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Improvement of conditions for the radioactive ion exchange resin immobilization in the cement Portland

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Abstract

The present work focuses on the optimization of the conditions of resin waste stabilization in cement matrices. The cemented resins matrices have been performed by mixing, in appropriate proportions, the radioactive resins, the Portland cement and sand with the water. Seven formulations have been carried out by incorporation the spent resin in amounts ranging from 8.3% to 15%. Study showed that we can increase the amount of the resin in the cement matrix from 8.3% to 12%. Under these conditions, the mechanical strength of the package increases by 73% and the porosity by 8%.

Leaching tests on the resulting package reveal that the formulation that incorporates 12-13% of the spent resin does not reject cesium. On either side, very low Cs departure of 11.4% is noticed for all formulations.

Key words: Cementation, ion exchange resin, leaching, compressive strength, porosity.

1. Introduction

Nuclear science and technology promotion for peaceful purposes are essentially dependent on the development of safety and the management of radioactive waste requirements. The subject of this work has been undertaken in the context of the << Unité de Recherche Mixte UMR>> between the National Centre of Science, Technology and Energy Nuclear (CNESTEN) and the University Hassan II Mohammedia - Casablanca (UHIIMC). It concerns the conditioning optimization of spent ion exchange resins used in purification of reactor water The resin which is the subject of our study is from the reactor TRIGA Mark II (rated power of 2 MW) of the National Center of Maamora (CENM) [1]. Cementation is one of many methods used for radioactive waste solidification [2]. It concerns low and intermediate level radioactive wastes such as the studied spent ion exchange resins. During this work, we aim to improve the confinement conditions of this kind of waste and to make the storage step more convenient, economical and environmental. The undertaken approach is to study the system spent resin - cement Portland (OPC) –sand-water [3] which are dependent on the amount of incorporated resins, physic-chemical conditions, characteristics and conditioning steps. The main objective of this research is to reduce in volume of cemented waste intended for storage without affecting its performances, reliability, efficiency and durability [4]. Taking into account the formulations and processes developed in previous works [5-9] including those used within the Exploitation of radioactive waste CNESTEN unity (UED), this study focuses on the research of the optimal conditions of the spent radioactive resins fixation and on the improvement of its physical and chemical properties auspicious for a sure and an enduring storage. Characterization of the final cemented resins matrix has been accomplished by measuring the strength, the porosity and the leaching of solid package. The study has been completed by the incorporation of ^{134}Cs in all formulations followed by the study of its leaching.

2. Materials, equipment and methods

Knowing that the quality of the coating matrix of the ion exchange depends on the conditions of the matrix preparation, and physic-chemical characteristics of materials (resin, cement, and sand)used in the preparation of the cemented package: The mastery and the optimization of these factors are necessary to carry out cemented drums with suitable characteristics adequate for the storage. In what follows, we give the main properties and preliminary measures undertaken for resins, cement, and sand. Next, we will give processes and experimental conditions for the preparation of cemented matrix and leaching study.

2.1. The ion exchange resin

The concerning action-exchange resin, recovered from the reactor of the Maamoura CEN, is a gel called Purolite NRW 37. in addition to the characteristics mentioned in table 1, the resin is formed by an assembly of three fractions whose diameters are respectively 0.315 mm, between 0.4 and 1.0 mm and higher than 1.25 mm. They contribute to the total mass by 0.2%, 80% and 3% respectively. These characteristics are responsible for the resin adsorption capacity. This resin is classified by the AIEA Agency among the intermediate level radioactive waste. Therefore, the contaminated resin requires an adequate conditioning before its storage. Among these conditioning types, the cementation is the most appropriate and the most used for the confinement of this resin.

main data	Specificproperties
Skeleton:	Cross-linked polystyrenic with DVB, gel type
Functionalgroup:	$R^-SO_3^-$
Physicalappearance:	amber beads, dark, translucent and transparent
Ionicform at delivery:	H^-
Moisturecontent:	40 % (form H^+)
Maximum swelling:	Na^+ -H^+ : 5%
Apparent density:	Around 800 g/l
Real density :	1.20 (form H^+)
Total Exchange capacity:	Min 1.7 eq/l (form H^+)

Table 1 : Characteristics of resin PUROLITE NRW 37 used in the Maamoura CEN reactor.

