THE CONDITIONING OF INCINERATOR ASHES: AN INCREASE IN THE ENCAPSULATION RATIO

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ABSTRACT

In France, in the field of nuclear industry, the procedure concerning conditioning of low and medium level incinerator ashes consists in embedding this waste in a polymer cement composite matrix.

In the course of examining the different basic constituents of the cement present in the reference matrix encapsulation which is made use of blast furnace slag, ordinary Portland cement and flying ashes, a substitution of these ashes by those actually coming from the waste to be processed was studied.

It's demonstrated that the embedding ratio can be further increased from 40 to 45% in a composite matrix, and from 20 to 35% in a cement matrix.

The encapsulation preliminary characteristics of the laboratory samples remained practically unchanged.

INTRODUCTION

An R & D program has been undertaken by the CEA in the frame of the processing of low and medium activity incinerator ashes in order to define an encapsulation process resulting in a package that would be stable with regard to properties compatible with storage center restrictions. Among the various lines of research, there is one in particular that concerns the future Melox plant, which will be fabricating mixed oxide nuclear fuel and which will produce, during its operation, contaminated waste, 30% of which will be treated by incineration. This will lead to several categories of ash classified according to their alpha radionuclide activity: the least active will be embedded in matrices.

At the beginning of the program involving Melox waste, three encapsulation matrices were chosen for subsequent selection:

- a cement matrix
- an epoxide type polymerized matrix
- a composite cement/polymer matrix.

The properties of each of these matrices were compared.

The study program was followed by a more detailed investigation of encapsulation in a mixed cement/polymer matrix, the most satisfactory.

During the optimization phase of this formulation, we reckoned that it was possible to increase the encapsulation rate by acting on the constituents of the cement and in particular by replacing the ashes composing the latter by the waste itself.

THE CHARACTERISTICS OF ASH

As the Melox plant is still under construction, the ashes we used for these tests were obtained from the incineration, in comparable conditions, of waste with a composition similar to that of the waste that will later be incinerated. The determination of their characteristics required the implementation of techniques such as Infrared Spectroscopy, X Ray, Spectroscopy Thermal Differential Analysis, Electron Scan Microscopy. The reference composition of the waste is given in Table I and the physico-chemical characteristics of the ashes in Table II.

TABLE I

Characteristics of Wastes

ORIGIN	PROPORTION (%)
PVC	50%
Neoprene	27%
Latex	15%
Cotton	4%
Kleenex	4%

TABLE II

Ashes Composition (ppm/ashes)

	10^3 ppm/ashes		10^3 ppm/ashes		10^3 ppm/ashes
C	8%	Ba	26	Cu	3.6
Si	240	P	15	Ni	1.2
Ca	130	Mg	14	Mn	0.8
Al	112	Fe	11.5	Cr	0.8
ZN	40	Ti	9		
Specific surface			3.5 ± 0.1 m^2/g		

The infra-red spectrum is characterized by:

- the 1624 cm^{-1} ray corresponding to water vibration
- the 3447 cm^{-1} ray attributed to associated OH bonding
- the largest ray is situated between 950 and 1050 cm^{-1} and corresponds in fact to a bundle of masked characteristics rays. These rays are essentially due to Si-O bonding. The large and ill-resolved aspect is prototypical of a poorly crystallized structure.

Observation with an electron microscope with high magnification revealed an amorphous texture close to vitrification (Figs. 1 and 2); exceptionally rods (Fig. 3) and platelets (Fig. 4) were detected.

The determination of pozzolanic activity was carried out using small test tubes 2 cm in diameter and 4 cm high with lime/ash and cement/ash mixtures in which we followed the evolution of the mechanical resistance and the kinetics of hydrate formation and lime consumption by means of differential thermal analysis. The ashes are first mixed dry with the lime; the mixing water is then added so as to obtain normal

