CONDITIONING OF SPENT ION EXCHANGE RESINS BY EMBEDDING IN COMPOUND MATRICES

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ABSTRACT

In ion exchange resin (IER) embedding by the epoxide process, the polymerization temperature peak can be a limit, due to the damages possibly occurring in the solidified IER form.

Two evolutions of the epoxide process, using compound matrices, are presented :

- the epoxide sand process, where the embedding matrix contains, added to an epoxide resin, an inert filler constituted of "Fontainebleau Sand".

The properties of the ternary IER - Epoxide - Sand system were studied : results of laboratory experiments and those on a full scale campaign are given.

- In the second process, an epoxide cement compound matrix is used for the IER solidification.

Two cements, i.e. blast furnace slag cement or flying ash cement, were tested, mixed with an hydrophilic epoxide binder.

Applied to mixed bed or pure cationic or anionic IER, the formulation, gives a high embedding ratio and good qualities to the final product.

These results allow to plan further industrial development.

INTRODUCTION

In France several processes using polymers are used for the solidifying of the spent ion exchange resins coming from the nuclear fuel cycle, especially those utilized in the coolant condensate purification process, or those from the water of irradiated fuel storage pools.

Solidification by the epoxide process has been developed by the CEA, and applied by TECHNICATOME on an industrial scale : this process is based upon the use of a two component epoxide system, with an epoxide liquid resin, the reticulation of which is obtained by addition of an amine hardener having special hydrophilic properties.

One limitation of the process is the height of the polymerization temperature peak : because of the amount of water in the waste form, the polymerization temperature, has to be lower than 100°C.

In order to increase the range of use of epoxide compounds, different works were launched to reduce the polymerization reaction exothermicity.

New embedding agents called compound matrices, were tested : they contain, mixed with a two-component epoxide system, a third component, which can be either an inert filler such as glass beads, or sand with a high silica content, or an hydraulic binder, i.e a cement with specific properties.

The results, presented hereafter, are obtained through two different processes :

- in the first case, I.E.R are embedded with an epoxide - sand matrix, where the epoxide binder is mixed with a special sand, called "Fontainebleau Sand",
- in the second case, the embedding agent is an epoxide cement matrix composed of one part of a two component epoxide system and one part of a cement, added with its hydration water : a special cement is needed such as blast furnace slag cement.

To carry out the study on these two processes, the methodology is the following :

- the first step, done on a laboratory scale, is a feasibility work, in which the optimized formulation is determined, based on the research of the acceptable higher embedding ratio. This work is continued by a characterization step, where the main properties of the solidified waste form are determined according to the following criteria :
  - after polymerization of the sample :
    hardness measurement : the test is carried out by measuring the driving of a special pin placed under a calibrated mass - Hardness Shore D Test, according to DIN 13505 norm
    water swelling : a control of the sample dimensions is performed at 7,14, 21 days of water immersion,
  - on freshly mixed embedded samples :
    polymerization exotherm measurement : the sample is placed in adiabatic conditions in order to measure the evolution of the temperature versus time,

- the second step is a full scale transposition of the formulation. This work is carried out using 100 l or 200 l metallic drums, and a pilot plant called SETH 200, specially designed by TECHNICATOME for the I.E.R solidification. The exothermicity of the polymerization reaction can be measured by equipping the drums with thermocouples before pouring.

EPOXIDE SAND PROCESS

Laboratory Experiments

In this solidification process, the embedding agent contains a two-component epoxide system and "Fontainebleau Sand"-SiO_2, content 98 %, grain size 0 to 300 micrometers, used as a heat releasing agent.

Ion exchangers are ROHM and HAAs products (cationic IR 120, anionic IRA 400 used in pure or mixed bed : in this case IR. 120/IRA 400 = 2/3 - 1/3). After 1 day of immersion, IER dewatered by pumping are first mixed in the filler, then added with the epoxide binder. After mixing, the product is poured into cylindrical molds.

Different series of samples have been made in order to allow the different tests to be performed.

- Appearance and Density

  After 2 days of hardening, the solidified samples containing different weights of IER, epoxide and sand are homogeneous, completely embedded with no free particles at the surface.

  It must be pointed out, that the final product will have a different density, depending on the mixing speed and the air emulsified within the epoxide sand product.

  According to these mixing conditions, the density may vary between 0.7 and about 1.1.

