# THE ASBESTOS CEMENT CONTAINER AND ITS CHARACTERIZATION PROGRAM

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## ABSTRACT

A new type of packing container is designed in France, by SGN, for the reprocessing wastes conditioning: the asbestos cement container (CAC) made by the industrial process for pipes fabrication. Two types of CAC are studied, differing from each other by their wall thickness. The technology of which SGN is in charge is presented.

A characterization program is operated by CEA in view of satisfying to regulatory requirements. Emphasis is placed upon the radionuclides migration study, through different asbestos cement samples.

## INTRODUCTION

For the technological wastes coming grom the COGEMA reprocessing plants, a new type of conditioning container is studied : the asbestos cement container (in french CAC). Two types are designed, according to the origin of the wastes, differing from each other by the thickness of their walls :

- A 50 mm thick CAC, for non α wastes, i.e. wastes coming from laboratories, such as cells or glove boxes out side equipment. This kind of wastes is primarly conditioned in 100 l metallic drums, compacted to "pressed cakes" put in a 200 l metallic drum, placed in the storage container.
- A 75 mm thick CAC, for α wastes, i.e. wastes coming from not cells ; this kind of material includes process equipments, such as pumps, or mechanical apparatus : these wastes are put in a canister, and then placed in the storage container.

In the two cases, the space, between the canister or the 200 l drum, and the CAC, is filled with a special cement grout. This grout contributes to the radionuclides confinement, adding its own characteristics to those of the asbestos cement barrier.

The asbestos cement container is being designed by SGN which is in charge of the technological development.

Moreover, for this container, designed to be used on a large scale, a characterization program, including several stages has been built for COGEMA, by the CEA. The CEA is in charge of the characterization work.

### Development History

Asbestos cement material was selected by SGN several years ago, in view of developing :

- Either high integrity containers for radioactive waste conditioning.
- Or tubing of high performance and quality for radwaste storage and disposal.

Most of the materials selected all around the world for this kind of application are of two types :

- Reinforced concrete, based on a well known matrix (cement) but uneasy to characterize as an industrial container, (local and non homogeneous steel reinforcement often with uncertainties concerning the quality insurance for the manufacturing.
- Polymer based container, with a high cost and a short term experience, leading to some uncertainties about their durability.

Furthermore, the evolution of specifications on radwastes leads to very large Research and Development and test programs, especially for new materials. The corresponding cost is difficult to support either by the customer, or by the process owner.

The development by SGN of asbestos cement material is a new trend in this field. Its different stages are summarized in Fig. 1.

The main points are highlighted hereinafter :

1) Material selection

Taking into account the features indicated above, the main selection criteria were as follows :