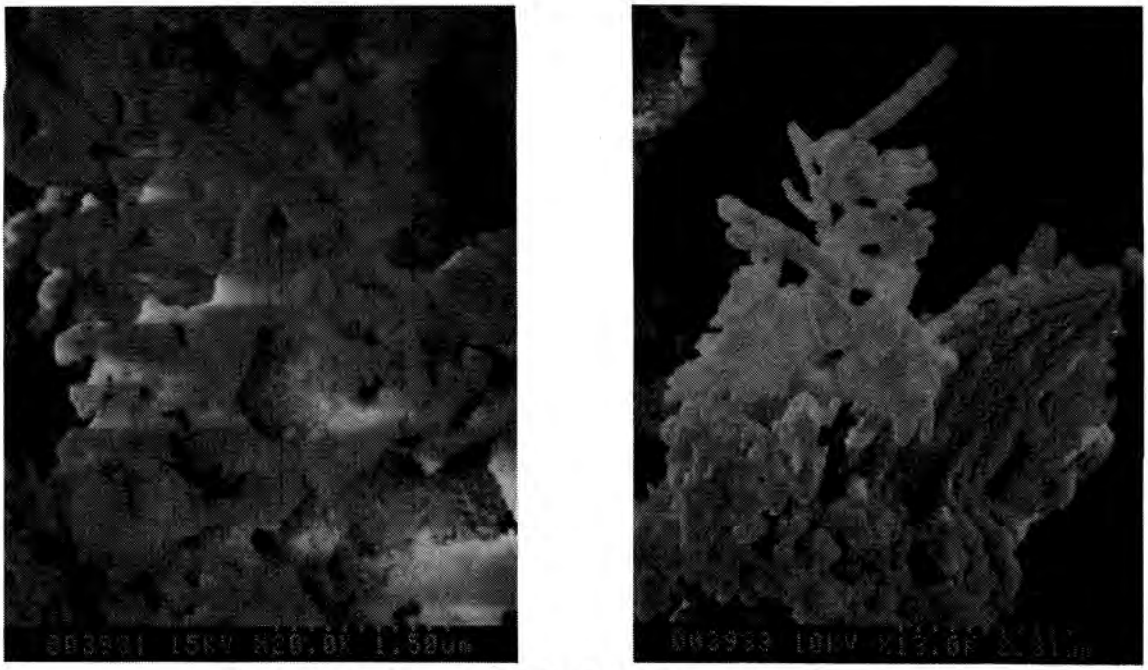

Fig. 1. Observations of ashes by electronic scanning microscopy.

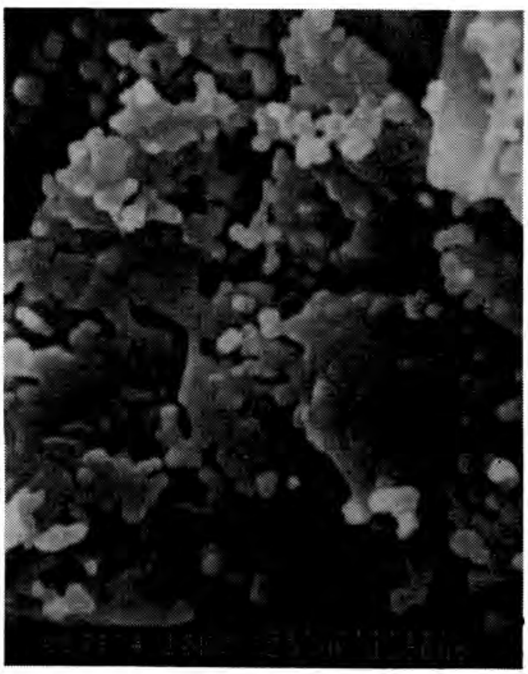

Fig. 2. Observations of ashes by electronic scanning microscopy.

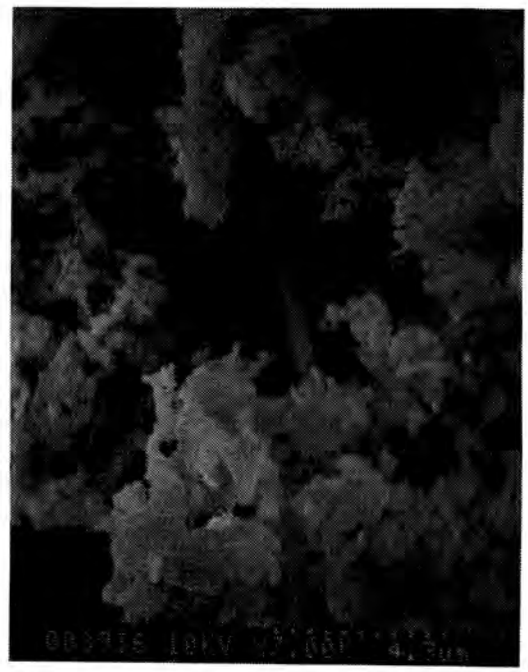

Fig. 3. Observations of ashes by electronic scanning microscopy.