- Hardness

  As observed with polymer embedded waste forms, the hardness of epoxide sand IER increases with time till stabilization. This evolution is shown for different sample composition in Table I : it can be noticed that, for pure epoxide - IER or epoxide sand IER forms, hardness is in the same range.

- Swelling Tests

  These tests are performed on cylindric samples carefully machine surfaced, for metrology determination. The dimensional change and weight variation of samples immersed during a 21-day period, in Cadarache tap water, is shown on Table II.

Calorimetric Measurements

Using an adiabatic cell, equipped with a thermocouple, placed in the middle of the freshly molded sample, gives the polymerization exotherm, from which the solidification temperature peak and the corresponding time are obtained.

These values are summarized in Table *III for 4 typical* compositions : between samples n° 1 and n° 4, the peak temperature decreases by about 18-20°C.

The ternary diagram presented in Fig. 2 summarizes the different compositions having been fabricated. In this figure, the special hachured area represents the feasibility area, obtained from the results of the different tests : high embedding ratio, hardness measurement, swelling and polymerization peak temperature.

In this area, the formulation chosen to perform the full scale test will be :

IER - Epoxide - Sand : 50/40/10.

Quality of the Product

Microscope examinations have been carried out on epoxide sand IER forms, prepared by cutting and polishing. They show the silica grains located between the IER, with a thick film of epoxide binder around the IER beads.

Full Scale Tests

In order to apply the laboratory formulation at full scale, a 200 l drum fabrication campaign was performed, using the pilot plant SETH 200, designed for the IER solidification by the epoxide process, and equipped with a sand feeding device.

The objectives of this campaign were, first, to check the temperature range of use of two different epoxide systems, by measuring the polymerization exotherm obtained in 200

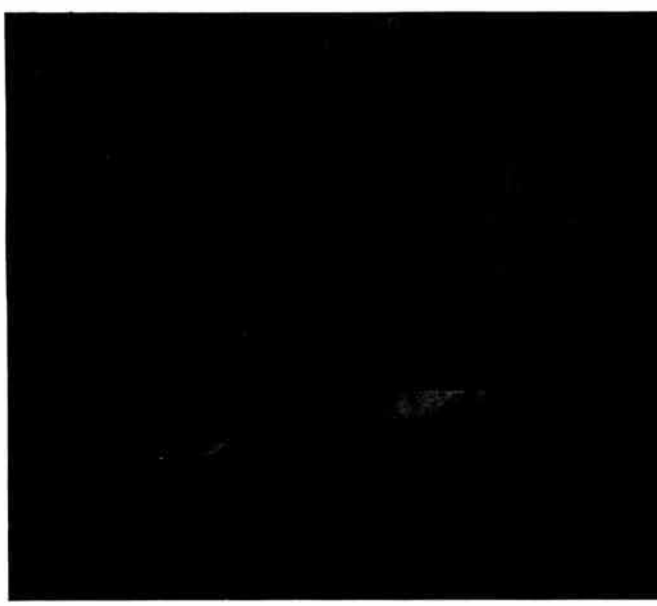

Fig. 1. Feasibility Diagram. View of IER - Epoxide - sand embedded forms.

TABLE I

IER Epoxyde-Sand-System-Hardness and Density for Different Compositions.

N°	Ratio IER : Polymer sand	IER g IRA400 (1)	IER g IR120 (2)	Polymer g Epox.	Polymer g Hardn.	Sand g	Density	Hardness Shore D 2 days	Hardness Shore D 15 days
1	50:50:0	30.05	45.07	46.93	28.07	0	1.046	6.48	63.3
2	50:45:5	30.05	44.98	42.17	25.33	7.54	1.066	6.50	64.6
3	50:40:10	30.07	44.98	37.47	22.57	15.01	1.066	6.00	63.4
4	50:35:15	30.01	45.04	52.85	19.68	22.58	1.082	4.41	61.9
5	45:50:5	27.01	40.53	46.97	28.14	7.57	1.082	8.00	64.9
6	45:45:10	27.00	40.55	42.17	25.38	15.07	1.103	8.30	64.0
7	45:40:15	27.05	40.50	57.48	22.48	22.50	1.136	7.00	64.7
8	45:35:20	27.07	40.57	32.85	19.72	30.01	1.116	4.75	63.5
9	40:50:10	24.03	36.02	46.95	28.13	15.03	1.128	6.75	66.0
10	40:45:15	24.01	36.07	42.25	25.40	22.51		23.5	66.8
11	40:40:20	24.04	36.05	47.57	22.47	37.57		22.5	68.9
12	40:35:25	24.01	36.05	32.82	19.75	37.52		19.5	65.9
13	35:50:15	21.04	31.88	45.91	28.09	22.57		24.0	64.8
14	35:45:20	20.99	31.53	42.16	25.40	40.07		25.0	66.8
15	35:40:25	21.03	31.51	42.49	22.50	38.48		24.5	69.7
16	60:40:0	36.01	53.98	37.57	22.57	0.		15.4	64.2
16'	60:40:0	36.57	53.97	37.57	22.15	0.			
17	55:40:5	33.0	49.49	37.57	22.52	3.50.		17.0	64.6
17'	55:40:5	33.07	49.57	37.52	22.52	7.57.			