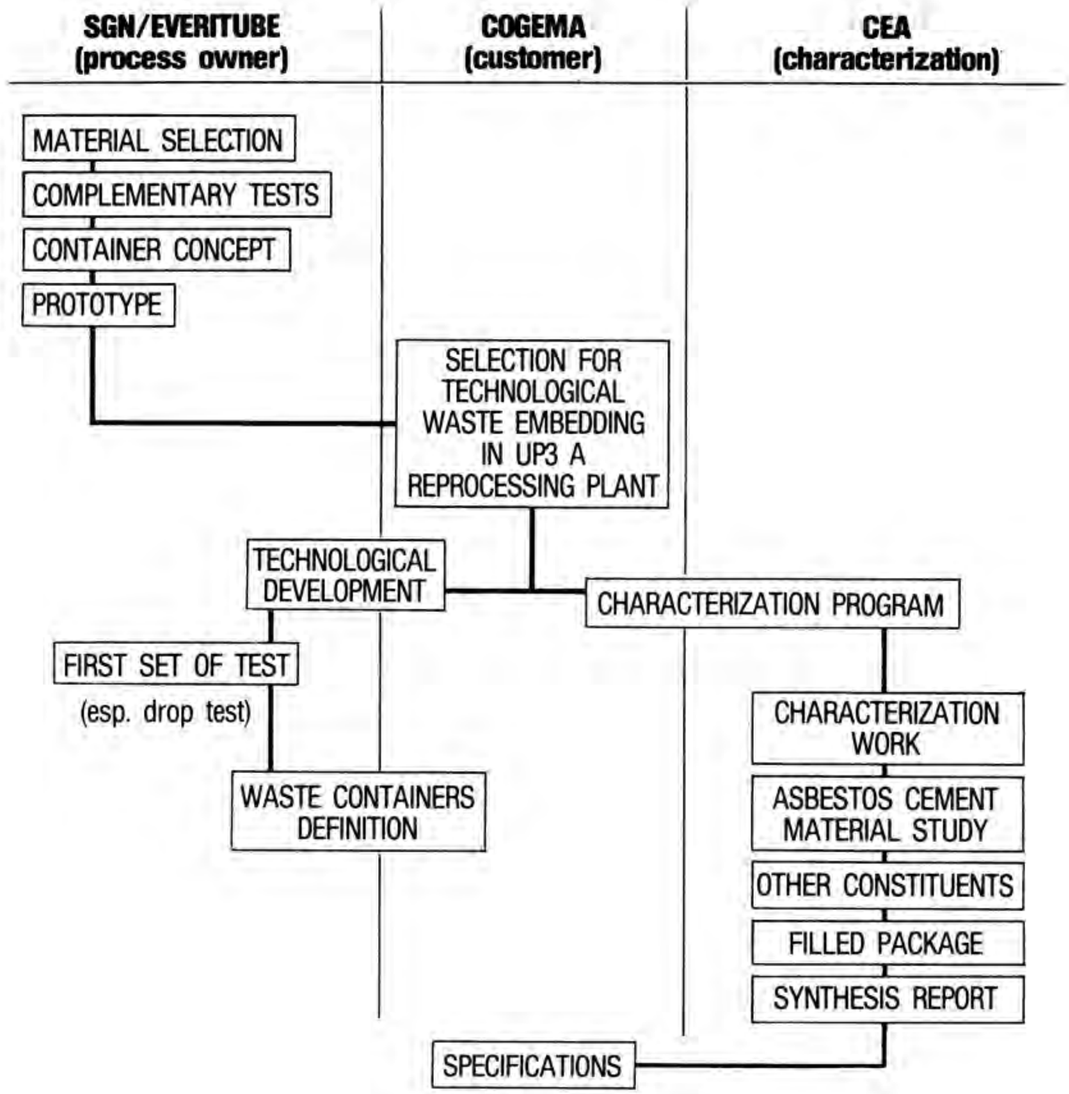


Fig. 1. Progress Chart of Asbestos-Cement Material Development.

- Well known material, and an industrial one in a wide range of countries.
- Very simple manufacture process, with an already well proven quality insurance program (for industrial pipe application).
- Long term industrial experience (over 50 years) in underground piping for sewage water.
- High mechanical resistance, without any steel reinforcement (compressive strength : 80 MPa and 120 MPa, on solid samples depending upon the direction of application. Other values are given on tubular samples - Table 3).
- Corrosion and ageing properties quite good, and already known and published (existing international committee).
- High temperature resistance for special applications.

2) Complementary tests

Taking into account the properties of the asbestos cement material which were already available, the first technical survey was completed by some additionnal tests, such as :

- Temperature and fire resistance.
- Chemical resistance (6 months, 3N nitric acid in a Ø 150 mm container).
- Resistance to gamma irradiation (up to $6.10^9$ rads integrated dose).

3) Selection by COGEMA and technological development

On the basis of the technical survey, the container concept and the various prototypes realized by SGN, COGEMA decided to select this material and adapt the container concept to the embedding of technological wastes coming from UP3A - UP2 800 reprocessing plants of La Hague.

Together with the unit design study, COGEMA and SGN developed and tested the container itself, taking into account the particular requirements of the waste types and the conditioning process.

4) Characterization program

At this final stage, COGEMA decided to apply the remaining characterization program on the different industrial container items, allowing to check out the agreement with the French safety authorities requirements regarding such kind of waste.

This work has been undertaken by CEA, and will be described further.

Finally, the asbestos cement container must be considered from two points of view :

- The material itself, already characterized, either by industrial experience or by complementary tests in CEA, according to the safety authorities recommendations.
- The container technology, which has to be adapted together with the customer, according to the particular application requirements. As an example, the concept developed together with COGEMA is briefly described hereinafter.

Technological Waste Container Technology

The technological wastes coming from UP2-UP2 800 reprocessing plants are mainly of two types :

- Various wastes (paper, plastics, gloves...) in sealed metallic drums or plastic cans.
- Discarded equipments (pumps, valves, ejectors...) in sealed casings.

The basic principle of the conditioning unit is to embed these cans, drums and casings into asbestos cement containers without breaking the confinment. This is carried out in 3 main steps :

- Waste disposing into the container and lid placing.
- Cement grout injection.
- Sealing with epoxyde resins.

An example of the resulting waste package is described in Fig. 2.

Provided that the activity level is in agreement with the IAEA recommendations, the waste package will be in A category for transport of radioactive wastes.

Two types of containers have been designed for UP3, according to the beta gamma activity level and alpha content in the initial waste, but with the same conception and conditioning method.

- 50 mm thickness (wastes issuing from intervention zones).
- 75 mm thickness (wastes issuing from hot cells).

The main components of the container are :

- An asbestos cement shell, cut out from an industrial pipe and machined for this application.
- A lid, consisting of an asbestos cement plate, a steel one, and steel anchors, all sealed together.

Two holes are machined in to the lid (one for injection of grout and one as vent).

- A lock ring, ensuring that the waste drum or casing will be stable inside the container during and after the grout injection.
- The bottom part, similar to the lid.

A special micro-concrete (or grout) is injected through the hole all around the waste canister. Different compositions of grout have been tested including cements with secondary constituents, like high furnace slag. Actually studies are carried on to obtain the definitive formulation.

After drying, an epoxyde resin is injected on the top part of the container, ensuring the final sealing of the waste package.

Asbestos Cement Container Characterization Program

This program includes 3 phases :

1. Characterization of asbestos cement material.
2. Characterization of the container.
3. Characterization of the filled package.

The first part of the work will be described in this paper[1].