consistency. All the mixing operations were carried out with a RILEM 32 type mixer. The binder is then poured into the molds. In the case of the ashes being studied, no hardening was observed after 28 days, it therefore seems that the ashes have no pozzolanic activity; this was confirmed by the differential thermal analysis where no decrease of the lime peak was noted after first 14, then 28 days.

ASH PROCESSING/TREATMENT OF ASHES

Reference Treatment

A test program allowed three encapsulation matrices to be compared (1):

- a cement matrix (three types of cement were examined: CPJ 45, CLC 45 and aluminous cement);
- an epoxide polymer matrix;
- a mixed matrix composed of CLC cement and epoxide polymer.

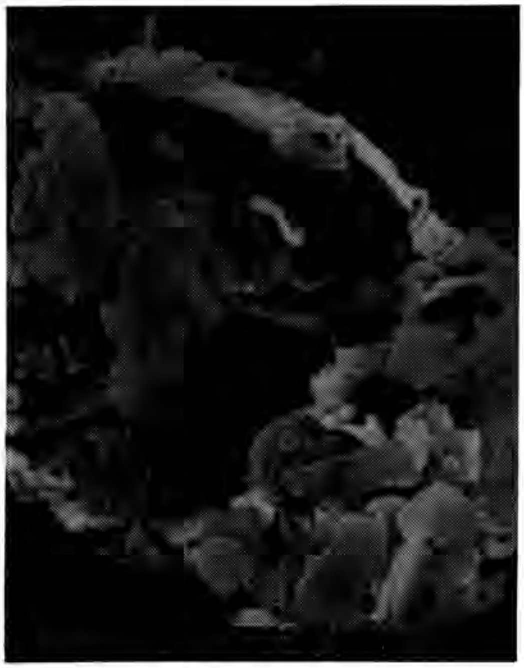

Fig. 4. Observations of ashes by electronic scanning microscopy.

The best encapsulation rates are obtained with polymer and polymer/cement matrices.

The criteria chosen for this comparison were:

- feasibility for which it was shown that encapsulation rates of 20% in weight were obtained for cement and that 40% were obtained for the polymers and the mixed polymer/cement matrix;
- the leaching of alpha radionuclides for which the mixed matrix gave the best results;
- radiolysis resistance for which the lowest rate of radiolysis on Pu 238 spiked samples, after an α integrated dose close to 2.10^7 Gy, was produced by the polymer matrix, whereas the composite matrix gave an intermediate result between the polymer and the cement;
- mechanical resistance, for which the best restilts were obtained with the polymer matrix.

These results allowed the development of an encapsulation process for incinerator ashes in a mixed cement/epoxide polymer matrix with the following proportions for each constituent:

- epoxide polymer 30% of the weight
- CLC cement and water 30%
- ashes 40%

in the following ratios:

water/cement = 0.5 - hardener/resin = 0.5

Improvement of the Encapsulation Ratio

The overall encapsulation cost has not only to take into account the cost of the process, but also the subsequent storage cost of the packages. With this in mind, and on the basis of the processes that had already been studied, we attempted to increase the encapsulation ratio.

The main idea is to replace *one of the basic* constituents of the cement we use for the cement or mixed cement/polymer matrices by the ashes to be encapsulated.

Encapsulation Tests

The constituents of the CLC cement we use are the following:

clinker	51%
slag	24%
ashes	25%

Using these basic constituents, we made cements, ash encapsulations in cement and in a mixed cement/polymer matrix. The methodology used for this study is as follows:

- fabrication of samples by means of laboratory equipment with the aim to evaluate the feasibility of the process with regard to the quantity of ash that is introduced,
- characterization of the samples thus obtained in relation to the following criteria:
  - measurement of the solidification temperature as a function of time by means of a Langavant calorimeter on an approximately 600 g mass of the mixture,
  - measurement of the resistance to the compression of the hardened samples,
  - measurement of the water resistance of the samples: the mass of the samples is measured according to time during their immersion in water.

