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Effect of partial substitution of the sand by the fireclay in cementitious matrix of confinement of ions exchange resins.

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- ✓ Compressive strength

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Abstract
In Morocco, the spent radioactive ion exchange resins are generated from the purification of the water circuits of the nuclear reactor TRIGA MARK II of the Center for Nuclear Studies of Maamoura (CENM). A strategy for the effective management of these wastes from generation to storage is necessary to ensure their safe handling, conditioning and storage to avoid detrimental effects on health and the environment. The immobilization of radioactive waste of low and intermediate activity in cement matrices, which constitutes the first barrier to curb the radiation of these wastes, is the most widely used technique for producing radioactive waste packages that are compliant with regulatory requirements. The incorporation of clay in mortar produces similar materials to ordinary cement mortar but with superior characteristics. The aim of this study is to find a new formulation of a cement matrix of confinement of ions exchange resins by gradually substituting the sand in the mortar by a fireclay. The monitoring of physical, chemical properties and the influence on the mechanical behavior of mortars has identified, an optimal formulation consisted of 52.57% of cement, 10.4% sand, 8% of fireclay, 15.153% of the water and 13.915% resin. Indeed, the compressive strength for this formulation is 7.4292 MPA seems most suitable for packaging resins.

1. Introduction
In Morocco, the management of radioactive waste has become a major concern of the government, scientists and users of nuclear techniques. Radioactive waste showed low and intermediate activities in different sectors; for example. In the TRIGA MARK II CNESTEN, (National Centre of Energy, Science and Nuclear Techniques of Rabat) and generally in institutes and research laboratories and industries.
This management must be performed in a rigorous framework to ensure safe solutions for all radioactive waste, without losing sight of the permanent need for protection of the risk posed by these wastes, for present and future generations on the environment [1-3].
The immobilization of radioactive waste of low and intermediate activity in cement matrices, which constitutes the first barrier to curb the radiation of these wastes, is the most common used technique for producing radioactive waste packages that are compliant with regulatory requirements [4-6].Indeed, the incorporation of clay in mortar produces similar materials to ordinary cement mortar but with superior characteristics [7-11].
The purpose of this work is to study the gradual substitution of sand by the fireclay in the cement matrix of confinement of spent ion exchange resins, which is from the reactor TRIGA Mark II of the CNESTEN, in an attempt to improve the mechanical properties of the mortar. This study consists in characterizing materials used for confection of the mortars. In this context, we conducted a series of tests, including mortars with a report W/C (water /cement) constant. This work also consists in analyzing the mechanical properties with rates ranging from 0 to 12% for the addition of fireclay. The results of these tests are compared with those of a witness mortar. Analyses of Diffraction of the X-rays and fluorescence X were carried out on the fireclay.
This article is devoted also to solve the problems related to the behavior of materials in order to find a good matrix of confinement of the radioactive waste treated by the CNESTEN. This matrix must ensure storage under

conditions in conformity with the requirements of safety and security [1]. The choice of materials must be judicious and optimized on the basis of scientific, technical and economic criterion.

2. **Experimental**

2.1. *Materials*

2.1.1. Portland Cement

The used Portland cement (CPJ 35) is cement whose technical characteristics comply with the Moroccan standard NM 10.1.004.

2.1.2. Sand

The sand used on a laboratory scale complies with the Moroccan standard NM 10.1.020. We also use this sand for industrial applications for the confinement of radioactive waste.

2.1.3. Fireclay

We substituted the sand in the cementitious matrix by a commercial fireclay, which is a silico-aluminous material, who in the presence of water, reacts with the calcium hydroxide to form "hydrated" compounds possessing the properties of cements [12-15].

2.1.4. Water

The water used is the tap water, the physical-chemical characteristics are:

- pH :7.381
- Ionic conductivity: 672µs (cell constant 1.045).

2.1.5. Ions exchange resins

The ions exchange resins [3, 16] MDP- 15 type as clear spherical beads, are used in the purification of water circuits of the reactor and in the storage pools of spent fuel from TRIGA Mark II reactor type Purolite NRW 37. These are cation exchange resins strongly acid gel-type. Ions exchange resins is a process by which ions contained in a solution are removed to be replaced by an equivalent amount of other ions of the same electrical charge. The physical-chemical properties of the ions exchange resins shows in Table 1.

