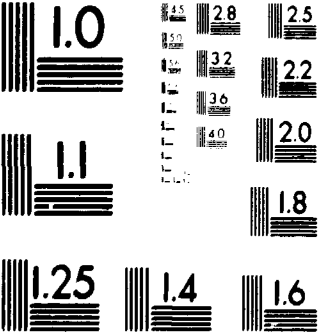


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

ISSN/0393-6309

ENEA- RT/PAS/89/35 .

G. CAROPRESO, G. DE ANGELIS

EVALUATION OF THE PROPERTIES OF CEMENTED LOW LEVEL WASTES THROUGH AN EXTENSIVE CHARACTERIZATION PROGRAMME

25 pages.

IT9100013

COMITATO NAZIONALE PER LA RICERCA E PER LO SVILUPPO DELL'ENERGIA NUCLEARE E DELLE ENERGIE ALTERNATIVE

ISSN/0393-6309

ENEA

COMITATO NAZIONALE PER LA RICERCA E PER LO SVILUPPO
DELL'ENERGIA NUCLEARE E DELLE ENERGIE ALTERNATIVE

EVALUATION OF THE PROPERTIES OF CEMENTED LOW LEVEL WASTES THROUGH AN EXTENSIVE CHARACTERIZATION PROGRAMME

G. CAROPRESO, G. DE ANGELIS
ENEA - Dipartimento Protezione Ambientale e Salute dell'Uomo, Centro Ricerche Energia Casaccia

RT/PAS/89/35

Testo pervenuto nel dicembre 1989
Progetto Enea: Smaltimento rifiuti
radioattivi o pericolosi (ED)

Lavoro presentato alla «1989 Joint International Waste Management Conference».
Kyoto, Giappone, 23-28 Ottobre 1989

RIASSUNTO

I rifiuti radioattivi condizionati devono soddisfare una serie di requisiti relativi all'imballaggio, allo stoccaggio provvisorio, al trasporto e allo smaltimento definitivo.
A questo riguardo i vari organi di controllo richiedono il possesso di diverse proprietà, di maggiore o minore rilevanza.
Oltre alla regolamentazione per il trasporto l'attenzione viene generalmente rivolta alle proprietà chimico-fisiche e meccaniche, alla stabilità termica, all'acqua e alle radiazioni, nonché alle possibilità di smaltimento.
La valutazione di tali requisiti richiede la formulazione di una serie di procedure sperimentali. A tale scopo, un esteso programma per la caratterizzazione di rifiuti a bassa attività solidificati in cemento è stato intrapreso presso l'ENEA Casaccia, nell'ambito del Terzo Programma Quinquennale (1985-1989) della Comunità Europea sulla Gestione dei Rifiuti Radioattivi (Contratto FI1W-0101-I(A)).
Tre tipi di effluenti di interesse generale sono stati presi in considerazione: resine di scambio ionico granulari, concentrati di evaporazione da centrale BWR (Solfati) e fanghi di filtrazione.
Su tali effluenti sono stati condotti esperimenti sia in scala laboratorio, sia in scala industriale.

SUMMARY

The immobilized radioactive wastes have to fulfill the demands for packaging, interim storage, trasportation and final disposal.
For this purpose the possession of various properties, more or less relevant, are required by authorized agencies.
In addition to transport regulations the attention is generally focused on physico-chemical and mechanical properties, thermal, radiation and water stability, as well as confinement ability.
The assessment of such requirements needs the set up of experimental procedures. With this in mind an extensive programme for the characterization of cemented low level wastes has been undertaken at ENEA Casaccia in the frame of the Third (1985-1989) European Communities Programme on Radioactive Waste Management (Contract No. FI1W-0101-I(A)).
Three types of waste streams of general interest have been taken into account: bead ion-exchange resins, BWR evaporator concentrates (Sulphates) and filter sludges.
Both labo. and full scale experiments have been carried out.

CONTENTS

1. INTRODUCTION

Very strict requirements in order to minimize the environmental impact of solidified waste forms were recently imposed by the Italian Regulatory Body (1).

They can be summarized as follows:

a) compressive strength: not less than 500 N/cm^2;

b) freezing-and-thawing cycles: no cracks after at least 30 cycles (24 hours each) from -40 to +40 C ($RH > 90\%$); compressive strength not less than the above mentioned limit;

c) radiation stability: after exposure at 10^6 Gy of radiation, compressive strength must not be less than 500 N/cm^2;

d) fire resistance: solidified wastes must behave as non-burning or at least self-extinguishing materials, according to ASTM D635-81;

e) leachability: conditioned waste must display high leaching resistance, evaluated by using long-term test methods;

f) free standing liquids: absent, according to ANSI/ANS 55.1;

g) biodegradability: unchanged mechanical strength after bacterial attack;

h) water resistance: no cracks after immersion in tap water for 90 days; maintenance of the compressive strength value.

