

**CEMENT ENCAPSULATION OF LOW-LEVEL RADIOACTIVE SLURRIES OF COMPLEX CHEMISTRY**

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ABSTRACT

Investigations have been carried out to solidify in cement a low-level radioactive waste of complex chemistry which should be produced in a new plant designed to process radioactive effluents from CEA Cadarache Research Center. Direct cementation comes up against a major problem: a very long setting time of cement due to strong inhibition by borates from the waste. A two-stage process, including a chemical treatment prior to immobilization, has been elaborated and the resulted material characterized.

INTRODUCTION

The French Atomic Energy Commission has undertaken studies to design a new nuclear plant to process low- and intermediate-level radioactive aqueous effluents produced on Cadarache Research Center (1). Because arising from various activities, these effluents are characterized by highly variable chemical and radiological compositions. After treatment, they should lead to A- and B-category wastes, as defined by the French Legislation. While vitrification has been selected for B-category wastes conditioning since it allows important volume reduction together with high confinement properties of the matrix, cement has been chosen to encapsulate A-category wastes. Cementation is indeed a good compromise between investment cost and matrix quality, all the more since confinement may be, for the most radioactive packages, reported on a high integrity container which would allow respect of near-surface disposal requirements.

This paper is devoted to cementation of the low-level radioactive waste. It reports investigations carried out at the laboratory scale in order to elaborate a formulation which would be acceptable both from the process and disposal viewpoints.

WASTE CHARACTERISTICS

The A- category waste should be composed of a slurry resulting from seeded-ultrafiltration and of an evaporator concentrate with a salinity which may reach 600 g.L⁻¹. For the need of the study, a synthetic waste was prepared from non radioactive simulated effluents. Its composition is given in Table 1.

Table 1 : Chemical composition of the synthetic waste used in the study.

Solid Phase		Liquid Phase			
Fe(OH) ₃	5.3%	NO ₃ ⁻	145.8 g.L ⁻¹	Na ⁺	43.7 g.L ⁻¹
Fe(OH) ₂	17.5%	PO ₄ ³⁻	11.2 g.L ⁻¹	K ⁺	1.6 g.L ⁻¹
Cu(OH) ₂	4.3%	SO ₄ ²⁻	17.2 g.L ⁻¹	Ca ²⁺	1.2 g.L ⁻¹
BaSO ₄	35.2%	Cl ⁻	30.8 g.L ⁻¹	NH ₄ ⁺	1.7 g.L ⁻¹
Fe(CN) ₆ K _{4-x} Ni _x	24.1%	B	5.6 g.L ⁻¹		
CaHPO ₄	13.6%	NO ₂ ⁻	2.4 g.L ⁻¹		
Expressed as % of total weight of solid in the sludge					
Density		1.21			
Dry extract (mass ratio)		27.5%			
pH		8			

EXPERIMENTAL**Preparation of synthetic waste**

The sludge was prepared from a dilute effluent obtained from dissolution in demineralized water of sodium and potassium salts (analytical grade) at the following concentrations: NaNO₃ 18.5 g.L⁻¹, KH₂PO₄ 0.9 g.L⁻¹, Na₂SO₄ 1.3 g.L⁻¹, NaCl 5.6 g.L⁻¹, NaNO₂ 0.14 g.L⁻¹ and H₃BO₃ 1.7 g.L⁻¹. A three-stage treatment was then carried out, as expected in the industrial process:

- phosphate precipitation with calcium hydroxide (2.2 g.L⁻¹) so as to improve efficiency of the following steps,
- chemical treatment devoted to sorption of radionuclides through addition of reagents (Fe(NO₃)₃.9H₂O 1.25 g.L⁻¹, FeSO₄.7H₂O 3.44 g.L⁻¹, CuSO₄.5H₂O 0.69 g.L⁻¹, Ba(NO₃)₂ 2.5 g.L⁻¹, Fe(CN)₆K₄.3H₂O 1.67 g.L⁻¹ and NiSO₄.7H₂O 1.11 g.L⁻¹),
- concentration of the floc by a factor 12.25 using seeded-ultrafiltration.

