

## CEMENT USE FOR RADIOACTIVE WASTE EMBEDDING AND DISPOSAL PURPOSES

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### Abstract

The use of cement-based materials in Nuclear Industry sets problems which drastically differ from those of Civil Engineering. Some problems and issues are emphasized, dealing with cement embedment of salt-laden solutions, mortar grouting and radionuclide confinement.

## 1. INTRODUCTION

The essential part of the waste production in France comes from Nuclear Power and Reprocessing plants, Nuclear Centres and fuel element factories. Waste management policy provides shallow-land burial for radioactive wastes with an alpha emitter activity not exceeding 3.7 MBq/kg (0.1 Ci/t). The production of low level wastes is estimated at 500,000 m<sup>3</sup> for 30 years, mostly consisting of ion exchange resins embedded in polymers, high-salt-laden concentrates and technological wastes immobilized in cement-based materials.

High level wastes ("C" wastes) as well as transuranic wastes ("B" wastes) will require isolation in deep geologic formations. They are mainly generated by the reprocessing of spent fuel. Type C waste is a vitrified waste form in a stainless steel canister that contains fission products with long-lived alpha emitting radionuclides. "B" wastes such as sludges, hulls and caps and contaminated equipments are embedded in bitumen or mortars.

In all cases, hydraulic binders are widely used for embedding materials and for civil engineering work and barrier construction. In this matter, they represent about 70 % of the materials used in a shallow land disposal. A large variety of problems must be solved dealing with the composition determination, mixing and placing of cement pastes, mortars and concretes, the cement hydration in contact with salt-laden solutions, the radionuclide confinement of waste forms and

engineered barriers, the durability of concrete under environmental conditions [1-2]. The aim of this paper is to emphasize the problems specially encountered and the issues adopted in Nuclear Industry.

## 2. EMBEDMENT IN CEMENT-BASED MATERIALS

On the basis of ANDRA specifications for homogeneous waste packages, radioactive effluents have to be embedded in a matrix in the form of a uniform dispersion of radioactive products. No standing water is tolerated and the waste forms have to meet the acceptance criteria listed in Table 1, for shallow-land disposal.

Table 1  
Acceptance criteria concerning immobilized homogeneous wastes

Bleeding (%)	0	Annual fraction leached	
compressive strength (MPa) :		. $\alpha$ emitters	< $10^{-4}$
. 20 days	> 15	. tritium	< $5 \cdot 10^{-2}$
. 90 days	> 20	. $\beta\gamma$ emitters :	
		3.7 < A <sup>(1)</sup> < 37	< $10^{-1}$
		37 < A <sup>(1)</sup> < 370	< $10^{-2}$
		A <sup>(1)</sup> > 370	< $7 \cdot 10^{-3}$

(1) A = initial activity in MBq/kg

Each liquid waste differs in its specific chemical composition and thus represents a new case to be studied. The aim is to precipitate the salt-ladened concentrates into less soluble compounds to avoid water leaching. Before cementation, boron contained in the PWR effluents is usually made insoluble by the precipitation of calcium borate,  $\text{Ca}([\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O})$  ( $\text{CBH}_6$ ). However, for the concentration encountered, this compound is not stable in cement chemical environment (Figure 1) and a delay in setting is observed.

After setting, a shift of the ettringite X-ray pattern is observed which is attributed to partial substitution of  $\text{SO}_4^{2-}$  tetrahedra in the ettringite structure by  $\text{B}(\text{OH})_4^-$ .

For example, the composition of charlesite (mineral of ettringite group) is given below:



This property of the ettringite type phases can be used to efficiently immobilize boron. For instance, the X-ray pattern of Figure 2 shows that the calcium quadribooroaluminate,  $\text{Ca}_6\text{Al}_2[\text{B}(\text{OH})_4]_4(\text{OH})_{14}\cdot 24\text{H}_2\text{O}$  (QBA) is stable in contact with cement pore water and that there is no setting delay. Notice that the shift of the X-ray pattern with time (after 2 months) is attributed to the presence of  $\text{SO}_4^{2-}$  ions. The mechanism of partial substitution of  $\text{SO}_4^{2-}$  tetrahedra in the ettringite structure is not very well known.