In addition a series of tests and analyses are commonly included in a full characterization programme in order to get further elements of knowledge and understanding of the behaviour of solidified waste (2).

Moreover, as outlined in Table I, both immobilized waste form and container are to be taken into account. Actually the disposal drum represents a further barrier against the release of radionuclides to the environment (3).

Three different waste streams of general interest have been considered in this paper: bead ion-exchange resins, filter sludges and BWR evaporator concentrates (Sulphates). The relative incorporation in cement was performed according to the recipes reported in Table II.

2. CHARACTERIZATION OF CEMENTED WASTE FORMS

2.1 Evaluation of the process parameters

The general properties of cement/waste mixes are reported in Table III. Some of them are relevant process parameters, whose influence on the properties of the final products is well known. Under this respect a detailed knowledge of the composition and the physical state of the waste streams is required, while a rigorous control of the above mentioned parameters is necessary.

Both the cementation process and the properties of the final product are strongly influenced by the water content. Cements are often

Table I
Characterization of cemented
low level wastes

Physico-chemical properties
- Porosity - Voidage
- Gas permeability
- Density
- Shrinkage or swelling
- Homogeneity of the waste form
- Free liquid
- Water content
- Initial and final set time
- Thermal conductivity
- Heat evolution
- Ultrasonic pulse velocity through the material
- Elastic modulus
- Shear modulus
- Poisson's ratio

Mechanical properties
- Compressive strength
- Tensile strength
- Flexural strength
- Impact resistance
- Surface hardness
- Abrasion resistance

Confinement ability
- Radionuclide diffusion in waste package liner
- Leaching resistance
- Water permeability
- Water solubility of the matrix
- Gas release under temperature and pressure

Stability
- Thermal cycling
- Radiation stability
- Water immersion stability
- Fire resistance
- Biodegradation resistance

General properties
- Chemical composition of wastes
- Waste/matrix interaction
- Filling of packaging
- Waste/matrix ratio
- Radionuclide inventory
- Dose rate
- Surface contamination
- Stackability

Packaging and liner quality
- Container tightness
- Packaging and corrosion resistance
- Packaging quality
- Dimensional tolerances

Table II
Composition of waste/cement mixes
(recipes for 1 kg)

Pozzolanic/bead ion-exchange resins, PZ/IER

Cement	599.30 g
Water	171.77 g
Amberlite IR 120*	114.85 g
Amberlite IRA 400*	114.85 g

* Both types of resin containing about 50 w.% of water

Portland/filter sludges, PC/FS

Cement	517.90 g
Water	307.30 g
Diatomaceous earths	74.80 g

Portland/BWR evaporator conc., PC/S

Cement	654.68 g
Water	264.00 g
Sodium sulphate	70.94 g
Potassium chloride	1.60 g
Decon-solution	8.78 g

Table III

Composition and general properties of waste/cement mixes

	PZ/IER	PC/FS	PC/S
Water/cement	0.477	0.497	0.416
Dry waste/cement	0.149	0.081	0.079
Weight reduction factor, K_m = Waste weight/final product weight	0.401	0.382	0.345
Volume reduction factor, K_v = Waste volume/final product volume	0.60	0.61	0.61
Consistency of the mix	plastic	semi fluid	fluid
Free standing water	absent	absent	absent
Bulk density, kg/m3 x 10E3	1.74	1.86	2.05
Set time:			
- initial	3h 10m	3h 50m	4h 30m
- final	4h 20m	5h 35m	6h 35m

referred as hydraulic because they react with water to form pastes which subsequently set and harden. This is an advantage for the wastes containing a high quantity of water, which plays a double role in the mix: chemically react with cement components to form hydrated products and contribute to the workability of the paste. Sometimes an excess of water is also required for pumping the waste from the storage tank to the mixing station.

Without any exception all the properties of the final products are influenced by the water/cement ratio. So a compromise has often to be reached between process needs and product quality.

The consistency of the mix, which is a measure of its workability (depending on both water/cement and waste/cement ratio), can be measured by dropping ball apparatus (BS 4551), flow table (ASTM C230), or Marsh funnel viscometer (API 13B). The last method is applied to very liquid pastes. Other things being equal, a fluid mix is preferable, while an excessive amount of water has to be avoided, because it can result in excessive bleeding (standing water not chemically bound). Bleeding is a sedimentation phenomenon (settling of solids in cement paste), governed by the laws of liquid flow in a capillary system. ASTM C232-71 is a suitable standard for its evaluation.