Before starting the spent resin cementation procedure, humidity and pH were adjusted according to the following protocols:

- **Preconditioning humidity**

The wet resin collected from the reactor is stored temporarily in the drums. Its humidity decreases with time due to the water evaporation. The humidity has been measured periodically to keep stable water/cement ratio (W/C) (the water bought by the resin is deduced from the mixing water). After a preliminary study, we adopt along this work the following protocol [10]:

A masse (m_i) of ion exchange resin is heated to 105 °C in an oven for 48h. After the dry heat, the resin is weighed (m_f) and its humidity is calculated according to equation1:

$$H = \frac{m_f}{m_i} \times 100 \qquad \textbf{eq (1)}$$

- **Preconditioning of the resin acidity**

Resin acidity at the outlet of the reactor can disrupt the stability and strength of the cemented matrix. Indeed, previous works [11] showed that strong acid waste can degrade the cement cohesion and decreases its resistance. To avoid these constraints, 50 g of previously dried resin in the open air are added 500 ml of bidistilled water. The mixture is stirred for 50 minutes during which ten successive and spaced measures of pH are carried out by the pH meter WTW bran, model 730 inLab. The technique used in the pH measurement is consistent with standard measurements (ISO 10390:2005 - Soil quality - Determination of pH) [12, 13]. Under these conditions, the final pH stabilized at a value of 5.04 is adequate to optimal cementing the spent resin

- **Characterization of the used resin**

The grain structure characterization of the air dried resin is performed using an optical microscope of Brand Optika.

2.2. Portland cement

The cement used in this work is an ordinary Portland cement (OPC-35N).It is manufactured in Temara cement factory. This type of cement widely used in the civil engineering sector consists of a mixture of clinker and gypsum finely ground. It is composed mainly by calcite ($CaCO_3$), Quartz (SiO_2), Alite (3CaO (SiO_2)), and

Belite (2CaO (SiO_2)) [14]. The diffractogram obtained by the mark PanalyticalX'Pert Pro MPD apparatus shows (Fig 1) that the minerals identified in Portland cement are consistent with the previously mentioned species.

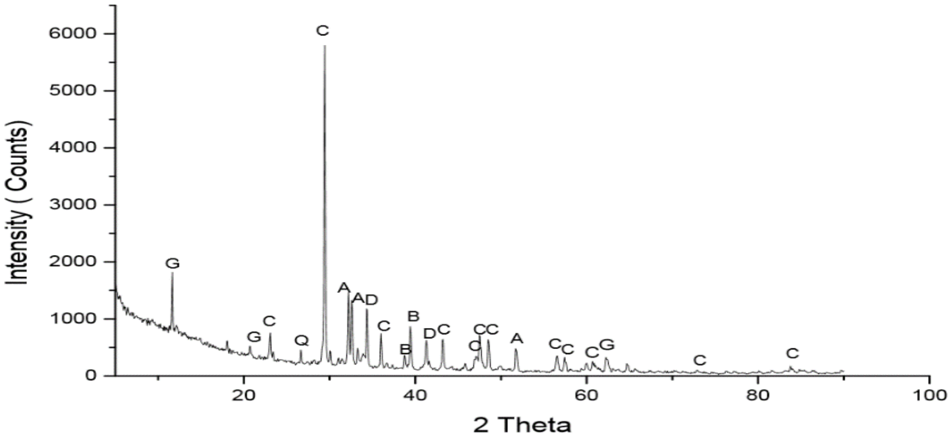

Figure 1 : RDX of cement.
C: Calcite; Q: Quarts; A: Alite; B: Belite; G: gypsum D: other components (Mg, AL,).

