CONCRETE ENCAPSULATION OF ION EXCHANGE RESINS: FROM R&D TO AN INDUSTRIAL PACKAGING FACILITY

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ABSTRACT

Due to the amount of spent ion exchange resins generated by the nuclear industry, the need has emerged for an effective long-term packaging method to accommodate this type of waste. The concrete encapsulation process meets this need and provides a relatively simple means of treatment. France and other countries have launched numerous R&D projects in this area.

This paper reviews the problems associated with packaging spent ion exchange resins using hydraulic binders and describes the methodology adopted by the CEA and SGN for the related development. In addition, progress is reported on the work undertaken with reference to specific examples.

INTRODUCTION

Spent ion exchange resins account for most of the low-and intermediate-level radioactive waste generated at the nuclear power plants operated by Electricité de France (EDF). A substantial portion of these resins are also generated by other centers such as the spent fuel reprocessing plants run by Cogema and some research laboratories operated by the French Atomic Energy Commission (CEA). Domestic output totals approximately 300 m^3 a year.

Such a volume of waste has amply justified research into specific treatment and disposal processes. The goal was therefore to define, among several possible alternatives, a simple-to-operate and cost effective process that would enable maximum volume reduction in compliance with the standards established for approval of the final waste packages.

In the initial stages, concrete encapsulation quickly emerged as the most attractive solution. However, the poor results obtained with its first commercial application, particularly regarding compliance with specifications of the waste storage authority, prompted the CEA and SGN to conduct further studies to identify and solve the problems encountered. This was achieved by devising appropriate treatment techniques and formulations, and by developing suitable technologies for their specific application to ion exchange resins.

IER CONCRETE ENCAPSULATION PROBLEMS

Problems Associated With Encapsulation

Ion exchange resins are not inert with respect to an encapsulation matrix which comprises hydraulic binding agents. The hydration of the cements includes solubilization in the mixing water of its anhydrous constituents such as Ca^{++}, Na^{+}, K^{+}, SO_4^{-} and OH^{-}. In contact with this solution, the resins react chemically through ion exchanges according to their affinities and the laws of chemical equilibrium. The cement hydration mechanisms are then upset by depletion of the solution in ion species which are essential for proper hydration, and by the release of undesirable ions. These exchanges affect the preparation of the encapsulated materials by acting on the rheology of the material (stiffening, false set, flocculation). The setting of the encapsulated material may subsequently be affected: acceleration, delay and hydrated material with poor mechanical resistance.

The physical and chemical phenomena involved are complex and not yet fully understood. Various observations or interpretations have been proposed in the literature: an ion exchange mechanism (OH^{-}/SO_4^{-} in the case of anionic resins) causing resin bead shrinkage or swelling (12), swelling under water of encapsulated materials containing cationic resins (2), shrinkage of resins due to the release of heat produced during hydration followed by an increase in encapsulated material volume during immersion, resulting in the emergence of internal tensions (3).

It is usually thought (4) that only packages with an initial high compressive strength (around 30 MPa after 28 days) can withstand immersion without significant deterioration. In fact, two aspects should be considered in the development of an ion exchange resin encapsulation formula.

Physical Aspect

The quantity of ion exchange resins encapsulated in the cement paste has a major impact on the properties of the encapsulated material. Compressive strength, R_c, is expressed as a function of the ratio P (where P = (volume of water + volume of IER)/volume of the encapsulated material) as follows:

$$R_c = K\, e^{aP} \quad (a < 0)$$

This equation is similar to the one which describes the variation in mechanical strength of a paste as a function of its porosity. For example, the compressive strength of the pure cement paste (R_c = 95 MPa) is reduced by two thirds when the waste loading (expressed as the ratio between the apparent volume of the water-saturated resins and the total volume of encapsulated material) reaches 50% (5).

Similarly, the dimensional stability of the immersed encapsulated materials depends to a large extent on the amount of incorporated ion exchange resins. It has been demonstrated experimentally that the swelling of encapsulated materials under water reaches unaccep-table levels for waste loadings of 62 and 70% (6, 7).