Table 1: Physical-chemical properties of the ions exchange resins

Hydrocarbon skeleton	Polystyrenique crossed to the DVB's gel type
Functional group	$R^- SO_3^-$
Physical appearance	Dark amber, translucent beads
Ionic form of delivery	H^-
Moisture content	51 55% (form H^+)
Maximum swells	Na^+ - H^+: 5%
Temperature limit	120 ° C
pH Limited	0-14
Apparent density	About 800 g/l - actual density: 1.20 (form H^+)
Total Exchange capacity	Min 1.7 eq/l (form H^+).

2.1.6. Mixer 3R

The mixer 3R is a device that provides a mixture of high homogeneity while reducing mixing time.
The mixer properties:
- Automatic mortar mixer capacity: 5 liters
- Automatic sand Introduction
- Automatic Mortar Mixer comes with stainless steel bowl 4.7 liter capacity
- Power supply: 380V, 50Hz
- Dimensions: 340 x 460 x 700 mm
- Weight: about 28 kg.

2.1.7. Press carver 4350.L

This is a manual hydraulic press for determining the resistance to compression type Carver Model (4350.L) S / N (4350-362), maximum capacity of 24,000 Pounds and is controlled by weight.

2.1.8. Column of sieves, type 3R

- For sand

The analysis is done in a series of sieves (0.08 mm, 0.20 mm, 0.40 mm, 0.80 mm, 1.60 mm).

- For fireclay

The analysis is done in a series of sieves (88 µm, 74 µm, 62 µm, 37 µm).

2.2. X-Ray diffraction Analysis

The fireclay was analyzed with a P Analytical diffractometer X PERT POWDER copper anticathode (λCukα = 1.5406 Å).

2.3. X-Ray Fluorescence Analysis

XRF is a non-destructive analytical method for materials. This is a quantitative and qualitative analysis of the elements which are present in the sample. An analysis of the fireclay was carried out by the S1Turbo SD system.

2.4. Protocol for the preparation of samples.

The pastes are prepared in a standard mixer-EN 196-1 [17] following the procedure described in EN-196-3 [18] on the normal consistency of pure pastes. Firstly, we have introduced the necessary amounts of sand, cement, ion exchange resin and fireclay. For one minute and the mixture of ingredients was carried out dry in the mixer.
To avoid overflow, the necessary amount of water is gradually added. The bowl containing the mixture was placed in the stirrer and under a slow speed for 1min.Then under more rapid agitation speed for 2 min. The mortar was introduced resulting in cylindrical specimens of 10 × 5.5 cm and vibrated during few seconds. The walls of cylindrical specimens have been previously brushed with oil (type Sika Iron M) which is a release agent. Once the mortar in test tubes, it vibrates the whole for a few seconds. Mechanical tests were performed on samples to determine their resistance; the release was done after the following periods: 7 days, 14 days, 21 days and 28 days.

2.5. *Formulation tests*

The objective of this study is the formulation of a cement matrix by gradually substituting the proportion of sand by a fireclay as filler. We follow the effect of this substitution on the compressibility of the specimens while keeping the W/C ratio constant. The various alternative tests are gathered in Table 2. A test without substitution of sand by the fireclay will serve as a witness. It will compare the effects of the substitution of sand by the fireclay on the mechanical resistance of the matrix.

Table 2 : Formulation tests

	%/weight (g)	**Cement**	**Sand**	**Fireclay**	**Water**
witness	%	57.14	20	0	22.85
	weight (g)	1828.57	640	0	731.43
Test 1	%	57.14	18	2	22.85
	weight (g)	1828.57	576	64	731.43
Test 2	%	57.14	16	4	22.85
	weight (g)	1828.57	512	128	731.43
Test 3	%	57.14	14	6	22.85
	weight (g)	1828.57	448	192	731.43
Test 4	%	57.14	12	8	22.85
	weight (g)	1828.57	384	256	731.43
Test 5	%	57.14	10	10	22.85
	weight (g)	1828.57	320	320	731.43
Test 6	%	57.14	8	12	22.85
	weight (g)	1828.57	256	384	731.43

3. Results and discussion

3.1. *Quantitative chemical analyses of fireclay*

The chemical composition of the fireclay was determined by x-ray fluorescence. The results obtained are expressed in mass percent (Table 3).