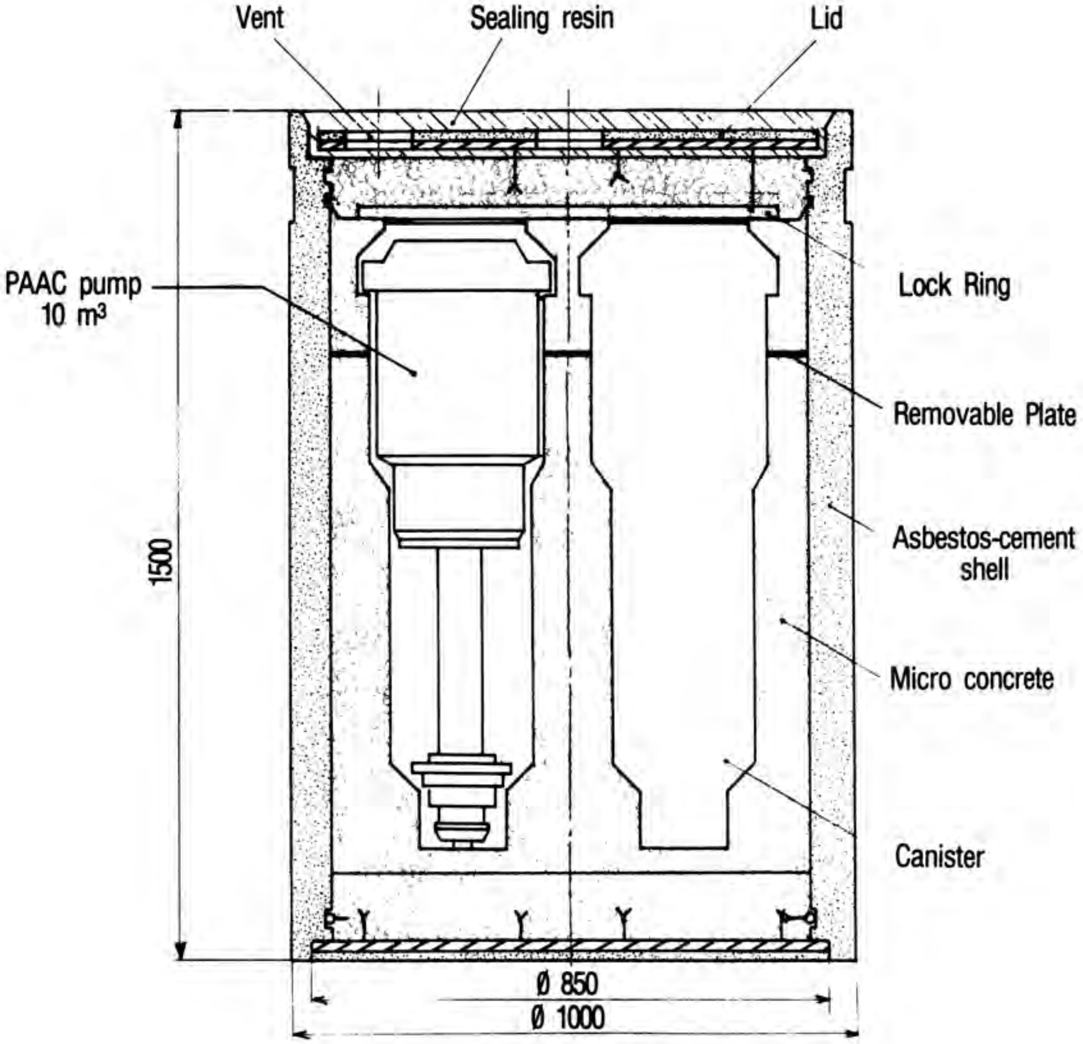


Fig. 2. "α" C.A.C. (Each figure expressed in mm)

## Asbestos Cement Material Characterization

The industrial standard product composition is the following :

CPA 55 cement (OPC) : 85 - 87 %.
Asbestos : 13 - 15 %.

Different kinds of cements are available in France.

Some of them contain secondary constituents like flying ashes or high furnace slag. A comparative work has been made on asbestos cement compositions, using different cements, especially in view to know the retention properties of these materials, towards alkaline elements, such as Cesium, release.

Tables I and II give the composition of the considered cements and their constituents analysis.

The characterization work contains :

- Mechanical tests.
- Thermal cycles resistance measurements.
- Physical measurements.
- Radionuclides migration tests.

The number of samples, with various geometry used in this work, reaches several hundreds (200 tubes for mechanical tests, 120 discs for migration tests).

TABLE I

Different cements composition

| | | |
|---|---|---|
| CPA 55 : OPC | : Reference product | |
| Content | : Clinker Portland 97 % | |
| CPJ 45 : Content | : Clinker Portland 65 % + Secondary constituents 35 % | |
| CLC : Content | : Clinker 25 to 60 % + Flying ashes 20 to 45 % + High furnace slag 20 to 45 % | |
| CHF : Content | : Clinker 25 to 60 % + High furnace slag 40 to 75 % | |

TABLE II

Mean chemical analysis

| Constituents | Clinker Portland % | High furnace slag % | Flying ashes % |
|---|---|---|---|
| $SiO_2$ | 19 to 25 | 25 to 30 | 42 to 50 |
| $Al_2O_3$ | 2 to 8 | 13 to 20 | 16 to 30 |
| $Fe_2O_3$ | 1 to 5 | 2 to 5 | 5 to 10 |
| CaO | 62 to 67 | 45 to 50 | 2 to 4 |
| MgO | 0 to 3 | 1 to 4 | 1 to 2 |
| Alcalis | 0,2 to 0,3 | 1 | 5 |

## Physical and Mechanical Tests

The following tests have been made[2]:

- Mechanical tests :
  . Crushing strength (Radial compression).
  . Bursting strength, by internal hydraulic pressure.
  . Axial compression strength.
- Thermal cycles :
  . Crushing strength measurement after :
    - Freezing and defrosting cycles - 25 times.
    - Temperature increase up to 80°C (176°F).
  a) during 48 h.
  b) during 1 month.
- Physical measurements :
  . Water permeability.
  . Dry product density.
  . Water absorption.
  . Dimensional variation, after immersion in water.
  . Pore spectra using the mercury porosimeter.

Experimental conditions

- All the tests are executed, using normalized procedures, like Normes Françaises NF and Fiches Techniques CEA.
- The samples used for mechanical tests and for thermal cycles are normalized ones (tubes : Ø 150 mm, e = 15 mm, L = variable).

Results

All the measurements are summarized in Tables III, IV, V.

