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New matrix cement-zeolite for the cementation of radioactive waste: study of the physical properties and mechanical performances

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Abstract

In the aim to improve the physical properties and the mechanical performance of the confinement matrix of spent of use Ion Exchange Resin (IER) considered among the radioactive waste of low and medium activity of long-lifetime, various formulations of the cementitious matrix based of different percentages of zeolite raining form 2% to 10% by weight of cement with a step of 2% have been developed. The physical properties (compactness) and the mechanical performance (the compressive strength) of the new cement- zeolite matrix have been investigated. The obtained experimental results from the different formulations elaborated showed that the partial substitution of cement by the zeolite improves significantly the physical properties and the mechanical performances of the last one, this is due mainly to the pozzolanic properties of zeolite related to their reactive SiO_2 and Al_2O_3, Which react with $Ca(OH)_2$, released during the hydration of cement and transforming it into aluminates and gels C-S-H. In consequence, the microstructure of the hardened cementitious matrix has improved; its compactness and its mechanical resistance of compression were increased also.

Keywords: *Radioactive waste; spent radioactive resin; cementation; zeolite; compactness; compressive strength.*

1. Introduction

The Ion Exchange Resins (IER) are widely used in a nuclear facility as a macromolecule for the purification of nuclear reactor water circuits and the treatment of liquid radioactive waste [1–8]. After it's used, the radioactive resin must be treated and managed in an appropriate manner in order to minimize their potential danger to the human health and the environment [9]. Several techniques have been developed to reduce this danger, namely the bituminization [10], the verification [11] and the cementation [12, 13]. The last one is the most widely used in that it has many advantages, such as the simple installation of its equipment's, the low temperature during the hydration and the low cost on one hand [2, 12–21]. On the other hand, the cementation of IER presents problems, namely the low mechanical of compressive strength of the package during of its conditioning, the low resin charge and the possibility of a strong leaching of radionuclides [22]. The optimization of the cementitious process of resin used in low and medium activity resulting from the purification of the of nuclear reactor water circuits TRIGA MARKII of the Center of Nuclear Studies of Maâmora (CENM) (CNESTEN-Morocco) have been required a much research work aimed to improve the containment conditions of this type of solid radioactive waste in formulated mortars [23, 24–30], as well as the method of immobilizing the capsules of used sealed sources [31] or the coating of the archives of the packages . In this context, our study focuses initially on increasing the charge of spent radioactive resin in the cementitious matrix and in a second time optimizing by improving the mechanical and physical performance of this package by incorporating an inorganic addition "zeolite". Various formulations of the containment matrix of IER have been developed at different percentages of zeolite ranging from 2 to 10 % by weight of cement with a step of 2%. The influence of zeolite on the physical properties and mechanical performance of the cementitious matrix was evaluated using the compactness and the compressive strength at the young age, medium-term and long-term. The obtained results from the different formulations tested showed that the addition of zeolite significantly improves the physical properties and mechanical performances of the cementitious matrix, namely the increase in the compactness and the improvement of the compressive strength at all ages.

2. Material and methods

2.1. Materials

2.1.1. Cement

The cement used in this work is a Portland cement with additions (CPJ-45N). This type of cement 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 ($2CaO.SiO_2$), Tricalcium aluminate ($3CaO.Al_2O_3$) and tetracalcium aluminate ($4CaO.Al2O_3.Fe_2O_3$). Its chemical composition is assembling in table 1 and its mineralogical analysis by X-Rays Diffraction (XRD) is presented in Figure (1).