1 - Water content of IR-120 48,01 %
2 - Water content of IRA-400 47,86 %

TABLE II

Immersion Test on Epoxide-Sand-IER Samples-Evolution of Dimensions

N°	Ratio % IER : Polymer sand	Before immersing Weight g	Before immersing Height cm	Before immersing Diameter cm	After immersing Weight g	After immersing Height cm	After immersing Diameter cm	Weight change %
1	50:50:0	80.53	4.491	5.718	86.37	4.50	5.224	7.3
2	50:45:5	76.88	4.782	5.216	85.60	4.803	5.226	10.3
3	50:40:10	79.45	4.589	5.397	88.07	4.584	5.399	10.6
4	50:35:15	78.19	3.501	5.354	84.30	3.486	5.354	7.8
5	45:50:5	80.82	4.485	5.384	86.70	4.467	5.398	7.3
6	45:45:10	84.85	3.758	5.374	87.86	3.745	5.374	3.5
7	45:40:15	82.21	4.195	5.374	87.90	4.195	5.373	6.9
8	45:35:20	75.28	4.109	5.363	83.62	4.100	5.368	1.1
9	40:50:10	83.53	4.805	5.402	89.30	4.871	5.400	6.9
10	40:45:15	82.35	4.884	5.395	88.38	4.875	5.401	7.3
11	40:40:20	76.14	4.326	5.374	84.28	4.080	5.477	10.7
12	40:35:25	78.07	4.075	5.374	84.60	4.318	5.374	8.4
13	35:50:15	82.60	5.100	5.393	87.77	5.101	5.391	6.3
14	35:45:20	82.62	4.783	5.276	87.10	4.789	5.276	5.5

TABLE III

Influence of IER and Sand on Polymerization Heat

N°	Ratio IER : polymer : sand	Initial temperature °C	The highest solidification temperature °C	Time of peak appearance in hours
1	50 : 50 : 0	-	73	9 : 55
2	60 : 40 : 0	26.2	60.5	11 : 53
3	55 : 40 : 5	28.9	60.3	14 : 37
4	50 : 40 : 10	27.0	54.2	11 : 31

The appearance of these 4 samples is shown on figure n° 1.

TABLE IV

The Ends of tHis Hachured Area Represent the Limits of an Acceptable Formulation

Location	IER w.%	Epoxide w.%	Sand w. %
D1	60	40	0
D2	45	50	5
D3	45	40	15

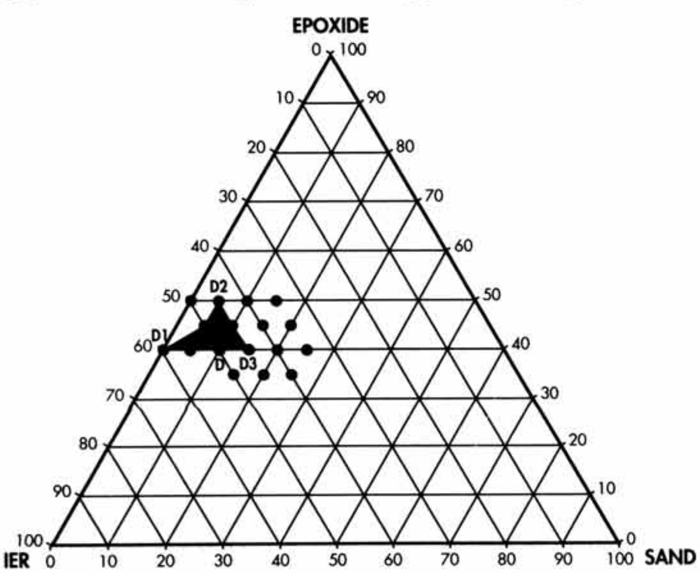

Fig. 2. IER Epoxide sand process.

l drums, and then to compare the properties of pure epoxide - IER and epoxide - sand - IER packagings.

