition of sodium and/or lithium hydroxide with Na/Li ratios from 1 to 100. A white gel-like compound precipitated instantaneously. The solution was filtered and the solid was washed several times with isopropanol and dried at room temperature under vacuum since it was very sensitive to dehydration.

The solids were analyzed by using X-ray diffraction according to the protocol described in Section 2.2 and the filtrates were analyzed using ICP-AES to get information on the sodium and lithium contents in the solid.

3. Results and Discussion

3.1. Influence of lithium salts on the hydration rate of calcium sulfoaluminate cement

3.1.1 Experiments on cement suspensions

Lithium strongly accelerated the hydration of CSA cement. To enable the investigation of the early stages of hydration, the system was slowed down by increasing the water-to-cement (w/c) ratio. Sampling to analyze the composition of the aqueous phase was also easier. Figure 1 reports the evolution of the electrical conductivity of a cement suspension (w/c ratio of 10) when the solution contained lithium hydroxide (1 mmol/L).

As for calcium aluminate cements (Damidot, D. *et al.* 1996), four stages could be defined:

I – Dissolution period: some ions were released in solution due to the dissolution of anhydrous cement phases, and the electrical conductivity increased rapidly.

II – Induction period: the electrical conductivity reached a plateau, meaning that the composition of the aqueous phase remained almost constant. Dissolution and precipitation rates were low and similar, leading to a pseudo-stationary state. This period, also characterized by a low thermal activity, mainly corresponded to hydrate germination.

III – Massive precipitation period: the electrical conductivity decreased rapidly due to the massive precipitation of hydrates which consumed ions from the solution. To counterbalance this depletion of ions, the dissolution of anhydrous phases was accelerated, leading to a second increase in the electrical conductivity.

IV – Deceleration period: during the last period, dissolution and precipitation reactions continued to compete, but with a decreasing rate. The remaining quantity of anhydrous phases decreased and the surface of cement grains was progressively coated by hydrates which acted as a diffusion barrier for water. The electrical conductivity showed little variations.

Under the same experimental conditions, suspensions were filtered at selected times corresponding to characteristic points of the electrical conductivity curve. The solutions were analyzed by ICP-AES and the solids by X-ray diffraction and thermogravimetry. It was noticed that the electrical conductivity reached its minimum when sulfates were exhausted from the solution.

As long as sulfates were detected in solution, the main precipitated hydrates were ettringite and aluminum hydroxide according to mass balance equation (1). Once sulfate was exhausted, formation of calcium monosulfoaluminate hydrate occurred (equation (2)).

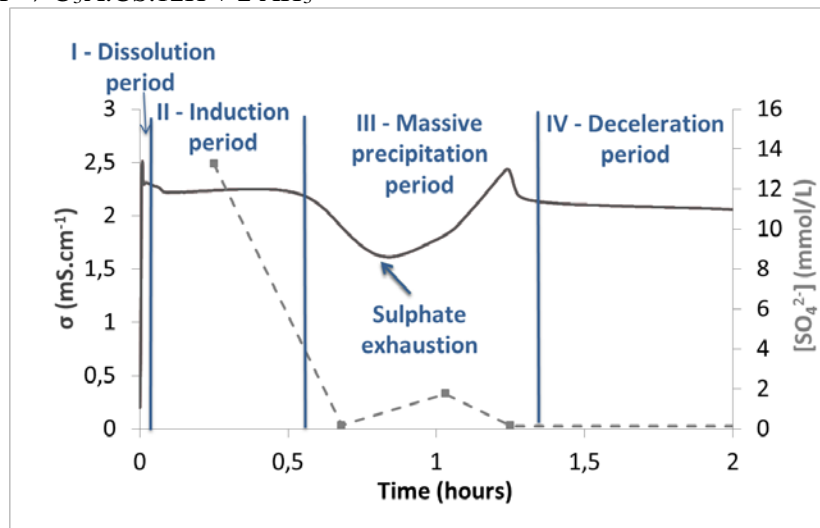
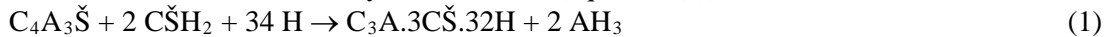


Figure 1 Evolution of the electrical conductivity during hydration of CSA cement by a 1 mmol/L lithium hydroxide solution ($w/c = 10$, $T = 25^\circ\text{C}$)

To investigate the influence of different mixing solutions on the hydration rate of CSA cement, the starting time of the massive precipitation period was determined for various lithium salts at a concentration of 1 or 10 mmol/L (Figure 2).

Massive precipitation occurred much more rapidly with the lithium hydroxide solution than with water. This acceleration could be attributed to lithium ions rather than to hydroxide ions. Indeed, it was still observed with lithium nitrate, whereas sodium hydroxide did not cause any significant change as compared with water.

This accelerating effect of lithium ions was also studied (Figure 3) as a function of the lithium concentration in the mixing solution, varying from 0 to 10 mmol/L, which corresponded to molar quantities of lithium per gram of cement (Li/C ratio) between 0 and 0.1 mmol/g. The accelerating effect of lithium increased with the Li/C ratio within the range 0 – 0.02 mmol/g and, for higher ratios, the magnitude of the acceleration remained constant (plateau effect).

