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Calcium sulfoaluminate cement blended with OPC: A potential binder to encapsulate low-level radioactive slurries of complex chemistry

Céline Cau Dit Coumes [a,*], Simone Courtois [b], Sandrine Peysson [c], Jean Ambroise [c], Jean Pera [c]

[a] *Commissariat à l'Energie Atomique, DTCD/SPDE/L2ED, CEN Valrhô, 30207 Bagnols-sur-Cèze cedex, France*
[b] *Université Aix-Marseille II, Laboratoire EA(MS)^2, Avenue Gaston Berger, 13625 Aix-en-Provence cedex, France*
[c] *INSA Lyon, URGC-Matériaux, Domaine Scientifique de la Doua, Bâtiment J. Tuset, 12 Avenue des Arts, 69621 Villeurbanne cedex, France*

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ABSTRACT

Investigations were carried out in order to solidify in cement a low-level radioactive waste of complex chemistry obtained by mixing two process streams, a slurry produced by ultra-filtration and an evaporator concentrate with a salinity of 600 gxL^{-1}. Direct cementation with Portland cement (OPC) was not possible due to a very long setting time of cement resulting from borates and phosphates contained in the waste. According to a classical approach, this difficulty could be solved by pre-treating the waste to reduce adverse cement–waste interactions. A two-stage process was defined, including precipitation of phosphates and sulfates at 60 °C by adding calcium and barium hydroxide to the waste stream, and encapsulation with a blend of OPC and calcium aluminate cement (CAC) to convert borates into calcium quadriboroaluminate. The material obtained with a 30% waste loading complied with specifications. However, the pre-treatment step made the process complex and costly. A new alternative was then developed: the direct encapsulation of the waste with a blend of OPC and calcium sulfoaluminate cement (C$\bar{S}$A) at room temperature. Setting inhibition was suppressed, which probably resulted from the fact that, when hydrating, C$\bar{S}$A cement formed significant amounts of ettringite and calcium monosulfoaluminate hydrate which incorporated borates into their structure. As a consequence, the waste loading could be increased to 56% while keeping acceptable properties at the laboratory scale.

1. Introduction

It has long been a common practice to incorporate low- and intermediate-level radioactive wastes into cement [1]. In particular, the use of cement to immobilize concentrates or sludges from water treatment is attractive [2]: *(i)* the process is relatively simple and inexpensive, *(ii)* water from the waste is used for cement hydration, *(iii)* properly set compositions are characterized by good self-shielding and high compressive strength, and *(iv)* the high internal pH of cement systems precipitates and thus confines many radionuclides.

Cementitious materials intended for radioactive waste encapsulation usually include substantial amounts of ordinary Portland cement (OPC) in their formulation. However, wastes produced by nuclear activities are very diverse and, under certain circumstances, chemically react with cement phases or mixing water, thus reducing the quality of the product. These reactions often result in inhibition, retardation or acceleration of the cement hydration process. In some cases, chemical interactions between waste and cement proceed slowly without affecting hydration, but eventually result in the deterioration of the waste form in storage or disposal, for instance by swelling and cracking.

Two approaches may be considered to reduce or eliminate adverse waste–cement interactions: *(i)* to perform a chemical pre-treatment of the waste streams in order to convert interfering species into compounds stable in cement, or *(ii)* to select a binder which would show a better compatibility with the waste, such as calcium sulfoaluminate cement (C$\bar{S}$A).

C$\bar{S}$A cements have been manufactured and successfully used on an industrial scale in China for about 20 years [3–5]. The clinker is prepared by burning mixtures of limestone, bauxite and gypsum of appropriate compositions, ultimately to moderate temperature (1300–1350 °C, which is 100 to 150 °C lower than that required for OPC). Industrial wastes or by-products such as fly ash, blast furnace slag, “red mud” (a largely unwanted product of the Bayer process for alumina purification) or phosphogypsum can also be used as raw components which provide additional environmental advantages [6–9]. C$\bar{S}$A clinker is mainly composed of ye'elimite ($C_4A_3\bar{S}$), belite (C_2S) and an Al-rich ferrite [10]; after cooling, it is ground with gypsum. By increasing the proportion of gypsum (typically from 10 to 25%), a series of cements, ranging from rapid-hardening to shrinkage-compensating, and eventually to self-stressing, can be produced [5]. C$\bar{S}$A cement pastes harden through the formation of an initial ettringite skeleton, and its subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate hydrate, C–S–H, alumina and ferrite gel [11,12]. A possible hydration scheme has been proposed by Glasser et al. [13] (Table 1). The contents of ettringite and calcium monosulfoaluminate

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* Corresponding author.
E-mail address: celine.cau-dit-coumes@cea.fr (C. Cau Dit Coumes).

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Table 1
Possible hydration scheme of $C\bar{S}A$ cements [13].

$C\bar{S} + 2H \rightarrow C\bar{S}H_2$
$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_3A\cdot 3C\bar{S}\cdot H_{32} + 2AH_3$
$C_2S + 2.6H \rightarrow C_{1.1}SH_{1.7} + 0.9CH$
$C_4A_3\bar{S} + 18H \rightarrow C_3A\cdot C\bar{S}\cdot H_{12} + 2AH_3$ (in case of excess ye'elimite as compared to gypsum)
$4CH + AH_3 + 6H \rightarrow C_4AH_{13}$
$3C_4AH_{13} + 2C_3A\cdot 3C\bar{S}\cdot H_{32} + AH_3 \rightarrow 6C_3A\cdot C\bar{S}\cdot H_{12} + 34H$
$AH_3 + 3CH + 3C\bar{S}H_2 + 20H \rightarrow C_3A\cdot 3C\bar{S}\cdot H_{32}$ (in case of excess gypsum as compared to ye'elimite)
CH and C_4AH_{13} would be transitory products only.
In $C\bar{S}A$ cements, C–S–H typically occurs as C–S–H(I).