2.4. Sand

The sand that used as additive in the cementation Protocol complies with the NM 10.1.020 (EN 196-1) standard [15]. Characterized by its siliceous morphology, the sand is chemically inert towards the components of the mixture. In light of the previously results [16] which demonstrated, that the uses of sand of the size of 0.2 mm reinforce the mechanical resistance of the cemented resin matrix. The used sand, for the preparation of all formulations has a particle size ranging from 0.08 to1.6 mm to where 0.2 mm fraction is dominant (Table 2).

Table 2 : Sand size distribution.

Size (mm)	Percentage (%)	Cumulative percentage (%)
1.6	0.53	99.66
0.8	0.86	99.13
0.4	2.50	98.26
0.2	91.33	95.76
0.08	4.43	4.43

2.5. Phase of the cementation of resin

To accomplish the cementation process under our experimental conditions, we used three operating modes; all modes are prepared with the same formulation (Formulation 1, Table 4). It is based on the mixture in 207 mL of water, Portland cement (510 g), sand (200g) and the resin (83g).

- **Mode 1:** This procedure involves two steps; the first is to stir in a mortar, for 60s at a speed of 140 revolutions/s a mixture of cement and sand in the water. In the second phase, the resin is added to the above mixture, and the all is stirred for 120s at a speed of 240 rev/s.
- **Mode 2:** In this operating mode, the mixture containing cement, sand, resin and water is mixed for 180s. During the first 60s the mixture was stirred at a slow speed (140 rev/min), after, the mixing was continued with higher speed (240 rev/min) for 120s.

- **Mode 3:** this method involves three steps: first are stirred in water, a quantity of cement for 60s at a speed of 140tours/min. After addition of sand, in the second step the mixture is stirred for 60s at the same speed. In the final phase, the resin is added and the mixture was stirred for 60s at a rate of 240tours/min.

Table 3: Compressive strength of three modes at 28 days of cure.

	Mode 1	Mode 2	Mode 3
compressive strength (MPa)	3.62	2.49	2.12

Taking into account the preliminary results mentioned in table 3, the moulds having a diameter of 6 cm and a height of 10 cm, are prepared for all formulations according to the mode 1.

2.6. Preparation of cemented resin matrix

The mixing of the components of the formulation is carried out using a standard mixer brand 3R, type automatic mortar mixer with the capacity of 5 L.

2.7. Formulations

Several formulations have been tested according to the experimental data determined previously, especially those concerning the quantity of resin ranges from: 10% to 15% [16]. 7 formulations have been selected and performed. Each formulation composition is detailed in table 4.

Table4: composition of the formulations for a kilogram of mixture.

Formulation	Cement (g)	Sand (g)	Resin (g)	Water (g)
1	510	200,2	83	206,8
2	510	190	100	200,0
3	510	190	110	190
4	510	190	120	180
5	510	170	130	170,5
6	510	190	140	160
7	510	185	150	155

The sand/cement ratio (S/C) in all formulations is between 0.39 and 0.33. The ratio (E/C) is stable at 44%.

2.8. Compressive strength and porosity study

Compressive strength tests for each formulation are performed at different ages of the matrix: 7, 14, 21, 28, 40, 60, 90 days (fig, 3, 4, 5). They are made using a brand press Carver Model (4350.L) S/N (4350-362). The results are given in MPa (mega Pascal).

The porosity is measured according to the following Protocol [17]: the matrix is emerged in the water for 4 days until saturation. The volume V_i and the mass M_i of the matrix are measured after saturation respectively, and then it is placed in the oven at 105 ° C for 3 days. The mass measured at the exit of the oven is designated by M_f . The calculation of the porosity is deduced by the formulae 2 [18]:

$$P = \frac{(m_i - m_f)}{V_i} \; x\, 100 \qquad \text{Eq (2)}$$

2.9. Lixiviation

- Ions exchanges resins contamination

In order to study the leaching behavior of ions exchanges resins, it is essential to work with a contaminated resins. The contamination is carried out according to the following protocol:

In a container of 500 mL, the resin is added to a volume (V) of ^{134}Cs taken from a stock solution which has a specific activity Am = 3.16 Bq / g. The mixture is stirred at room temperature for 30 minutes.