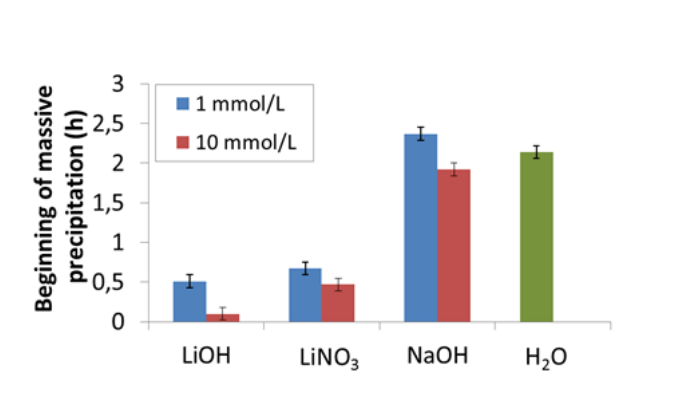


Figure 2 Time of occurrence of the massive precipitation period when CSA cement is hydrated by different mixing solution (salt added at a concentration of 1 or 10 mmol/L, w/c = 10, T = 25°C)

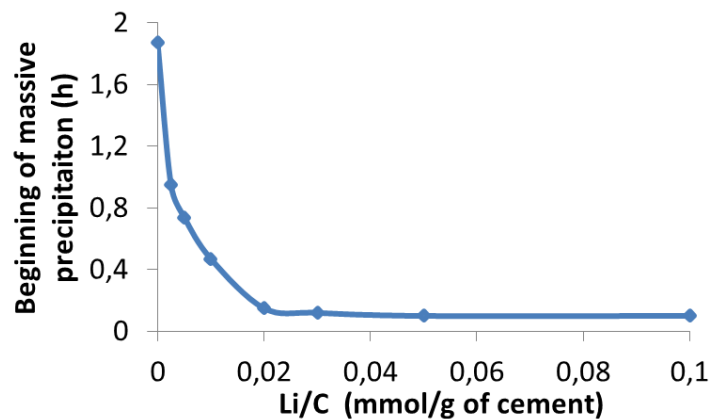


Figure 3 Time of occurrence of the massive precipitation period when CSA cement is hydrated by lithium hydroxide solutions of increasing concentration (w/c = 10, T = 25°C)

3.1.2 Experiments on cement pastes

Complementary experiments were performed on a cement paste (w/c = 0.6) hydrated by a lithium hydroxide solution. The lithium-to-cement (Li/C) ratio was set to 0.03 mmol/g (initial lithium concentration of 50 mmol/L), such concentration corresponding to the beginning of the plateau effect pointed out in Figure 3. The evolution of the phase assemblage was characterized by X-ray diffraction and thermogravimetry, whereas the interstitial solution was expressed using pressure and analyzed after increasing periods of hydration (Figure 4).

Gypsum was fully consumed 30 minutes after mixing. Up to 3 hours, the precipitated hydrates were ettringite, traces of calcium monosulfoaluminate hydrate and poorly crystallized aluminum hydroxide. This latter was already detected by thermogravimetry analysis (weight loss at 250°C) 5 minutes after mixing. The lithium concentration in the interstitial solution was below the detection limit (0.1 mg/L) from the first characterization time (15 min). This result showed that lithium was totally incorporated in a solid phase during the first stages of hydration.

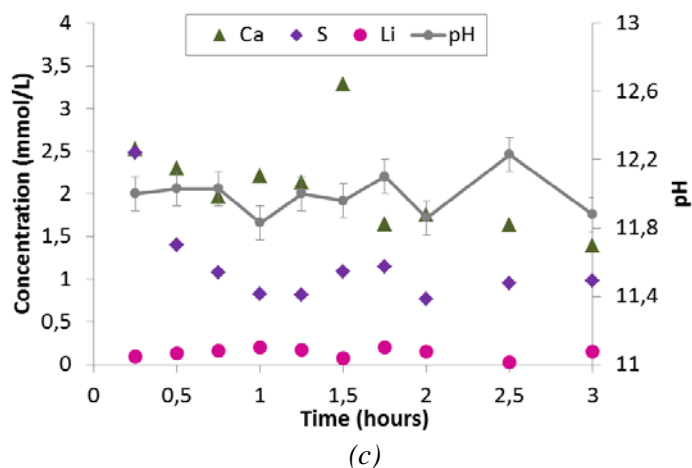
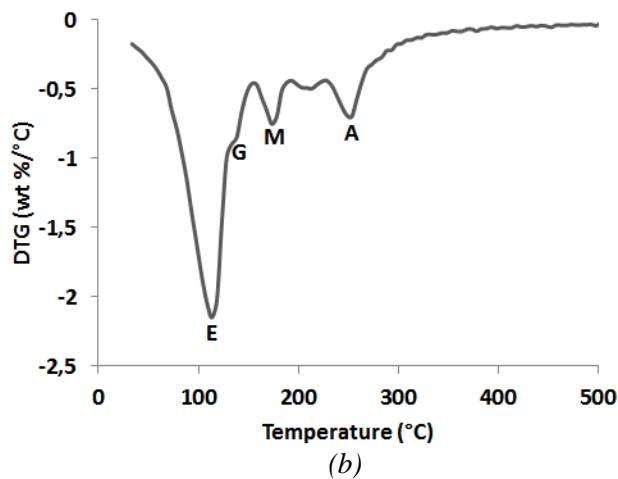
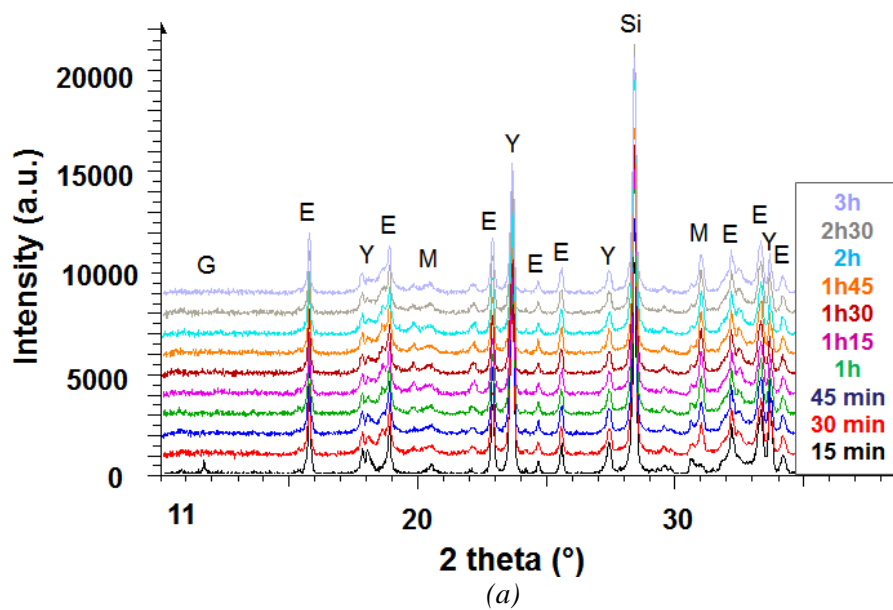