These results are used to improve the embedment in cement of ion exchange resins coming from the primary cooling circuit of PWR [3].

### 3. MORTARS FOR GROUTING AND INJECTION

Grouting of solid wastes or mortar injection to fill up the annular gap between the type B wastes and the host medium (Figure 3) has required the development of an empirical formulation model; it relies on the physical characteristics of the components, taking into account the two contradictory properties: fluidity and compacity.

The sand volume represents the most important part of mortars; this implies that mortar properties depend on the characteristics of the sand skeleton. Experiments were carried out to determine the most appropriate grain size distribution of the sand with regard to the required properties of the mortar such as fluidity, homogeneity, compaction and shrinkage. The seven different types of sand described in Figure 4 were studied. A large granular range was chosen to get a better discrimination of their behaviour. For a given overall volume (70%) of the sand, the mortar composition was determined for each type of sand, previously characterized by its void ratio,  $u_s$ , and specific area,  $S_s$ . The results presented in Figure 5 show that shrinkage increases with the proportion of cement paste in the mortar. Binary type sands, having the lower void ratio, (Table 2) give mortars which exhibit the smallest shrinkage; on the other hand, monogranular sand leads to higher shrinkage.

These results clearly demonstrate that sand granular skeleton has a strong effect on mortar properties. A smaller void ratio induces a decrease in the amount of cement paste to be used and consequently less heat generation occurs during setting, smaller shrinkage and less cracking; smaller specific area leads to a decrease in the water/cement ratio and consequently to lower permeability and to an increase in material homogeneity.

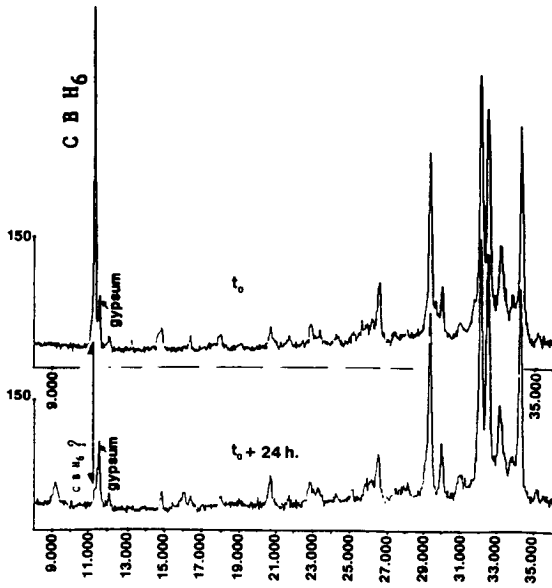


Figure 1. X-ray diffraction analyses of  $CBH_6$  before cement hydration ( $t_0$ ) and after 24 hours of hydration (blended cement type CLC). Notice the absence of hydrates (such as  $Ca(OH)_2$ ) on the X-ray pattern.

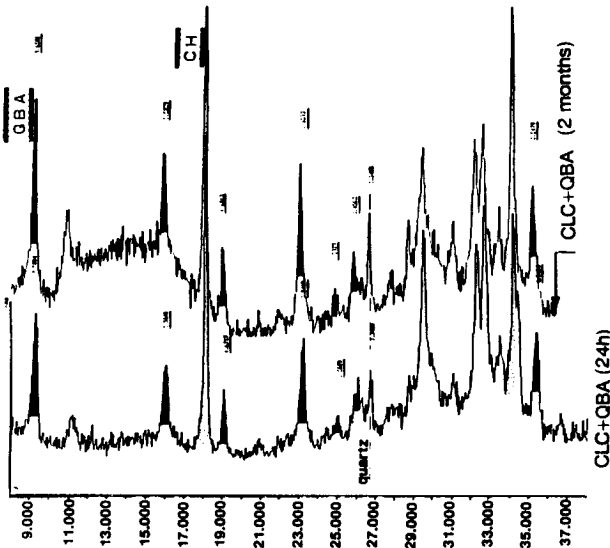


Figure 2. X-ray diffraction analyses of a mixture CLC cement + QBA after 24 hours and 2 months of hydration. CLC = slag and fly ash cement.