- Lixiviation process

The matrices of cemented ions exchanges resins were emerged after 16 days of cure in distilled water. The water volume is fixed such a way that every matrix was surrounded on each side by 2 cm. After 105 days of immersion in the same water volume, leachant has been analyzed for radioactivity by an Hyper-pure Germanium Detector with a relative efficiency of 30%. The activity has been calculated by the software “Genie 2000”. [19]

$$R = \frac{A\ V}{A_0\, S\, T} \qquad \text{(Eq 3)}$$

where R is the leaching rate (cm/s), A is the radioactivity leached constituent (Bq/Kg) , V is the sample volume (cm^3) , A_0 is the initial radioactivity (Bq/Kg) ,S is the exposed surface area of the matrix (cm^2) and T is the duration of leaching (s).

3. Results and discussion

3.1. Optical microscopy

The resin characterization by optical microscopy stored before its cementations shown as photographs in Figure 2.

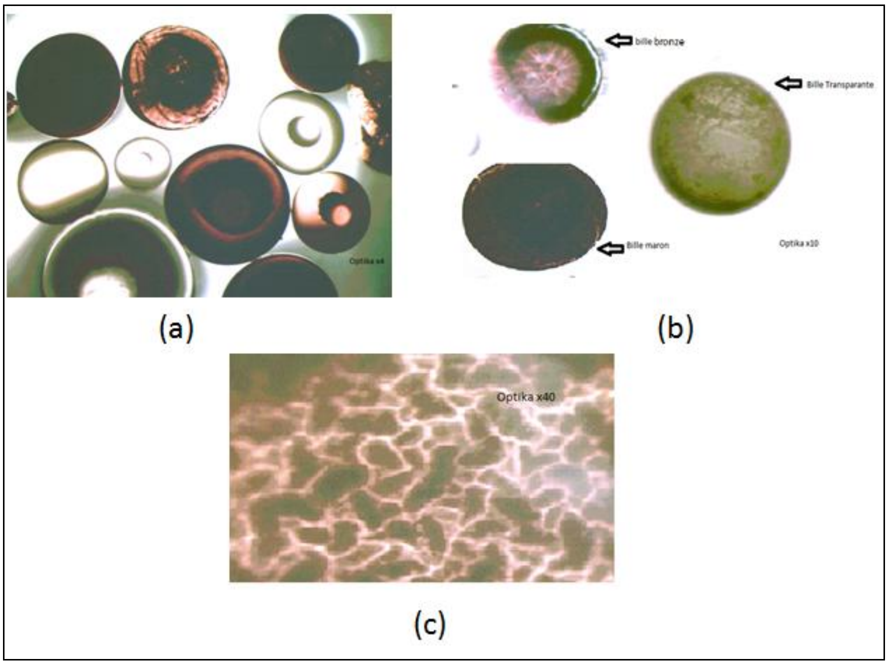

Figure 2: resin beans observed with different enlargement: (a): an enlargement of 4; (b): an enlargement of 10; (c): an enlargement of 40.

The images obtained by optical microscopy show that the morphology of the resin has not been modified during its use in the reactor and during its storage before cementing operation. It is composed of dark grains; translucent and transparent (**Fig 2**). Its porous nature is due to the concentration of porosity in the center of the grains.

3.2. Strength of the package strength

The compressible strength variation according to the solidification time for formulations 1, 2, 3, 4, and then for 4, 5, 6, 7 are shown in Figures 3 and 4 respectively.