Figure 4 Hydration of CSA cement with 10% gypsum in the presence of a lithium hydroxide solution (Li/C = 0.03 mmol/g of cement, w/c = 0.6, T = 20°C) at early age : (a) X-ray diffraction patterns (E = ettringite, G = gypsum, M = monosulfate, Y = ye'elimite, Si = silicon); (b) TGA analysis of a 5 minute-old sample (E = ettringite, G = gypsum, M = monosulfate, A = aluminum hydroxide); (c) Evolution of pH and composition of the pore solution

3.1.3 Discussion: possible mode of action of lithium

Lithium strongly accelerates hydration of CSA cement. It is readily precipitated at an early age. A leveling in the acceleration occurs however at high concentration. A similar influence has already been described for calcium aluminate cement (Damidot, D. *et al.* 1996). Two mechanisms would be involved (Rodger, S.A. and Double, D.D. 1984; Backe, K.R. *et al.* 2001; Matusinovic, T. *et al.* 1994):

- at low concentration of lithium, precipitation of Li-substituted aluminum hydroxide with accelerated nucleation rate as compared with pure aluminum hydroxide;
- at higher concentration of lithium, precipitation of lithium aluminate hydrate $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ which serves as nucleation site for aluminum hydroxide precipitation.

In both cases, precipitation of aluminum hydroxide occurs more readily, which accelerates the whole hydration process.

In this study, precipitation of well crystallized $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ was never observed. However, poorly crystallized aluminum hydroxide was detected by TGA from the first characterization time, 5 minutes after mixing. Coprecipitation of a mixed hydroxide, comprising aluminum and but also small amounts of lithium, seems likely.

To check the feasibility to incorporate lithium in $\text{Al}(\text{OH})_3$, some syntheses of amorphous aluminum hydroxide were performed in the presence of lithium: the Li/Al ratio was progressively increased from 0 to 0.5. The product, which formed almost instantaneously, was characterized by ^{27}Al MAS-NMR (Figure 5). In agreement with literature, aluminum in $\text{Al}(\text{OH})_3$ was mainly in octahedral coordination (AlO_6), but tetrahedral (AlO_4) and pentahedral coordinations (AlO_5) were also noticed. Isobe (Isobe, T. *et al.* 2003) showed that amorphous aluminum hydroxide comprises subunits of AlO_4 , AlO_5 and AlO_6 which are bound through hydrogen bonds with a wide distribution of bonding strengths. The pentahedral coordination was not observed anymore when lithium was present. The chemical shift of the main peak corresponding to octahedral aluminum showed no variation, but its full width at half maximum decreased progressively when the Li/Al ratio increased. This indicated a better definition of the crystallographic site. At a Li/Al ratio of 0.5, the compound was not amorphous anymore: it exhibited well resolved X-ray diffraction lines characteristic of crystalline $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$.

These results thus confirmed the possibility to incorporate lithium into aluminum hydroxide with only slight modification of the crystallographic structure.

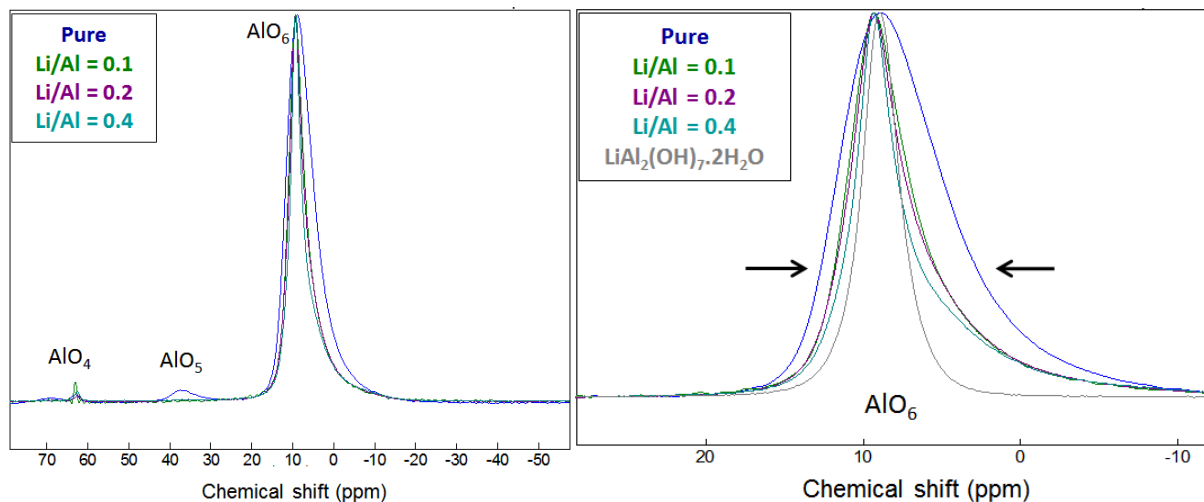


Figure 5 ^{27}Al -MAS NMR spectra of aluminum hydroxide (synthesized in the absence and in the presence of lithium) and of hydrated lithium aluminate $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$