Mechanical tests measurements show a similar behavior for the 4 asbestos cement formulations The permeability test and pore spectra measurement show that CHF and CLC compositions have particular properties : low permeability and small pores.

TABLE III

Asbestos cement material
Mechanical tests
- ( ) statistic error on 5 measurements -

| Test | Cement | CPA | CPJ | CHF | CLC |
|---|---|---|---|---|---|
| Crushing strength MPa | Without treatment | 45,90 (1,87) | 47,69 (1,55) | 36,53 (1,77) | 37,35 (1,52) |
| | 48 h immersed | 44,46 (2,63) | 48,77 (2,22) | 47,58 (3,27) | 42,97 (2,23) |
| Bursting strength MPa | Dry | 22,23 (1,72) | 26,15 (1,76) | 23,70 (1,07) | 20,31 (4,12) |
| | 48 h immersed | 20,27 (1,60) | 23,27 (2,33) | 22,12 (2,70) | 19,88 (1,97) |
| Axial compression MPa | Dry | 89,51 (6,21) | 87,02 (7,87) | 81,09 (7,25) | 79,22 (7,84) |
| | 48 h immersed | 69,22 (4,83) | 56,82 (8,93) | 69,03 (8,23) | 61,14 (6,92) |

TABLE IV
Asbestos cement material
Thermal cycles measurements

| Test | | CPA | CPJ | CHF | CLC |
|---|---|---|---|---|---|
| Crushing strength MPa | Freezing Defrosting cycles (25) | 43,04 (1,96) | 48,59 (2,29) | 43,26 (1,87) | 39,25 (2,37) |
| | 80°C during 48 h | 38,95 (1,64) | 43,27 (1,37) | 39,93 (0,67) | 37,33 (2,96) |
| | 80°C 1 month | 36,78 (3,24) | 43,61 (1,39) | 40,69 (2,19) | 36,51 (2,49) |

TABLE V
Asbestos cement material
Physical measurements

| Test | | CPA | CPJ | CHF | CLC |
|---|---|---|---|---|---|
| Density | | 1,69 (0,02) | 1,71 (0,02) | 1,55 (0,03) | 1,55 (0,03) |
| Water absorption | | 20,4 (0,6) | 20,8 (0,3) | 27,0 (1,1) | 24,1 (1,6) |
| Dimension variation ↗ | | + 0,04 (0,12) | + 0,12 (0,08) | + 0,12 (0,04) | 0 (0,09) |
| . length . diameter | | + 0,07 (0,14) | + 0,07 (0,07) | 0,07 (0,21) | 0 (0,14) |
| Permeability $m.s^{-1}$ | | $1,07x10^{-11}$ | $5,45x10^{-12}$ | not measurable at 60 bar | $6,4x10^{-11}$ |
| Pore spectra | Mean Radius Å | 260 | 330 | 200 | 220 |
| | Hg vol. $cm^3g^{-1}$ | 0,11 | 0,14 | 0,12 | 0,15 |

Radionuclides Migration Tests

Studies are carried out on the diffusion coefficient measurements concerning four radionuclides and four asbestos cement compositions[4]. The nuclides have been chosen as representatives of the true technological wastes activity, coming from reprocessing plants. These are :

- Tritium, as tritiated water - β emitter.
- Cesium ($^{137}Cs$) and Strontium ($^{85}Sr$) - γ emitters
  . $^{85}Sr$ has been used for the possibility of detection of its 514 keV γ ray with a Ge-Li detector : it simulates the $^{90}Sr$ - β emitter - behavior.
- Plutonium ($^{238}Pu$) - α emitter.

The asbestos cement compositions are those tested in the mechanical tests.

It must be noted that the tritiated water method is used for the water diffusion coefficient measurement.

Experimental conditions

Experiments are carried out in diffusion cells with two compartments separated by the diffusion barrier to be tested. Samples are plane discs with variable thickness. (Fig. 3).

Standard diffusion cells characteristics are :

- Material : vinyl polychloride.
- Compartment volume : 100 ml.

Asbestos cement samples characteristics are :

- Ø : 7 cm.
- e = 0,15 - 0,4 - 0,8 - 1,2 cm.

The two compartments of the diffusion cell are filled with lime water (pH = 13).

The radionuclide is put under the nitrate form -except for tritium, used as tritiated water-, in the first compartment, and the radioactivity is measured in the second compartment.

For $^{137}Cs$, $^{85}Sr$, the activity range is 50 µCi and for $^{238}Pu$, is 2 mCi.

Results and interpretation

Experiments on asbestos cement/CPA 55 composition

- Tritiated water

Results are shown on Fig. 4 and Table VI.

The values of the tritiated water diffusion coefficient $D_e$, are on the same range :

$D_e \simeq 2.10^{-3}$ cm².d⁻¹. It is shown that tritiated water transfert follows the Fick theory[4].

TABLE VI
Tritiated water diffusion

| l (cm) | $D_e$ (cm².d⁻¹) | θ = α | $t_i$ (d) |
|---|---|---|---|
| 0,175 | $1,8 \times 10^{-3}$ | < 8 % | |
| 0,4 | $1,9 \times 10^{-3}$ | ∿ 32 % | ∿ 4 |
| 0,8 | $3,2 \times 10^{-3}$ | ∿ 28 % | ∿ 9 |
| 1,2 | $1,9 \times 10^{-3}$ | ∿ 16 % | ∿ 20 |

- $^{137}Cs$

Table VII and Fig. 5 show the diffusion measurements about Cesium.