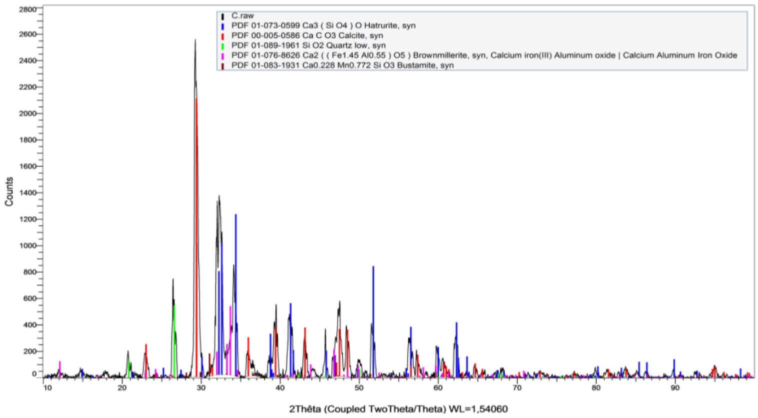

Figure 1: Analysis by X-Rays Diffraction (XRD) of cement

The spectrum delivered by the XRD in Figure 1 shows that the predominant crystallographic structures in the Portland cement used in the cementation of the ion-exchange resin are the calcite $CaCO_3$, the alite Ca_3SiO_5, and the quartz SiO_2.

2.1.2. Zeolite

The zeolites are inorganic polymers, based on a three-dimensional crystalline skeleton of TO_4-type tetrahedral. T represents a generic atom: it is generally a silicon atom, which corresponds to a tetrahedron SiO_4, or aluminum, forming an AlO_4 tetrahedron (Figure. 2). These tetrahedral are connected to each other by oxygen atoms, so each oxygen atom is actually divided by two tetrahedral [32].

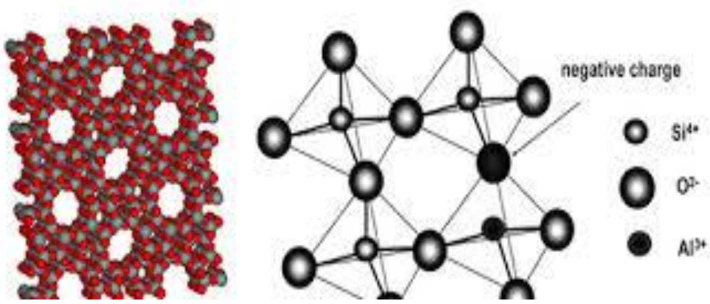

Figure 2: Structure of zeolite

The Figure (3) shows the crystalline structure of the zeolite. Its chemical and mineralogical compositions are illustrated in Table (1).

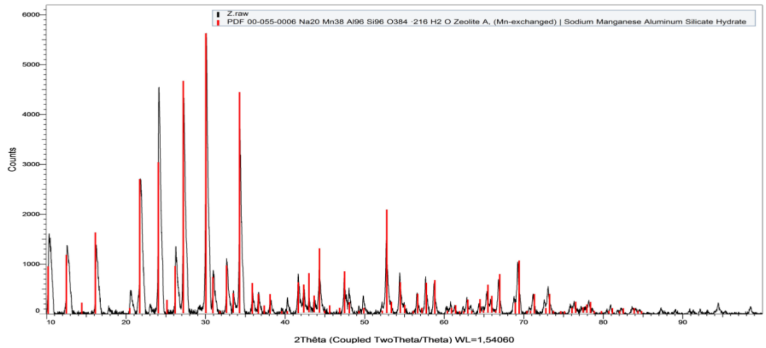

Figure 3: Analysis by X-Rays Diffraction (XRD) of the zeolite

The analysis of the results deduced by the spectrum (Figure 3), obtained by the XRD, shows that our addition (zeolite) presents an average quantity of sodium, quartz, alumina and some trace of iron. From the results presented in Table (1), we found that the chemical compositions of cement and zeolite are strictly different. In fact, the cement is very rich in calcium oxide (CaO) (61.8%) and silica (SiO_2) (19.2%), whereas the zeolite is rich in sodium oxide (Na_2O) (27.90%), silica (SiO_2) (27.20%) and aluminum oxide (Al_2O_3) (25%).