3.2. Influence of sodium borate on the hydration rate of CSA cement

3.2.1 Rate of hydration

The heat flux released during CSA cement hydration by demineralized water or by a sodium borate solution ($[\text{B}] = 1 \text{ mol/L}$, $\text{pH} = 11$) was investigated using isothermal microcalorimetry ($T = 25^\circ\text{C}$)

(Figure 6). Sodium borate delayed hydration by increasing the duration of the period of low thermal activity. For a boron concentration of 1 mol/L and a pH adjusted to 11.0, the heat flux reached its maximum after 80 hours. In comparison, the maximum heat flow of the reference sample prepared with water was recorded after about 3 hours.

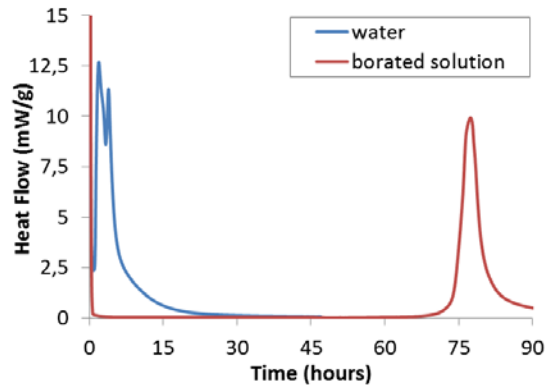


Figure 6 Heat flow produced during the hydration of CSA cement by water or by a sodium borate solution ($[B]_{\text{tot}} = 1 \text{ mol/L}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 25^\circ\text{C}$)

3.2.2 Phase assemblage and composition of the pore solution

The mineralogy and pore solution composition of a paste specimen prepared with CSA cement and a sodium borate solution ($[B]_{\text{tot}} = 1 \text{ mol/L}$, $\text{pH} = 11$) was carefully investigated (Figure 7).

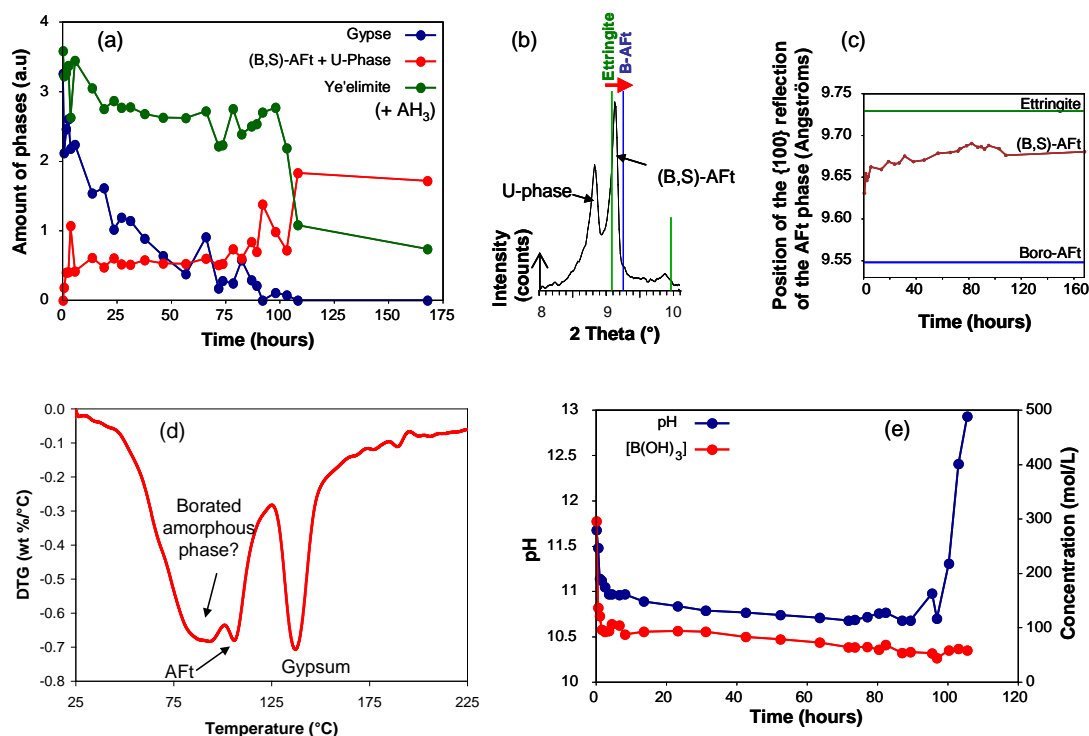


Figure 7 Hydration of a CSA cement by a sodium borate solution ($[B]_{\text{tot}} = 1 \text{ mol/L}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 20^\circ\text{C}$). (a) Mineralogical evolution inferred from XRD analysis. (b) Shift of the $\{100\}$ reflection of the precipitated AFt-type phase compared to ettringite and B-AFt. (c) Evolution of the position of the $\{100\}$ reflection of the (B, S)-AFt phase during hydration. (d) TGA analysis of a 24h-old sample. (e) Evolution of pH and boron concentration of the pore solution during hydration.