Table 3:X-Ray Fluorescence of the fireclay

	Oxides composition (%)					
	Al_2O_3	SiO_2	P_2O_5	K_2O	TiO_2	Fe_2O_3
Fireclay	43.00±0.67	53.82 ±0.50	0.68 ±0.04	0.91 ±0.01	0.13±0.01	1.35 ±0.01

3.2. X-Ray analysis

The diffraction pattern (Figure 1) shows that the main mineral phases present in this sample are **:** Quartz (SiO2), the Mullite (3Al2O3, 2SiO2) and Cristobalite (SiO2).

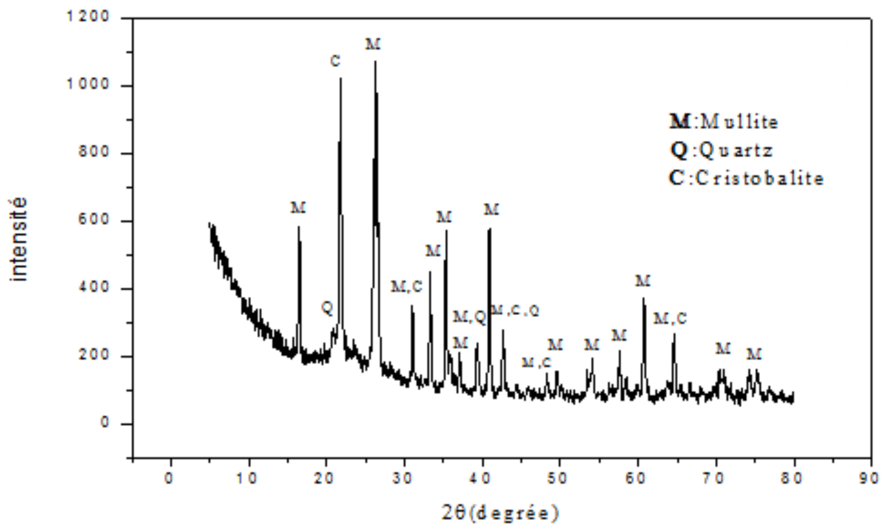

Figure 1: The diffraction pattern of fireclay

3.3. Particle size analysis

Particle size analysis showed (Figure 2) that the majority of the grains constituting the sand has an average size of 0.2 mm and a relatively high fineness rate of 0.08 mm; indicating that our sand is standardized according to the standard NM 10.1.020 (EN 196-1) [19].

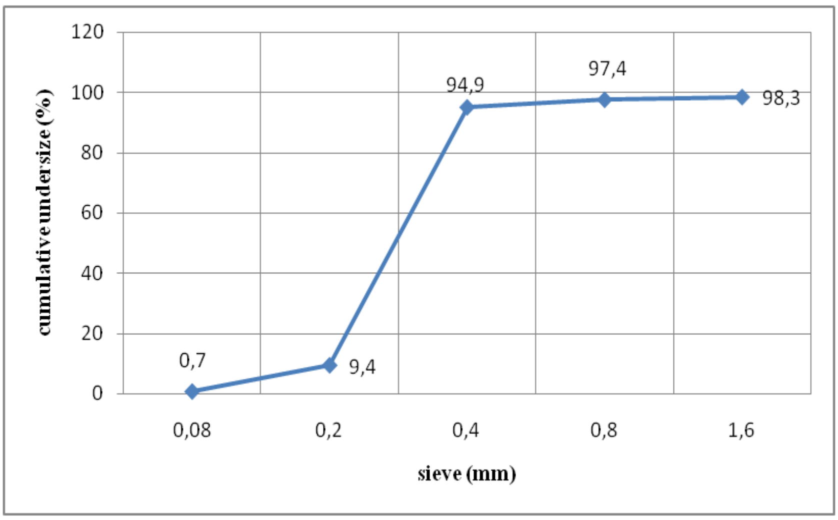

Figure 2: Variation of size particle of the sand

3.4. Size analysis of fireclay

All of the grains constituting the calcined clay are of large size (88 µm) at a very small size (37 µm) and it means that our clay is low in the file (Figure 3).