A waste loading of 50% therefore provides a good tradeoff between the achievement of adequate encapsulated material properties for disposal in a surface repository and a sufficient reduction in waste volume.

Chemical Aspect

Analysis of chemical interactions between the cement and the resins shows that each type of resin reacts in a specific way depending on its own properties and those of the attached ions. Changes occur in the composition of the liquid phase when the ion exchange resins are mixed with the cement paste.

For cationic resins (Fig. 1) a decrease in the alkali concentration, and hence in the basicity of the pore solution, is observed. These reactions can cause the paste to thicken during mixing due to significant changes in the pH.

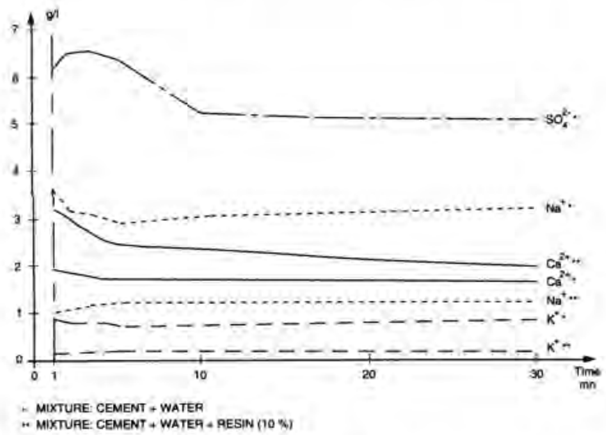

Fig. 1. Ion species of the pore solution for a cement paste with and without resin.

The example given in Fig. 2 is for "mixed bed" resins initially containing boron and lithium, for which the high concentrations of Li^+ and $B(OH)_4^-$ ions are found in the pore solution. These two ions have opposite effects on the paste setting time, since the Li^+ ion decreases this time due to activation of the binder aluminous phase and the $B(OH)_4^-$ increases it due to the formation of insoluble calcium borates on the surface of the cement grains.

When the resins contain OH^- ions, the paste stiffens during mixing due to the precipitation of hydrated aluminates.

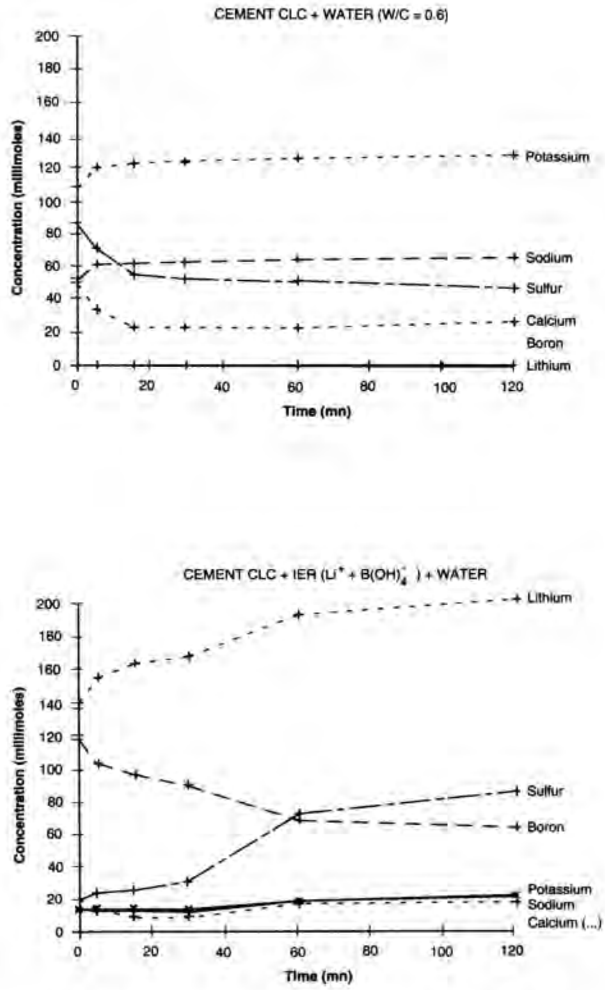

Figure 2 : Concentrations in the pore solution during mixing

Fig. 2. Concentrations in the pore solution during mixing.