The XRD patterns recorded up to 95 h showed that very few amounts of ye'elimite dissolved until the depletion of gypsum (Figure 7-a). Note that the heat flow peak accompanying the acceleration of

hydration was recorded about 10 h earlier in the calorimetric experiment (Figure 6). However, the samples for the mineralogical investigation were cured at 20°C, instead of 25°C for the calorimetric study. This temperature difference could explain the slightly different rates of hydration in the two experiments since it is well known that CSA cement hydration is highly thermo-sensitive (Berger S., *et al.* 2011).

The slow dissolution of ye'elimite was accompanied by the precipitation of an AFt-type phase. Its {100} reflection exhibited a small deviation towards higher angles as compared with pure ettringite (Figure 7-b). This could be explained by the partial substitution of sulfate anions by borate anions in the structure of ettringite. Wenda and Kuzel (Wenda, R. and Kuzel, H.J. 1983) showed indeed that borate can completely substitute for sulfate in AFt phases. Poellmann (Poellmann, H. *et al.* 1993) additionally demonstrated that a large range of solid solutions exists between ettringite and the AFt phase containing boron. When the hydration degree increased, the amount of AFt-type phase increased, and the angular position of its {100} reflection approached that of pure ettringite (Figure 7-c), which could be explained by the progressive release of sulfates by dissolution of the anhydrous phases. When gypsum was exhausted, massive dissolution of ye'elimite occurred, accompanied by massive precipitation of the AFt-type phase. Small amounts of U-phase were also evidenced by XRD. It is an AFm-type phase, similar to calcium monosulfoaluminate hydrate, where some calcium cations are substituted by sodium cations. Its precipitation could be expected given the very high concentration of sodium in the mixing solution due to the pH set to 11 with sodium hydroxide. No other AFm-type phases could be detected.

Thermogravimetry analysis performed on a 1d-old paste confirmed the presence of residual gypsum and of small amounts of an AFt-type phase (Figure 7-d). An additional important weight loss was also recorded at 80°C, corresponding to a compound not detected by XRD, and thus amorphous or poorly crystallized. Complementary experiments were performed in order to identify this compound. The pore solution was extracted by pressing the cement paste and characterized for its pH and chemical composition (Figure 7-e). After an abrupt decrease from 11.6 to 11.0 at the very beginning of hydration, the pH showed little variation as long as gypsum was present, slightly decreasing from 11.0 to 10.75. About nine tenths of the borate ions were rapidly depleted. The solution also comprised high contents of sulfates (between 300 and 400 mmol/L), resulting from the progressive dissolution of gypsum, but calcium concentration remained very low (close to 20 mmol/L). The precipitation of an amorphous or poorly crystallized borate mineral containing calcium may be assumed from these results. It could explain the rapid stiffening of the cement paste observed experimentally shortly after mixing.

Formation of a calcium borate with possible $C_2B_3H_8$ stoichiometry has already been postulated to explain the strong retarding effect of borate ions on PC hydration (Roux C., 1989). However, the cement paste investigated in this study also comprised high sodium contents and thermodynamic calculations of the most stable phase assemblage rather predicted the precipitation of ulexite, a mixed borate mineral containing sodium and calcium ($NaCa[B_5O_6(OH)_6](H_2O)_5$) (Champenois, J.B. *et al.* 2015).

Ulexite was synthesized according to Casabonne's protocol (Casabonne Masonnave, J.M. 1987) and was analyzed by ^{11}B MAS-NMR (Figure 8). Its spectrum showed two main peaks for chemical shifts within the range [18.5; 14] ppm and [3.5; -1.5] ppm, corresponding to tricoordinated and tetraordinated boron atoms respectively. ^{11}B -MAS NMR analysis was also performed on cement paste samples aged of 6 and 24 h. As for ulexite, the spectra exhibited two peaks at [4; -1.5] ppm and [19; 13] ppm, showing the presence of boron both in tetrahedral and trigonal coordinations respectively. The ratio between the tetrahedral and trigonal sites was however much higher than in ulexite. This could be explained by assuming the precipitation of two boron-containing phases: ulexite, but also the mixed AFt-type phase containing borate and sulphate anions, as previously evidenced by X-ray diffraction and thermogravimetry analysis. Indeed, Champenois *et al.* (Champenois, J.B. *et al.* 2012) have shown that boron is tetrahedrally four-fold coordinated by oxygen in the crystal structure of the AFt phase. In comparison, the spectrum of a one-year old sample only exhibited one sharp peak characteristic of boron in tetrahedral coordination in the AFt phase. This

spectroscopic analysis thus supported previously reported thermodynamic calculations predicting the transient precipitation of ulexite at an early age in the cement paste hydrated by the sodium borate solution.

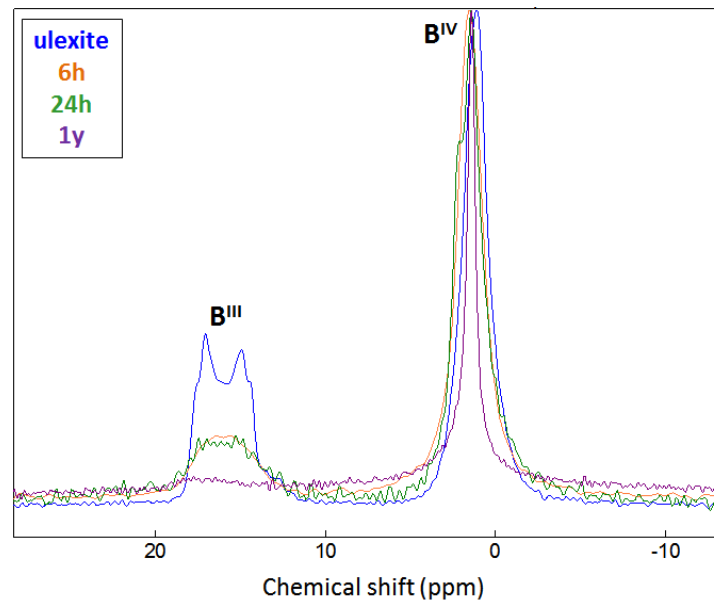


Figure 8 ^{11}B -MAS NMR spectra of ulexite and of cement paste samples hydrated by a sodium borate solution after 6 h, 24 h and 1 year. ($[\text{B}]_{\text{tot}} = 1 \text{ mol/L}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 20^\circ\text{C}$)