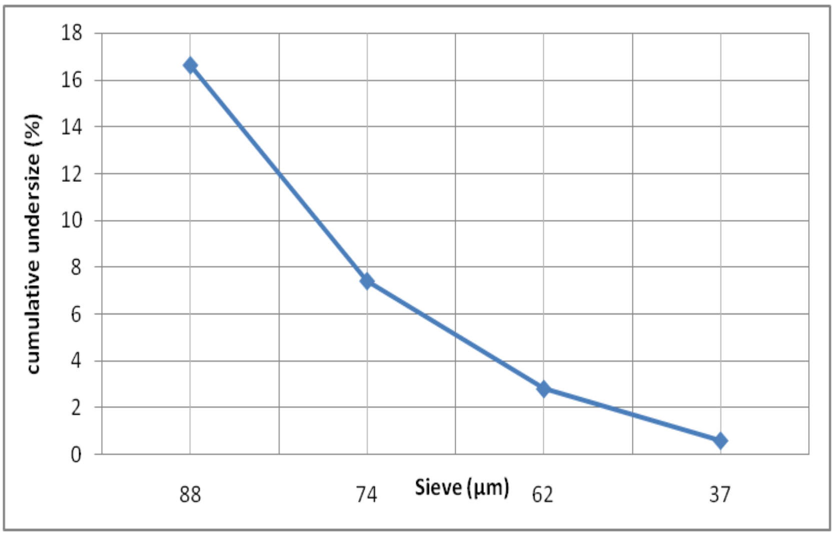

Figure 3: Grading curve of the fireclay

3.5. Results of tests formulations

We measured for samples of different formulation, the compressive strength as a function of curing time ranging from 7 to 28 days (Figure 4).

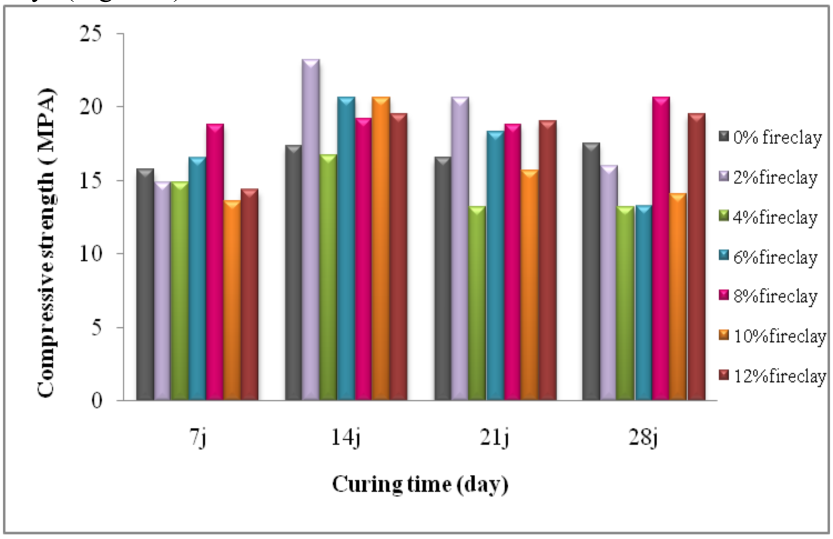

Figure 4: Effect of curing time on the compressive strength

From Figure (4), which shows the mechanical of compressive strengths at an early age (2 days), medium-age (7 days and 14 days) and long-term (28 days) of the new formulation matrix based on different percentages of fireclay as in function of age, we noticed that the compressive strengths of all the mortars formulated by these additions increase with age and with the percentages introduced. This improvement can be explained by the dual role of fireclay:

- Filling the tiny voids in the mortar due to its very high fineness,
- Pozzolanic effect, silica it contains will combine with portlandite after hydration reactive clinker phases to form C- S -H as the following reaction:

$3CaO.SiO_2 + H_2O \longrightarrow CSH + Ca(OH)_2$;

$CaO + SiO_2 + H_2O \longrightarrow CSH$[14, 16].

On the other hand, we noted the effect of curing time on the compressive strength (Figure 4) shows that at 28 days, the best resistance corresponds to the incorporation of 8% of fireclay in the mortar.

However, according to several studies [20-24] there are three main effects of additions: a granular effect, a physical- chemical effect and a chemical effect.

3.6. Confinement of ions exchange resins in the matrix

The best obtained formulation corresponding to 8% of fireclay, has enabled us to study the incorporation of radioactive waste in the matrix according to the percentages varying from 3.479 % to 13.915 % in order to determine the maximum rate of this waste that we can confine in the studied matrix (Table 4) .