Shorthand notations: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $H = H_2O$, $\bar{S} = SO_3$, $F = Fe_2O_3$.

hydrate are very sensitive to the amount of added sulfate: the former dominates in a gypsum-rich environment, whereas the latter tends to increase in a gypsum-deficient system [14]. Water requirement for rheology is broadly similar for OPC and $C\bar{S}A$ cement [15]. However, while a W/C ratio of 0.4 is theoretically adequate to ensure complete hydration of OPC, this ratio might exceed 0.55 for $C\bar{S}A$ clinker blended with sufficient gypsum. It has been shown that the chemical water demand increases with the gypsum content up to a maximum which corresponds to the maximum ettringite yield [5]. If properly formulated, $C\bar{S}A$ cements give high early strength: Pera and Ambroise [16] reported the development of a concrete with 40 MPa compressive strength after 6 h, and 55 MPa strength after one day. Good durability is reported, especially in sulfate environments [17,18], and expansion can be controlled by adjusting the amount of gypsum added [19]. Recently, $C\bar{S}A$ cements have been used to stabilize wastes containing heavy metal salts [20–23]: ettringite and calcium monosulfoaluminate hydrate, the two main phases formed, can accommodate substitutions, as shown in Table 2 [24–26].

In this paper, the cementation of a low-level radioactive waste of complex chemistry, containing significant amounts of phosphates and borates, is investigated. Three approaches are described and compared: *(i)* using OPC, *(ii)* pre-treating the waste, and conditioning with a blend of OPC and calcium aluminate cement, and *(iii)* embedding in a blend of OPC and $C\bar{S}A$ cement.

2. Experimental

2.1. Waste composition

The low-level radioactive waste considered in this study was a mixture of a slurry resulting from ultra-filtration with an evaporator concentrate having a salinity up to 600 gxL^{-1}. A simulated waste was made from non-radioactive synthetic effluents by dissolving sodium and potassium salts (analytical grade) into demineralised water. Its properties are given in Table 3.

2.2. Reactants for waste encapsulation

Various binders were used: two Portland cements (CEM I 52.5 PM ES CP2 from Lafarge Le Teil, and CEM I 52.5 PM from Vicat Montalieu), a calcium aluminate cement (Fondu from Lafarge), and a $C\bar{S}A$ clinker (TS from Belitex). Their mineralogical compositions are compared in Table 4. Some formulations were improved by adding non-densified silica fume (Pechiney ND-LAU 71) and siliceous sand with fine granulometry (<350 µm). The grout workability was enhanced by using a superplasticizing admixture made of polycarboxylic ether for Portland cement (Glenium 21 from MBT), or of polysaccharide ether for $C\bar{S}A$ (Addilose M12 from Avebe). A water-retaining agent including starch ether (Opagel FP6 from Avebe) was used in case of high W/C (water/cement) ratio.

Table 2
Some reported ion substitutions in ettringite and calcium monosulfoaluminate hydrate [25,27] and references therein].

Ettringite $C_3A\cdot 3C\bar{S}\cdot 32H$	Ca^{2+} site	Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}
	Al^{3+} site	Cr^{3+}, Si^{4+}, Fe^{3+}, Mn^{3+}, Ni^{3+}, Co^{3+}, Ti^{3+}
	SO_4^{2-} site	$B(OH)_4^-$, CO_3^{2-}, Cl^-, OH^-, CrO_4^{2-}, AsO_4^{3-}, SeO_4^{2-}, VO_4^{3-}, BrO_3^-, NO_3^-, MoO_4^{2-}, ClO_3^-, SO_3^{2-}, IO_3^-
Calcium monosulfoaluminate hydrate $C_3A\cdot C\bar{S}\cdot 12H$	Al^{3+} site	Cr^{3+}, Fe^{3+}, Ga^{3+}
	SO_4^{2-} site	HBO_3^{2-}, CO_3^{2-}, Cl^-, OH^-, Br^-, I^-, NO_3^-, ClO_3^-, IO_3^-, ClO_4^-, MnO_4^-, CrO_4^{2-}, $Fe(CN)_6^{3-}$, $S_2O_3^{2-}$, WO_4^{2-}

Table 3
Chemical composition of the synthetic waste used in the study.

Solid phase		Liquid phase			
$Fe(OH)_3$	5.3%	NO_3^-	145.8 gxL^{-1}	Na^+	43.7 g L^{-1}
$Fe(OH)_2$	17.5%	PO_4^{3-}	11.2 gxL^{-1}	K^+	1.6 g L^{-1}
$Cu(OH)_2$	4.3%	SO_4^{2-}	17.2 gxL^{-1}	Ca^{2+}	1.2 g L^{-1}
$BaSO_4$	35.2%	Cl^-	30.8 gxL^{-1}	NH_4^+	1.7 g L^{-1}
$Fe(CN)_6K_{4-x}Ni_x$	24.1%	B	5.6 gxL^{-1}		
$CaHPO_4$	13.6%	NO_2^-	2.4 gxL^{-1}		
Expressed as % of the total weight of solid in the sludge					
Density (solid + liquid)					1.21
Mass of solid phase per litre of sludge					332.8 g
Dry extract (mass ratio)					27.5%
pH					8

2.3. Protocols

Chemical pre-treatments of waste were carried out in a stirred and thermoregulated 1 L-reactor. Mixing was performed with a standard (European standard EN 196-1) mortar mixer according to the following sequence: (1) introduction of the powders and pre-mixing at low speed for 3 min, (2) addition of waste and possibly of water, (3) mixing at low speed for 1.5 min, addition of superplasticizer if necessary, and (4) mixing at high speed for 1 min.