3.2.3 Discussion: possible mode of action of sodium borate

A thermodynamic study has shown that ulexite is stable when pH is comprised between 10.5 and 12 (Champenois, J.B. *et al.* 2015). In the investigated system, the pH remained close to 11, within the stability domain of ulexite, as long as gypsum was present. The exhaustion of gypsum was accompanied by a pH increase up to 13. Ulexite was then destabilized and cement hydration strongly accelerated.

The transient precipitation of ulexite thus seemed to play a key role in the control of the cement reactivity at an early age: as long as this phase was present, ye'elime dissolved very slowly.

3.3. Simultaneous influence of lithium and sodium borate on the hydration rate of CSA cement

3.3.1 Rate of hydration

The combined influence of borate and lithium ions on CSA cement hydration was investigated using isothermal calorimetry on paste samples prepared by mixing CSA cement with a 1 mol/L boron solution and a pH adjusted to 11.0 by addition of lithium and sodium hydroxides.

Figure 9 plots the time at which the heat flow reached its maximum versus the initial Li/C ratio in the cement paste. Adding lithium ions accelerated the hydration, as in absence of borate ions, by reducing the duration of the period of low thermal activity. A leveling effect in the acceleration was also noticed for Li/C ratios inferior to 0.05 mmol/g of cement, and a plateau effect was remarked for higher ratios.

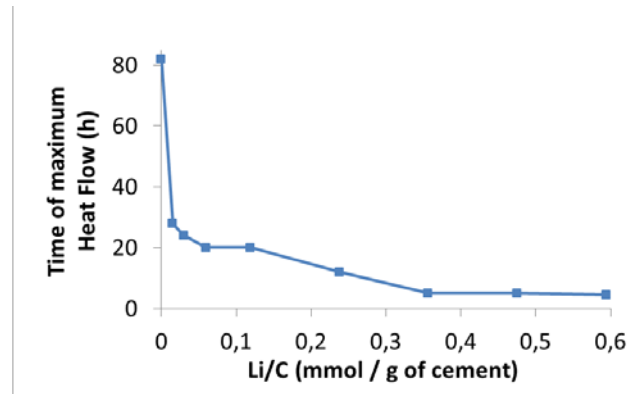


Figure 9 Heat flow recorded under isothermal conditions: influence of the initial LiOH concentration in the mixing solution on the hydration of a CSA cement hydrated by a sodium borate solution ($[B]_{\text{tot}} = 1 \text{ mol/L}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 25^\circ\text{C}$)

3.3.2 Phase assemblage and composition of the pore solution

Hydration stops were carried out on paste samples between one and sixty hours of hydration (Figure 10). The mixing solution exhibited a total boron concentration of 1 mol/L, a lithium hydroxyde concentration corresponding to a Li/C ratio of 0.03 mmol/g, and a pH of 11.0, adjusted with NaOH.

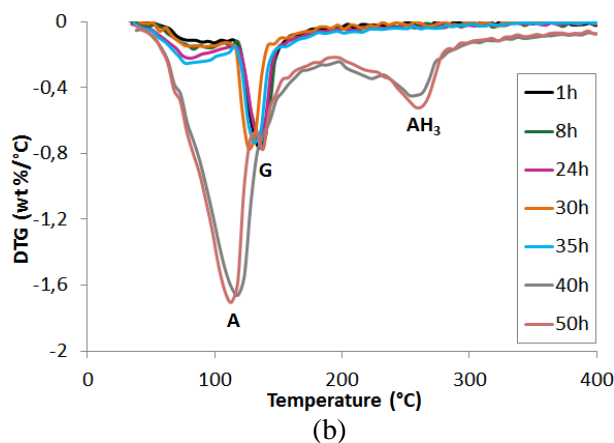
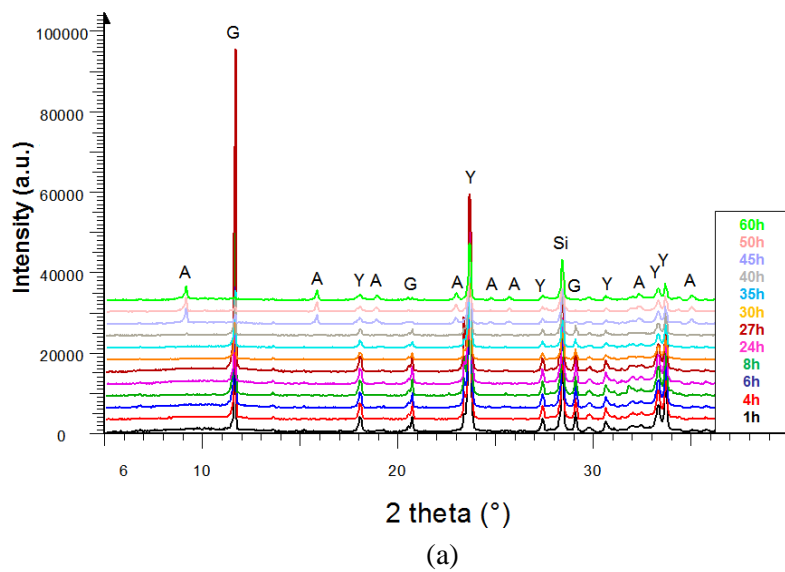