PROCESS APPLICATION DIFFICULTIES

In addition to the conventional problems associated with the treatment and packaging of nuclear waste (confinement, biological shielding, remote dismantling capability of some equipment), the use of resin concrete encapsulation based on a formulation raises the specific problems detailed below:

Mixing

Commercial application must be comparable to laboratory implementation despite the scale effect. The main criterion for selecting an appropriate mixer is clearly its capability to homogenize in a minimum time (mixing efficiency), although it is just as important to maintain satisfactory fluidity and stability of the paste.

Verification

The properties of the encapsulated material are verified in detail on the basis of a formulation established in the laboratory according to specifications of the waste disposal authority. Verification of the concrete encapsulation process is therefore essential to ensure approval of the waste at the repository.

As a result, most of the work entails improving the accuracy and the reproducibility of the batching proportions used in the formula. While current technologies offer reliable solutions to the problem associated with conventional batching by weight (for water, cement, aggregates, etc.), the batching of the encapsulated resin waste is complex and must be determined on a case-by-case basis.

Process Waste

Treatment of the resins may generate additional waste which has to be eliminated. Such process waste includes:

- ammonia offgases when part of the resin active sites arae occupied by ammonia ions (NH_4^+);

- liquid effluents produced by a specific preliminary chemical treatment carried out before concrete encapsulation, or by dewatering the waste to increase the waste loading;
- solid waste mainly resulting from retention in the mixer.

OBSERVATIONS

The above-mentioned problems involving waste and matrix interaction were not detected until special laboratory research had been conducted. Technological deployment difficulties in fact too often mask such physical and chemical incompatibilities between the waste and the encapsulating material, thus preventing a selective interpretation of the phenomena involved. Working with the engineering contractor, the operator also attempts to improve certain technological aspects by stepping up efforts on process waste problems or by striving to increase productivity, while often minimizing the importance and the difficulties associated with securing approval of the final waste package.

CEA/SGN METHODOLOGY FOR RESEARCH AND PROCESS DEVELOPMENT

The CEA and SGN propose to apply a joint interactive development methodology, on a case-by-case basis, associating the laboratory and the engineering contractor. The participants are thus able to conduct their applied research and process industrialization in a pilot facility to maximize the resulting benefits.

The actions specific to each case are described below. Information must be exchanged at every stage to ensure proper implementation of the program.

Knowledge of Initial Waste Properties

At this stage chemical and radiological analyses of the waste are carried out to detail the input data received from the waste generator. This stage also identifies and studies the special problems associated with resin collection, transfer, batching and preliminary treatment (if necessary). The first in-line verification techniques (sampling for chemical analyses and in-line beta/gamma spectrometry) are also implemented at this stage.

Formula Precharacterization On Laboratory Samples

At this stage the tests are usually conducted on simulated waste, which entails some representativeness problems. The measurements or analyses conducted (Fig. 3) must predict the behavior over time of the fresh and hardened material under different curing conditions. Structural studies and porosity measurements are carried out to monitor hydration of the cement and identify the newly crystallized phases. In some instances, it may be necessary at the precharacterization stage to have an initial idea of the radionuclide containment capacity of the encapsulated materials. The test adopted is a leach test performed on small samples doped with radioactive elements. For ion exchange resin encapsulation in a cement matrix, special attention is given to the consistency of the paste, the setting time, the dimensional variations and the mechanical strength of the encapsulated materials stored in air, under water or at 100% humidity.

Representative Scale Feasibility Tests

These tests are carried out and used to select a mixing technology and specify concrete encapsulation procedures. The basic concepts of the future packaging process are detailed in this stage, which is approached with a "rough" encapsulation formula and carried out on scaled-down industrial equipment.

