Optimization study of the cementitious matrix for the confinement of radioactive ion exchange resins: preparation and characterization

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ABSTRACT

In order to optimize the formulation of the conditioning matrix of the Ion Exchange Resins (IER) (MBD-15), considered as radioactive waste generated by the TRIGA MARK II nuclear reactor of the CENM, we carried out several tests by fixing the percentage of cement and by modifying the percentages of the resins to be confined (0 - 14%) and that of water. On the other hand, we performed another test to illustrate the role of an aggregate such as sand, in the cement matrix. The measured response of all the tests carried out is evaluated by the compressive strength of the matrix, after a time of 7, 14 and 28 days of confinement. The results obtained show that the maximum amount of IER that can be incorporated into a formulation without the package losing its strength is 12%. The addition of an aggregate (sand) in the cement matrix increases its compressive strength.

Keywords: *Radioactive waste, Formulation, Containment matrix, Radioactive waste packaging.*

1. INTRODUCTION

Low- and intermediate-level radioactive waste comes from all stages of the nuclear fuel cycle and is conditioned to ensure its safe management. The present study concerns the treatment for long-term storage of low- and intermediate-level long-lived radioactive waste [1].

The conditioning of this type of effluent consists in mixing it with cement to form, by hardening, a solid, stable and durable final product, easier to manage during storage and final disposal [2] [3].

For environmental reasons, much work has been done to produce cemented eco-packages with good mechanical strength that are capable of confining large quantities of radioactive waste. In addition, many formulations for cementing radioactive waste were developed by adding pozzolanic substances such as kaolinite, bentonite, zeolite, blast furnace slag, silica fume and natural red clays, and fly ash [4-11]. These mineral mixtures had different properties and improve the performance of solidified waste in different forms and by different means.

In this context, many works are carried out in collaboration with the CNESTEN, which is responsible for the management of radioactive waste. All of this work has focused on improving the conditioning of IER by cementing [12]. In spite of these efforts, it has proved to be very difficult to incorporate large quantities of IER without altering the compressive strength and porosity of the cement mix [13].

The present study, which constitutes a continuation of this work, proposes the design of new formulations for the cementing of IER with ordinary Portland cement of class 45 in the presence of an addition which is the finely ground red brick waste, designated by RBW.

Mortars made by mixing the brick waste powder have a longer service life and high mechanical strength [14]. The manufacture of RBW is designed by natural clays containing quartz, feldspar and other accessory minerals. The function of clay minerals is to provide plasticity while feldspar acts as a flux to decrease the melting point and quartz is used to fill the space in the bricks. The plastic mixture is then shaped, dried and heated. Heating destroys the crystalline structure of the clay, which produces amorphous pozzolanic substances. The heating temperature is approximately between 450 and 800 °C [15]. The amorphous substances produced are mostly aluminosilicates which react with lime in the presence of water to form calcium silicate hydrate ($3CaO.2SiO_2.7H_2O$) and tetracalcium aluminate hydrate ($4CaO.Al_2O_3.19H_2O$) which give the hydraulic character to the mortars according to equations (1) and (2). [16].

$Al_2O_3.2SiO_2 + 2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O$ (eq1)

$Al_2O_3.2SiO_2 + 7Ca(OH)_2 + 19H_2O \rightarrow 4CaO.Al_2O_3.19H_2O + 3CaO.2SiO_2.7H_2O$ (eq2)

The formation of these products, in the form of interlocking crystals, improves the strength of concrete. which, justifies their use in the construction of many historical buildings since ancient times [17].

In the light of these data on the contribution of RBW on the quality and durability of concrete, by adding it to portland cement, we have carried out formulations by replacing proportions of sand by RBW. The objective is to reinforce the durability of cement matrices for the containment of solidified waste, to isolate radioactive waste from the environment. In this context, new formulations were carried out in order to study the compressive strength and porosity of the cementitious matrices of confinement of IER, allowing moreover, to increase the mechanical strength of the cementitious matrices of confinement of IER. This allows the containment matrix to contain more IER. Consequently, this allows a reduction in the volume of the packages intended for storage.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Cement

The cement used CPJ 45 is a cement whose technical characteristics are in accordance with the Moroccan standard NM 10.1.004. CPJ 45 is a portland cement, resulting from the grinding:

- Clinker (+70%).
- Gypsum to regulate the setting [18].
- The complement to 100% of one or more secondary constituents such as fillers, pozzolan or fly ash.