Cement mixes always contain an amount of air voids, whose presence cannot be avoided but only controlled. As a matter of fact the presence of air voids can be useful in improving the frost resistance, but an excess of them can adversely affect the leachability. This is the reason why they should be included between 3% and 5%, as measured by the air porosimeter (UNI 6395).

Very important are also the setting and hardening of cement paste. The former includes both initial and final set, the relative times being measured by means of the Vicat needle (BS 4550). Apart from some particular cases both rapid and slow setting are to be avoided for reasons to do with both processing and waste form properties.

The hardening of set cement may require a long period of time, but most of the final strength is reached within 28 days (4). To this end the curing conditions should be carefully controlled. Usually they require a temperature of 20 +/- 2 C and a relative humidity not less than 90%.

During the curing period of cement paste hydration reactions occur which bring to the formation of calcium silicates, calcium aluminates and calcium aluminoferrite. The exothermal nature of such reactions is proved by the heat evolved, as recorded by the thermocouples embedded in the sample. The exotherm peak temperature (Table IV) should be kept as low as possible, in order to avoid crack formation due to the shrinkage which follows the initial expansion.

Normally hardened cement pastes shrink (the movement continuing over a long period of time), due to the smaller volumes, with respect to the reactants, occupied by the products originated during the hydration reactions. Expansion may occur in some pastes (e.g. in the early stages of hydration of blast furnace cement), but it is more evident when certain types of wastes, such as ion-exchange resins or Sulphate solutions, are incorporated. The trend of the expansion as a function of time is illstrated in fig. 1.

Of course the process parameters, whose correlation with the quality of the solidification product is more and more evident, have to be conciliated with the maximum amount of waste which can be incorporated, in order to account for the economic factors involved. Normally the use of cement brings to a volume increase of about 100% or more with respect to the volume of the original waste.

2.2 Mechanical properties

With the aim at a proper assessment of the quality of cement pastes the evaluation of inter-related mechanical properties cannot be disregarded. Such properties are time dependant, being developed during months; however, because a 28 day curing is enough to reach strength values quite close to those obtained after one year, this is taken as reference.

The following equation relates the velocity V of ultrasonic waves (54 kHz) through the material, the elastic modulus E, the density ρ, and Poisson's ratio μ:

$$V^2 = (E/\rho)(1-\mu)/(1+\mu)(1-2\mu) \qquad (1)$$

The Poisson's ratio is a measure of the rigidity of the material: the lower μ, the more rigid the material. Similarly higher ultrasonic pulse velocities indicate higher strengths in specimen.
Pulse velocity and elastic modulus can be related empirically with compressive strength. Relationships of the type

$$E = K \times R^n \qquad (2)$$

have been proposed, where E = Elastic Modulus (GPa), K = Constant, R = Compressive Strength (MPa), and n = Fractional Power ($n < 1$).

Compressive strength (UNI 6132-72), surface hardness, tensile (ASTM C191-77) and flexural (ASTM C348-80) strength give an idea of the behaviour of cement materials under mechanical stress (fig. 2), while drop (5), impact (5), and dispersibility test (6) simulate severe accident conditions.

2.3 Confinement ability

The possibility that water comes in contact with the solidified waste in the disposal site has to be seriously taken into consideration.

From this point of view the interactions between water and final waste forms are to be examined. They mainly concern the possible impact on the product integrity (cracks and swelling may occur by immersion in water) and the release of radionuclides to the environment. The former

Table IV
Exotherm peak temperatures

Cement/waste	400 l drum	
	centre	surface
PZ/IER	84.0	47.8
PC/FS	84.3	51.8
PC/S	123.8	78.9