At this stage, a mixer is selected with an appropriate technology, maximum capacity, special accessories, etc. The batching and feed devices for the constituent materials, as well as the special draining and rinsing equipment, are tested.

Waste packages of 100 to 200 liters are also poured using simulated waste. The tests include verification to ensure that the properties of the encapsulated material are identical to those obtained on small samples using standardized specimens taken after mixing or specimens taken from the packages after hardening.

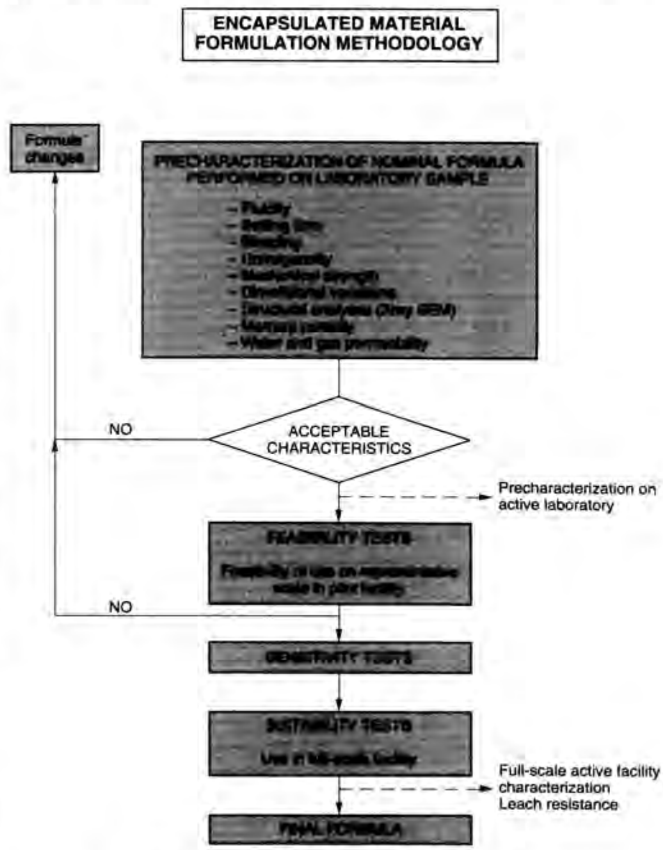

Fig. 3. Formulation methodology.

Sensitivity Tests

The laboratory sensitivity tests must enable determination of the formula composition range which provides acceptable properties for the encapsulated material with allowance for variations in the composition of the waste itself. Using a reference formula and imposing further batching accuracy constraints, if necessary, comprehensive pilot tests are performed to validate all concrete encapsulation procedures, adjust batching parameters which affect overall accuracy, reproducibility or reliability of the process, and optimize in particular the draining and rinsing systems after quantitative determination of the retained waste.

Suitability Tests

At this stage in the study, the concrete encapsulation formula and process are fully defined and the full-size facility is built. Suitability tests are performed to verify that the facility produces a high-quality waste package which meets the technical specifications of the French National Radwaste Management Agency (Agence Nationale pour les Déchets Radioactifs; Andra). The characterization tests are performed, including in particular leach tests on full-size waste packages if justified by their radioactivity. Andra approval for disposal of the packages in a surface repository is contingent on the results of the characterization tests.

The synergy at play between the CEA and SGN in this area, which aims at combining the development of an appropriate formulation with a pragmatic approach to process industrialization, ensures the future operator of a qualified process featuring optimum reliability and low operating costs in compliance with the final waste specifications required by the storage authority.

APPLICATION TO EDF AND COGEMA WASTE

The CEA and SGN have developed several processes for resin encapsulation using hydraulic binders, in collaboration with the main radwaste generators in France, EDF and Cogema. Other processes are also now under development.