The evaporator concentrate was simulated by dissolving sodium and potassium salts in demineralized water (NaNO_3 436 g.L^{-1} , NaCl 110,4 g.L^{-1} , H_3BO_3 74,4 g.L^{-1} , Na_2SO_4 40,4 g.L^{-1} , KH_2PO_4 37,2 g.L^{-1} , $(\text{NH}_4)_2\text{SO}_4$ 14,7 g.L^{-1} and NaNO_2 8,2 g.L^{-1}).

The sludge and evaporator concentrate were finally mixed within the proportions of 58% and 42% in volume.

Reactants for waste encapsulation

Two hydraulic bindings were used: a Portland Cement with a high silica content (CPA CEM I 52.5 PM ES CP2 from Lafarge) and a calcium aluminate cement (Fondu Lafarge). The formulation was optimized by adding non densified silica fume (Péchiney ND-LAU71) and siliceous sand with a fine granulometry (<350 μm) (Sifracco NE34). The grout viscosity was reduced by using a superplasticizing admixture (Glenium 21 from MBT).

Protocols

Mixing was performed with a normalized (EN 196-1) mortar mixer according to the following sequence:

(1) introduction of the waste and possibly of the water, (2) mixing at low speed, (3) addition of the pre-mixed pulverulents (cement, sand and silica fume) while maintaining slow stirring, (4) addition of superplasticizer if necessary, and (5) mixing at high speed for two minutes.

Elaborated materials were characterized by measuring various parameters according to normalized procedures: bleeding (NF P 18-359), setting time (EN 196-3), heat of hydration (NF P 15-436), shrinkage of prismatic samples (4*4*16cm) during curing at 20°C in a sealed bag or in air with humidity of 65% (NF P 15-433), swelling of 4*4*16cm samples during curing at 20°C under water (NF P 15-433), bend strength and compressive strength of 4*4*16cm specimens cured at 20°C in air, sealed bag, or under water (EN 196-1). Mineralogical analyses of the solidified materials were performed using powder X-ray diffraction (Bruker D8), while microstructure was investigated with scanning electron microscopy (SEM – JEOL JSM 820). For leaching tests, phosphates, sulfates, nitrates and chlorides were analyzed using respectively ICP, ionic chromatography, potentiometry and colorimetry.

RESULTS AND DISCUSSION

Direct encapsulation of waste in Portland Cement

A first formula (Table 2) was calculated assuming: (i) a waste incorporation rate of 50% in volume, (ii) a water/cement ratio of 0.5 (proportions by mass), (iii) no addition of free water (which means that water for cement hydration is only provided by the waste), and (iv) a silica fume/cement ratio of 6% in volume (which is a commonly used value in formulation).

Table 2 : Formula I (for 1L grout).

Waste	Portland cement	Silica Fume	Sand
500 mL	877.2 g	37.6 g	545.1 g

The resulting material showed very good workability, but a setting time higher than 8 days, which was much too long for industrial application (ideal setting times ranging from 4 to 24h).

After 7 days of curing in moist air (20°C, humidity of 95%), a sample was taken from the non hardened paste and cryodesiccated. A polished section was examined using reflected light microscopy and SEM combined with X-ray microanalysis. No hydration product was detected at the periphery of the clinker grains. The presence of phosphorus (very likely as phosphate) in the matrix was localized between cement grains and was associated with calcium, thus indicating the precipitation of calcium phosphate.

Among the constituents of the waste, phosphates and borates are known to be strong retarders of cement setting and hardening, retardation being caused by the formation of protective layers over the cement grains due to precipitation with calcium (2). It seems however that phosphates were not involved since they were precipitated in the matrix, but not at the surface of the cement grains. The strong inhibition should thus have mainly resulted from borates. When pH is within the range 4.5-12, borates are for a part under the polyboric forms $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$. According to Roux (3), those species would instantaneously form an amorphous gel, probably $2\text{CaO}.3\text{B}_2\text{O}_3.8\text{H}_2\text{O}$, at the surface of the grains, thus preventing further hydration. Moreover, the major role of borates is supported by previous results which showed that wastes free from boron but containing phosphates twice as more concentrated as in this study could be easily solidified with Portland cement.

Cementation of chemically pre-treated waste

A chemical treatment of the waste was defined in order to limit the strong interaction between cement and boron.