Table 4
Chemical and mineralogical compositions of cements.

Cement	Ordinary Portland cement		Ordinary Portland cement		Calcium aluminate cement		Calcium sulfoaluminate clinker	
Reference supplier	CEM I 52.5 PM ES CP2 Lafarge Le Teil		CEM I 52.5 PM Vicat Montalieu		Fondu Lafarge Fos/mer		TS Belitex	
Oxides (% weight)								
SiO_2	19.9		21.3		3.7		7.50	
Al_2O_3	5.4		3.8		39.5		30.41	
Fe_2O_3	2.6		4.0		16.0		8.57	
CaO	65.0		65.3		38.0		44.22	
MgO	1.4		1.0		–		0.59	
K_2O	0.9		0.4		<0.4		0.17	
Na_2O	0.1		0.1		<0.4		0.04	
SO_3	3.4		2.2		–		6.54	
TiO_2	–		0.2		–		1.08	
SrO	–		–		–		0.25	
Loss on ignition	1.0		1.4		0.7		0.32	
Minerals[a] (% weight)	C_3S	65.6	C_3S	66.3	CA (major)		$C_4A_3\bar{S}$	53.5
	C_2S	16.0	C_2S	11.2	$C_{12}A_7$		C_2S	21.2
	C_3A	4.0	C_3A	3.3	C_2S		C_4AF	16.3
	C_4AF	5.6	C_4AF	12.0	C_2AS		CT	9.0
	Gypsum	4.8	Gypsum	4.2	C_4AF			
	Carbonate	2.8	Carbonate	2.0				

[a] Quantitative phase composition estimated using the Bogue calculation for OPC clinker, and measured for $C\bar{S}A$ clinker (data provided by Belitex).

Table 5
Criteria to assess the quality of solidified waste forms.

Fluidity after mixing	Cemented waste should have a low viscosity after mixing in order to allow easy emptying of the drum, and thus to minimize amounts of rinsing water.
Setting time	Final set should be higher than 6 h to avoid any setting in the mixer in case of technical hitch, and lower than 24 h to enable good output of the conditioning unit.
Bleeding	The material should not exhibit any bleeding after 24 h.
Heat of hydration	The temperature rise resulting from cement hydration should not affect the package integrity.
Compressive strength	Compressive strength after 90 days of curing under water at 20 °C should exceed 8 MPa.
Dimensional stability	Any expansion or shrinkage which may damage the matrix or container should be precluded.

Waste forms were measured according to standard procedures: bleeding (French standard NF P 18-359), Vicat setting time (EN 196-3), shrinkage of prismatic samples (4×4×16 cm) during curing at 20 °C in a sealed bag or in air (relative humidity of 65%) (NF P 15-433), swelling of 4×4×16 cm specimens cured at 20 °C under water (NF P 15-433), flexural and compressive strengths of 4×4×16 cm samples cured at 20 °C in air, sealed bag, or under water (EN 196-1), and heat of hydration using the semi-adiabatic method (EN 196-9). This latter consisted in introducing a sample of 1575±1 g of freshly made grout into a cylindrical container having a volume of approximately 800 cm^3. The container was placed into a calibrated calorimeter (with a coefficient of total heat loss below 100 Jxh^{-1} xK^{-1} for a temperature rise of 20 K) in order to determine the quantity of heat emitted in accordance with the development of temperature. The temperature rise of the sample was compared with the temperature of an inert sample in a reference calorimeter. At a given point in time, the heat of hydration of the cement contained in the sample was calculated by summing the heat accumulated in the calorimeter and the heat lost into the ambient atmosphere throughout the period of the test. The desirable criteria were defined by taking into account both process requirements and near-surface disposal specifications (Table 5).

Table 6
Investigated cement–waste formulations.

Formulation ref.	Chemical pre-treatment	Embedding in cement		Main parameters
I	No	Waste	500 mL	W/C = 0.5
		OPC[a]	877.2 g	τ = 30%
		Silica fume	37.6 g	
		Sand	545.1 g	
II	Yes	Waste	500 mL	W/C = 0.56
				OPC/CAC
	$Ca(OH)_2$[b] 43 g	OPC[a]	745.8 g	90/10
	$Ba(OH_2 \cdot 8H_2O$[c] 61 g	CAC	85.2 g	τ = 30%
	Stirring at 60 °C	Silica fume	35.6 g	
	for 5 h	Sand	515.4 g	
		Water	27.5 g	
		Plasticizer[d]	0.5%	
III	No	Waste	537.2 mL	W/C = 0.92
		OPC[e]	153 g	OPC/$C\bar{S}A$
		$C\bar{S}A$	357 g	30/70
		Plasticizer[f]	0.2%	τ = 56%
		Water-retaining agent	0.15%	

W/C = water/cement ratio, τ = waste loading (mass %).