2.1.2. Sand

The sand used in the preparation of cemented resin forms is a river sand characterized by its siliceous or silico-limestone morphology. It complies with the NM 10.1.020 standard (EN 196-1). The sand used has a dominant grain size of 0.2 mm. According to the results of previous work, this grain size contributes to the improvement of the mechanical performance of cemented resin forms [19].

2.1.3. Bricks

The brick used in this study, was collected from a construction site near the laboratory. Before its characterization and use, the RBW was crushed, in order to reduce its granulometry and to increase its specific surface.

2.1.4. Ion exchange resin (IER)

The IER used in this work as a solid radioactive waste generated by the nuclear reactor of the nuclear studies center of maâmoura – Morocco is a cross-linked polymer in the form at a base of different structures (cationic and anionic) (Fig1). It consists of an assembly of three particle sizes: ofthe grains with a diameter of less than 0.31 mm, 80% of the grains with a diameter of 0.4 mm and 1.00 mm and 3% of the grains with a diameter greater than 1.25 mm.

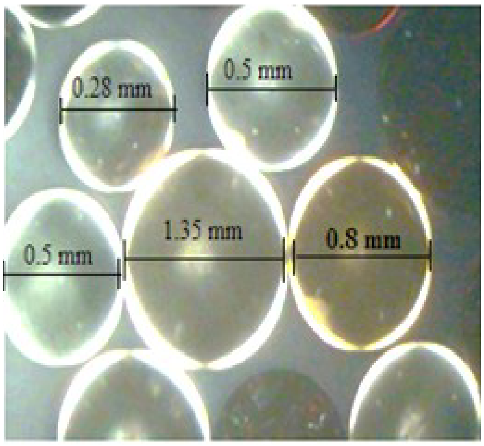

Figure 1. Morphology of the ion exchange resins used

2.1.5. Mixing water

The water used in this study is drinking tap water with a pH of 7.38 and an ionic conductivity of 672 µs. It contains all the requirements of the P18-303 standard.

2.2. Methods

2.2.1. Method of sample preparation

All cemented resins forms were prepared as following:

The prepared materials are weighed according to the formulation and placed in the container of an automatic mortar mixer of the brand 3R in the following order: sand, cement, and bricks. After mixing at a slow speed for the 60s, the resins and water are added, the mixture is mixed in the first step at a slow speed for 60s and thereafter, at a higher speed equal to 240 rpm for 120 s. The obtained paste is cast in cylindrical molds, 8.4 cm high, and 4.2 cm in diameter. These molds are precoated with form release oil to facilitate the demolding of the cemented resins forms after 3 hours of curing. The cemented resins forms are recovered and placed in a space chosen for curing under normal temperature and pressure conditions[11].

2.2.2. Formulations

In order to optimize the quality of the resin containment matrices, previous work has been done. They increased the used resin loading from 8.3% used at CNESTEN to 12% designated by [12]. The present study aims to further improve the physical properties and mechanical performance of the long-lived radioactive spent Ion Exchange Resin (IER) containment matrix by using red brick waste as an addition. Several formulations were carried out, substituting the sand with the brick waste at different percentages ranging from 0% to 10%, with a step of 2% (Table 1). In order to see the impact of substitution rates on the mechanical strength and porosity of the 12% IER containment matrix.

Cement %	Sand %	RBW %	Resin %	Mixing water %
53	17.76	0	12	17.24
53	15. 76	2	12	17.24
53	13. 76	4	12	17.24
53	11. 76	6	12	17.24
53	9. 76	8	12	17.24
53	7. 76	10	12	17.24

Table 1. Composition of the cement formulations with 14.38 % IER.

2.3. Materials characterization

2.3.1. Granulometry

The RBW was ground, in order to reduce its granulometry and increase its specific surface, we proceed to an automatic grinding using the RM 200 Mortar Mill. The sieving is done by sieves of diameter (88µm, 74µm, 62µm, and 37µm).

2.3.2. Chemical characterization

The chemical composition of the red brick waste powder was analyzed by X-ray fluorescence (XRF) using a portable system, Energy Dispersion, model Bruker S1 Turbo SD X-ray Spectrometer. Loss on ignition (L.O.I.), determined by mass loss up to 1000°C.