Table 1: Chemical composition of cement and zeolite

Content (%)	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Cl**
Cement	61.80	19.20	7.80	3.16	2.01	2.40	0.82	0.10	0.01
Zeolite	0.016	27.20	25.00	0.021	0.232	0.06	0.031	27.90	0.001

2.1.3. Ion-exchange resin

The ion exchange resin that is the subject of our work as a solid radioactive waste generated by the nuclear reactor of Maâmoura CEN -Morocco is a crosslinked polymer in the form of beads. It consists of an assembly of three particle sizes: 0.2% of the grains with a diameter of less than 0.31 mm, 80% of the grains with a diameter between 0.4 mm and 1.00 mm and 3% of the grains with a diameter greater than 1.25 mm. Characteristics of the ion-exchange resin are shown in Table (2).

Table 2: Characteristics of the ion-exchange resin

Physicochemical properties of the resin	
Skeleton	Polystyrenica crossed to the gel type DVB
Functional grouping	$R^{-} SO^{-3}$
Physical appearance	Translucent dark, amber beads
Ionic form at delivery	H^{-}
Moisture content	51 65% (form H^{+})
Maximum swells	Na^{+} - H^{+} : 5%
Temperature limit	120 ° C
pH limit	0-14
Apparent density	About 800 g/l
Real density	1, 20 (form H^{+})
Total Exchange capacity	Min 1.7 eq/l (form H^{+})

2.1.4. Radiological characterization of ion-exchange resin by gamma spectroscopy

The gamma ray spectroscopy consists of measuring the energy and counting the number of photons emitted by IER in a natural or artificial way for a given duration. From the obtained results at Table (3), it is then possible to identify different radioelements (qualitative analysis) and to determine their concentration (quantitative analysis) in our radioactive waste (IER).

Table 3: The radioelements present in the resin

Natural radioelement		
Radioelement	**Activity (Bq/kg)**	**Detection limit (Bq/kg)**
Chain of U - 238		
Th - 234	<	66.7
RA - 226	<	6.6
PB - 214	<	1.7
Chain of Th - 232		
AC - 228	<	2.5
PB - 212	<	1.0
BI - 212	<	1.0
TL - 208	<	1.6
Chain of U - 235		
U-235	<	3.0
K-40		
K-40	<	16.5
Artificial radionuclides		
Radioelement	Activity (Bq/kg)	Detection limit (Bq/kg)
CS - 137	<	0.5
CS - 134	<	0.4

I-131	<	0.5

The results of the analysis of the following natural and artificial radioelements such as $^{-134}$Cesium, $^{-137}$Cesium, $^{-131}$Iodine, U^{238} family, ^{234}Th family (Thorium), ^{235} U (Uranium) and K4 Potassium) on a sample of IER show that the activity values of these radioelements are below the detection limits of the measurement system, which shows that this resin is very low radioactive.

2.2. Method the solidification of ion-exchange resin

The tested specimens are prepared by first mixing the cement and the wet resin of a moisture content of an around about 64% after we added the water and then the salt. The resulting mixture of water / (cement + zeolite) ratio = 0.40 is poured into cylindrical molds 5.5 cm in diameter and 10 cm in height previously oiled to facilitate demanding. The samples are then gently vibrated by a vibrator type Trakita VR 250D to remove the air pockets. After a set time, the samples were removed and stored in a relatively humid room until crushing time (7, 4, 21, 28 and 90) days.

3. Results and discussions

3.1. Physical properties

The physical properties of the different formulations developed have been examined using the compactness of the cylindrical specimens (Figure 4). The obtained results are described in the Figure (5).

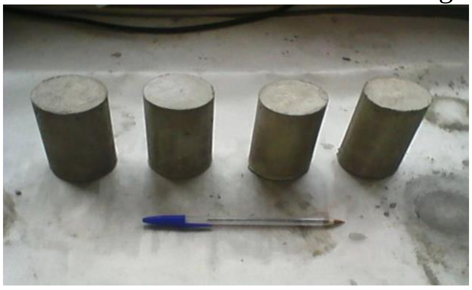

Figure 4: The specimen test

3.1.1. Compactness

The compactness is an essential characteristic of the containment matrix of IER, it demonstrates the ratio between the absolute theoretical volume (Eq 1), that is to say without vacuum, of the dry matrix and its apparent volume (Eq 2). It is, therefore, factor in the durability of containment package.

