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Evaluation of the mechanical behavior of the matrix of the radioactive waste containment according to the physical and chemical state of organic and inorganic macromolecular binders

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Abstract

New formulations of the containment matrix of Ion Exchange Resin (IER) were studied depending on the physical and chemical state of the inorganic and organic macromolecular binder. The prepared formulations containing a macromolecular organic binder polyepoxide in its powder state (grain size = 0, 40 µm) and the inorganic solid macromolecular binder (zeolite 4A) is characterized by the improvement of the compressive strength as mechanical properties. The obtained improvement is synonymous with the good dispersion of fine particles of both the inorganic and organic macromolecular binder in the IER containment matrix.

Keywords: *Radioactive waste, IER, polyepoxide binder, zeolite, containment protocol, compressive strength*

1. Introduction

When produced, radioactive wastes have a solid, liquid or metal form. To be easily and safely handled, they are often used in the form of waste packages. The package could guarantee that radioactive elements in the waste do not migrate. The latter constitutes a barrier between the radioactive elements and the storage medium [1]. At the Center of Nuclear Studies of Maâmora (CENM), the containment of radioactive wastes with low and intermediate activity such as the used Ion Exchange Resins (IER), after their use in the purification of water of nuclear reactor is in cementations packages [2,3]. The latter is an ideal material for the imprisonment of IER because of its good mechanical, physical and chemical properties [4]. Cementing gave an initial ratification [5-7], which prompts researchers to the field of radioactive waste management to focus more on optimizing the cementing process [8-11]. In this context, we have studied our old study of [12-14] performance optimization of IER confinement matrix while introducing this time new organic (poly-epoxide resin) and inorganic (zeolite 4A) macromolecular binders to the basic formulation of the containment matrix.

2. Materials and methods

The general objective of this study is to improve the containment of IER by the optimization of the basic formula adopted by the Waste Operations Unit (UED / CENM). To achieve this objective, we performed several formulations namely: cement matrix without any macromolecular binder; cement matrix with liquid organic macromolecular binder; cement matrix with organic macromolecular granulate binder and powder (epoxy resin) ; and cement matrix with inorganic macromolecular binder (zeolite 4A).

2.1. Cement

The cement used in this work is a Portland cement with additions (CPJ-45N). This type of cement which is widely used in civil engineering consists of a mixture of finely ground clinker and gypsum. It consists mainly of tricalcium silicate ($3CaO.SiO_2$), di-calcium silicate ($2CaO.SiO_2$), aluminum, tricalcium inate ($3CaO.Al_2O_3$)) and tetracalcium aluminate ($4CaO.Al_2O_3.Fe_2O_3$).

Table 1: Mineralogical composition of cement

compounds	Composition	Shorthand	Rate
Silicate tricalcique	$3CaO.SiO_2$	C_2S	45 - 65%
Silicate bicalcique	$2CaO.SiO_2$	C_3S	15 - 35%
Aluminate tricalcique	$3CaO.Al_2O_3$	C_3A	4 - 14%
Aluminoferritetétracalcique	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	10 - 18%

2.2. Ion Exchange Resin

The ion exchange resin is an insoluble cross-linked macromolecular matrix of water which, in contact with a solution, can exchange ions therein with other ions of the same sign from the solution. The main characteristics of the resin used in this work are given in the following table: [15]

Table 2 : Physico-chemical properties of the ion exchange resin

skeleton	**Polystyrene crossed with the gel type DVB**
functional grouping R- SO3	R- SO3-
physical aspect	Billesambrefoncé translucent
Ionic form in delivery	H-
Moisture content	51-65 % (H+ form)
swelling up	Na+ -H+ : 5%
Temperature Limit	120°C
PH limit	From 0 à 14
Apparent Density	Approximately 800 g/l
real Density	1, 20 (H+ form)
total éxchange Capacity	Min 1,7 eq/l (H+ form)
The particle size of the resin	
Less than 0,315 mm :	0,2 max
0,4<X<1,0 mm	80% min
more than 1,25 mm	3% max