**Table 2**  
**Characteristics of the seven studied sands**

Sand type	binary eutectic 1	binary 2	basin-shaped 3	"flat" 4	bell-shaped 5	mono-granular 6	concave 7
$U_s$	0.164	0.295	0.367	0.394	0.445	0.563	0.386
$S_s$	45.49	83.03	58.07	50.40	42.73	31.82	31.95

( $cm^2/g$ )

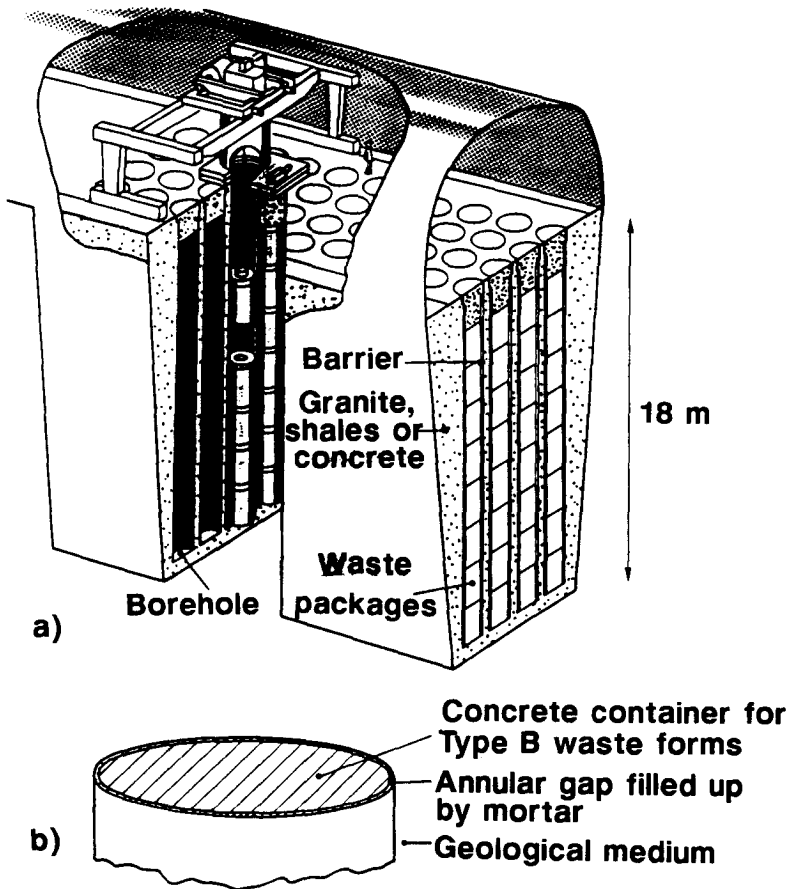


Figure 3. Type B waste. Disposal reference concept in vault.