TABLE VII
Diffusion coefficients of Cs

| l (cm) | $D_e$(cm².d⁻¹) | $t_i$(d) | α | $D_x$*(cm².d⁻¹) | $t_e$(d) |
|---|---|---|---|---|---|
| 0,15 | $3,0.10^{-3}$ | 5 | 4 | $7,5.10^{-4}$ | 13,5 |
| 0,4 | $1,0.10^{-3}$ | 40 | 1,5 | $6,7.10^{-4}$ | 108 |
| 0,8 | $0,6.10^{-3}$ | 70 | 0,72 | $8,3.10^{-4}$ | 346 |
| 1,2 | $0,11.10^{-3}$ | 100 | 0,05 | $2,2.10^{-3}$ | 295 |

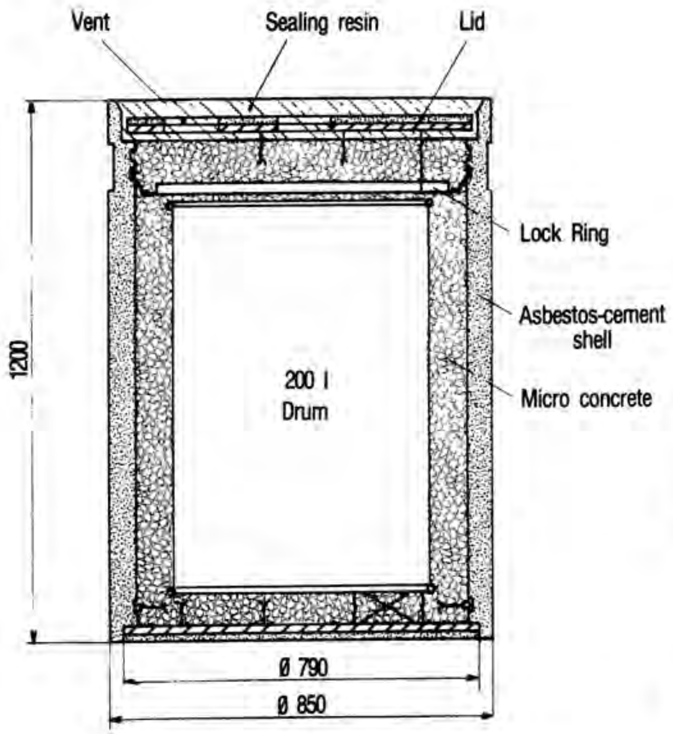


Fig. 3. "Non α" C.A.C.

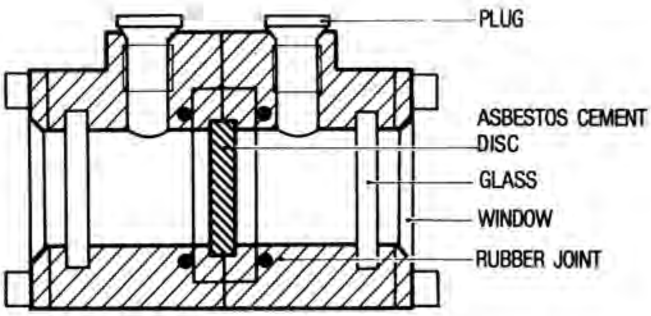


Fig. 4. Diffusion Cell for Asbestos Cement Samples.