The characteristics of the fabricated samples are given in Tables III, IV and V.

TABLE III

Composition of Cement Samples (%)

	CLC (%)	SAMPLE (%)	SAMPLE (%)
Ordinary Portland cement	51	51	51
Blast Furnace Slag	24	24	24
Flying Ashes	25	0	0
Waste Ashes	0	25	25
Gypsum	4	4	0

Swelling Tests

These tests were carried out using cylindrical samples fabricated in the laboratory and immersed in demineralized water. We compared the variation of mass of a cement sample with samples obtained by replacing the ash constituent by "waste" ashes. The results thus obtained are given in Fig. 5.

Measurements of Polymerization Heat

Polymerization heat was measured at the moment of casting and as a function of time on a sample of approximately 600 g placed in an adiabatic cell. The temperature was measured by means of a thermocouple set in the center of the sample. The maximal polymerization temperature as well as the time required to reach this peak are given in Table VI.

TABLE IV

Composition of Embedded Samples (%)

	CLC Embedded Sample	Sample 3 Water/cement 0.4	Sample 4 Water/cement 0.6
Ordinary Portland Cement	51%	51%	49.5%
Blast Furnace Slag	24%	24%	21.5%
Flying Ashes	25%	0%	0%
Waste Ashes	0%	25%	30%
Waste Ashes	20%	20%	20%
Embedding rate	20%	34.3%	32.5%
Feasability	Good	Good	Liquid past
Compression strench (MPa)	22	48	13

TABLE V

Composition of a Polymer/Cement Embedded Sample

Cement CLC	Ordinary Portland Cement	10.2
	Blast Furnace Slag	4.8
	Flying Ashes	0
	Waste Ashes	5
	Water	10
Polymer	Epoxide resin	20
	Hardener	10
Waste	Waste Ashes	40

The cement obtained from waste ashes has a maximal polymerization temperature that is comparable to that of the reference CLC cement (Fig. 6); the time required to attain this temperature is twice as long however, due to the absence of any pozzolanic activity in the ashes (Table VI).

The encapsulation of ashes in these two types of cement brings about a drop in the solidification temperature of more than 10 degrees compared to cement alone; the same remark as in the previous case can be made if one compares the times required to reach the exothermal peaks (Fig. 7).

The solidification temperature of ash encapsulated in a composite polymer/cement matrix, in which the ash constituent of the cement has been replaced by "waste" ashes, is close to that of the reference encapsulation (Fig. 8).

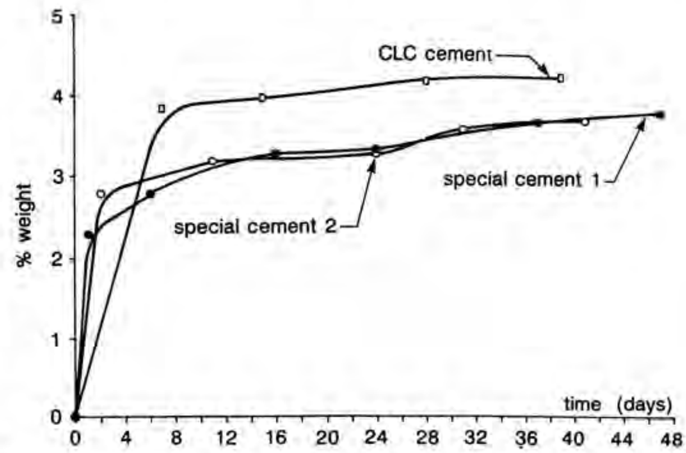

Fig. 5. Weight variation during water immersion.