Table 4: Confinement of ions exchange resins formulation

	%/weight (g)	Cement	Sand	Fireclay	Water	Wet resin
Test 7	%	57.14	12	8	22.85	0
	weight(g)	1828.57	384	256	731.43	0
Test 8	%	56	11.6	8	20.921	3.479
	weight(g)	1792	371.2	256	669.472	111.328
Test 9	%	54.86	11.2	8	18.982	6.958
	weight(g)	1755.52	358.4	256	607.424	222.656
Test 10	%	53.71	10.8	8	17.044	10.436
	weight (g)	1718.72	345.6	256	545.408	333.952
Test 11	%	52.57	10.4	8	15.153	13.915
	weight (g)	1682.24	332.8	256	484.896	445.28

3.7. Results of confinement of ions exchange resins in the cementitious matrix

The results of effect of the curing time variation on the compressive strength for different rates of ions exchange resins incorporated in the mortar with are collected in Figure 5.

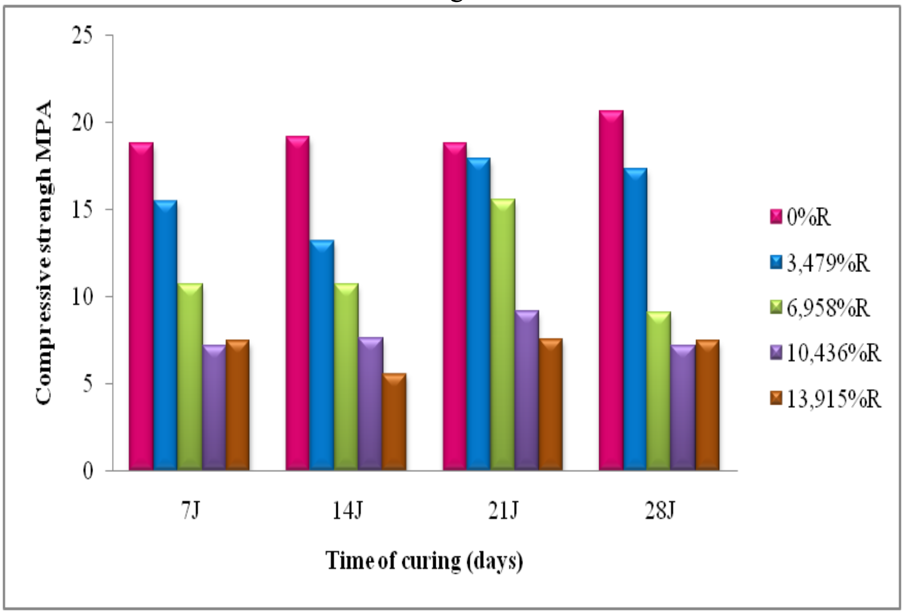

Figure 5: Effect of curing time on the compressive strength at various rate of confinement of ions exchange resins in the cementitious matrix.

After the Figure (5) that displays the compressive strengths at an young age (2 days), medium-age (7 days and 14 days) and long-term (28 days) of the new formulation confinement matrix based on 8% of fireclay in presence of various rate of ions exchange resins as in function of age, we seen that the compressive strengths of all the mortars formulated by these additions in presence of ions exchange resins decrease with age and with the percentages introduced. This decrease in compressive strength can be explained the presence of various rate of confinement of ions exchange resins in the formulation matrix based on 8% of fireclay negatively influences the mechanical performance in particular the mechanical resistance to the compression.

By comparison with previous studies [16, 25, 26] conducted in the laboratory of UGDR, we conclude that this work permitted to find better values of the compressive strength. Thus the studied matrix has better performance.

Conclusion

The formulation study shows that:

- The compressive strengths increase when substituting sand by fireclay. It means an improvement of the compactness by three effects that act simultaneously and in a complementary way: physical effect, physico-chemical and chemical (pozzolan).
- The fireclay can be has a pozzolanic reactivity: there is an adhesion of lime by the silica grains to form calcium silicate hydrate (C-S-H).
- The formulation confinement of ion exchange resins, better performance was observed for the following composition: 52.57% cement, 10.4% sand, 8% of fireclay, 15.153% of water and 13.915% of ions exchange resin which results in a better mechanical resistance to compression of 7.4292 MPa.

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