According to literature, two strategies have been investigated to cement wastes with high contents of borates:

- addition of calcium hydroxide to precipitate boron into calcium hexahydroborite $\text{CaO}.\text{B}_2\text{O}_3.6\text{H}_2\text{O}$ (3, 4).
- addition of calcium hydroxide and aluminates in order to precipitate boron into calcium quadriboroaluminate $3\text{CaO}.\text{Al}_2\text{O}_3.2\text{Ca}[\text{B}(\text{OH})_4]_2.\text{Ca}(\text{OH})_2.30\text{H}_2\text{O}$ (QBA) (3, 5).

The former has been used to encapsulate PWR evaporator concentrates with boron up to 40 g.L⁻¹. However, two disadvantages should be mentioned: (i) there is still a significant retardation in cement setting, and (ii) calcium hexahydroborite is unstable in cement and is progressively converted into calcium mono- or quadri-boroaluminate.

The latter would be more effective to reduce setting inhibition. It was thus investigated in this study.

Given the presence in the waste of sulfates and phosphates together with borates, a two-stage process had to be defined: (1) pre-treatment consisting in the addition of calcium hydroxide and barium hydroxide and stirring at 60°C during 5 hours, and (2) embedding of the waste with a mixture of Portland and calcium aluminate cements.

During pre-treatment, phosphates and sulfates were precipitated into calcium phosphate and barium sulfate, this latter phase being stable in cement on the contrary to gypsum which would have been formed if only calcium hydroxide had been used. Conversion of sulfate into barium sulfate prevented delayed formation of ettringite in the hardened matrix, and the resulting risks of swelling and cracking. Reaction was however slow at ambient temperature. At 60°C, quantitative insolubilization required 5 hours. Under these conditions, phosphate precipitation was achieved within 30 minutes. As for boron, its concentration slightly decreased during the first hour of treatment, but then increased up to its initial value.

In the cementation step, the most common calcium aluminate cement (Fondu Lafarge) was used as a source of aluminate to precipitate boron into QBA with calcium hydroxide remaining from the first step.

If both steps had been performed simultaneously, sulfate precipitation, because of its slow kinetics, wouldn't have been quantitative before cement setting.

Optimized pre-treatment conditions and cementation formula are given in Table 3.

Table 3 : Reactants for pre-treatment of 1L waste and cementation formula (II) for 1L grout.

Pre-treatment		Ca(OH) ₂			Ba(OH) ₂ .8H ₂ O		
		42 g			61 g		
Formula II	Pre-treated waste	Portland cement	Calcium aluminate cement	Silica fume	Sand	Water	Plasticizer
	500 mL	745.8 g	85.2 g	35.6 g	515.4 g	27.5 mL	0.5% (*)

(*) mass ratio relative to cement

Characterization of materials prepared according to formula (II)

Effect of pre-treatment on cement setting was spectacular: initial and final set, measured with a Vicat needle, occurred 7h and 11h45min after mixing.

The fresh paste did not exhibit any bleeding. Figure 1 shows the temperature and heat evolution curves determined by semi-adiabatic calorimetry. Two main peaks were observed, whereas only one peak was obtained for a material prepared according to formula (II) but with waste replaced by water. Hydration kinetics of the various cement phases (CA, C₃S, C₂S, C₃A, C₄AF) might be affected in different ways by the waste constituents, which would cause a decoupling of hydration reactions.

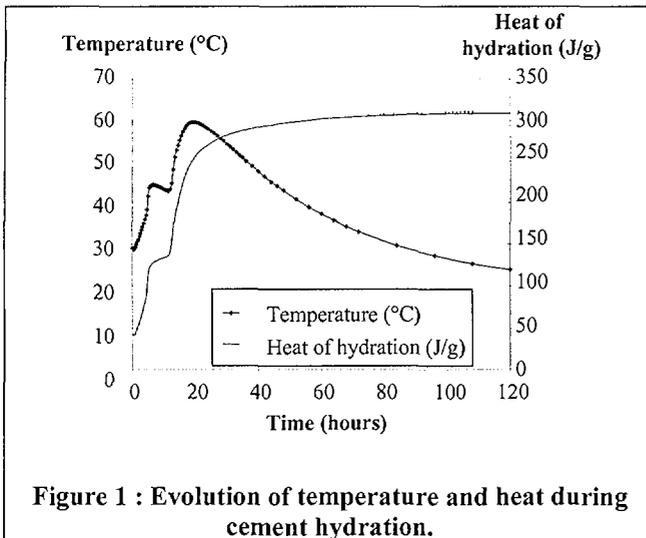


Figure 1 : Evolution of temperature and heat during cement hydration.