These processes differ according to the properties of the waste to be treated, which leads to an approach that may vary with the current stages of progress. The developments made with these processes for the three main types of ion exchange resin produced by the nuclear industry are:

- resins used to purify PWR plant secondary system water for EDF;
- resins to purify spent fuel storage pool water prior to reprocessing, for Cogema;
- resins from PWR treatment units of the primary system and secondary drains for EDF.

RESINS USED IN PWR PLANT SECONDARY SYSTEM WATER

The Waste

The resins are used by EDF to purify steam generator blowdown in PWR power plants. Owing to the low level of radioactivity circulating in the secondary system water, the waste has a very low activity concentration ($\leq 10^{-2}$ Ci/m^3). However, it is saturated with various combined chemical elements resulting from the addition of anti-corrosion agents. These elements may include morpholine, ammonia and hydrazine, which are not very stable.

The volume of waste produced annually per 900 MWe unit is about 8 m^3. This waste usually consists of 2/3 cations and 1/3 anions.

The Process

The treatment and packaging process developed and adopted for this specific case is a batch process. It is carried out in two separate steps:

Chemical Pretreatment

This operation is performed to saturate the active sites of the waste with stable ions having greater affinity, which eliminates chemical interactions within the matrix by inhibiting the exchange capacity of the resins. It is also carried out to eliminate undesirable chemical elements, particularly the ammonia, by shifting the equilibrium in solution.

Concrete Encapsulation

The pretreated waste is encapsulated in concrete using a formulation suited to the final properties required. A slag cement matrix limits the exothermal effects of the binder hydration reactions.

Technological Developments

The main technological choices and developments made principally concern the mixing technology and the waste batching proportions.

Use of a Guedu-type stainless steel mixer frequently adopted for batch applications in the chemical and pharmaceutical industry offers the combined advantages of suitable encapsulation performance (waste loading of 50 to 75% by volume), homogeneity and low retention. Adaptation of this equipment to nuclear environment constraints led SGN to focus more particularly on development of the rinsing systems (with special stationary nozzles and a rotating spray cleaning head), and on the encapsulated material draining equipment (piston holder) to limit external decontamination and consequently reduce the generation of process waste.

The ion exchange resins are batched in a dosing pot. This mainly permits:

- elimination of excess supernatant required for transfer of the resins;
- achievement of a stable, reproducible state for the waste;
- process verification by producing a constant predetermined quantity suited to the preparation of a batch.

The principle employed is simple and batching is carried manually by the operator.

Applications

In 1988, on the basis of the process developed, SGN received from EDF an order to supply a mobile system for encapsulating steam generator blowdown resins produced by the P'4 and N4 series PWR units. The system is used for a total of eighteen 1300 MW units.

Its main characteristics are:

- capability to handle twelve 55-gallon drums a day enabling a daily resin packaging total of more than 1 m^3;
- easy assembly and disassembly of the treatment and packaging modules by the operators within three days;
- transport by normal road convoy in view of the overall dimensions.

RESINS FOR FUEL STORAGE POOL WATER PURIFICATION

The Waste

The ion exchange resins used by Cogema to purify the water in spent fuel storage pools before reprocessing are usually regenerated prior to draining and stored until packaging at a later date. These resins are of the low- or intermediate-level type (10 to 400 Ci/m^3) and have varying physical properties (bead shape, crushed or mixed with other materials).

The Process

The process adopted for packaging ion exchange resins in bead form is comparable to the one described above for steam generator blowdown resins. Some adjustments in the treatment and formulation were necessary to improve the final properties of the packaged waste before disposal in a surface repository. Verification of the confinement properties required for the encapsulation material has led in particular to an adjustment of the maximum waste loading (approximately 50% by volume) and optimization of the pretreatment operations.

Technological Developments

The basis of the technological development is the same as for the steam generator blowdown resins. However, most of the equipment adopted in this case has to be adapted for use in a highly radioactive waste environment.

Specification of a mixer with dimensions compatible with the removal facilities in the radioactive area led SGN to develop equipment which can be used for remote disassembly operations. This special equipment includes the mixer tank, a piston holder and a lid.