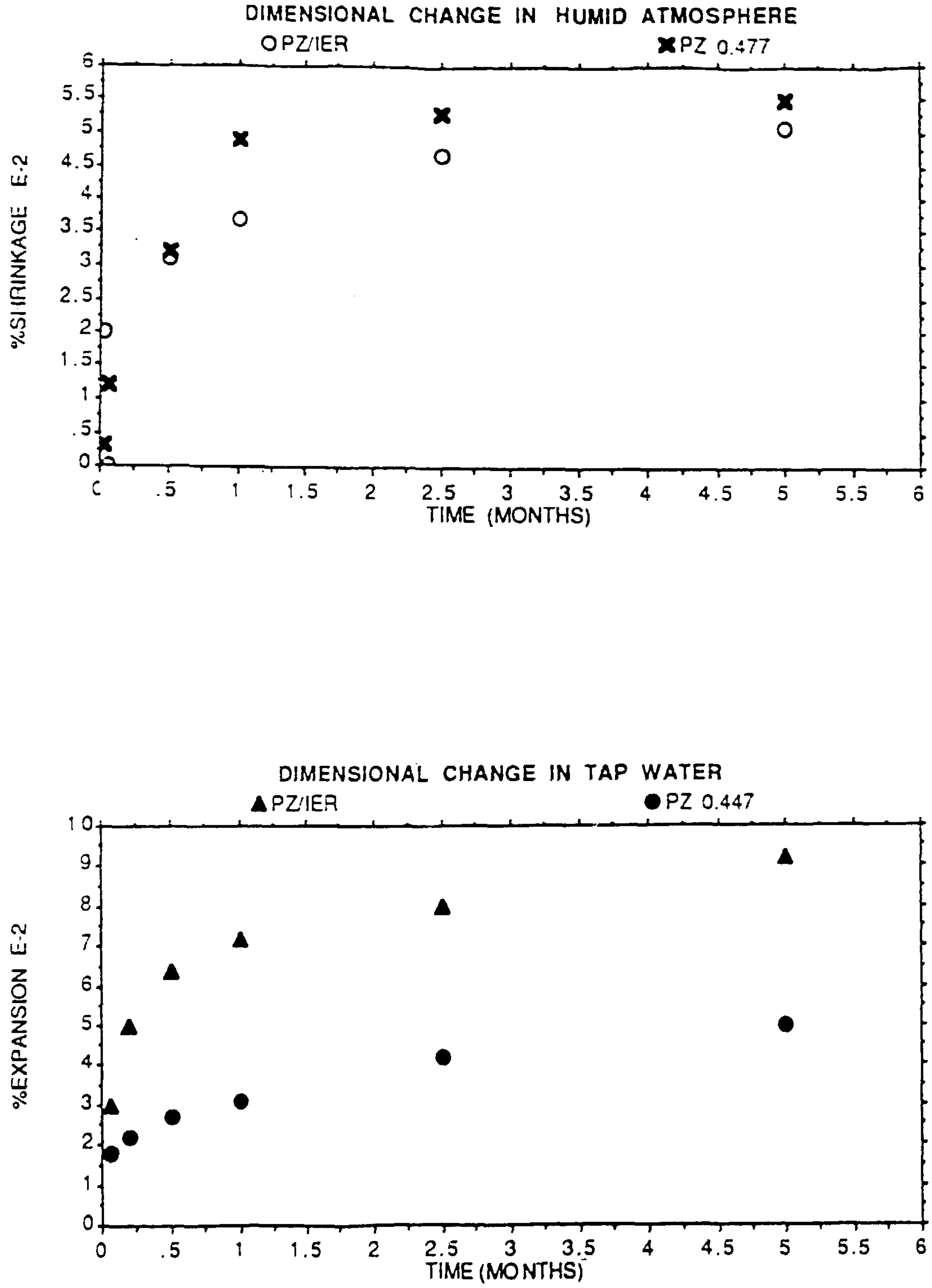


Fig. 1 Dimensional changes of cemented resins in humid atmosphere (RH > 90%) and in tap water