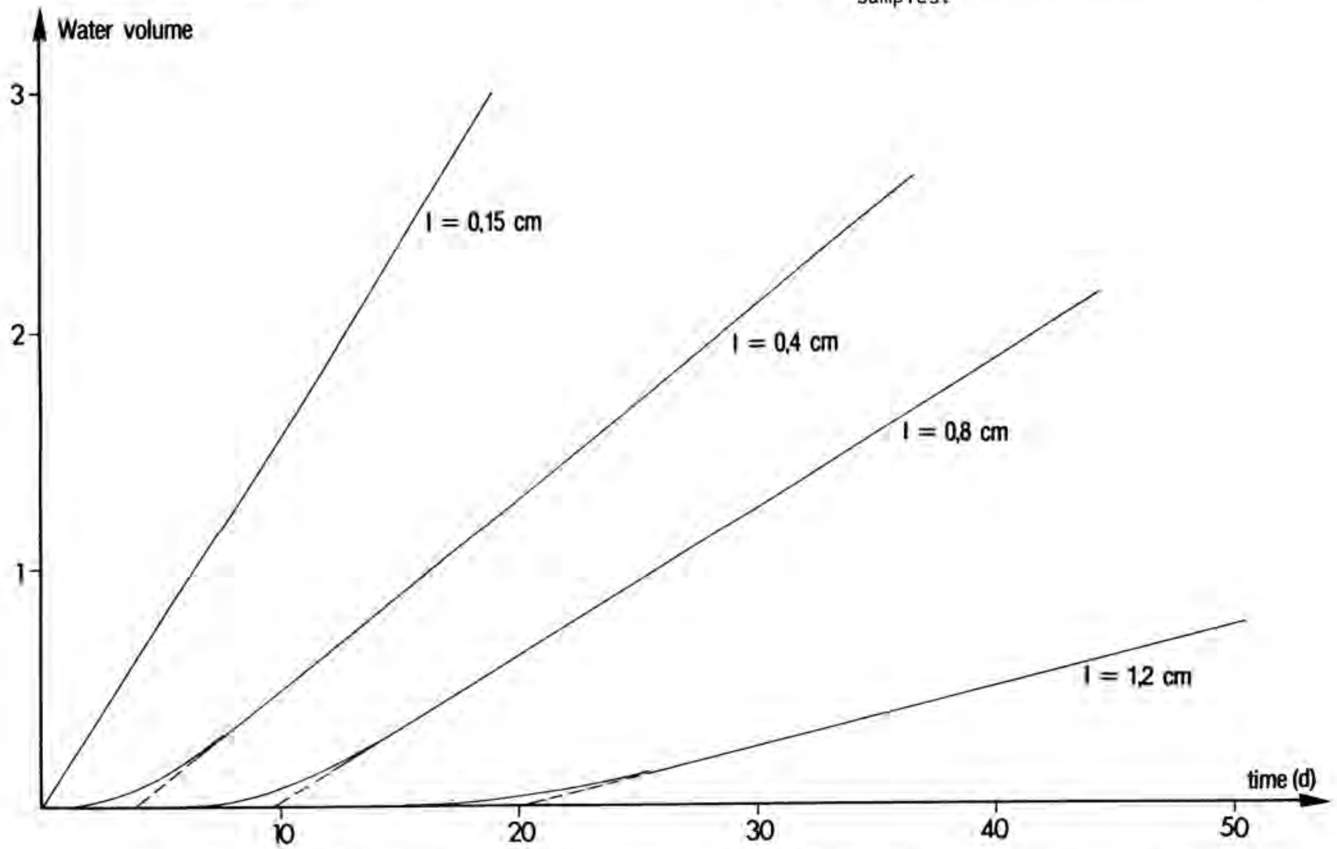


Fig. 5. Asbestos Cement CPA 55-Tritiated Water Diffusion in Samples With Increasing Thickness.

The effective diffusion coefficient $D_e$, measured with samples having increasing thickness are a bit different : the variation of $D_e$ is in the $3.10^{-3}$ cm².d$^{-1}$ to $1.10^{-4}$ cm² d$^{-1}$ range. It is known that the Fick's theory gives $D_e = c^{ste}$ for whatever will be the discs thickness -when the stationnary state is reached-.

- $^{85}$Sr : comparison with $^{137}$Cs

Figure 6 shows the diffusion curves for $^{137}$Cs and $^{85}$Sr, obtained with a 0,15 cm thick disc. Values for $^{137}$Cs and $^{85}$Sr $D_e$ are on the same range :

- $D_e$ (Cs) = $3.10^{-3}$ cm².d$^{-1}$.
- $D_e$ (Sr) = $0,7.10^{-3}$ cm².d$^{-1}$.

Nevertheless, the equilibrium times (which is the point where the tangent of the curve cuts the time axis) are quite different : $T_i$ (Cs) = 5 d and $T_i$ (Sr) = 60 d. This equilibrium time can be calculated for a 1,2 cm thick disc : $T_i$ (Sr) = 10 y.

- $^{238}$Pu

In the experimental conditions -pH = 12 - 13- the plutonium hydrolyses : a gelatinous precipitate is formed in the first compartment of the cell. No activity can be detected in the second one, whatever the barrier thickness chosen. This fact shows that asbestos cement material is quite convenient for the plutonium embedding.

- Comparison between four asbestos cement compositions Cesium diffusion

The results of tests carried out over a long period of time (300 d) are shown on the Fig. 7. The diffusion curves coming from asbestos cement samples using the four cements (CPA - CPJ - CHF - CLC) are different from each other. The phenomena don't follow the classic diffusion theory ; nevertheless the diffusion curves observation reveals that the asbestos cement composition using cements with secondary constituents (particulary flying ashes and high furnace slag) have special retentional properties against Cesium release. (Fig. 8).

CLC > CHF > CPJ > CPA.

## CONCLUSION

Starting with the well-known and industrial material, a high quality container adapted to the conditioning of technological wastes from COGEMA reprocessing plants, has been developped.

French regulations (projet de règle fondamentale de sûreté n° III.2.e for shallow land burial) prescribes a characterization program.

For the asbestos cement container the characterization program in 3 stages has been introduced. The first stage, corresponding to the material characterization has been done : four asbestos cement compositions have been studied. Their physico-mechanical characteristics, and their properties towards the diffusion of four radionuclides representatives or real waste activity have been described.

The program will be continued through the characterization of the other container constituents, and by the filled package one.

A methodology with two independant parts appears :

- Conditioning process study.
- Conditioning characterisation work.

The application of this methodology, added to industrial experience, gained for COGEMA, and also the large range of industrial standard pipes, allow to consider a development field.

The main additionnal applications to be foreseen are :

- A reconditioning of special wastes.
- Conditioning of large wastes (dismantling ones).
- Packaging for conditioned wastes with poor mechanical properties (such as bituminized ones).