The resin batching principle was retained and optimized to permit automation of the batching cycles. The development of monitoring instruments (level detectors) during overall testing on the pilot facility enabled validation of the waste batching procedures during decentralized operation.

The development of solutions providing the accuracy required by the formulation for batching the various constituent materials also validated the feasibility of packaging for the type of ion exchange resins considered.

Applications

In 1989 Cogema commissioned SGN to perform development and engineering studies for a stationary system to package resins now stored at its reprocessing plant in La Hague, France. The proposed actions include:

- validation and qualification of the main stages in the pilot and full-scale packaging process for the mixer;
- initiation of the end product characterization to secure approval for disposal in a surface repository;
- performance of a summary preliminary design study of the system.

In view of the positive results obtained during the previous development stages, Cogema recently requested consideration of new types of resins (particularly crushed or mixed) and inclusion of specific features of this waste in the development work now under way. The current direction thus favors offering more flexible, versatile solutions for packaging process waste, including the various forms of ion exchange resins employed.

REACTOR ION EXCHANGE RESINS CONTAINING BORON

The Waste

The ion exchange resins to be encapsulated are anion exchange resins from the boron recycle system of the Fessenheim nuclear power plant. They contain approximately 1 eq. $B(OH)_4^-$ per liter of ion exchange resin.

Radiochemical analysis results indicate that the concentration of radionuclides trapped by the ion exchange resins is low and below the encapsulation threshold specified by Andra. The ion exchange resins therefore only need to be immobilized in a matrix to avoid dispersion.

The Process

In this case no pretreatment is performed on the waste, which is encapsulated in a portland and aluminous cement matrix. A waste loading of 50% has been adopted.

The experiments conducted on 1.5-liter batches enabled the preparation of high-quality encapsulated materials. The following properties were measured for these materials:

- setting time of approximately one week;
- acceptable dimensional variations for the samples subjected to different curing conditions (Fig. 4); After six months of curing the swelling under water is less than 400 microns per meter and shrinkage when stored in air is approximately 1 mm/m.
- high mechanical strength reaching 40 MPa after six months curing under water.

In view of these promising results, feasibility testing was initiated with the preparation of 100-liter packages. Three months after setting of the encapsulated material, five 8-cm-diameter core samples were taken in the package and 8-cm-high cylinders were cut from the core samples.

The results of the density and compressive strength measurements are given below with indication of the sample position:

Samples	Density (Mg/m^3)	Compressive Strength (MPa)
Horizontal-Top	1.85	29
Horizontal-Mid	1.79	27
Horizontal-Bot	1.80	23
Vertical-Mid	1.85	21
Vertical-Bot	1.80	18

The results show that the waste package has acceptable mechanical properties since the mean compressive strength after 90 days is greater than 20 MPa. Differences in density and strength were however measured, depending on the sampling height. This heterogeneity, which was not visible to the naked eye on a package cross section, required improvement of the mixing process.

In addition, subsequent feasibility tests will have to be supplemented by the use of industrial facilities and the program will have to be extended to include sensitivity studies.

CONCLUSION

Pending the development of more advanced treatment processes such as incineration or chemical destruction, which could provide attractive alternatives, the CEA and SGN are offering an economical industrial solution for the disposal of spent ion exchange resins stored at nuclear facilities. Concrete encapsulation of the waste can rapidly provide "relief" to waste generators who are looking for qualified commercial