C = 1-P Equation 1

With, P = [Mi-Mf]/v Equation 2

P: Porosity

M_i: Mass of the specimens' saturation in water, M_f: Mass of the specimens parboiled for 3 days at 105 ° C, V: Apparent volume of the specimens. The Figure (5) shows the variation of the compactness of the matrix of containment of IER.

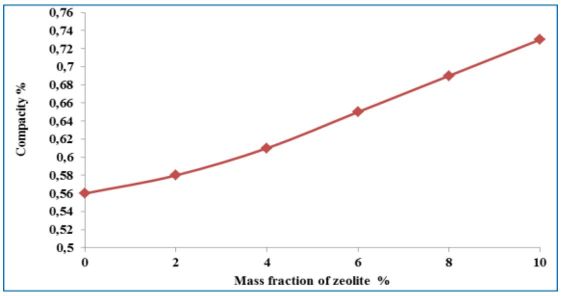

Figure 5: Variation of compactness as a function of mass fractions of zeolite

At the Figure (5) which presents the compactness of the cementitious containment matrix of IER based on different percentages of zeolite. The compactness increases progressively as a function of the mass fractions of our addition; this increase is logically explained that when cement-water mixtures start into contact with the zeolite, the aluminosilicate of zeolite begins to decompose under the attack of OH^-. The species of depolymerized, such as $[SiO(OH)_3]^-$ and $[Al(OH)4]^-$ react with Ca^{2+} released during the hydration of cement and convert to aluminates and gels C-S-H. The microstructure of the cement matrix at hardened stat is improved and consequently, this compactness has been increased.

3.1.2. Mechanical performance

The mechanical performances of different formulations realized have been evaluated by the compressive strength of cylindrical specimens. A total of 140 samples was prepared and tested at different contents of resin (0.2, 4, 6, 8, 10, 12, 14, and 16%) and zeolite (2, 4, 6, 8, 10%). The compressive strength of the different formulations developed is measured after five curing time (7, 14, 21, 28, 90 days) using a manual hydraulic press of the type of Carver 4350. The obtained results are presented in the Figures (6, 7 and 8) where each graph point represents the average of two tests.

3.1.3. Compressive strength of cementitious matrix without additions

The results of the compressive strength of the cementitious confinement matrix IER without additions are described in Figure (6).

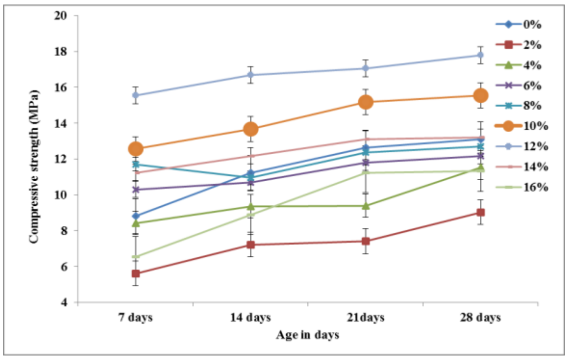

Figure 6: Compressive strength as a function of percentage of resin from 0% to 16%

According to the Figure (6), the mechanical performance of a cementitious matrix of containment of IER, determined by the compressive strength, increased as a function of the quantity of waste (IER) until to 14% where it decreases, Which allowed us to conclude that the maximum quantity of waste that can be incorporated into a formulation without the package lose its mechanical performance is 12% which presents the saturation point. If we exceed this percentage the package was late its compressive strength.

3.1.4. Compressive strength of cementitious matrix with zeolite

The Figures (7 and 8) illustrate the variation of compressive strength at the young age (7 days) medium (14 days) and long-term (28 days and 90 days).