It shows that:

- For all formulations, the resistance increases gradually with the time of solidification. This increase has slowed in general after 40 days.
- Among all tests, the formulation 4 is characterized by the higher values. The maximum value being equal to 8 MPa is observed after 90 days.
- This formulation has incorporated 12% of the resin (Table 4). This value is much higher than 8.3% previously used in cementing procedures in the CNESTEN. This result is of great importance, it reduces the amount of conditioned spent resin to be stored.

The curves shape representing the variation of the resistance versus solidification time **(Fig 3, 4**), shows a linear increase in resistance between 7 and 28 days before adopting a slow rate between 28 and 90 days. This suggests the existence of two solidification mechanisms; the first has rapid kinetics, whereas the second is characterized by a slow solidification velocity. These two mechanisms need to be elucidated in order to identify the sites and the binding forces of the resin in solid matrix.

The package strength variation according to the used formulations in this work (Fig. 5) shows that the strength increases gradually from the formulation 1 to 4, and then decreases linearly until the formulation 7. The maximum value 6.50MPa is observed for the formulation 4.

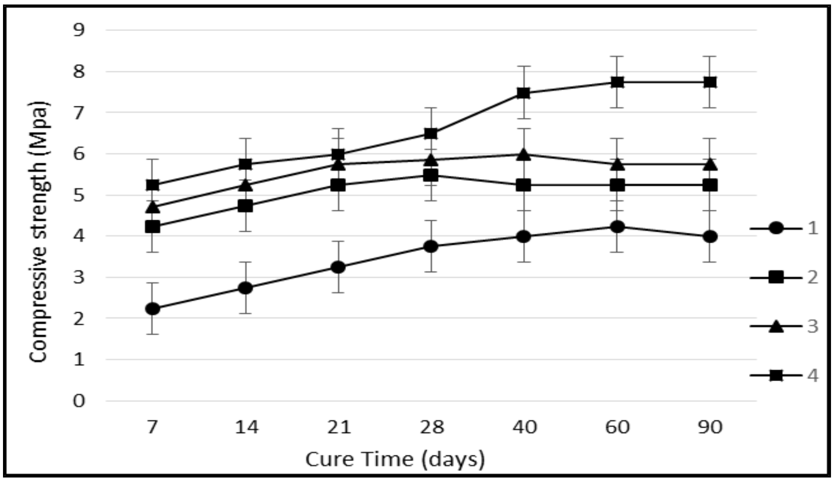

Figure 3: strength of the package of formulations 1, 2, 3, 4 at different curing time.

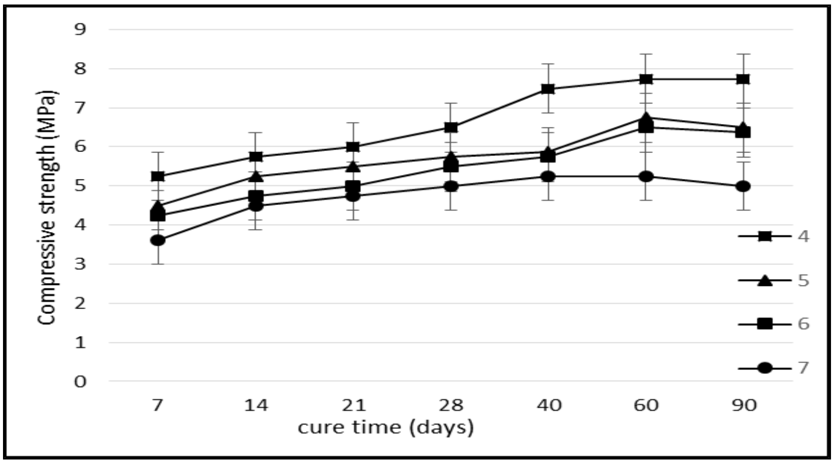

Figure 4: strength behavior for formulations 4, 5, 6, 7 at different curing time.