Figure 10 Hydration of CSA cement by a lithium/sodium borated solution ($[B]_{\text{tot}} = 1 \text{ mol/L}$, $\text{Li/C} = 0.03 \text{ mmol/g}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 20^\circ\text{C}$) at an early age : (a) X-ray diffraction patterns (A = AFt phase, G = gypsum, Y = ye'elimite, Si = silicon); (b) TGA analyses (A = AFt phase, G = gypsum, AH_3 = aluminum hydroxide)

Until 35 h, gypsum and ye'elimite were slowly consumed. However, the samples submitted to thermogravimetry analysis exhibited a significant weight loss at 80°C, which indicated the precipitation of an amorphous or poorly crystallized hydrated compound with loosely bound water. Dehydration occurred in the same range of temperature than ulexite observed for the {CSA + sodium borate} system.

After 40 h, hydration accelerated: gypsum and ye'elimite were consumed more rapidly, and precipitation of an AFt-phase and aluminum hydroxide occurred. The thermograms also showed the massive precipitation of aluminum hydroxide. No lithium borate hydrate was detected.

Figure 11 shows the evolution of the pore solution composition with ongoing hydration. During the first hour of hydration, about two thirds of the borate ions were depleted from the solution. A drop in the sodium concentration was also noticed. On the contrary, the lithium concentration remained almost constant. The pH was close to 11.7. The sulfate concentration was quite high, close to 300 mmol/L, whereas that of calcium was about ten times lower. These results were consistent with the precipitation of a sodium borate compound possibly comprising calcium, such as ulexite.

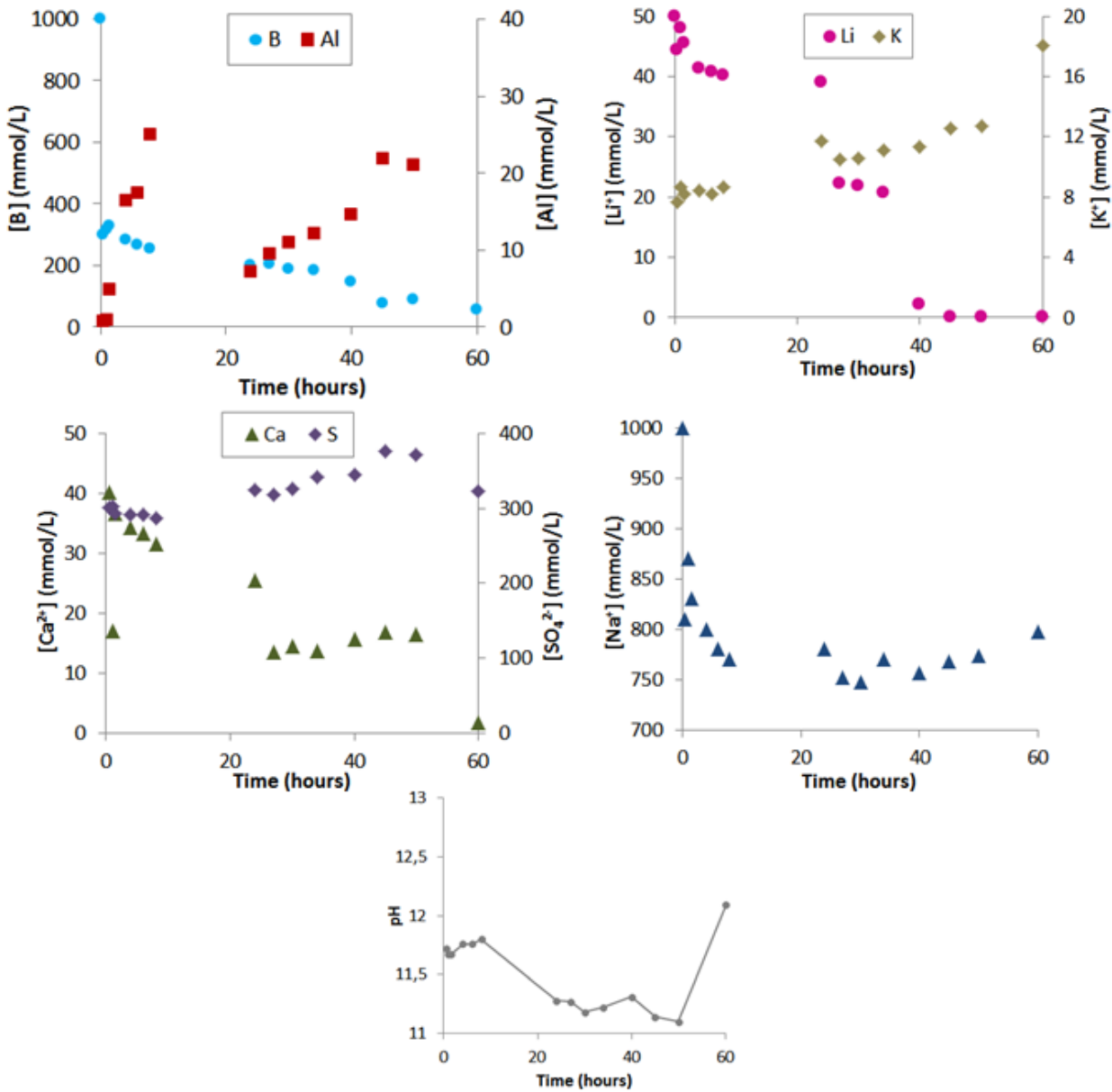


Figure 11 Hydration of CSA cement by a lithium/sodium borated solution ($[B]_{tot} = 1 \text{ mol/L}$, $Li/C = 0.03$, $pH = 11$, $w/c = 0.6$, $T = 20^\circ\text{C}$) at an early age: evolution of pH and composition of the pore solution during hydration

The lithium concentration began to decrease after 30 h and fell below the detection limit after 50 h. It should be noted that hydration accelerated during this period, leading to massive precipitation of aluminum hydroxide which could incorporate lithium.