2.2.3. Calculation of the moisture content of the resin

The moisture content is a very important factor in the formulation process, it is measured periodically to keep the amount of water used in the formulation preparation stable. This allows us to keep a fixed (Water/Cement) ratio of 0,4 [20].

The moisture contentis measured according to the following procedure [21]: An initial mass (m_i) of 1 Kg of spent IER is dried in the oven at a temperature of 105°C for 48 hours. After measuring the final mass (m_f) of the dried resin, the moisture content is calculated by the formula 1 (Gressier, n.d.).

$$\mathbf{H\,(\%)} = \left(\frac{m_i - m_f}{m_i}\right) \times 100 \qquad \text{Eq.1}$$

2.3.4. IER pH measurement

The IER pH measurement is made according to the standard (ISO 10390:2005 - Soil quality - Determination of pH) (Walkley, 2003). The pH value is given using the Grubbs test [22]. The pH measurement of used ion exchange resins is performed according to the following protocol: The resin is dried in the open air in the laboratory for one week. A mass of 50g of the dried resin is diluted in 500g of double-distilled water according to the resin/water ratio 1/10. The mixture is stirred for 50 minutes. In the end, pH is measured using a pH meter of the brand WTW model pH meter Inolab 730. After each measurement, the same operation is repeated10 times.

2.3.5. Mechanical strength tests

Compressive strength tests of the cemented waste forms were performed at different curing times (7, 14, 21, 28 and 90 days) using a Carver (4350.L) S / N (4350-362) press model, capacity up to 24,000 pounds. During this test cemented waste forms was placed between the plates of the press, on which an increasing uniaxial force was exerted manually until it rupture. Each retained value of the compressive mechanical strength is an average value of the three tests values.

2.3.6. Measurement of the IER packages porosity

The porosity of cemented resins forms was measured according to the protocol mentioned in a previous work [23]. Each cemented waste form involves completely emerging in distilled water to it saturation. After 3 days of immersion, Cemented resins forms was removed and wiped with an absorbent paper. To ensure that saturation conditions were reached, the saturated mass of the cemented waste form M_i was weighed twice at 3-hour intervals until that the obtaining mass gain percentage G (%) became less than 1 (Eq 2).After the measurement of the mass M_i and the volume V_i of the saturated cemented waste forms, it was placed in an oven for 3 days at 105°C. The mass and volume measured at the outlet of the oven were designated as M_f and V_f respectively.

Since V_i is equal to V_f, the calculation of the porosity is deduced from the expression (Eq 3).

$$G(\%) = \frac{(M ¿¿ i - M_{i-1}) \times 100}{M_i} < 1\,\% ¿ \qquad \text{Eq.2}$$

$$P = \frac{(M_i - M_f)}{V} \times 100\,\%\, Eq.3$$

3. Results and discussion

3.1. Raw materials characterization

3.1.1. Spent Ion Exchange Resins

The moisture content of the IER used all along this work is about 50,7 %. And its pH value of measured before cementation using the Grubbs test varies between 5 and 6. However, these values are consistent with those of previous work [26].This states that this pH range leads to carried out cemented IER forms with appreciable quality.

3.1.2. Characterization of red brick waste

3.1.2.1. Granulometric analysis of red brick waste

The results of the particle size analysis of the red brick waste are given in Table 2. Analysis of these results shows that the dominant particle size is 88 µm. This meets the requirements for the use of fillers in cement matrices NFP 18-501.

Sieve (µm)	**Refusal (g)**	**Cumulative Refusals %**
88	790	79
74	115	90.5
62	68	97.3
37	18	99.1
Fond	9	100

Table 2. Particle size distribution of red brick waste

3.1.2.2 Physicochemical Analysis of red brick waste

The table shows the chemical element contents of used RBW obtained by XRF. It indicates that silicon oxide (SiO_2) is the main component of RBW. SiO_2 represents about 55.2 %. Aluminum oxide and iron oxide are present in RBW with contents of 15.42% and 6.95%, respectively. The analysis of the data in the table also shows the presence of CaO at a content of 8.90 %.