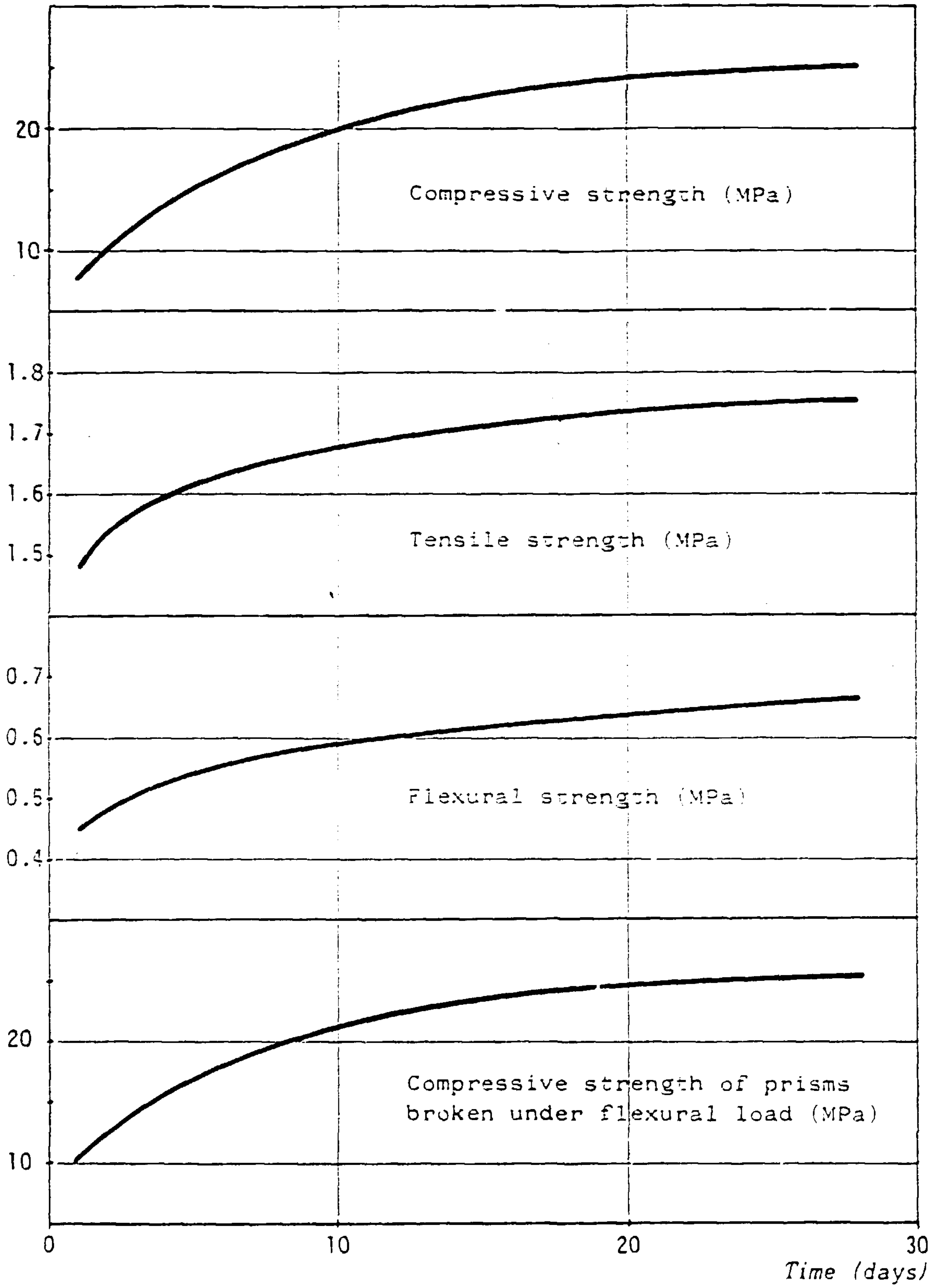


Fig. 2 Mechanical properties of cemented resins

can be easily assessed by visual inspection and control of the mechanical strength; the latter requires an exhaustive analysis of intrinsic properties, which depend on both waste and matrix.

Disruption phenomena due to water immersion are often shown by cemented bead ion-exchange resins and BWR evaporator concentrates as well, due to the high volume increase and subsequent stress caused by water uptake or chemical reactions. Other types of waste are usually less detrimental in this concern.

The leachability is undoubtly the property which better accounts for the retention capacity of solidified waste forms.

Leach tests using deionized water as leachant were conducted at +40 C (7). The results, obtained with chemical tracers ($CsCl$ and $SrCl_2$), are reported in Table V.

As an example the percentage of release as a function of time for Cs and Sr is reported in fig. 3 for cemented bead ion-exchange resins.

A long series of experiments showed that leachability is strongly influenced by parameters like pH, chemical composition of the leachant and temperature, while scarse or no effect is caused by pressure variation.

Accurate studies brought to the conclusion that leaching phenomena are determined by many factors, which can be associated with the waste embedded (like chemical speciation, precipitation, adsorption, buffering capacity, etc.) or with the matrix (porosity, diffusion of ions in the pore system, hydraulic conductivity).

In particular porosity and permeability play an important role. Thus accurate measurements of these parameters are required.

Water permeability can be determined by direct methods, under high or low pressure, based on the application of the Darcy's equation

$$dq/dt = K \times A \times i \tag{3}$$

where:

dq/dt = volumetric flow rate (m^3/s)

K = hydraulic conductivity (m/s)

A = cross sectional area of the porous medium (m^2)

i = hydraulic gradient, which is dimensionless, being the head of water driving the flow (m) divided by the distance over which the flow takes place (m).

