Influence of sodium borate on the early age hydration of calcium sulfoaluminate cement

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ABSTRACT

Calcium sulfoaluminate (CSA) cements are potential candidates for the conditioning of radioactive wastes with high sodium borate concentrations. This work thus investigates early age hydration of two CSA cements with different gypsum contents (0 to 20%) as a function of the mixing solution composition (borate and NaOH concentrations). Gypsum plays a key role in controlling the reactivity of cement. When the mixing solution is pure water, increasing the gypsum concentration accelerates cement hydration. However, the reverse is observed when the mixing solution contains sodium borate. Until gypsum exhaustion, the pore solution pH remains constant at ~10.8, and a poorly crystallized borate compound (ulexite) precipitates. A correlation is established between this transient precipitation and the hydration delay. Decreasing the gypsum content in the binder, or increasing the sodium content in the mixing solution, are two ways of reducing the stability of ulexite, thus decreasing the hydration delay.

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1. Introduction

Calcium sulfoaluminate (CSA) cements requiring less energy and producing less CO_2 than Portland cement during their manufacture are receiving increasing attention in the context of sustainable development [1,2]. They can have highly variable compositions, but all of them contain ye'elimite, also called Klein's compound, in their clinker [3–6]. In this article, we will consider only sulfoaluminate belite cements in which ye'elimite ($C_4A_3\bar{S}$[1]) predominates over belite (C_2S) [7]. 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) [8]. Besides, CSA cements are of interest to stabilize hazardous wastes [9–15]. It has been shown recently that belite calcium sulfoaluminate cements with high ye'elimite contents may have good potential for the conditioning of borate-containing radioactive wastes: their rate of hydration is less retarded by borate ions than that of ordinary Portland cement [16–19]. Besides, they form by hydration large amounts of AFm and AFt phases [20–24]. However, the mechanism by which concentrated sodium borate solutions modify the hydration of CSA cements is still not fully understood. The speciation of boron in the cement paste also needs some clarifications. In addition to the AFm and AFt phases, other borate minerals can potentially form at high pH in the presence of calcium (frolovite CBH_4, hexahydroborite CBH_6, C_2BH, $C_2B_3H_8$, inyoite $C_2B_3H_{13}$ and nobleite CB_3H_4) [25–28]. Moreover, since the concentrated borate waste contains sodium, sodium borates should also be considered (NBH_8, NB_2H_{10}, NB_5H_{10}), as well as a mixed borate mineral containing sodium and calcium (ulexite $NC_2B_5H_{16}$) [25].

This work aims at giving new insight into the influence of sodium borate on the early age hydration of calcium sulfoaluminate cements with variable gypsum contents, as well as on the processes involved. A better understanding of the chemical evolution of such systems will help optimize the CSA cement-based recipes developed for the conditioning of radioactive borate-containing waste.

2. Experimental

2.1. Materials and specimen preparation

Several CSA cements were prepared by mixing a ground industrial CSA clinker (Belitex KTS 100) ($d_{10} = 2.5$ μm, $d_{50} = 15.1$ μm, $d_{90} =$

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[1] Shorthand cement notations are used in this article: C = CaO, S = SiO_2, $\bar{S}$ = SO_3, A = Al_2O_3, H = H_2O, T = TiO_2, B = B_2O_3 and N = Na_2O.

Table 1
Mineralogical composition of CSA clinker.

Minerals	$C_4A_3\bar{S}$	C_2S	$C_{12}A_7$	CT	MgO	Others
Weight %	66.2	13.5	9.4	2.6	0.9	7.4

49.8 μm, BET specific surface area = 4.8 m²/g) with the appropriate amount (0% to 20% by weight of cement) of analytical grade gypsum (d_{10} = 5.4 μm, d_{50} = 18.7 μm, d_{90} = 52.4 μm, BET specific surface area ~0.5 m²/g) for 15 min. The mineralogical composition of the CSA clinker is reported in Table 1. In the clinker, ye'elimite predominated over belite and mayenite. The other minor constituents, mainly phases containing titanium and iron, could be regarded as hydraulically inactive.

Cement pastes were prepared using a water to cement (w/c) ratio of 0.6. There were two main reasons for choosing such a high ratio.