Oxides	**Al_2O_3**	**SiO_2**	**Fe_2O_3**	**CaO**	**K_2O**	**TiO_2**	**P_2O_5**
	15.42 ± 0.54	62.2 ± 0.54	6.95 ± 0.03	8.90 ± 0.02	2,57 ± 0.02	0.97 ± 0.01	0.71 ± 0.05

Table 3. Chemical composition in % of RBW

3.1.2.3. Mineralogical analysis of red brick waste

The mineralogical composition of the admixture can have some consequences on the properties of the final product. As shown in the figure, the main crystalline phase of the red brick powder is quartz and other compounds in the mineralogy of ceramic materials, such as hematite, feldspar ($K_2Al_2Si_6O_6$) are present in minor amounts. This is in agreement with the high content of SiO_2 and Al_2O_3 obtained by XRF. However, a diffuse band between 20° and 30°2θ was observed (Fig.2). This band probably shows the presence of amorphous substances derived from the high amounts of calcined clay minerals [26].

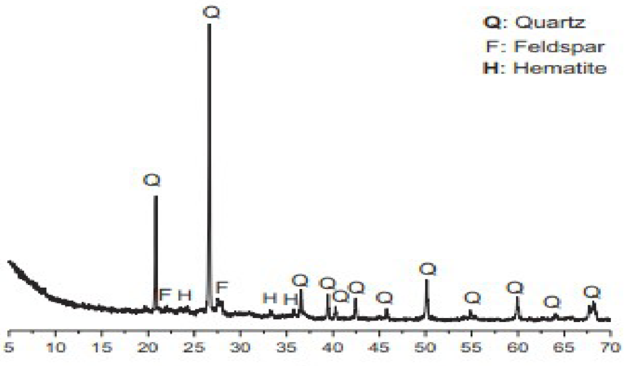

Figure 2. X-ray diffraction (XRD) spectrum of the RBW material used.

3.2. Characterization of the cemented resins forms

3.2.1. Compressive strength of cemented resins forms

The durability of solidified waste forms is paramount to isolate radioactive waste from the environment. The results of compressive strength tests of cemented waste forms containing different contents of red brick waste powder at different curing periods (7, 14, 21, 28, and 90 days) are presented in Figure 3.

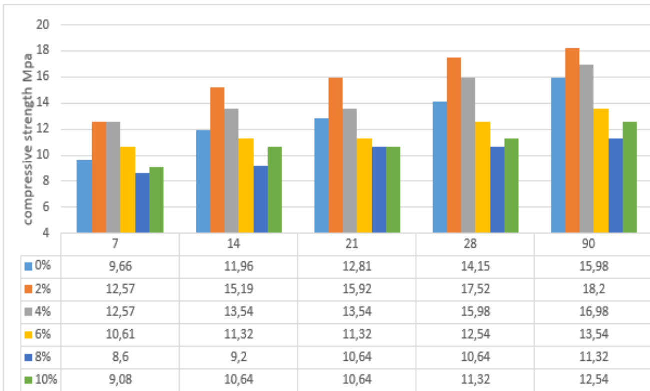

Figure 3. Histogram of the variation of the compressive strength as a function of curing time at different RBW addition rates.

All manufactured cemented resin forms have a 28-day compressive strength greater than 8 MPa. This shows that the cemented waste meets the requirements of the NFP 18-406 standard. This stipulates that containment packages must have a mechanical strength greater than 8 MPa [27] [13].

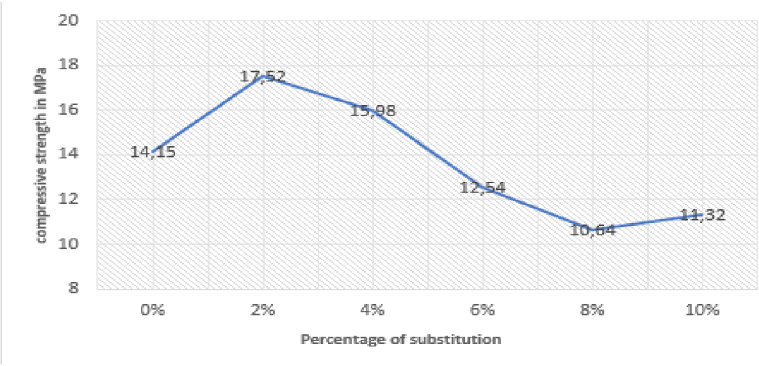

Figure 1: Strength as a function of the percentage of substitution by RBW at 28 days of age

Limiting ourselves to the curing time of 28 days (Fig.4), the variation of strength as a function of the proportions of RBW addition at 28 days confirms that the strenght is maximum and equal to 17.52 for the content of RBW addition equal to 2%.