The porosity of cement can be measured by different methodologies, according to the range of pore size. The most suitable is the Mercury Intrusion Porosimetry (MIP), based on the Washburn equation:

$$r = 2\sigma \cos \vartheta / P \tag{4}$$

where:

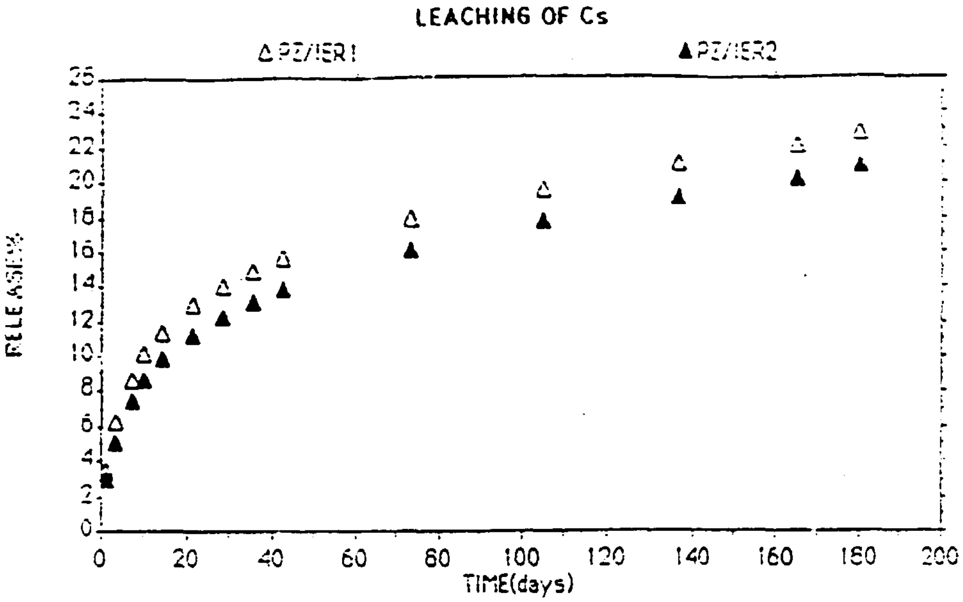
r = pore radius (A)

σ = liquid surface tension (dynes/cm)

ϑ = contact angle of the liquid used

Table V
Leaching of Cs and Sr
(after 105 days)
from cemented samples
(average of two values)

cement/waste	PZ/IER		PC/FS		PC/S	
chemical tracer	Cs	Sr	Cs	Sr	Cs	Sr
leaching rate (Kg/m2.s)	1.0 10^{-7}	2.2 10^{-8}	7.5 10^{-8}	8.0 10^{-9}	3.0 10^{-7}	1.9 10^{-8}
leaching factor (m/s)	2.9 10^{-11}	1.2 10^{-11}	4.0 10^{-11}	4.3 10^{-12}	1.4 10^{-10}	9.3 10^{-12}
cumulative leached fraction % (m)	0.18	0.02	0.16	0.02	0.65	0.05
% release	21.9	2.9	22.4	2.6	74.3	5.1



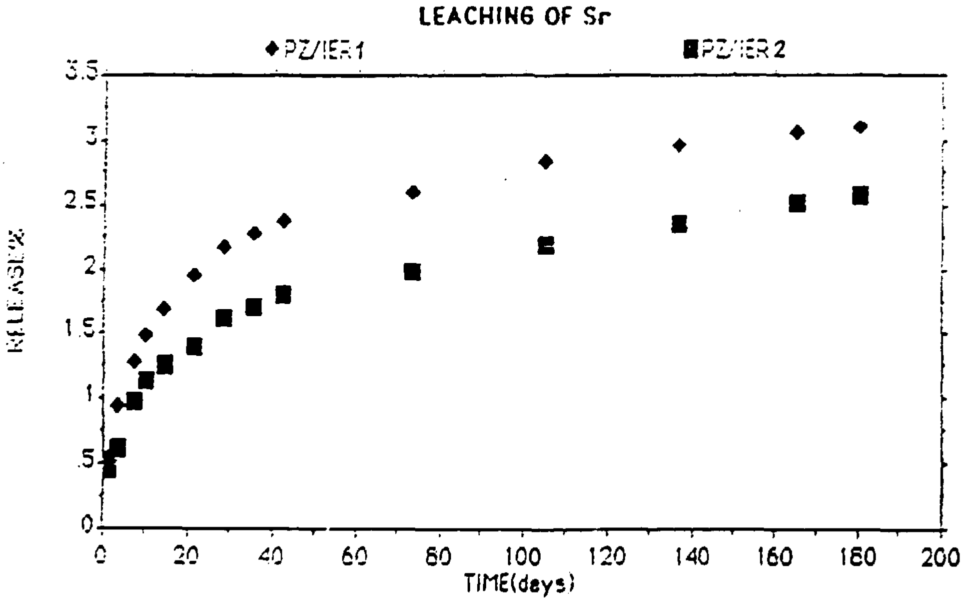


Fig. 3 % release vs. time for Cs and Sr from cemented resins immersed at +40 °C in deionized water

P = external pressure applied (kg/cm^2

Using mercury as penetrating liquid (σ = 480 dynes/cm; θ = 140), the following relationship is practically obtained:

$$r = 75,000/P \qquad (5)$$

The results are usually reported as cumulative pore volume (cm^3/g) as a function of pore diameter.