[a] CEM I 52.5 PM ES from Lafarge Le Teil.

[b] The calcium hydroxide concentration was calculated assuming precipitation of hydroxylapatite and QBA ($[Ca^{2+}] = 1.67[PO_4^{3-}] + 0.75[B]_{tot}$).

[c] Barium was introduced in slight excess ($[Ba^{2+}]/[SO_4^{2-}] = 1.08$) as compared to the stoichiometry of $BaSO_4$.

[d] Glenium 21, content expressed as mass ratio (%) relative to cement.

[e] CEM I 52.5 PM from Vicat Montalieu.

[f] Addilose M12, content expressed as mass ratio (%) relative to cement.

Supplementary mineralogical analyses of the solidified materials were performed using powder X-ray diffraction (Siemens D8, $\lambda_{K\alpha1}(Cu) = 1.54056$ Å, 2θ range: 5–60°, steps of 0.02°, 2 s/step), while microstructure was investigated by scanning electron microscopy (Philips XL PX6631/01, voltage 15 kV, SE imaging, EDS analysis). Porosity was characterized using mercury intrusion porosimetry (Micromeritics Autopore III-investigated pressures ranging from 0.8 to 5,300,000 psia) on 1 cm^3 samples dried under vacuum at room temperature. Static leaching tests were performed on monolithic (4×4×4 cm cubes) and crushed (grain size below 1 mm) samples. The samples were immersed under demineralised and decarbonated water, with a 10 mL/g liquid to solid ratio. The reactors were sealed and stirred for 24 h at room temperature. Leachates were then filtered at 0.45 µm and analysed using ICP (B) and ionic chromatography (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-).

3. Results and discussion

3.1. Direct encapsulation of waste in Portland cement

A first formulation (Table 6) was calculated assuming: *(i)* a waste loading of 30% by mass (or 50% by volume), *(ii)* a W/C ratio of 0.5, *(iii)* no addition of free water (which means that water for cement hydration was provided by the waste), and *(iv)* a silica fume/cement ratio of 6%. Silica fume accelerated the hydration process by providing an increased number of nucleation sites for hydrates. Its pozzolanic activity with portlandite increased the compressive strength. Porosity was also decreased by denser packing.

The resulting material showed good workability, but had a setting time greater than 8 days, which was much too long for industrial application (ideal setting times ranged between 6 and 24 h). After 7 days of curing in moist air (20 °C, relative humidity of 95%), a sample was taken from the non-hardened paste and cryo-desiccated. A polished section was examined using reflected light microscopy. It revealed the absence of any hydration product around clinker grains. This strong inhibition of cement hydration may have resulted from the presence of phosphates and borates in the waste. Borates are reported to be strong retarders of cement setting and hardening [28–32]. Retardation may arise from surface adsorption, and possibly from the formation of protective layers over cement grains due to precipitation with calcium [33]. According to Roux [34], the borate inhibition effect might result from formation of amorphous $2CaO \cdot 3B_2O_3 \cdot 8H_2O$ from polyboric anions $B_3O_3(OH)_4^-$ and/

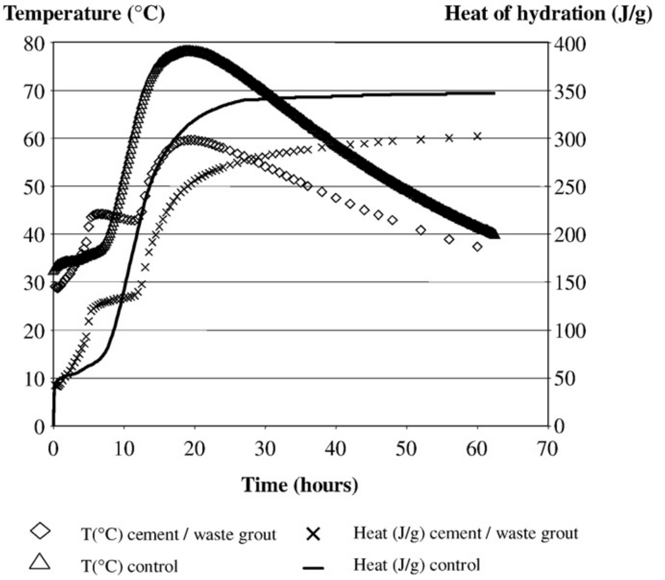


Fig. 1. Temperature rise and heat of hydration of the cement–waste material prepared according to formulation II (see Table 6). Comparison with a control grout elaborated with water instead of waste.

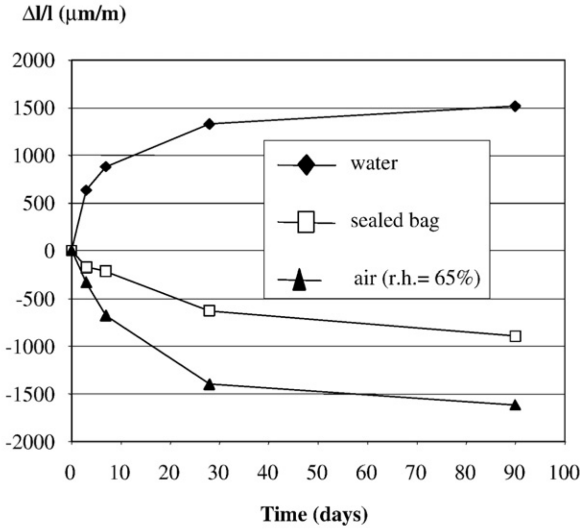


Fig. 2. Dimensional variations of 4×4×16 cm samples prepared according to formulation II (see Table 6) and cured at room temperature under water, air or in sealed bag.