These results are clearer by studying the variation of the gain in mechanical strength, as shown in Figure 5.It emerges that the mechanical performance of the containment matrix with 2 and 4% substitution of sand by the waste red brick, determined by the compressive strength, increases until 17.52 MPa thereafter it decreases progressively in the percentages 6, 8 and 10%, which allowed us to conclude that the maximum of red brick that can be introduced into the formulation is 2% of substitution, this amount presents the saturation point. If we exceed this percentage the confining matrix begins to lose its mechanical performance. This phenomenon is attributed to a decrease in the speed of the hydration reaction due to the appearance of a protective layer of Ca^{2+} adsorbed on the surface of the grains and the enrichment of the solution in aluminum ions, silicon and calcium hydroxide $Ca(OH)_2$.

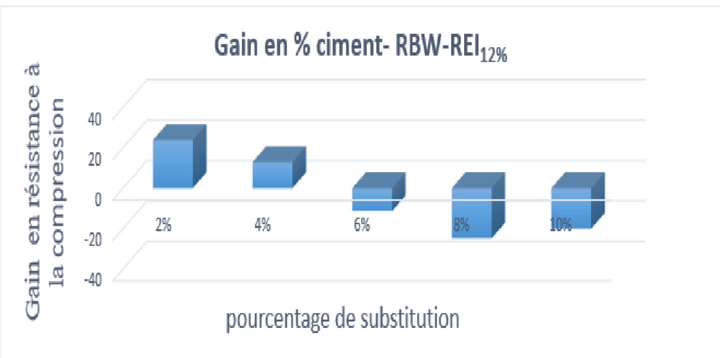

Figure 2: Histogram of the variation of the gain in Mechanical Strength as a function of the proportions of RBW additions at 28days.

On the other hand, the variation of porosity according to the proportions of RBW (Fig.6), shows that the porosity is low for the proportions in RBW equal to 2% and 4%, sign of the cohesion of their mixes.

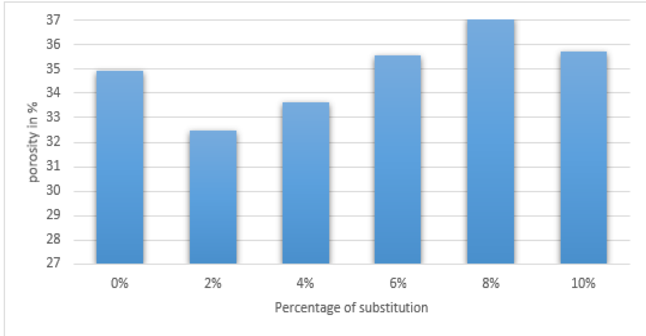

Figure 3: Histogram of the variation of porosity as a function of the proportions of RBW additions at 28days.

These results of the porosity of the cemented resin forms according to different percentages of substitution of RBW with sand correspond perfectly to the results obtained by the mechanical resistance. The porosity reaches its minimum at 2% substitution, then it increases progressively according to the percentage added of RBW powder. Indeed 2% RBW contributes to densify the cement paste by a physical effect which leads to a more compact stacking of the solid grains, and to modify the microstructure by reducing the pores of the cement matrix.

4. CONCLUSION

The work presented in this article is part of a collaboration between the National Center for Nuclear Energy, Science and Technology (CNESTEN) and the Hassan 2 University of Casablanca. It concerns the study of the contribution of red brick waste powder as a mineral addition to the cementing process on resin recovered from the Triga Mark 2 research reactor of CNESTEN after its saturation in radionuclides. The joint project between CNESTEN and our university aimed at designing and producing new formulations by replacing quantities of sand with the addition of waste brick. The study was carried out in three steps: (1) characterizations of the materials used, (2) preparation of a formulation without addition and other formulations containing respectively 2%, 4%, 6% and 8% in addition, (3) study of the characteristics of the cementitious mixtures prepared by these new formulations. The exploitation of the experimental results showed that the brick waste powder led to an increase in the RM compressive strength and a decrease in its porosity, which are two important characteristics that contribute to the cohesion of the packages to be stored. This is an encouraging result which is reflected in the increase of the quantity of resin confined in the cementitious matrix, and consequently reduction of the volume of the package to be stored.

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