2.4 Stability

The stability of cemented waste forms was verified by exposing the samples to different experimental conditions.

At the end of each test the compressive strength was checked and compared to that obtained after normal curing (Table VI).

2.4.1 Thermal cycling

Freezing-and-thawing cycles (24 hours each between -40 and +40 C; RH > 90%) combine in the same test two different challenges to the integrity of cemented waste forms: temperature variation and water absorption. If made with a strong thermal gradient they prove quite severe for cement samples, which show evident crumbling after a few cycles. On the contrary, cycles carried out by allowing the temperature to reach the upper and lower limit in a quite long period of time, are endured by the specimens and no visible damages appear.

Although the mechanisms are not well understood, it is quite clear that the pore structure of cement plays an important role in determining the frost resistance (4).

2.4.2 Fire resistance

The test was conducted according to ASTM D635-81 for plastic materials. As expected the only effects concerned the formation of shallow cracks for cemented resins.

It is known however that serious troubles can occur in the case of rehydration of Portland cements which experience a high relative humidity after a fire. Calcium oxide liberated from the lime present in cement rehydrates to calcium hydroxide with deleterious effects, leading sometimes to the disruption of a cement which had withstood a fire accident without actual disintegration.

Thermogravimetric analysis is highly helpful to understand the phenomena which take place by heating a cement sample from ambient temperature to 1000 C. They can be outlined in the following way:

20 - 200 C: loss of sorbed, capillary and cristallization water

200 - 250 C: water removal from hydrated iron oxide
($Fe_2O_3 \cdot xH_2O \rightarrow Fe_2O_3 + xH_2O$)

Table VI
Compressive strength (MPa)
of cemented wastes
(average of three values)

Cement/waste	PZ/IER	PC/FS	PC/S
Normal curing	25.0	42.5	35.5
Freeze-thaw cycles	22.5	45.5	44.0
Water immersion	23.5	52.0	46.5
Bacterial attack:			
- Pseudomonas aeruginosa	20.5	46.0	44.5
- Fungi	23.5	41.0	40.0

350 - 450 C: decomposition of calcium hydroxide
($Ca(OH)_2 \rightarrow CaO + H_2O$)

500 - 800 C: decomposition of calcium carbonate
($CaCO_3 \rightarrow CaO + CO_2$)

2.4.3 Water immersion stability

The stability of the solidified wastes immersed in water was extensively considered in a previous paragraph. It can be said, in addition, that sometimes the water absorption, strictly related to the porosity of the specimen, is measured.

Unfortunately the experiments for determining it, based on drying the sample to a constant weight, followed by water immersion and measure of the weight increase, give quite different results, consistent with the procedures used. The main reason of such discrepancies lies on the difficulties encountered in removing the water: at one extreme, drying at ordinary temperature may be ineffective; on the other hand, heating the samples at high temperature may remove some of the combined water. Anyway most good concretes are reported to have an absorption well below 10%.

2.4.4 Radiation stability

No visible effects were noticed after exposure to a dose rate of 487 Gy/h for 101 days (corresponding to a cumulative dose of 1.18×10^6 Gy). As to the compressive strength, it was uneffected by radiation exposure.

2.4.5 Biodegradation resistance

No bacterial growth of Pseudomonas aeruginosa (8) was noticed after incubation at 37 C and RH > 90% for three weeks. At the same way no growth of fungi (9) occurred after incubation at 30 C (RH > 90%) for the same time length. However, the methods followed are standard for polymeric materials and not for cement products.

2.5 Full scale tests

The tests on the full package included:

- stackability test
- drop test from 1.2 m
- penetration test
- drop test along the horizontal axis.

Each package was a 400 l drum and contained: pozzolanic cemented ion-exchange resins (R2, R3), Portland cemented filter sludges (F2, F3) and Portland cemented BWR evaporator concentrates (C2, C3).