In order to confirm the formation of ulexite, cement pastes aged from 30 minutes to 60 hours were analyzed by ^{11}B -MAS NMR (Figure 12). At 30 min, 1 h30 min, 6 h and 24 h, boron seemed to be precipitated only as ulexite. The fractions of tricoordinated and tetraordinated boron were almost equal to those of synthetic ulexite. At 60 h, a decrease in the fraction of tricoordinated boron was observed, as well as a refinement of the peak corresponding to tetrahedral boron. This could be explained by the additional precipitation of a mixed AFt phase containing borates and sulfates. This phase, which was actually observed by X-ray diffraction, is characterized by a sharp peak at a chemical shift of 0.9 ppm, corresponding to boron tetrahedrally four-fold coordinated by oxygen.

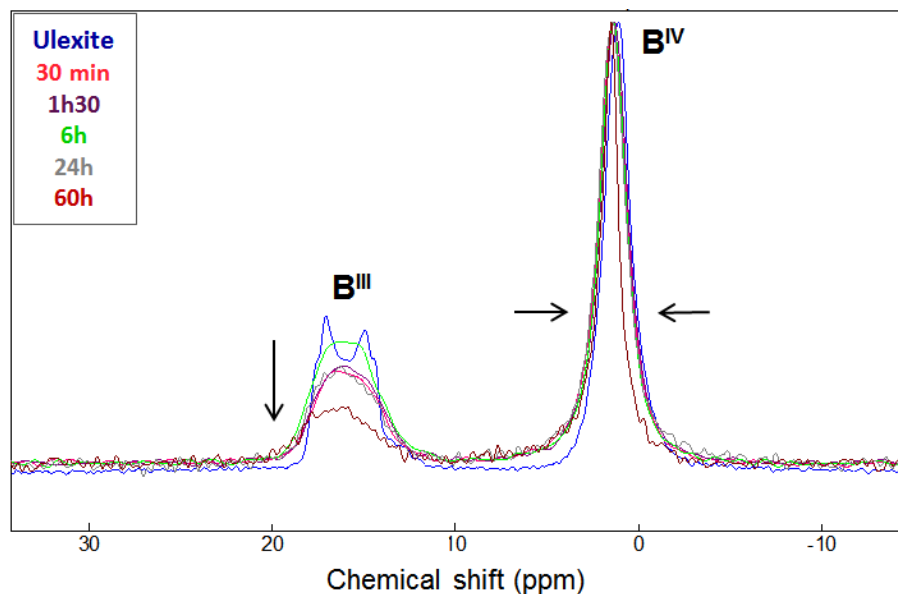


Figure 12 Comparison of the ^{11}B -MAS NMR spectra of synthetic well-crystallized ulexite and of cement pastes hydrated by a sodium and lithium borated solution ($[\text{B}]_{\text{tot}} = 1 \text{ mol/L}$, $\text{Li/C} = 0.03 \text{ mmol/g}$, $\text{pH} = 11$, $w/c = 0.6$, $T = 20^\circ\text{C}$)

3.3.3 Discussion: possible mode of action of sodium and lithium borate

When sodium borate and lithium hydroxide were introduced simultaneously in the mixing solution, the mechanisms identified for each species seemed to be simply superimposed without mutual interactions.

Precipitation of poorly crystallized ulexite occurred in the first minutes after mixing, slowing down the dissolution of ye'elimite. However, lithium enabled to limit the retardation due to sodium borate by shortening the period of low thermal activity. Precipitation of Li-substituted aluminum hydroxide with accelerated nucleation rate as compared with pure aluminum hydroxide likely speeded up the whole hydration process. It can be noted that the stage of accelerated hydration began whereas ulexite and gypsum were still present. In the absence of lithium, hydration accelerated only when gypsum was exhausted, which resulted in a pH increase causing the destabilization of ulexite. This destabilization of ulexite was not necessary anymore in the presence of gypsum.

4. Conclusion

When borate and lithium ions were introduced separately in the mixing solution, lithium was shown to accelerate the hydration of CSA cement with 10% gypsum whereas borate ions retarded it.

- As for calcium aluminate cement, lithium could accelerate the precipitation of aluminum hydroxide, which is known to be a key factor controlling the duration of the period of low thermal activity. Studies on simplified systems, consisting in synthesizing aluminum

hydroxide in presence of lithium, confirmed that lithium can be incorporated into aluminum hydroxide with only slight structural changes.

- On the contrary, borate ions caused the precipitation of poorly crystallized ulexite at an early age. As long as ulexite was present, dissolution of ye'elimite was strongly slowed down. The duration of the period of low thermal activity increased with the amount of ulexite precipitated, and the acceleration of cement hydration occurred only when this phase was destabilized.

These two mechanisms seemed to be superimposed without interaction when borate and lithium ions were simultaneously introduced in the mixing solution.

- The acceleration effect of lithium resulting from a shortening of the period of low thermal activity was still observed, as well as the levelling off at high lithium concentration.
- Transient precipitation of ulexite seemed likely, as shown ^{11}B -MAS NMR characterization of cement pastes at an early age.

This work offers new prospects for the conditioning of borate-rich waste, which may be encountered in the nuclear industry, using a calcium sulfo-aluminate cement: the retardation effect of borate ions can be simply counteracted by adding small amounts of lithium to the mixing solution.

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