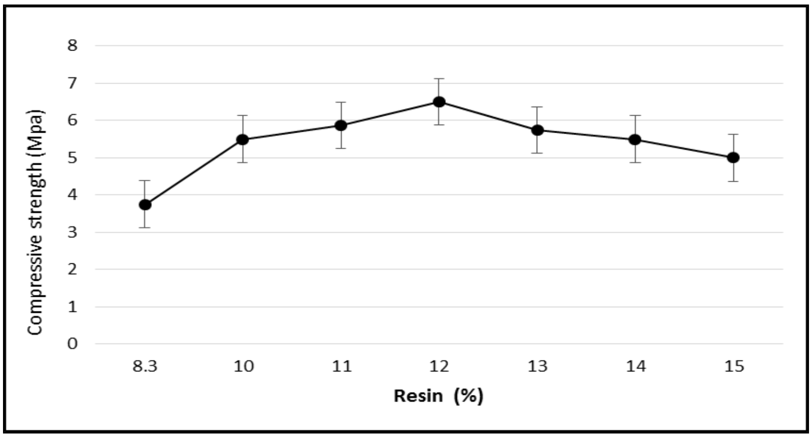

Figure 5: Strength of the package at the age of 28 days.

3.3. Porosity

In conclusion, this study has implemented a new protocol for securing radioactive resins. The final product containing 12% of resin is characterized by an increase in resistance of 73% over the previous procedure. The variation of the porosity according to percentage of the resin (Fig. 6) shows that:

- Porosity decreases progressively until the formulation 4 to which it reaches the value of 40.62%. Subsequently, the porosity increases progressively to the formulation 7.

These results are perfectly consistent with the literature that shows that the mechanical strength increases with the decrease in the porosity [20]. We deduce from results of porosity that the formulation with 12% of resins has a minimal permeability [21], which reinforces the resistance and minimizes leaching of the matrix during storage and final disposal of cemented waste [22].

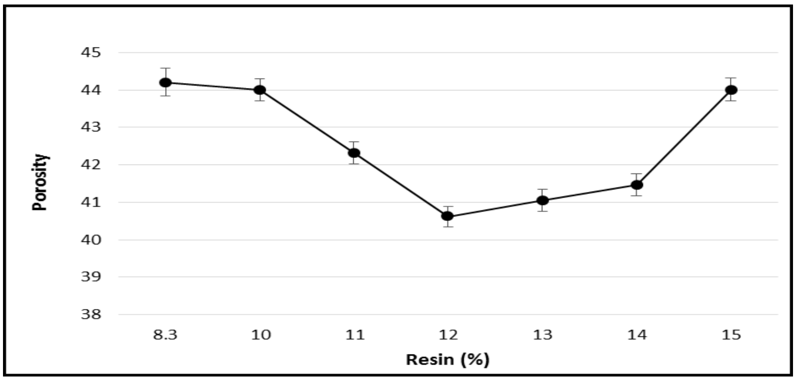

Figure 6: The variation of porosity relative to the percentage of the resin incorporated by formulations.

3.4. Lixiviation

The results of leached activity and leaching rate are given in figures 7 and 8 respectively.

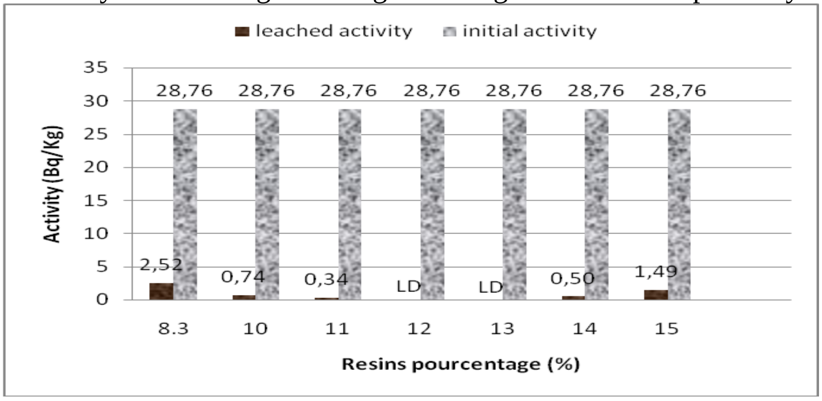

Figure 7: leached activity behavior relative to the percentage of the resin incorporated by formulations.