or $B_3O_3(OH)_5^{2-}$ when pH is within the range 4.5–12. At higher pH, aqueous boron, mainly as $B(OH)_4^-$, would precipitate as crystallized $CaO\cdot B_2O_3\cdot 6H_2O$ or $CaO\cdot B_2O_3\cdot 4H_2O$, which allows cement hydration to progress. This assumption is consistent with the observations of Casabonne Masonnave: adding borates to a lime-containing solution caused the precipitation of amorphous $2CaO\cdot 3B_2O_3\cdot 8H_2O$ for pH and B/Ca molar ratios respectively within the range 9–10.9 and 6–12, whereas, at higher pH (11–13.5), crystallized $CaO.B_2O_3\cdot 6H_2O$ was formed provided the B/Ca molar ratio exceeded 2 [35]. More recently, Bell and Coveney [36] suggested that retardation caused by borate ions could result from their chemisorption on the silicate groups of calcium silicate hydrates, thus preventing growth of these hydrates. In the same way, phosphates have been shown to be retarders of cement hydration [28,29,37]. A systematic study of the hydration of cement pastes in phosphate-rich solutions (up to 50 gxL^{-1}) revealed that the delay increased with the phosphate concentration up to 25 gxL^{-1}, but then decreased at higher concentrations [2,38,39]. Rheological investigations carried out on cement pastes containing increasing amounts of phosphates also showed the occurrence of a discontinuity at the same phosphate concentration (25 gxL^{-1}). These results were explained by assuming two competing processes: adsorption of phosphates on the cement phases, which retarded hydration, and, at high phosphate concentrations, precipitation of hydroxylapatite, which did not retard. According to these results, the phosphate content in the waste (11.2 gxL^{-1}) suggests that retardation, at least in part, is due to an adsorption process which prevents dissolution of the cement particles.

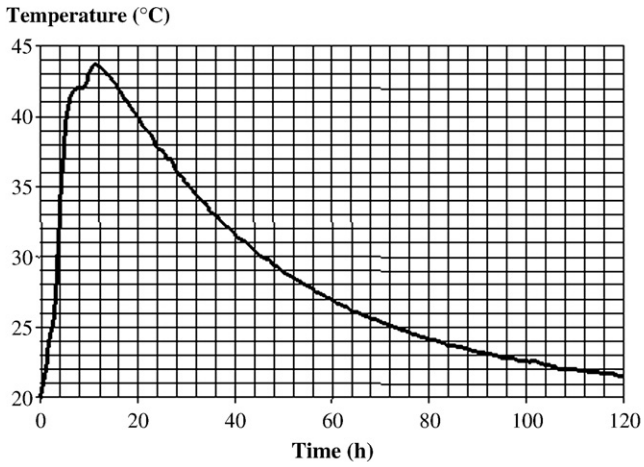


Fig. 3. Temperature rise of the cement–waste material prepared according to formulation III (see Table 6).

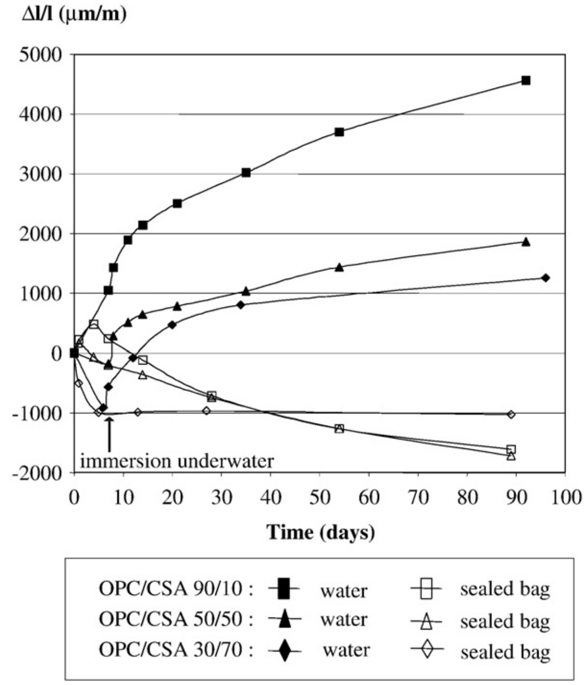


Fig. 4. Influence of the OPC/C$\bar{S}$A blend composition on the dimensional stability at room temperature of 4×4×16 cm samples prepared according to formulation III (see Table 6).

3.2. Cementation of a chemically pre-treated waste

Cementation of low-level radioactive wastes containing high levels of soluble salts has been extensively investigated. For example, the European Commission supported research on cement conditioning of nitrate, sulfate, and borate-rich waste streams in the 1980s [40]. Two main strategies have been used to cement wastes with high contents of borates:

- addition of calcium hydroxide to precipitate borates as calcium hexahydroborite $CaO\cdot B_2O_3\cdot 6H_2O$ [41–44],
- addition of calcium hydroxide and aluminates to incorporate borates into the AF_t phase $3CaO\cdot Al_2O_3\cdot 2Ca[B(OH)_4]_2\cdot Ca(OH)_2\cdot 30H_2O$ (calcium quadriboroaluminate QBA, or high boron-content AF_t) [9,45,46].