Figure 2 : Sodium-rich calcium silicate gel with micro-cracks

Bend and compressive strength of 4*4*16cm specimens were recorded for three types of curing (Table 4). Hardening was slightly more rapid for samples immersed in water but, after 28 days, the results were similar whatever the storage mode. Compressive strength largely exceeded the minimum value (8 MPa) required by ANDRA for any material immobilizing homogeneous type A wastes in a high integrity container.

On aging, 4*4*16cm specimens showed important dimensional variations: expansion under water and shrinkage in air or sealed bag (Table 5). However, no macroscopic damage could be observed after 90 days of curing.

Table 4 : Bend and compressive strength of 4*4*16cm specimens for 3 types of curing.

Time (days)	Water		Air-tight bag		Air (relative humidity of 65%)	
	Bend strength (MPa)	Compressive strength (MPa)	Bend strength (MPa)	Compressive strength (MPa)	Bend strength (MPa)	Compressive strength (MPa)
4	4.7	21	3.8	19.3	2.1	13.2
7	5.2	23.2	4.5	21.9	3.3	19.5
28	5.7	29.5	5.2	29.2	7.7	28.5
90	6.5	30.5	6.2	34.6	9.0	33.3

Table 5 : Dimensional variations of 4*4*16cm specimens for 3 types of curing.

Time (days)	Water		Air-tight bag		Air (relative humidity of 65%)	
	Swelling ($\mu\text{m}/\text{m}$)	Mass variation (%)	Shrinkage ($\mu\text{m}/\text{m}$)	Mass variation (%)	Shrinkage ($\mu\text{m}/\text{m}$)	Mass variation (%)
3	+630	0.45	-175	-0.13	-330	-
7	+655	0.73	-215	0	-680	-2.02
28	+890	1.08	-630	-0.03	-1400	-2.02
90	+1515	1.35	-895	-0.02	-1620	-1.08

Shrinkage could have three main components : autogenous shrinkage, thermal contraction after setting, and drying shrinkage for specimens stored in air. As for expansion, several assumptions should be considered (6): water penetration through diffusion and capillary suction, formation of expansive hydrates, anisotropic crystal growth, attraction of water due to colloidal behavior of phases such as ettringite...

XRD analysis and SEM observation were performed on samples after 90 days of curing under water. Only small amounts of ettringite, which was well crystallized as stubby rods in air bubbles, could be detected in the superficial zone (2mm thick) of the sample. This seems to preclude the hypothesis of ettringitic expansion. SEM showed however the presence of agglomerates (100 μm in size) of partly hydrated silica fume which formed a sodium-rich calcium silicate gel with numerous micro-cracks (figure 2). This result suggests that an alkali-silica reaction occurred in the matrix, involving the badly dispersed silica fume and the high amounts of sodium brought out by the waste. Expansion of the samples could thus have resulted from imbibition of water by the alkali-silicate gel.

A leaching test was carried out on a cylinder sample ($\phi=80\text{mm}$, $h = 100\text{mm}$) which was cured in water at 20°C for 28 days. The leachate was then analyzed. Nitrates and chlorides were detected in significant amounts (Table 6), the leached fraction being close to 8% (in mass) for each species. On the contrary, only traces of sulfate were present and the phosphate concentration was below the detection limit. This good result must have been due to the very low solubility of barium sulfate and calcium phosphate.

Table 6 : Leaching of nitrates, chlorides, sulfates and phosphates.

	NO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}
Initial mass in sample (g/kg of material)	28.62	6.50	5.74	9.30
Mass in leaching water (g/kg of material)	2.38	5.24×10^{-1}	4.97×10^{-3}	$< 2.76 \times 10^{-3}$
Leached fraction (% in mass)	8.3	8.7	0.087	<0.03

CONCLUSION

The elaborated material shows favorable properties in view of industrial application (fluidity, setting time below 24h despite the presence of borates, moderate heat of hydration), and it checks ANDRA specifications on homogeneous wastes immobilized in a high integrity container (no bleeding, compressive strength higher than 8MPa after 28 days of curing at 20°C under water). Further study is however under way (i) to improve dimensional stability by preventing alkali-silica reaction to occur, and (ii) to evaluate the sensitivity of the formulation towards a variation in the chemical composition of the waste.

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