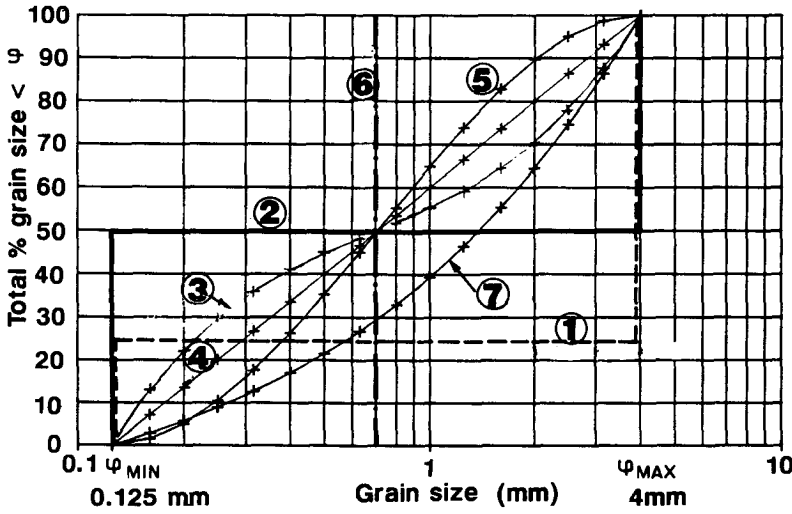


Figure 4. Grain size distribution of the seven studied sands. 1) binary eutectic (75%  $\phi_{max}$ -25%  $\phi_{min}$ ); 2) binary (50%  $\phi_{max}$ -50%  $\phi_{min}$ ); 3) continuous, basin-shaped; 4) continuous logarithmique ('flat'); 5) continuous, bell-shaped; 6) monogranular ( $\phi = \sqrt{\phi_{max} \cdot \phi_{min}}$ ); 7) concave (power law of Furnas type).

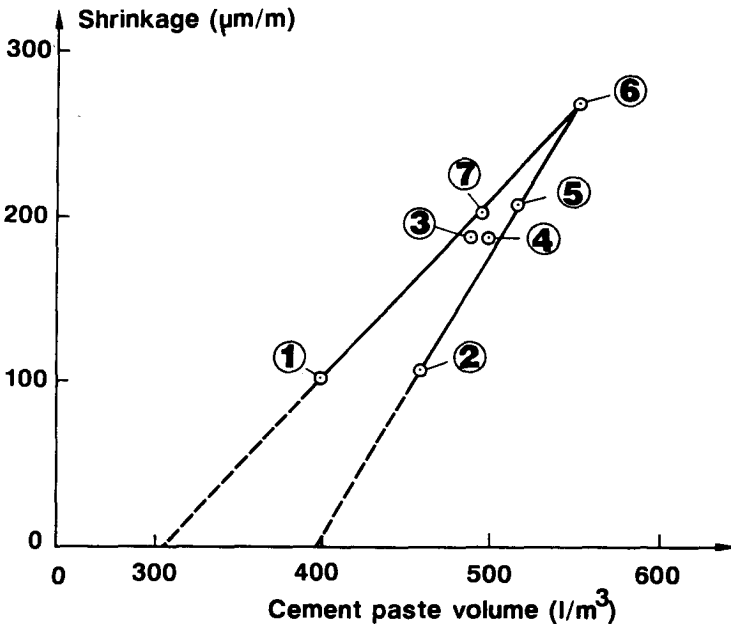


Figure 5. Shrinkage at 28 d of curing (in air-tight bag), as a function of the cement paste volume for the mortars studied (sample dimensions: 4 x 4 x 16 cm).

#### 4. CEMENT PROPERTIES WITH REGARD TO RADIONUCLIDE CONFINEMENT

Modelling of the migration processes in the different barriers has required a knowledge of the chemical behaviour of the radionuclides which are important for the safety evaluation of the disposal.

For example, studies were carried out at room temperature to measure the americium solubility in cement pore water. Americium was added to a  $\text{Ca}(\text{OH})_2$  saturated solution by means of different compounds: a) an acid solution of americium, b) in  $\text{Am}(\text{OH})_3$  form, c) at pentavalent state using  $\text{Na}_3\text{AmO}_2(\text{CO}_3)_2$ . The addition of potash allowed pH - and consequently ionic strength - to vary. Moreover, tests were performed for different values of  $\text{Am}/\text{Ca}(\text{OH})_2$  mass ratio and with interstitial pore water. The results, presented in Figure 6, can be summarized as follows [4]:

- Am is a chemical element which is very insoluble in contact with cement interstitial pore water; its solubility is about  $10^{-11}$  mole/liter,
- the solubility decreases rapidly during the first week but the equilibrium is only reached after about 10 weeks,
- the solubility of americium does not depend on the amount of Am and  $\text{Ca}(\text{OH})_2$ , on the solid phase ( $\text{Ca}(\text{OH})_2$  or cement), on the nature of Am compound initially added,
- the only parameter which is determinant is the pH; Am solubility increases with  $\text{OH}^-$  concentration when  $[\text{OH}^-]$  is higher than 1M.