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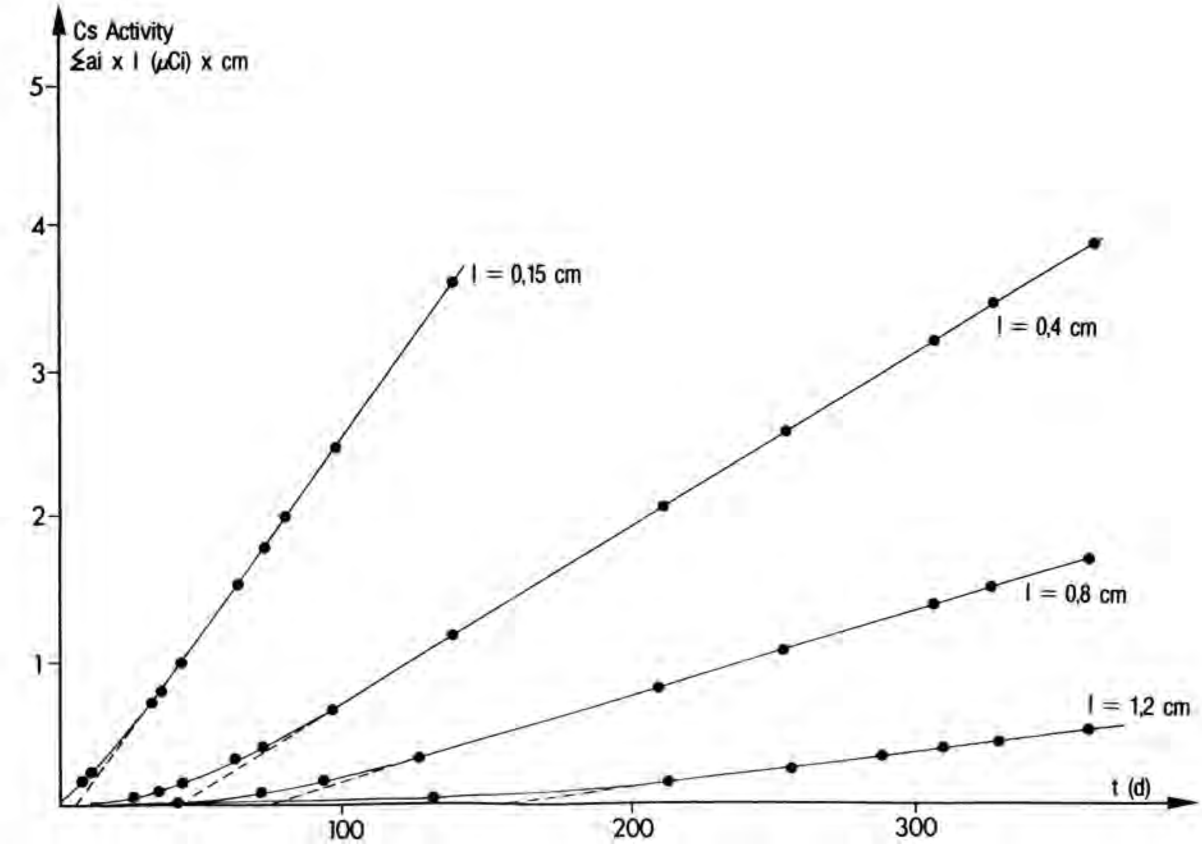


Fig. 6. Asbestos Cement CPA 55-Cesium Diffusion in Samples With Increasing Thickness.

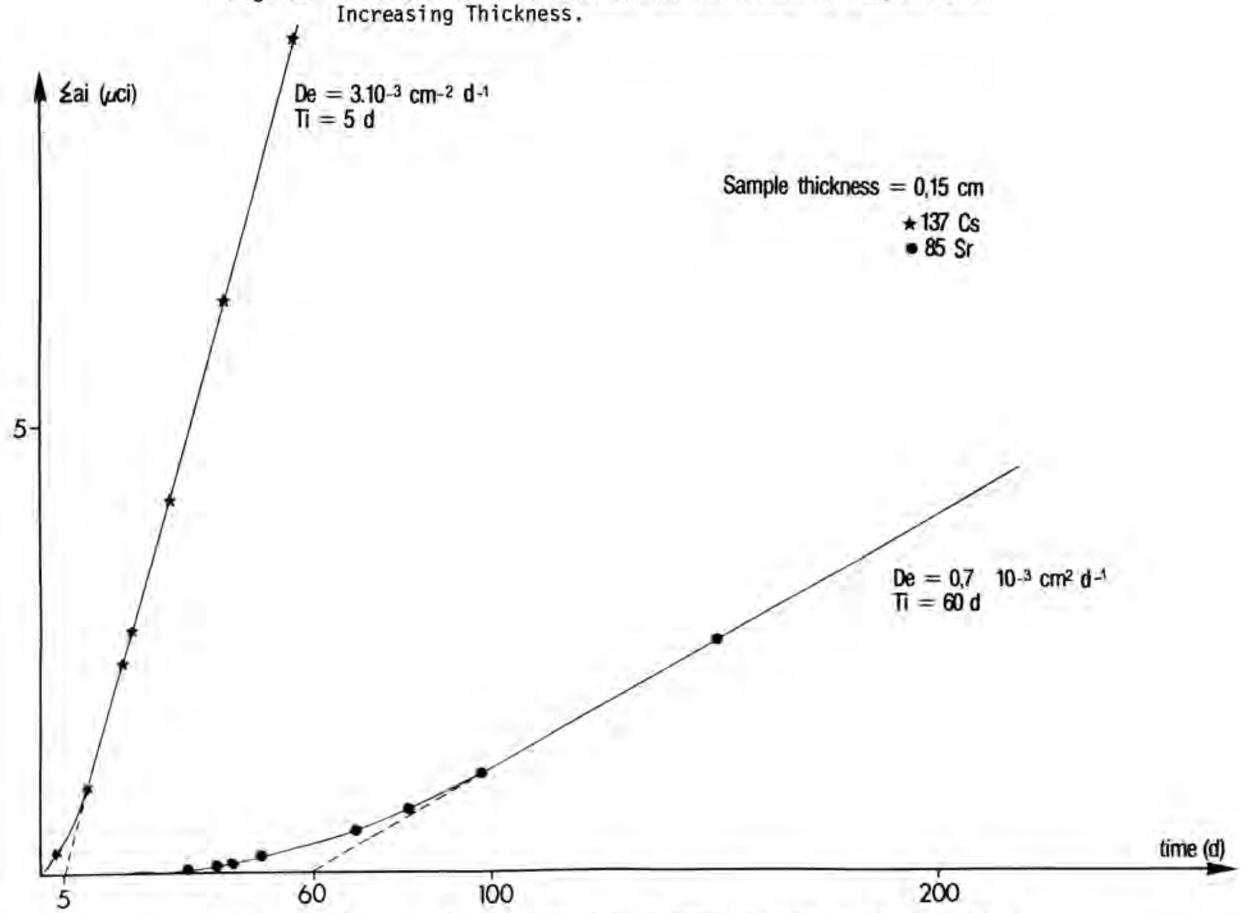


Fig. 7. Asbestos Cement CPA-55-Diffusion of Cesium and Strontium.