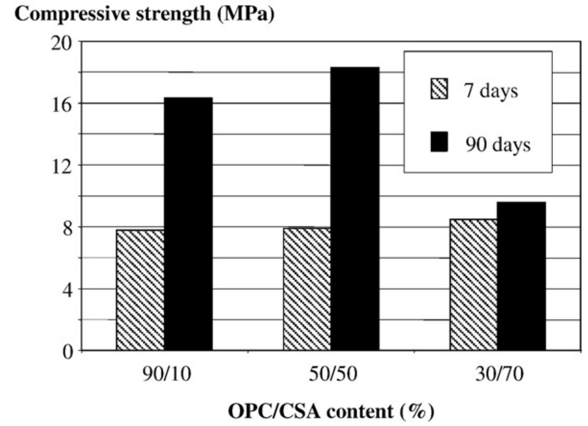
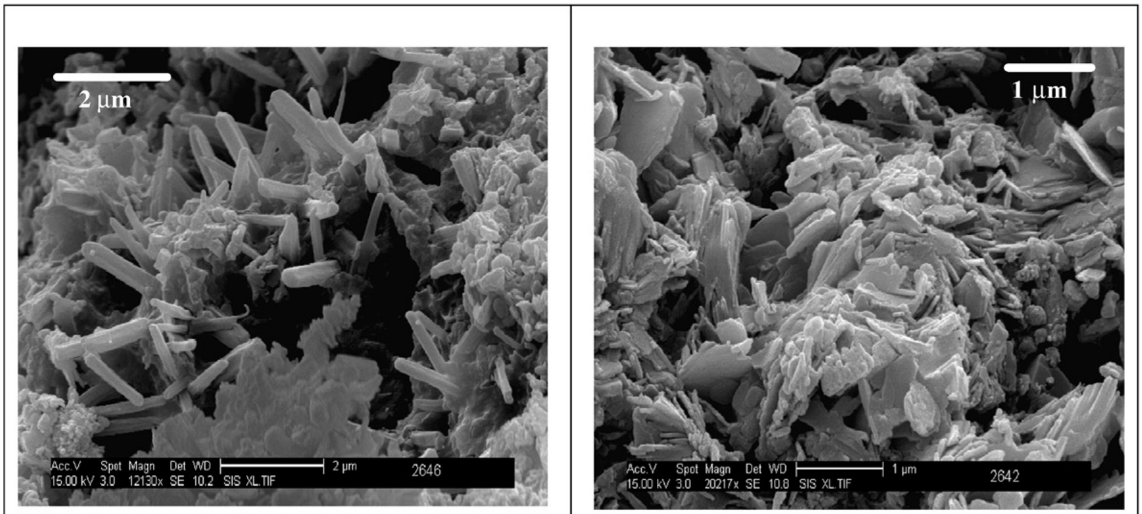


Fig. 5. Influence of the OPC/C$\bar{S}$A blend composition on the compressive strength of 4×4×16 cm samples prepared according to formulation III (see Table 6) and cured under water at room temperature.

The former has been used to encapsulate PWR evaporator concentrates with boron up to 40 gxL^{-1}. However, two disadvantages arise: *(i)* cement set is still retarded, and *(ii)* calcium hexahydroborite is unstable in cement and is progressively converted into calcium mono- or quadriboroaluminate. The latter, which is more effective to reduce set inhibition, was applied to the conditioning of the waste under study. The objective was to assess the properties of the resulting solidified waste forms, so as to get reference data for further comparison with new conditioning approaches.

Given the presence in the waste of phosphates, sulfates and borates, a two-stage process was defined (Table 6): *(i)* pre-treatment consisting of the addition of calcium and barium hydroxides and stirring at 60 °C for 5 h, and *(ii)* embedding of the waste with a mixture of Portland and calcium aluminate cements. During pre-treatment, phosphates and sulfates were precipitated as amorphous calcium phosphate and crystalline barium sulfate. In the cementation step, calcium aluminate cement (Fondu) was used together with calcium hydroxide remaining from the first step to precipitate boron into QBA. Waste loading in the matrix reached 30% by mass.

The fresh grout was fluid and did not bleed. Initial and final setting times were only 7 h and 11 h 45 min. Fig. 1 shows the temperature and heat evolution curves determined by semi-adiabatic calorimetry. The

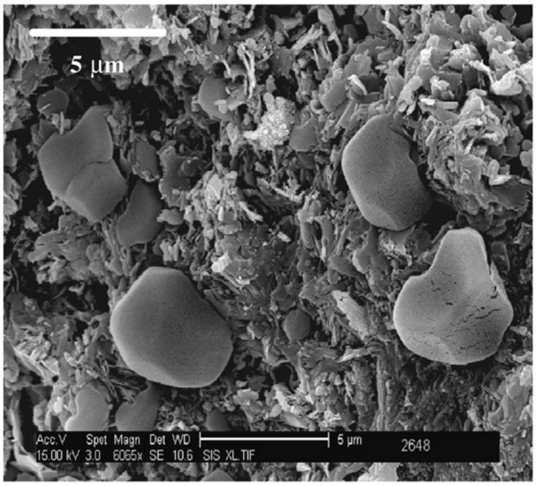


(a) SE – 15 kV - ×12130

acicular ettringite

(b) SE – 15 kV - ×2017

Platy crystals of calcium monochloroaluminate hydrate



(c) SE – 15 kV - ×6065

Sodium nitrate crystals

Fig. 6. SEM observation of a sample prepared according to formulation III (see Table 6) and cured for 6 months in sealed bag at room temperature.