Leaching rate as shown in figures 7 and 8 is maximal for the formulation 1 prepared with 8.3% of resins, and minimal for formulations 4 and 5 prepared respectively with 12% and 13%.

Lixiviation of ^{134}Cs decreases from the 8.3% to 12%. At 12% and 13% the leached ^{134}Cs is almost established in such a way that the activity of leached ^{134}Cs is below the detection limit of the detector. Next 13% lixiviation increases until 15%.

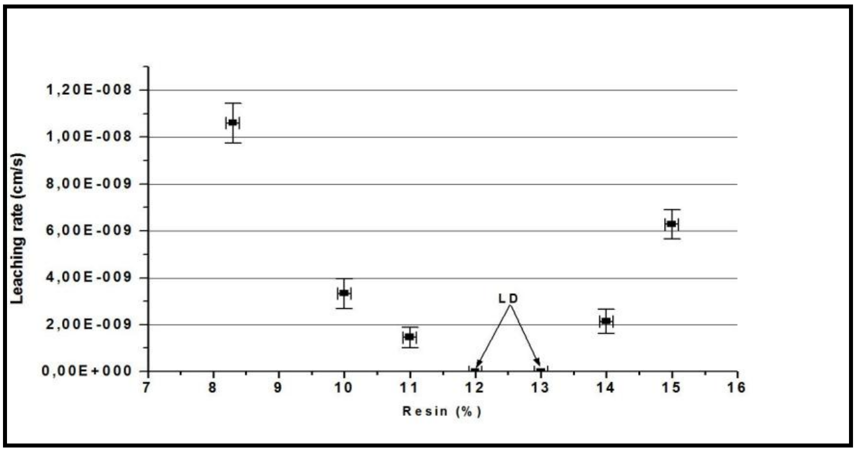

Figure 8: leaching rate variation activity relative to the percentage of the resin incorporated by formulations.
LD : the value of detected activity is below the detection limit of the detector. LD= 0.27 Bq/Kg.

Leaching of ^{134}Cs from cemented ions exchange resins behave the same way as the compressive strength and the porosity. According to the previously works[23-24], the improvement of mechanic and microscopic characteristic of mortar is due to the increasing of silicate calcium hydrate C-S-H, the mean component of mortar. Referred to the literature, the C-S-H (gel) is also the responsible of radioelement capture and retention [25-26]. After what preceded, we can conclude that the C-S-H produced by formulation 4 which contains 12% of resins, is more important than the C-S-H produced by the other formulations.

Conclusion

In conclusion of this work undertaken to improve the cementation of ion exchange resins used in the research reactor CNESTEN-Morocco, we have demonstrated that we could increase the percentage of incorporation of spent resin, from 8.3% to 12%. The optimum formulation is based on a mixture of 500 g of cement, 190g of sand, 120g of resin and 180 mL of water. Under these conditions, the resistance increased by 73%, the porosity decreased by 8.3% and the leaching resistance is reinforced compared to the previously used formulation. This protocol can lead to minimize cost and to reduce the storage space of cemented drums of this kind of waste. The profile of the variation of the resistance of the package prepared by the seven formulations suggests two modes of solidification: The first mode, characterized by relatively rapid solidification speed between 7 and 28 days. The second with slower solidification kinetics covers the period between 28 and 90 days. This phenomenon requires further study to determine the mechanisms of attachment of the resin in the solid cemented. Retention of Cs in the package designed and prepared by the formulation containing 12% of the used resin comfort stability of this package characterized by greater strength than those previously used in the containment of such waste kind.

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