As it is clear from Figure 6, americium solubility can be satisfactorily modelled by using our thermodynamic data or those of AERE [5]. The americium solubility is essentially due to the equilibrium between  $\text{Am}(\text{OH})_3(\text{s})$  and  $\text{Am}(\text{OH})_3^\circ$ . The data base used by other authors [5] leads to an overestimate of Am solubility.

The very low solubility of americium suggests that only a small quantity of this element is available for migration; this quantity is independent of the amount of Am initially added in the cement paste (provided of course it is higher than the Am solubility limit).

The previous solubility measurements (Figure 6) were performed either in batch tests (with lime and potash additions) or in the upper compartment of diffusion cells (containing lime, potash or synthetic interstitial pore water). The material used in the second case was a 3 mm thickness disk of portland cement paste (water/cement=0.38). In fact, diffusion measurements were difficult since the solubility was of the same order of magnitude as the detection limit. It is clear that the first step of Am migration is a precipitation in the upper compartment and probably at the surface, or within the cement; all the possible adsorption sites are then saturated before reaching the steady state of the diffusion process. It appears that leaching tests, if correctly interpreted, are more

appropriate to determine effective diffusion coefficients for very insoluble compounds.

On the other hand, diffusion tests were carried out with tritiated water which could be considered as a non-sorbing and mobile species. In the case of portland cement, the results available at that time can be summarized as follows:

- the effective coefficient,  $D_e$  ( $m^2/s$ ), is slightly higher for cement pastes than for mortars,

- $D_e(HTO)$  increases with the water/cement ratio,

- $D_e(HTO)$  does not depend on the thickness of the sample.

$D_e(HTO)$  value obtained at steady state for ISO mortars (water/cement=0.5) is about  $2 \times 10^{-12}$   $m^2/s$ . Slag and fly ash (CLC) cement behave differently since their complete hydration requires more than one year. For CLC cement,  $D_e(HTO)$  is the range of 2.5 to  $5 \times 10^{-13}$   $m^2/s$  depending on water/cement ratio and curing conditions of the mortars. This better behaviour of CLC cement is attributed to a finer distribution of the pore network.

Typical curves of tritiated water flow and radioactivity release are presented in Figure 7 in the case of a CLC mortar.

Finally, diffusion tests performed with caesium, which is less mobile than tritiated water, give the following results for portland cement samples:

- $D_e(Cs)$  increases with the water/cement ratio,

- $D_e(Cs)$  depends on the thickness of the sample and on the caesium concentration,

- $D_e(Cs)$  measured for caesium is lower than for tritiated water, by a factor of 3 to 4 with  $w/c = 0.5$  and by a factor of 10 and more for  $w/c = 0.3$  to 0.4.

Experiments were carried out during five years to measure the  $D_e(Cs)$  of CLC cement mortars. A mean value of  $6.0 \times 10^{-14}$   $m^2/s$  is obtained for a CLC ISO mortar. This enhances the better behaviour of CLC based materials with regard to caesium confinement.