– It should be noted that the chemical water demand of CSA cements is higher than that of Portland cement, and increases with the gypsum content of the binder [8]. In a previous work [29], it was shown that the minimum amount of water required for total hydration of cement comprising 80% clinker and 20% gypsum corresponds to a w/c ratio of 0.59 (0.54 by taking into account water brought by gypsum). The w/c ratio of 0.6 thus resulted from a compromise to avoid any stop in the hydration process due to lack of water while preventing any bleeding at an early age.
– From a more applied point of view, in the waste stabilization process, water is only brought by the waste. The higher the water content, the higher the waste loading in the cement matrix.

The mixing solution was either demineralized water or a solution containing 1 mol/L of borate ions at pH 11. In the latter case, the appropriate amount of boric acid was dissolved in demineralized water and the pH was set to 11 by adding analytical grade sodium hydroxide (960 mmol/L of NaOH for 1 mol/L of H_3BO_3). Such a solution mimics some contaminated waste streams generated by PWR nuclear plants. In the second part of the study, the sodium hydroxide concentration was varied from 0.85 mol/L to 1.12 mol/L while keeping the boric acid concentration constant at 1 mol/L, in order to get different pH values.

Mixing was performed for 5 min using a laboratory mixer equipped with an anchor stirrer and rotating at 100 r.p.m. Cement pastes were cast into airtight polypropylene boxes (7 mL of paste per box), and cured at 20 °C.

2.2. Specimen characterization

Hydration of the cement pastes was investigated using a highly sensitive Setaram C80-type microcalorimeter under isothermal conditions at 25 °C.

Cement hydration was also stopped after fixed periods of time, depending on the samples, by successively immersing the crushed paste into isopropanol and drying it in a controlled humidity chamber (with 20% relative humidity at 22 ± 2 °C). Crystallized phases were identified by X-ray diffraction with the Bragg Brentano geometry (Siemens D8 — copper anode λK$_{\alpha 1}$ = 1.54056 Å generated at 40 mA and 40 kV) on pastes ground by hand to a particle size of less than 100 μm. Before analysis, silicon was added to the samples (10% by mass of sample) and carefully mixed by grinding in a mortar to be used as an internal standard. The evolutions of the amounts of ettringite, monosulfate, gypsum, mayenite, ye'elimite, and of the boro-AFt phase were assessed from the XRD patterns by measuring the areas of characteristic reflections, standardized with respect to that of silicon (2θ = 9.08° for ettringite, 9.93° for monosulfate, 11.64° for gypsum, 33.42° for mayenite, 23.67° and 23.70° for ye'elimite, 9.2° for the boro-AFt phase, and 28.44° for silicon). Four test mixtures containing known fractions of clinker and gypsum were analyzed using this method. The error on the determination of the ye'elimite and gypsum contents ranged between 5 and 10%. Thermogravimetric analyses were carried out using a TGA/DSC Netzsch STA 409 PC instrument at 10 °C/min up to 1000 °C.

Some cement paste samples were characterized using ^{11}B-MAS NMR. The ^{11}B-MAS spectra were recorded at a Larmor frequency of 256.7 MHz using a Bruker Avance III 800 MHz (18.8 T) spectrometer. The spectra were made up of 64 free induction decays with a pulse length of 1 μs (π/10) and a relaxation delay of 5 s. The samples were spun at 20 kHz in a 3.2 mm probe. Experimental referencing, calibration, and setup were performed using solid powdered sodium borohydride. Solid $NaBH_4$ has a chemical shift of −42.06 ppm relative to the primary standard, liquid $F_3B \cdot O(C_2H_5)_2$ (where δ(^{11}B) = 0.00 ppm). The baseline was corrected by subtracting the background signal coming from the boron nitride stator of the probe. Spectral decomposition was performed using DMFit software [30].

The pore solution of the cement pastes was also extracted by compaction of 20 mL of sample using a Carver mechanical press at a pressure of 34 MPa. Its pH was then measured with a high-alkalinity electrode (Mettler Toledo Inlab Expert Pt1000 pH 0–14 T 0–100 °C) calibrated using three IUPAC pH buffers at 6.865 ± 0.010 (25 °C), 10.012 ± 0.010 (25 °C) and 12.45 ± 0.05 (25 °C) and its chemical composition

Table 2
Boron containing aqueous species and minerals added to the Cemdata07 database.