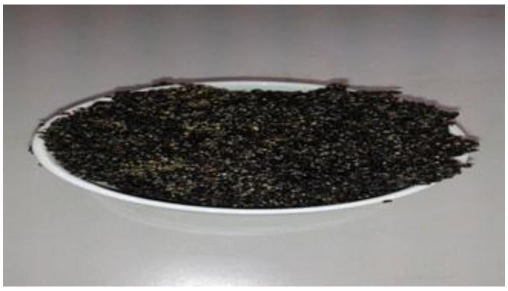


Figure 1: Ion exchange resin

2.3. Macromolecular epoxy resin

These commercial epoxy resins are thermoset polymers that are in liquid or solid form. They contain an epoxy grouping and result from the polycondensation of epichlorohydrin (CH_2CHOCH_2Cl) with a polyhydric alcohol or phenol [16-24], usually bisphenol A ($C_{15}H_{16}O_2$).

Epoxy resins have been extensively used in many industrial fields such as additives, construction, coatings and insulation materials for electrical devices, thanks to their many physical properties (chemical resistance, thermal properties, electrical and mechanical and good adhesion on many substrates).

Figure 2: Granular epoxy resin

2.4. Zeolite

Zeolites are structurally complex inorganic polymers based on a three-dimensional crystalline skeleton tétraèdres of TO_4 type. T represents here a generic atom: it is usually a silicon atom which corresponds to a SiO_4 tetrahedron, or to aluminum, forming an AlO_4 tetrahedron. These tetrahedral are linked to each other by oxygen atoms; each oxygen atom is therefore in fact shared by two tetrahedrons. The chemical composition of different zeolites is close to that of clays: they are more or less hydrated aluminosilicate. The very important difference at the crystallographic level is that clays have a layered or fibrous structure while the zeolites have a three dimensional structure. Most zéolithes have a high affinity for water when they are dry. The 4A zeolite has pores with a diameter of the order of 4 Å (1 Å = 10-10 m), a size that corresponds to a very strong binding energy with the water molecule.

2.5. Compressive strength

The compressive strength is an essential characteristic of the radioactive waste cementation matrix. It constitutes one of the basic parameters of our work. Its quantification was followed for all the studied

formulations. It is determined on cylindrical specimens of 10 cm height and 5.5 cm in diameter (Figure 3) after a time of 7, 14, 21, 28, 90 days of containment.

Figure 3: Glass tube of containment of IER

2.6. Formulations of the cementation matrix of the resin containment

The formulations we have made in this study are based on the conditioning of radioactive waste protocol adopted by UED / CENM as well as the one we described in our former study [12]

2.6.1 Formulations without macromolecular binders

Research in massive optimization of the amount of waste (IER), which may be incorporated in the formulation of the cement matrix without losing its mechanical and physical performance, has led us to primary formulations which are described in Table 3.

Table 3: Formulations without macromolecular binders

formulation	Cement (%)	Radioactive waste (IER) (%)	Water (%)
1	66.66	0	33.33
2	67.92	2	30.19
3	67.92	4	28,19
4	67.92	6	26.19
5	67.92	8	24.19
6	67.92	10	22.19
7	67.92	12	20.19
8	67.92	14	18.19
9	67.92	15	17. 19

2.6.2. Formulations with organic (epoxy resin) and inorganic (zeolite 4A) macromolecular binders

To evaluate the behavior of the epoxy resin and the 4A zeolite in the mechanical performance of the REI containment matrix, we performed in first time several formulations according to the morphology of the macromolecular binder. Tables 4, 5, and 6 show the composition of each formulation. Secondly, we have processed to quantify the mass of the inorganic macromolecular binder (zeolite 4A) (Table 7).