Measured and calculated Am solubility in alkaline media

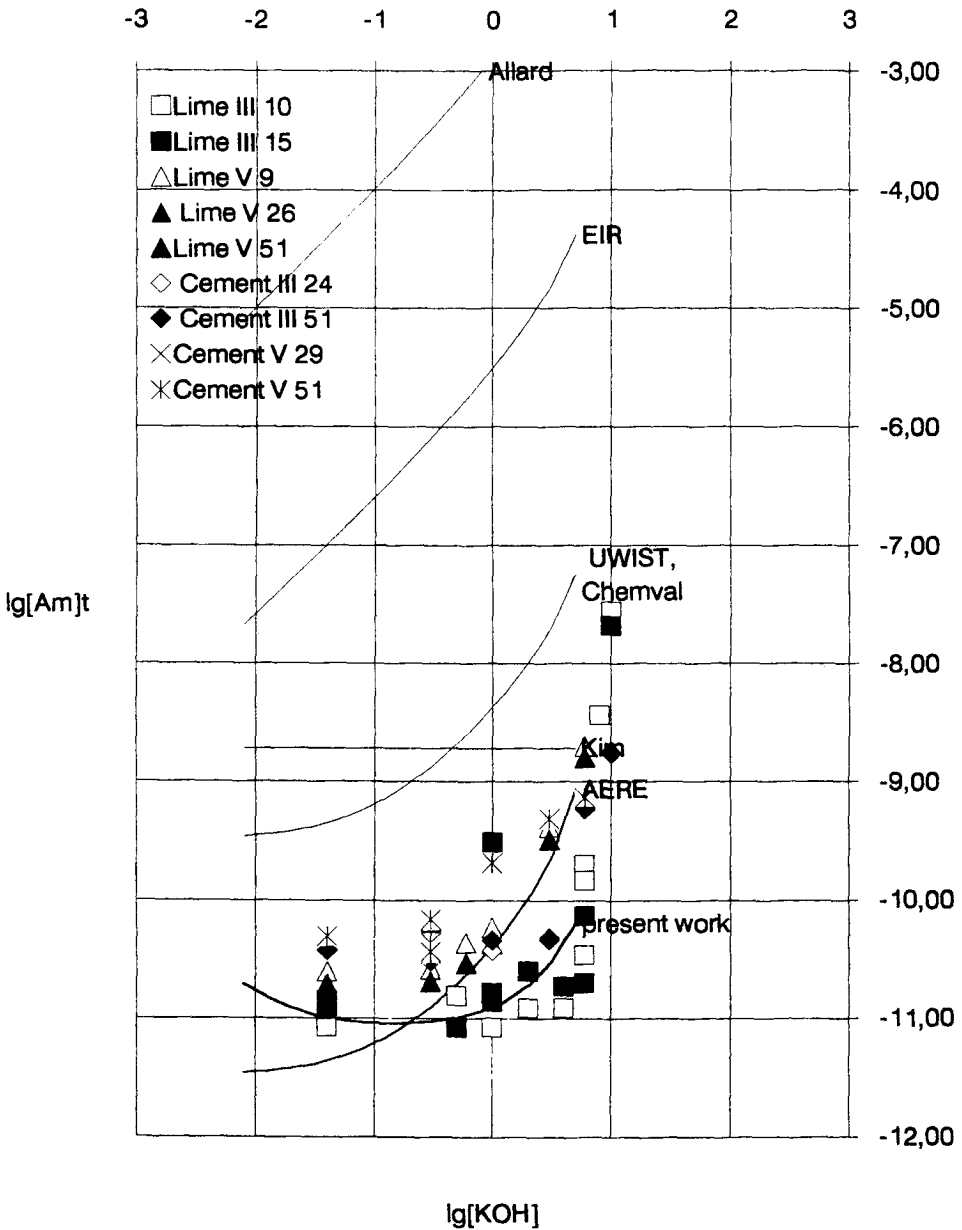
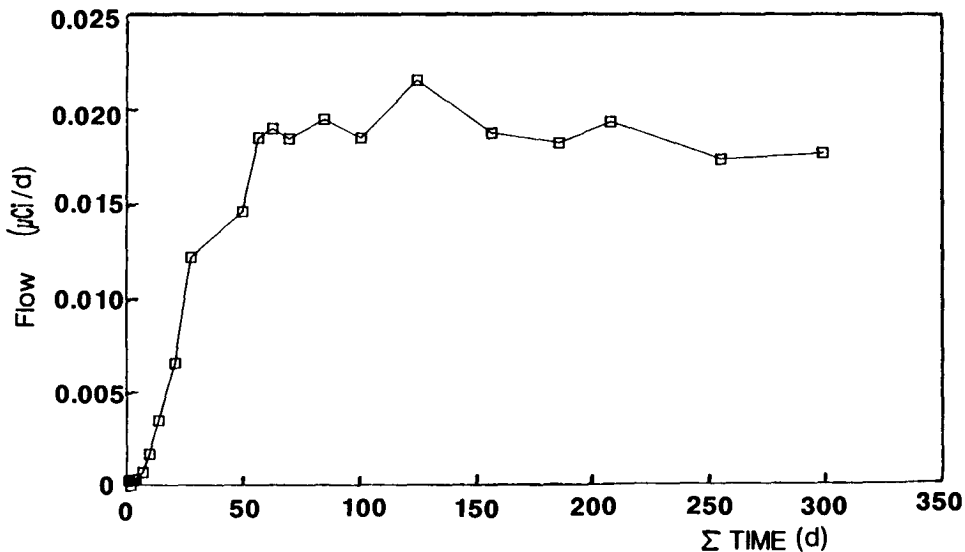
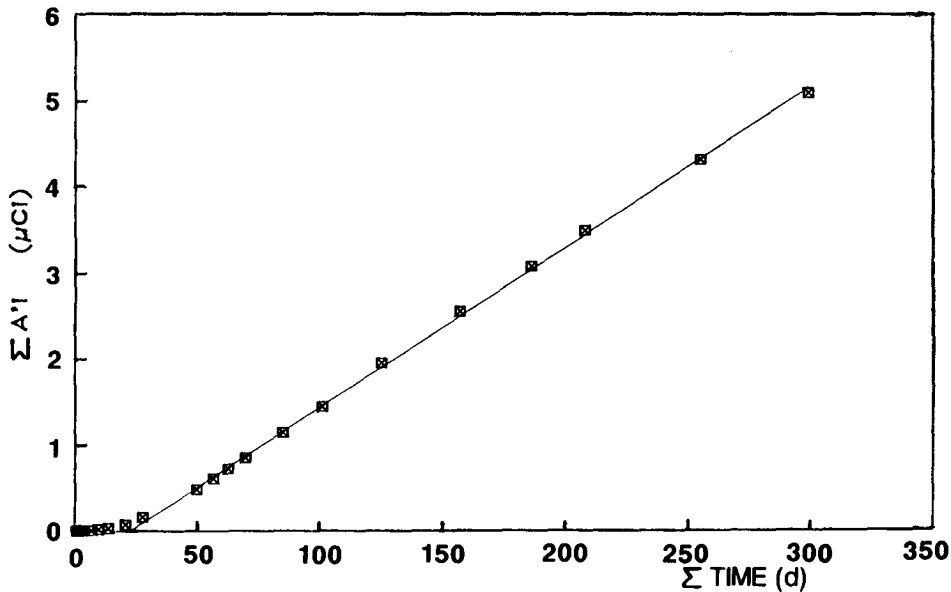


Figure 6. Solubility of americium under alkaline conditions. Experiment-calculation comparison (room temperature).



a) Tritiated water flow as a function of time



b) Tritiated water total release as a function of time

Figure 7. Diffusion test with tritiated water.  $De = 4.9 \times 10^{-13} \text{ m}^2/\text{s}$   
sample: CLC mortar (w/c = 0.42), curing time = 270 days

## 5. CONCLUSION

An overview of the different problems to be solved in Nuclear Industry is presented. Particular care in the choice of the different constituents of the cement based materials is recommended. As far as the embedment of salt-rich solutions is concerned, the use of an appropriate hydraulic binder allows more stable waste forms to be obtained after cement hydration; these improve radionuclide confinement.

The study of mortars for solid waste grouting or engineered barrier injection suggests the use of a binary sand to reduce the amount of cement paste to be used and consequently heat generation, shrinkage and potential cracking.

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