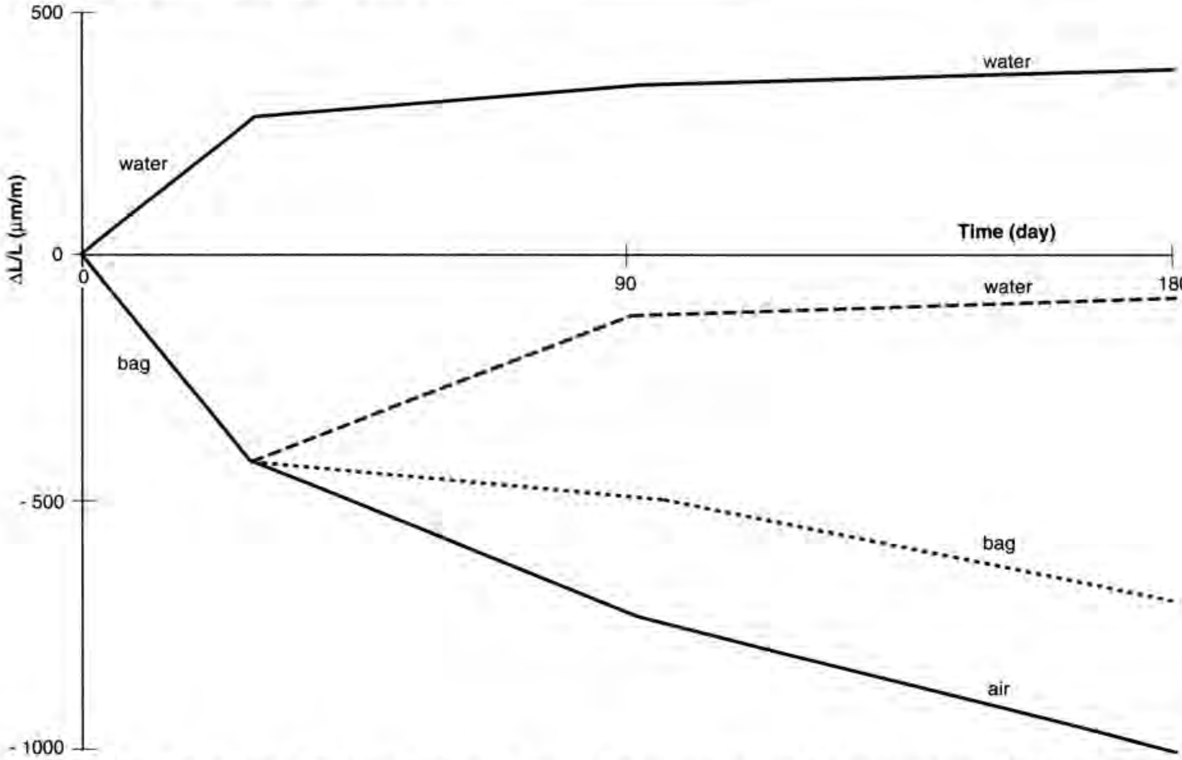

Fig. 4 - Dimensional variations as a function of time and curing conditions. Fessenheim waste forms (prismatic specimens: 4 x 4 x 16 cm).

packaging processes. In addition, the special efforts which have been dedicated to characterization of final waste forms relative to specifications of the French disposal authority ensure the production of high-quality encapsulated materials.

REFERENCES

1. O. BEIJER, PRAV Report No 1-36, 1980.

2. P. COLOMBO, R.M. NEILSON, BNL Report No 51615, 1982.

3. R. DAYAL, H. ARORA, M. MORCOS, NUREG Report No 3382, 1983.

4. S.E. PIHLA JAVAARA in compilation of Reports on Cementation of IER Wastes in Finland, Technical Research Center of Finland, 1983.

5. P. LE BESCOP, P. BOUNIOL, M. JORDA, Mat. Res. Soc. Symp. Proc. 176, 183-189, 1990.

6. P. LE BESCOP, "Conditionnement par les liants Hydrauliques de rÉsines Échangeuses d'ions Utilisées dans l'industrie Nucléaire", Mémoire CNAM, Paris, 1989.

7. P. LE BESCOP, R. ATABEK, Y. FITAMANT, J.P. GHYSELS, 1991 Joint International Waste Management Conference, "PWR Ion Exchange Resin Embedding in Cement, Proc. Vol. 1, p. 469-474, SEOUL, October 21-24, 1991.