maximum achieved temperature did not exceed 60 °C, which was acceptable since too high a temperature rise in a massive solidified waste form might induce thermo-mechanical constraints on the container, and micro-cracking of the material, with consequences to its long term durability. The heat output reached 300 Jxg^{-1} after 2 days, which confirmed that hydration of cement could occur, but the hydration rate was still slightly reduced (by a factor of 0.85) as compared to a control sample prepared with water instead of waste. The heat production occurred in two stages, instead of one for the control. Hydration kinetics of the various cement phases (CA, C_3S, C_2S, C_3A, C_4AF) might have been affected in different ways by the waste constituents, thus causing a decoupling of the hydration reactions.

Flexural and compressive strengths of 4×4×16 cm specimens were recorded for three types of curing. Hardening was slightly more rapid for samples immersed in water, but, after 28 days, the results were similar regardless of storage. Compressive strengths, ranging between 30 and 35 MPa, largely exceeded the minimum value (8 MPa) required by ANDRA (the French National Agency for Waste Management) for cementitious materials immobilizing homogeneous low-level radioactive wastes in a high integrity container.

On ageing, 4×4×16 cm specimens showed dimensional variations (expansion under water, and shrinkage in air or sealed bag) which were important during the first 28 days, but which then slowed (Fig. 2). No macroscopic damage could be observed after 90 days of curing. Shrinkage had two main components: autogenous shrinkage, and drying shrinkage for specimens stored in air. Autogenous shrinkage resulted from the depletion of water due to cement hydration, but could also be increased by progressive crystallization of hydrated salts, for instance $Ca(NO_3)_2 \cdot 4H_2O$, which decreased the free water content. Expansion under water was associated with water penetration through diffusion, capillary suction, and osmotic pressure gradient: the mass increase reached 1.5% after 90 days.

Pre-treating the waste was thus an effective way to suppress the inhibition of cement setting. At the laboratory scale, the formulation fulfilled all the quality requirements reported in Table 5. However, the complexity and cost of the conditioning process were increased.

3.3. Direct cementation of the waste with an OPC/$C\bar{S}A$ blend

Cementation of a non-treated waste was carried out with a blend comprising 70% $C\bar{S}A$ and 30% OPC (Table 6). $C\bar{S}A$ was used without adding more gypsum, sulfates being provided by the OPC and the waste. The effect of the change of cement on setting was striking: the waste incorporation rate could be increased up to 56% (by mass) while keeping the Vicat setting time below 24 h. The heat output due to cement hydration was rapid: the maximum temperature in the calorimeter was achieved 12 h after mixing (Fig. 3). However, the temperature rise (24 °C) remained lower than that recorded when the pre-treated waste was encapsulated with the OPC/CAC blend (30 °C), and more generally, was in the low part of the range of data (20–60 °C) usually measured on industrial cement–waste formulations under the same experimental conditions. Excessive heat release can be a problem in massive $C\bar{S}A$ concrete, since the rapid hydration of $C\bar{S}A$ cement leads to heat production over a short period of time. However, in the present case, the internal temperature remained moderate due to the low cement content and high W/C ratio of the recipe.

Table 7
Porosity distribution in a sample prepared according to formulation III and cured for 6 months in sealed bag.

Pore diameters (nm)	6–100 nm	100–600 nm	>600 nm	Total porosity
Volume fraction (%)	69.6[a]	25.2[a]	5.2[a]	46.5[b]

Sample composition: see Table 6.
[a] Of the total porosity.
[b] Of the sample.

Table 8
Leaching of anions from solidified waste forms prepared according to formulation III.

Leached fraction (%)	Monolithic sample	Powder
PO_4^{3-}	<0.03	<0.03
Cl^-	48.2	76.1
NO_3^-	41.1	79.6
SO_4^{2-}	6.8	7.6
B	4.6	8.8

Sample composition: see Table 6 — curing for 90 days in sealed bag.

Increasing the waste loading resulted in an increase in the W/C ratio (up to 0.92). A water-retaining agent had thus to be used to prevent bleeding of the fresh grout. Workability after mixing was satisfactory and could be maintained for 1 h, as assessed by slump measurements with a reference cone (minimum diameter 7 cm, maximum diameter 8 cm, height 4 cm) on ageing grout.

The blend composition was shown to be a key parameter to control the properties of the hardened grout. Decreasing the OPC content from 90% to 30% improved greatly the dimensional stability of the solidified waste forms, although decreasing compressive strengths (Figs. 4 and 5). The selected composition was thus a compromise to keep low dimensional variations, and compressive strengths above 8 MPa. Shrinkage of specimens cured in sealed bag was similar to that recorded for formulation II; swelling under water remained a little higher, but induced no macroscopic damage at the laboratory scale. This result will have to be confirmed at later age, as well as on large-scale experiments. The strong swelling observed for samples containing high amounts of OPC is consistent with previously reported results which concluded that ettringite produced under high portlandite concentration caused expansion, whereas the ettringite formation in low $Ca(OH)_2$-content mixtures did not result in expansion [47,48].