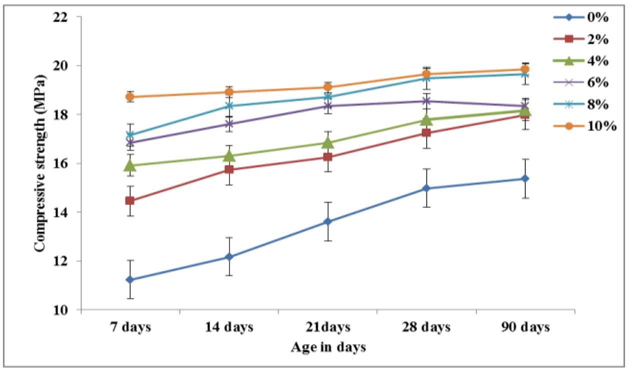

Figure 7: Compressive strength as a function of mass fraction of zeolite

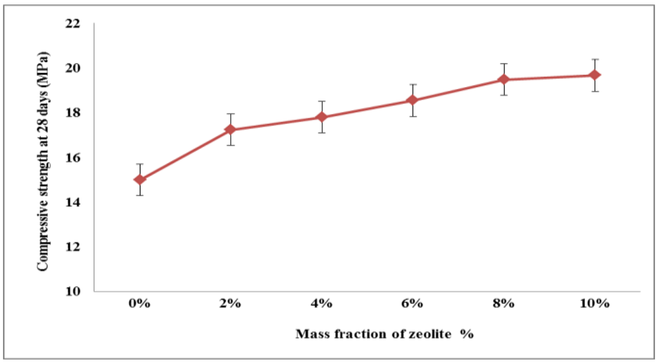

Figure 8: Compressive strength at 28 days as a function of mass fraction of zeolite

The results illustrated in the Figures (7 and 8) show that the compressive strength of cementitious of a containment matrix of IER increases with the mass fractions of zeolite in the matrix. Indeed; the particles of zeolite are finer than cement particles and can fill the interstitial voids between the grains of cement and IER. This stacking optimum granular would contribute thus a great increase in compactness and a reduction in the permeability of the matrix, which gives rise to an improvement in the compressive strength.

3.2. Gain of compressive strength

We calculated the gain in compressive strength at 28 days using the following formula (Eq 3).

$$G = [(CS_x - CS_C)/(CS_C)]*100 \qquad (3)$$

With: **G:** Gain in compressive strength at 28 days**;** CS_c: Compressive strength at 28 days of control matrix; CS_x: Compressive strength at 28 days of matrix with X% of zeolite, (X = 2%, 4%, 6%, 8%, 10%). The Figure (9) shows the gain of compressive strength at 28 days of the matrices with 2% to 10% of sunlight. The Figure (9) expresses the importance that plays the quantity of zeolite in the mechanical performance of matrix containment of IER. It shows that the formulations containing from 2 to 10% of zeolite have provided with a resistance which respectively exceeds the 22% to 31% the value recorded for the standard formulation.

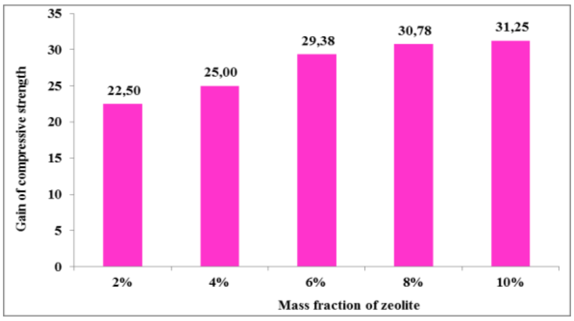

Figure 9: Gain of compressive strength at 28 days as a function of percentage of zeolite

3. Conclusion:

In the course of this work, we searched to optimize the formulation of the matrix confinement of spent ion exchange resin (IER) as radioactive waste on one hand by increasing its charge in the matrix and on the other hand by evaluating the influence of the addition of zeolite at various percentages ranging from 2 to 10% by weight of cement on the physical properties and the mechanical performances of this matrix. The obtained results from the different formulations elaborated show that:

- The incorporation of 12% IER into the cementitious containment matrix increases both the resin charge and improves the compressive strength of this matrix.
- The partial substitution of the cement by the zeolite increases, on one hand, the compactness of the matrix and on the other hand improves the mechanical performances of this new containment matrix since the mechanical compressive strength passing from 15 MPa to 20 MPa with a 10 % of Zeolite.

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