CONCLUSION

Using the process for encapsulating nuclear waste incinerator ash developed by the CEA Storage and Waste Department at Cadarache which consists in embedding the pulverulent ash in a matrix composed of CLC cement and an epoxide type polymer, we studied how to increase the encapsulation ratio as compared to this process, and in the case of encapsulation in a cement matrix. An increase is obtained by replacing the ashes constituting the cement by the waste to be

TABLE VI

Polymerization Temperature for Matrix and Embedded Samples

	Initial Temperature (°C)	Polymerization Temperature (°C)	Polymerization Time (h)
CLC matrix	25	65	17
Cement with waste ashes (CLM)	32	68	35
Ashes embedded in CLC cement	25	48	55
Ashes embedded in CLM cement	25	48	75
Ashes embedded in polymer/CLC matrix			
Ashes embedded in polymer/CLM cement	30	63	15

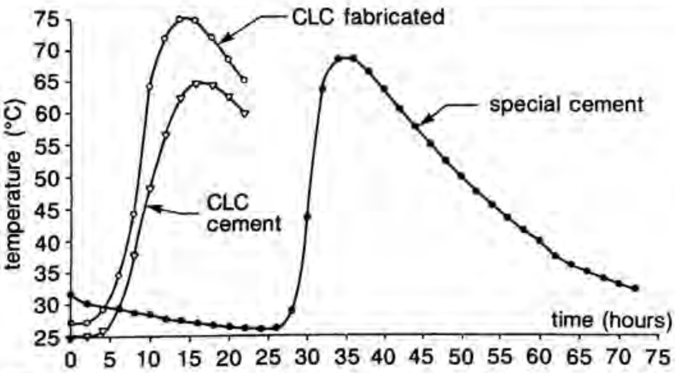

Fig. 6. Polymerization temperature comparison between CLC cement and special cement.

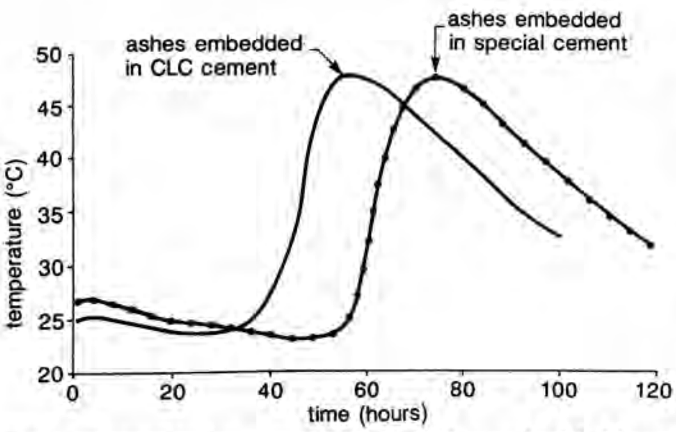

Fig.7. Polymerization temperature of ashes embedded in cement.

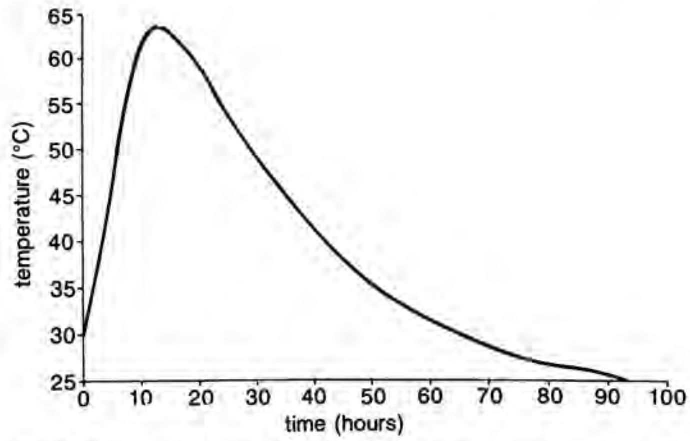

Fig. 8. Polymerization of ashes embedded in polymer/special cement matrix.

treated. We demonstrated that this value can be further increased from 40 to 45% in a mixed matrix and, from 20 to 35% in a cement matrix. The encapsulation characteristics of the laboratory samples remained practically unchanged.

A study program is underway in order to complete the determination of the characteristics of the encapsulations thus obtained: mechanical resistance and confinement efficiency on one hand and on the other the realization of scale packages with an encapsulation pilot plant.

REFERENCES

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