Figure 3 summarizes the main temperature data measured in different 200 l drums of IER embedded forms.

Four packages were made with pure epoxide binder using two Epoxide - Hardener ratios, i.e H/E = 0.5 or 0.6. Two different epoxide systems were used : they will be identified as A epoxide and B epoxide.

The use of pure epoxide matrix, with the embedding formulation IER/epoxide : 50/50 and epoxide-sand matrix, with IER/epoxide/Sand : 50/40/10 shows a significant result : the addition of Fontainebleau sand, to the epoxide binder - allows to obtain a temperature decrease of 8-10°C inside the embedded form.

Figure 4 shows the data obtained from a 28 d swelling test. An increase of the water absorption is obtained by using the compound binder.

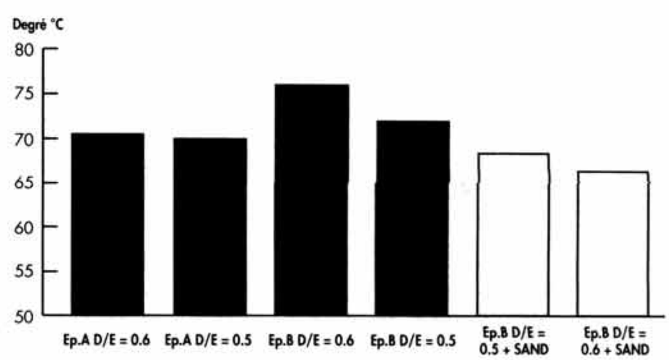

Fig. 3. Temperature elevation in 200 L drums.

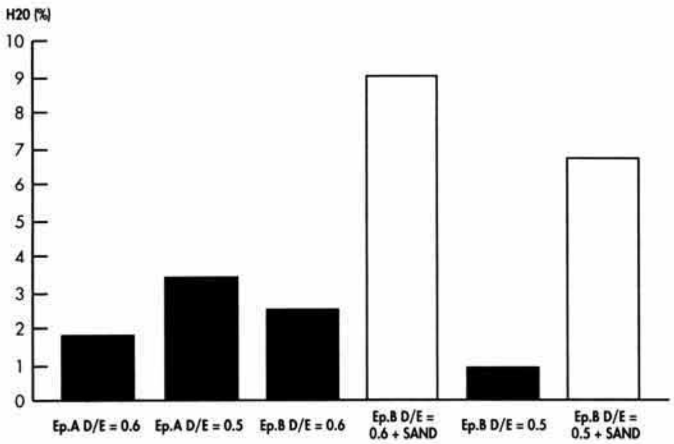

Fig. 4. 28 d immersion test. Variation of weight.

TABLE V

Polymerization Temperature in Different IER Embedded Forms

IER	Initial Temperature °C	Polymerization Temperature °C	Polymerization Time h
Mixed bed	25 °C	63 ÉC	12,5
Anionic IRA 400	25 °C	59 ÉC	15
Cationic IR 120	25 °C	66 ÉC	12

EPOXIDE CEMENT PROCESS

The epoxide cement process has been developed at the Cadarache Nuclear Research Center, for the solidification of LLW or MAW, especially for incinerator ashes [1,2]. In this process, the embedding matrix, is made of a hydraulic binder mixed to a two-component epoxide system. According to the nature of the waste to be solidified, the compound epoxide cement matrix has to be adapted : its components will therefore be different for dry waste such as pulverulent ash or for wet IER conditioning. In order to check the feasibility of the epoxide cement process on IER embedding, a laboratory study has been carried out.

In the case of IER, which are currently solidified after water saturation (1 day immersion) the compound matrix contains an hydrophilic epoxide binder, added with a special cement, having a poor hydration heat.