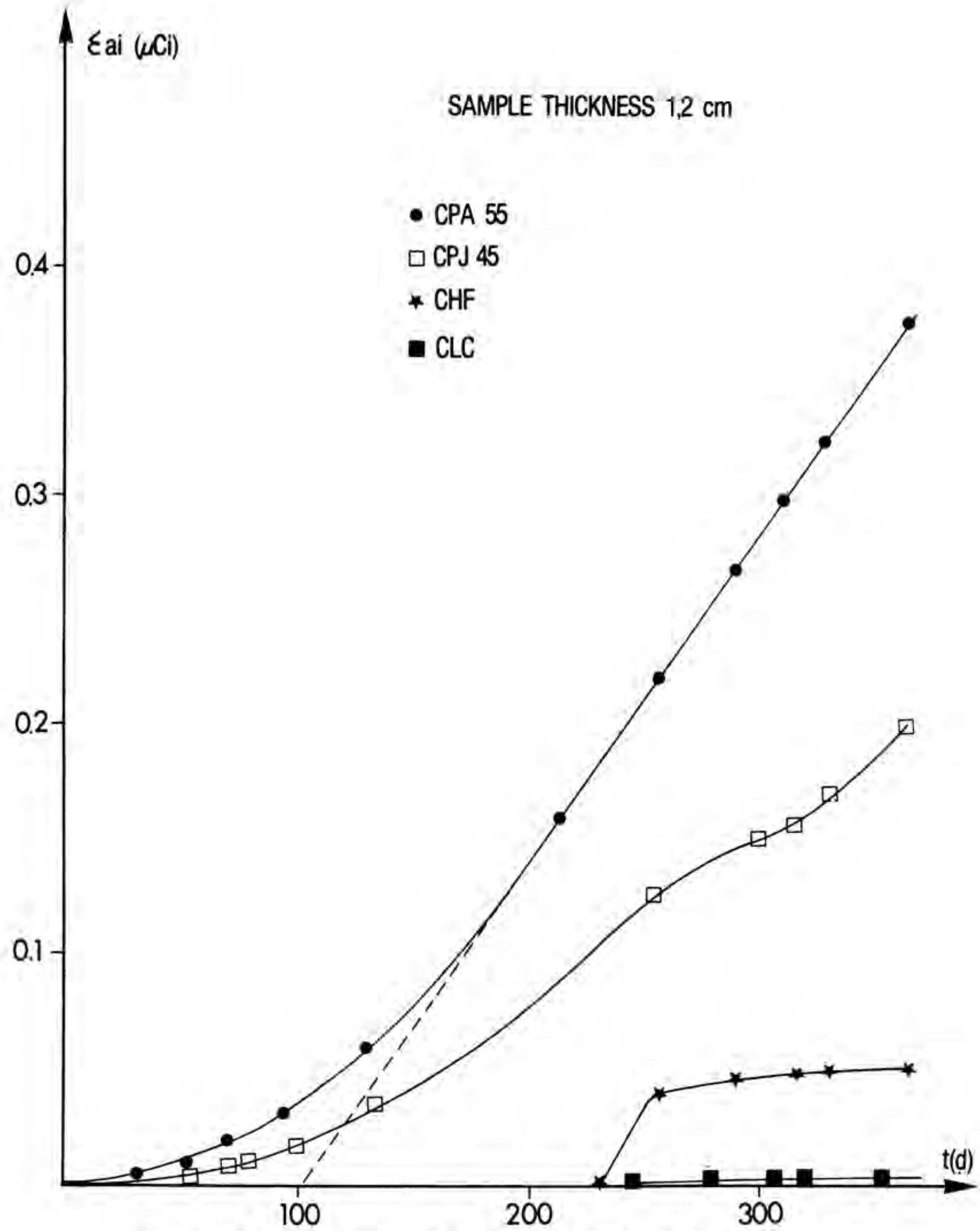

Fig. 8. Asbestos Cement - 4 Compositions Cesium Diffusion.

## APPENDIX

**Fick's theory**

First law : $\frac{dQ}{dt} = - D_e \frac{dc}{dx}$

Second law : $\frac{dc}{dt} = D_x^* \frac{d^2c}{dx^2}$

**Relation between the diffusion coefficients**

* $D_x^*$ : apparent diffusion coefficient.

* $D_x^* = \frac{D_x}{1 + \rho K_D \left(\frac{1 - \theta}{\theta}\right)}$

* $D_x = D_\nu \frac{\sigma}{\tau^2}$

$D_x$ : diffusion coefficient in matérial pores.
$D_\nu$ : diffusion coefficient in water.
$\sigma$ : striction.
$\tau$ : tortuosity.
$\rho$ : material density.
$K_D$ : distribution coefficient.
$\theta$ : porosity.

* $D_e = \theta \cdot D_x$ — $D_e$ : effective diffusion coefficient.

* $\alpha = \theta + \rho K_D (1 - \theta)$ — $\alpha$ : effective porosity.

. $t_i = \frac{l^2 - \alpha}{6 D_e}$ — $t_i$ : induction time. $l$ : sample thickness.

. $t_e = 0{,}45 \cdot \frac{l^2}{D_x^*}$ — $t_e$ : equilibrium time.