Table 4: Formulations with organic macromolecular binder (liquide époxy resin)

Formulation	Cement %	IER%	Water%	Liquid Polymer %
1	67.92	12	19.19	1
2	67.92	12	19.19	1.5

Table 5: Formulations with organic macromolecular binder (granular epoxy resin d / D = 37 / 250µm)

Formulation	Cement %	IER %	Water %	Granulated Polymer %
1	66.92	12	20.19	1

Table 6: Formulations with organic macromolecular binders (polymer powder 0.4 mm)

formulation	Cement %	IER %	Water %	Polymer powder %
1	66.92	12	20.19	1

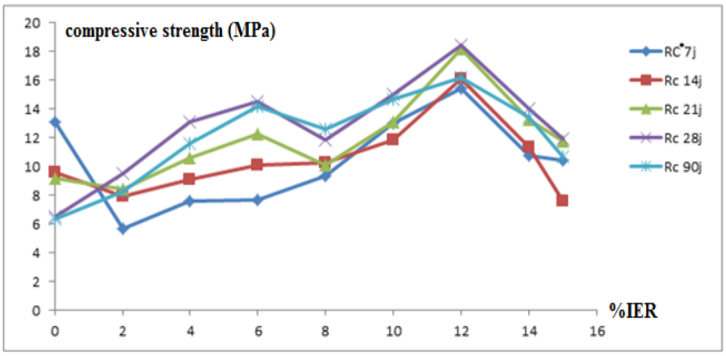
Table 7: Formulations with inorganic macromolecular binders (zeolite 4A)

Formulations	Cement	Water	IER	Zeolite 4A
1	66.92	20.19	12	1
2	66.42	20.19	12	1.5

3. Results and Discussions

The mechanical performance of the different produced formulations was evaluated by means of the compressive strength of cylindrical specimens. The obtained results were described by the following curves:

3.1 Formulation without a macromolecular binder



RC•: Compressive strength

Figure 5: Variation of the compressive strength of the formulations without a macromolecular binder

It is clear from Figure 5 that the mechanical performance of the IER containment matrix, which is determined by the compressive strength, increases depending on the amount of waste (IER), up to 14% and then it decreases. This allows us to conclude that the maximum amount of waste which may be incorporated in a formulation without the package losing its mechanical performance is 12%. In addition to this percentage, we see a drop in resistance.

3.2. Formulation with an organic macromolecular binder

To improve the obtained results of in the first experiments (2.6.1), we introduced some macromolecular binders in the formulation of REI containment matrix according to its physical state:

✓ Organic macromolecular binder polymer epoxy:

- Liquid
- Granular (EPO-NAN YA kind NPES-603)
- Powder (EPO-NAN YA kind NPES-607)

- ✓ Inorganic macromolecular binder: 4A zeolite

3.2.1. Liquid epoxy polymer.

The results of adding the epoxy polymer to the liquid state of 1% and 1.5% in the reference formulation formerly optimized are summarized in Figure 6

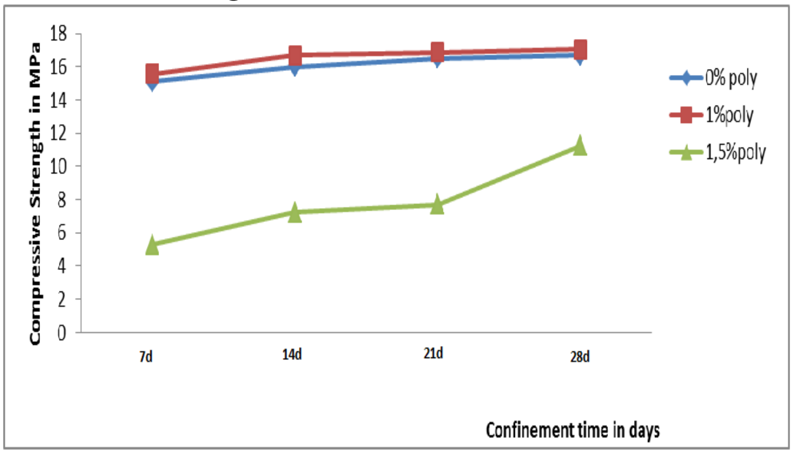


Figure 6: Variation of the compressive strength of the formulations with macromolecular organic binder (liquid)

From this figure, we see that the addition of a liquid organic macromolecular binder had no major effects on the mechanical properties of IER containment matrix since the resistance remains virtually unchanged to 1% of polymer in view of 0%, a significant decrease to 1.5%, which prompted us to use the macromolecular binder in its solid state.