The mineralogy of solidified waste forms was investigated by XRD on a sample cured for 6 months in a sealed bag at room temperature. The identified phases resulted either from crystallization of salts from the waste ($BaSO_4$, $NaNO_3$, $Na_3(NO_3)(SO_4).H_2O$), or from cement hydration (ettringite and calcium monochloroaluminate hydrate). Ye'elimite, the main component of $C\bar{S}A$, was totally depleted, thus indicating a high hydration degree. SEM observations confirmed the presence of acicular ettringite, homogeneously distributed in the cement paste, as well as chloroaluminate and sodium nitrate (Fig. 6). The porosity of the sample was characterized using mercury intrusion porosimetry. The total porosity was high (46.5% by volume), which resulted from the high waste loading, and thus the high W/C ratio of formulation III, but most pore diameters were below 100 nm (Table 7).

Two static leaching tests were carried out on the cemented waste after 90 days of curing in sealed bag. The first trial was performed on a cube, and the second one on a crushed sample. The compositions of the leachates after 24 h are reported in Table 8. Only small amounts of sulfates and borates were present and the phosphate concentration was below the detection limit. This result confirms the incorporation of these compounds in low-solubility phases. On the contrary, very high contents of nitrates and chlorides were detected, the leached fractions being close to 40% (blocks), or 75% (powder) for each species. SEM analyses showed the presence of many crystals of sodium nitrate. These salts, which are highly soluble, readily dissolved during the leaching test. Using a $C\bar{S}A$-based cement instead of pure OPC did not improve the confining of nitrates.

The reasons for the good performance of OPC/$C\bar{S}A$ blends to solidify the waste, despite high contents of borates and phosphates, have still to be clarified. The absence of setting inhibition probably results from the fact that $C\bar{S}A$ cement forms significant amounts of ettringite and calcium monosulfoaluminate hydrate which can incorporate borates (the strongest retarders) into their structure. Wenda and Kuzel showed that boron can substitute completely for sulphur in both AF_m and AF_t phases. They reported the existence of two boro-AF_t phases with a high

($C_3A \cdot Ca(B[OH]_4)_2 \cdot Ca(OH)_2 \cdot 36H_2O$) or low ($C_3A \cdot Ca(B[OH]_4)_2 \cdot 2Ca(OH)_2 \cdot 36H_2O$) boron content [49]. IR spectroscopy showed boron to be four-coordinated within the ettringite structure (i.e. existing as $B(OH)_4^-$). These authors also synthesized a fully boron-substituted AF_m phase with chemical formula $C_3A.CaHBO_3.11.5H_2O$. Boron was three-coordinated in this structure. Bothe and Brown [50] confirmed these results and performed a systematic study of the $CaO–Al_2O_3–B_2O_3–H_2O$ system at 23 °C. Poellmann et al. [51] additionally demonstrated that a large range of solid solutions existed between ettringite and the high or low boron-content AF_t phases. In this work, it was not possible to identify the phases incorporating borates because of their low concentrations relative to the detection limits of the characterization procedures. However, investigations on simplified systems are currently under way in order to investigate the hydration of $C\bar{S}A$ cement in a borate solution.

4. Conclusion

Three approaches were compared for cementing a low-level radioactive waste (LLW) of complex chemistry containing significant amounts of phosphates and borates. This waste, obtained by mixing a sludge resulting from ultra-filtration and an evaporator concentrate with a 600 gxL^{-1} salinity, is typical of streams generated by plants processing LLW effluents from nuclear centres. The main conclusions can be summarized as follows.

1. Direct cementation of the waste with OPC came up against unacceptably long Vicat setting times (above 8 days, while required setting times ranged between 6 and 24 h). Inhibition of the cement hydration was attributed to borates and phosphates, and arose from surface adsorption and possibly formation of protective layers over the cement grains due to precipitation with calcium.
2. This difficulty could be solved by pre-treating the waste: adverse cement–waste interactions are limited by insolubilizing the interfering species into compounds stable in cement. Because of the simultaneous presence of phosphates, sulfates and borates in the waste, a two-stage process had to be developed, including *(i)* addition of calcium and barium hydroxide to the waste stream and mixing for 5 h at 60 °C, followed by *(ii)* embedding the treated product from *(i)* with a blend of OPC and calcium aluminate cement. The treatment was designed to precipitate phosphate as calcium phosphate, sulfate as barium sulfate, and borate as an AF_t phase (calcium quadriboroaluminate). The material obtained for a waste loading of 30% by mass showed good properties (fluidity, final setting time of 11 h 45 min, moderate heat of hydration), and met the disposal specifications for homogeneous wastes solidified in a high integrity container (no bleeding, compressive strength higher than 8 MPa after a 90-day cure under water). However, the pre-treatment step increased the complexity and cost of the process.
3. Using blends of OPC and CSA cements seemed a promising alternative. Cement setting was not inhibited, which may have resulted from the fact that, when hydrating, CSA cement formed significant amounts of ettringite and calcium monosulfoaluminate hydrate which could structurally incorporate borates. Moreover, sulfates, which can induce deleterious effects in OPC-based materials (risk of swelling and cracking due to delayed formation of ettringite), were rapidly depleted by the hydration reactions to form non expansive ettringite in the early stages of hydration. Conditioning of the waste could thus be performed in one step, at room temperature, at an incorporation of 56%, which might allow a reduction of the number of packages produced by a factor 1.8. This laboratory work should however be supplemented by large scale experiments for a better assessment of the formulation (especially with regard to the heat output, as well as the dimensional variations and risk of cracking).

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