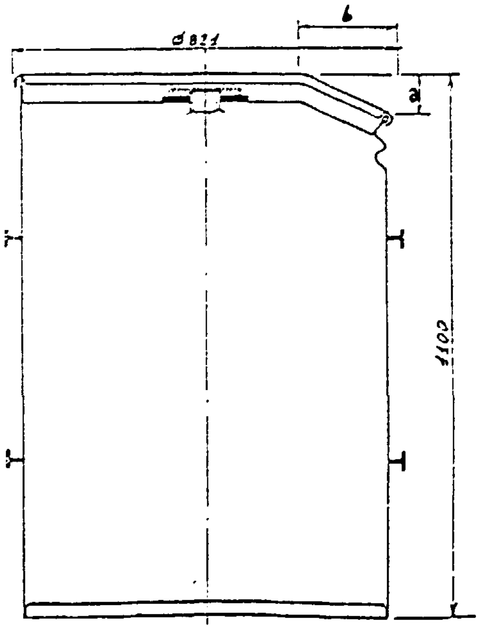
The method followed for the full scale tests was the one proposed by the IAEA (5),

2.5.1 Stackability test

The packages R2, F2 and C2 were subjected to a load of 3550 kg

Table VII
Deformations suffered by 400 l packages dropped from 1.2 m with the vertical axis inclined at about 28°

Drum	a (mm)	b (mm)
Pozz. cemented bead resins	70	340
Portland cemented filter sludges	70	340
Portland cemented evaporator conc.	70	330



(corresponding to 5 times the weight of the package), uniformly distributed on the top cover. No deformation occurred during the test.

2.5.2 Drop test from 1.2 m

The test, made on the same containers used for the stackability test, was conducted in order to concentrate the impact of the waste package in the area corresponding to the edge of the top cover, near the clippable lid. The drop was produced by means of a compressed air system. The inclination along the vertical axis was about 28°.

The damage due to the impact was limited to a restricted area of the drum (Table VII). The deformation suffered by the cover was not enough to separate it from the container, and, what is more, no release of material was noticed.

2.5.3 Penetration test

According to the IAEA requirements the penetration test was made with a bar of 6 kg, diameter of 3.2 cm and with a round edge, dropped from 2.1 m onto the surface of the drum.

Practically no damage was caused by the impact of the bar.

2.5.4 Drop test along the horizontal axis

The packages R3, F3 and C3 (identical to R2, F2 and C2) were dropped along their horizontal axis from 1.2 m.

The results of the test were like the ones due to the drop along the vertical axis, with some damage to the cover and without any release of material.

3. CONCLUSIONS

As discussed above several properties of the solidified waste forms are to be considered, in order to evaluate their behaviour under different experimental conditions.

The confinement of the radionuclides however can be assured only by the adoption of a multibarrier system (waste form/container/final repository), thus minimizing the environmental impact.

Further work is planned in this connection.

REFERENCES

1. ENEA-DISP, "Technical Guide No. 26: Management of Radioactive Wastes", (in Italian), Sicurezza e Protezione, No. 7, Jan-April 1985.

2. De Angelis, G. and Caropreso, G., "Characterization of products arising from the incorporation of low and medium level waste in cement or polymer matrix", RT/PAS/87/13, ENEA, C.R.E. Casaccia, Rome.

3. Hauser, W., Smailos, E., and Koester, R., "Long-term corrosion behaviour of metallic drums for low- and medium-level waste forms", *Proceedings of the Symposium on Conditioning of Radioactive Wastes for Storage and Disposal*, IAEA, CEC and NEA (OECD), 1982, pp. 283-292.

4. Lea, F. M., *The Chemistry of Cement and Concrete*, 3rd Edition, Ed. Arnold, 1970.

5. *Regulation for the safe transport of radioactive materials*, IAEA Safety Series No. 6, 1973 Revised Edition.

6. Lerch, R. E., Greenhalgh, W. O., Partridge, J. A. and Richardson, G. L., "Treatment and immobilization of intermediate-level radioactive wastes", *Management of Low-Level Radioactive Wastes*, Vol. 1, Pergamon Press, 1979, pp. 513-550.

7. "Long-term leach testing of solidified radioactive waste forms", ISO 6961, 1982.

8. "Standard practice for determining resistance of plastics to bacteria", ASTM G22, 1976.

9. "Standard practice for determining resistance of synthetic polymeric materials to fungi", ASTM G21, 1975.

Edito dall'ENEA, Direzione Centrale Relazioni.
Viale Regina Margherita, 125 - Roma
Finito di stampare nel maggio 1990
Fotoripr. e Stampa La Casa della Stampa
Via Empolitana 120/C - Tivoli (Roma)

Questo fascicolo e stato stampato su carta riciclata