3.2.2 Granular and powder epoxy polymer

The results of the addition of the powder and granular epoxy polymer in the formulation of the core matrix are illustrated in Figure 7:

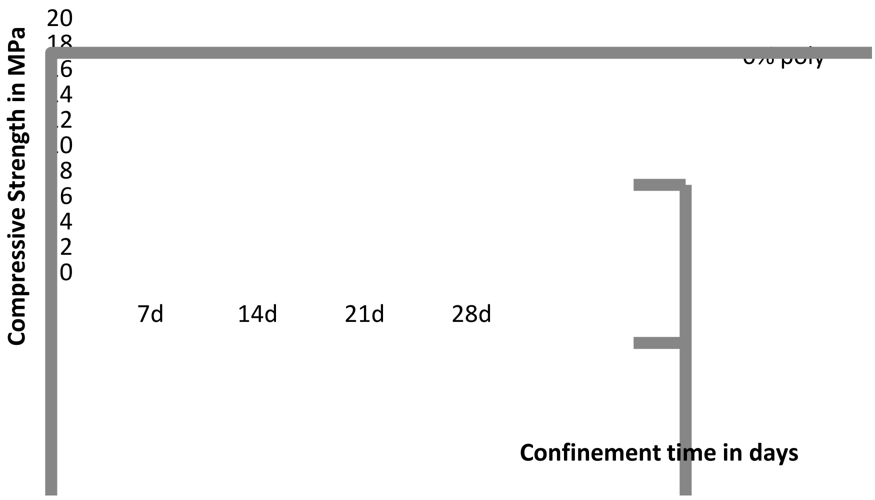


Figure 6: Variation of the compressive strength of the formulations with macromolecular organic binder (granular and powder)

The curves presented above allow us to appreciate the mechanical behavior of our test specimens according to confinement time. Thus, we can confirm that the addition of granular epoxy polymer whose grain sizes between 35 and 250 µm, had no positive effect on the resistance of the specimen, as the latter is low when compared to the reference specimens. By contrast, we found an increase in the compressive strength for the specimens containing the epoxy polymer in the powder form (grain size = 0, 40 µm).

3.2.3 Formulation with inorganic macromolecular binders (zeolite 4A)

The following figure shows the results of adding 1% and 1.5% of zeolite in the formulation of the IER containment matrix.

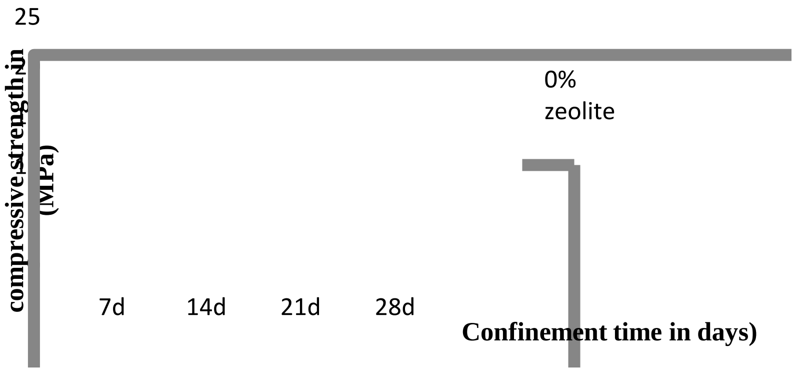


Figure 7: Variation of the compressive strength of the formulations with macromolecular inorganic binder (zeolite 4A)

According to the curves shown in Figure 8, we found that the mechanical behavior of the REI containment cylinder has been improved in a significant manner by the introduction of fine particles of zeolite. These fine particles occupy the interstices between the cement grains and those of REI, which minimizes the porosity of the specimen and subsequently increases its resistance.

4. Conclusion

In this work, we demonstrated the effect of the physical state of organic and inorganic macromolecular binders on the mechanical performance of the containment matrix of ions exchanging resins (IER).

In fact, the addition of a macromolecular organic epoxide polymer binder in its liquid state had virtually no effect on the compressive strength of the matrix. However, we noticed a significant improvement in the resistance in the formulations containing the same organic macromolecular binder in the granular state and then powder state in the formulations containing an inorganic macromolecular binder (zeolite 4A).

This increase in the obtained compressive strength is certainly due to the good dispersion of fine particles of both inorganic and organic macromolecular binders in the skeleton of the REI containment matrix.

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