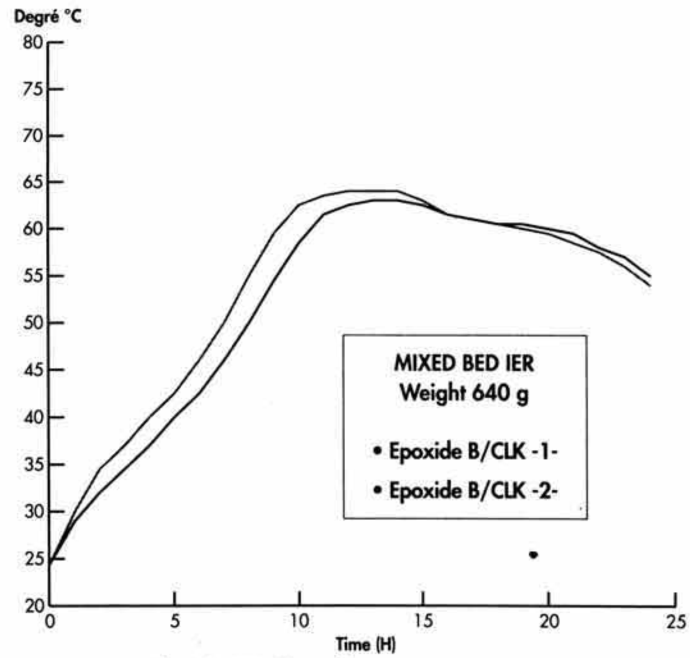

Fig. 5. IER-Epoxide-cement process.

Two cements were tested :

- a ternary cement containing ordinary Portland cement OPC 40 w %, blast furnace slag 30 w % and flying ash 30 w % - French appellation CLC -,
- a binary cement made of OPC w 20 % and blast furnace slag 80 w % - French appellation CLK.

Results - Discussion

The formulation work includes several parameters to be checked :

- properties of epoxide cement products are to be compared.
- in the epoxide-cement matrix, used to solidify wet IER, the addition of the water, needed to cement hydration must be quantitatively defined.
- For the epoxide - hardener system, which is an efficient part of the compound matrix, the hardener/epoxide H/Ep ratio also has to be defined, in order to know the influence of this parameter on the water absorption.

Properties of the Embedded Form :

In spite of the water saturation of the IER, a high hydration water to cement ratio is required. Also, using the B epoxide system previously quoted, the higher H/Ep ratio is chosen.

- The optimized value of the embedding ratio, i.e IER w. % to total weight of solidified form, is 0.4, which is approximately a factor of two superior than the value obtained with a cemented form.

- The value of Hardness (D Shore) is in the 66-76 range, 10 points higher than for pure epoxide form.
- The water absorption after a 28d immersion test is about 1-3 w. % : lower values are obtained, for a high w/c ratio. This can be explained by an osmotic pressure effect of the water inside and outside of the sample during the swelling test.

Polymerization Temperature :

The embedding process and formulation having been applied to the solidification of mixed bed IER and pure cationic or anionic IER. Laboratory experiments, using an adiabatic cell, were performed in order to measure thermal data on each type of embedded form. Table V summarizes the results :

Figure 5 shows the polymerization exotherm of epoxide cement - mixed bed IER samples : it should be noticed that the temperature peak is about 10°C lower than those obtained on pure epoxide IER solidified forms.

CONCLUSION

Two embedding processes using compound matrices are being developed on water saturated IER.The epoxide sand process was tested on a laboratory and industrial scale. Laboratory experiments show that the adding at 10 w. % range of an inert filler, constituted by a special "Fontainebleau sand" allows to moderate the liberation of heat during the time of hardening. The filler must have a very low grain size, in order to be located between the IER beads, without volume increasing and detriment for the IER embedding quality. Full scale experiments show good quality products, with an increased absorption of water. A second embedding process is the epoxide cement process.

The use, as an embedding matrix, of a compound binder constituted with a hydrophilic epoxide system and a blast furnace slag cement, allows an embedding ratio of 40 w. % of mixed bed or pure cationic or anionic IER. The embedded IER form is stable and fire resistant : moreover, using cement as a component of the solidification matrix gives the process an economical interest.

New experiments are being carried out, in order to characterize the epoxide cement IER embedded form, such as leaching tests, γ irradiation behavior. Moreover a full scale fabrication campaign is planned : further industrial development will depend on the results of this program.

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