Species		Formation reaction	Log K (T = 25 °C, P = 1 bar)	Ref.
Aqueous	$B(OH)_4^-$	$B(OH)_{3(aq)} + H_2O \rightarrow B(OH)_4^- + H^+$	−9.24	[43–47]
	$B_3O_3(OH)_4^-$	$3B(OH)_{3(aq)} \rightarrow B_3O_3(OH)_4^- + H^+ + 2H_2O$	−7.21	[33,48]
	$B_5O_6(OH)_4^-$	$5B(OH)_{3(aq)} \rightarrow B_5O_6(OH)_4^- + H^+ + 5H_2O$	−7.01	[33,48]
	$B_4O_5(OH)_4^{2-}$	$4B(OH)_{3(aq)} \rightarrow B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O$	−15.89	[33,49–51]
	$Al(OH)_3OB(OH)_2^-$	$B(OH)_{3(aq)} + Al^{3+} + 3H_2O \rightarrow Al(OH)_3OB(OH)_2^- + 4H^+$	−21.26	[52,55]
	$NaB(OH)_{4(aq)}$	$B(OH)_{3(aq)} + Na^+ + H_2O \rightarrow NaB(OH)_{4(aq)} + H^+$	−8.91	[33,53]
	$CaB(OH)_4^+$	$B(OH)_{3(aq)} + Ca^{2+} + H_2O \rightarrow CaB(OH)_4^+ + H^+$	−7.42	[53,54]
Minerals	Hexahydroborite	$2B(OH)_{3(aq)} + Ca^{2+} + 6H_2O \rightarrow$ Hexahydroborite $+ 2H^+$	−13.65	[25–28,54]
	Boric acid	$B(OH)_{3(aq)} \rightarrow$ boric acid	0.0438	[33]
	Inyoite	$6B(OH)_{3(aq)} + 2Ca^{2+} + 6H_2O \rightarrow$ Inyoite $+ 4H^+$	−19.72	[25–28,54]
	Borax	$4B(OH)_3(aq) + 2Na^+ + 5H_2O \rightarrow$ Borax $+ 2H^+$	−24.80	[25–28,54]
	$Na_2O \cdot B_2O_3 \cdot 8H_2O$	$2B(OH)_{3(aq)} + 2Na^+ + 4H_2O \rightarrow Na_2O \cdot B_2O_3 \cdot 8H_2O + 2H^+$	−18.55	[25–28,54]
	Nobleite	$6B(OH)_{3(aq)} + Ca^{2+} \rightarrow$ Nobleite $+ 2H^+ + 3H_2O$	−7.75	[25–28,54]
	Sborgite	$10B(OH)_{3(aq)} + 2Na^+ \rightarrow$ Sborgite $+ 2H^+ + 4H_2O$	−8.985	[25–28,54]
	Ulexite	$10B(OH)_{3(aq)} + 2Na^+ + 2Ca^{2+} + 4H_2O \rightarrow$ Ulexite $+ 6H^+$	−28.50	[25–28,54]
	4Boro-AFt	$4B(OH)_{3(aq)} + 2Al^{3+} + 6Ca^{2+} + 42H_2O \rightarrow$ Boro-AFt $+ 18H^+$	−123.80	[24,33]
	Boro-AFm	$B(OH)_{3(aq)} + 2Al^{3+} + 4Ca^{2+} + 17.5H_2O \rightarrow$ Boro-AFm $+ 14H^+$	−95.83	[24,33]
	U phase	$1.8 Al^{3+} + 4Ca^{2+} + Na^+ + 1.1SO_4^{2-} + 16.5H_2O \rightarrow$ U phase $+ 12.2H^+$	−78.96	[37]
	Ye'elimite	$4Ca^{2+} + 6Al^{3+} + SO_4^{2-} + 12H_2O \rightarrow$ Ye'elimite $+ 24H^+$	−350[a]	

[a] Arbitrary value allowing full dissolution of ye'elimite under the investigated conditions.