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The Callovo-Oxfordian as sand substitution in concrete: Effect on the confinement of the ion exchange resin

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Abstract: The present work aims to investigate the conditions for improving the containment of spent ion exchange resin (IER) as a radioactive waste, using powdered Callovo-Oxfordian clay (COx) as an addition to the cementitious matrix at different rates. The aim of this work was to investigate the influence of COx on the characteristics of cemented packages of spent (IER).
In this context, a cemented pack was made using Portland class 45 cement, sand, resin and water. And others are prepared by replacing the sand with COx, in the following proportions: (2%, 4%, 6%, 8% and 10%). The packages obtained with and without COx were measured for their compressive strength and porosity.

Keywords: Callovo-Oxfordian, Portland 45 cement, confinement, radioactive resin, mechanical strength.

1. INTRODUCTION

Nuclear energy is produced by nuclear power plants type pressurised water reactor. The water is treated with filters and ion exchange resins (IERs) to ensure the safety of personnel, to maintain the performance of the materials, and to avoid clogging the circuits [1].
After use, IERs become a solid waste [2] of low and medium activity with a long life, loaded with radioactive nuclides and cannot be reused, in this context they must be properly treated and disposed of in order to minimise the potential danger for the environment [3].
Conditioning consists of converting this radioactive waste into a solid form, enclosing it in containers and/or immobilising it [4], by solidification, coating or encapsulation in order to limit the possibilities of migration or dispersion of radionuclides during handling, transport and storage [5].

In many countries, immobilisation strategies for low-level radioactive waste are based on cementitious materials [6]. Cement solidification was developed in the 1950s and was the only method of solidifying radioactive waste before 1965 [7,8,9]. Due to the good physical, chemical and mechanical properties, low cost and stability, cement remains the best material for resin solidification.
Analyses and research on different types of cements have shown that, due to the requirements of the cementing process, Portland cements are still the most suitable for the solidification of waste concentrates [10]. Portland cement (CEM I) is a mixture of clinker, gypsum (or anhydrite) (3-5%) and mostly mineral additions such as fillers (calcite) up to 5%. [11] Clinker is composed of four main constituents, including C_3S, C_2S, C_3A and C_4AF, which will hydrate in the presence of water. It is the combination of these reactions that is defined as cement hydration.
As soon as the cement is put in contact with the mixing water, the 4 anhydrous phases of clinker and the mineral additions will dissolve in contact with the water to recombine into hydrates [12]. C_3S and C_2S are the major elements of clinker and their dissolution leads to the creation of the two hydrates which are the Hydrated Calcium Silicates Hydrates (C-S-H) and the Portlantide ($Ca(OH)_2$) symbolised CH . Other minor compounds are also formed during hydration, such as aluminium hydroxides, hydrated calcium aluminates or ettringite [13].

The C-S-H formed have a lower CaO/SiO_2 ratio than the CEM I hydrates, which has a double advantage,

- The equilibrium pH of C-S-H decreases with the Ca/Si ratio [14,15].

- The concentration of alkaline cations in the interstitial solution can be reduced, as the ability of C-S-H to bind Na+ and K+ ions increases as the Ca/Si ratio decreases [16].

The use of composite cements, obtained by replacing part of the Portland cement with minerals with pozzolanic or hydraulic properties, is becoming increasingly common in the conditioning and storage of radioactive waste [17]. The additions made make it possible to reduce manufacturing costs, limit the heat of hydration, etc., and also modify the cement hydration processes [18].

In addition, the Callovo-Oxfordian (COx) argillite has been selected as a potential geological barrier for the deep disposal of radioactive waste by Andra, the French National Agency for Radioactive Waste Management [19], The COx is composed of a clay matrix containing a few detrital grains of quartz and calcite, The average mineralogical composition of the COx argillite is as follows [20]: 45-50% clay fraction (mainly illite-smectite interbedded minerals with a fraction between 50 and 70% smectites, 20% carbonates, 22% quartz and 9% other minerals (feldspars, pyrite, dolomite and siderite)[21]. Some of these minerals are swelling, i.e., their volume increases on contact with water. This is mainly the case for smectite.
This property is particularly favourable for limiting the corrosion of metallic materials and the release of radionuclides [22], and its mineralogical composition gives it a relatively high resistance for a clayey rock, and a behaviour that is not very deformable, and that can be damaged above a certain load threshold. As far as short-term mechanical behaviour is concerned, the simple compressive strength of the clays is 21 MPa on average, in the middle of the formation studied [23].

During its contact with the cement components, the COx will be subjected to various coupled mechanical, hydraulic and thermal processes. One of the few studies conducted on the physico-chemical evolution of the interfaces between the COx clay and the cementitious materials is the one carried out by [24]. The study characterises the physico-chemical processes that take place on both sides of the cement paste/COx clay interface. The mechanical response of COx clays is strongly related to their water content, showing a low macroscopic strength and a more ductile response for higher water content. For example, [25] observed a higher Young's modulus not only for lower water content, but also for lower carbonate content. Other authors, for example, [26] have linked the effect of water content, and more specifically the drying and wetting processes, to the modification of the microstructure of the COx.

The present work, undertaken in this context, aims to study the impact of the addition of COx clay in the composition of the used cementitious matrix in the confining of IER experimentally by replacing the proportions of sand by COx, the protocol used consisting of two steps: the elaboration of the cementitious resin packages and the characterisation of the packages using the following analytical methods: X-ray fluorescence, compressive strength and porosity.

2. MATERIAL AND METHOD

In order to improve the physical and mechanical properties and to guarantee the stabilisation of the cementitious matrix, there are several formulations already in use and well tested by scientists, based on the modification of the type of cement used, the Water/Cement ratio noted W/C or the type of additives.

A. *Properties of the materials used*

The preparation of containment mortars requires various materials including:

1) *Cement*

The type of cement used in our study is ordinary commercial Portland cement class 45, which complies with Moroccan regulations NM 100.1.004. The following table shows the mineralogical composition and X-ray fluorescence analysis of CPJ 45.

SiO_2	20,64	**K_2O**	0,67	**Clinker**	70
Al_2O_3	3,93	**TiO_2**	0,27	**Gypsum**	2,5
Fe_2O_3	2,99	**MnO**	0,07	**Limestone**	32,5
CaO	59,41	**P_2O_5**	0,22	**C_2S**	23,05
MgO	1,40	**Na_2O**	0,02	**C_3S**	47,85
SO_3	2,27	**SrO**	0,058	**C_3A**	5,35
				C_4AF	9,10

Table 1 : The mineralogical and chemical composition of CPJ 45 (%)

2) *sand*

The sand used in the preparation of our samples complies with the NM 10.1.020 standard (EN 1961), and is characterised by a siliceous morphology, chemically inert, and with a dominant grain size of 0.2 mm.

Sieve (mm)	Mass (g)	Cumulative refusals (%)	Cumulative sieves (%)
1,6	2	0.2	99,9
0,8	6	0.6	99.7
0,4	54	5.4	99.1
0,2	934	93.4	93.7
0,08	3	0.3	0.3

Table 2: Grading distribution of the sand

3) Mixing water

The water used is tap water with a pH of 7.38 and an ionic conductivity of 672 µs.

4) The Callovo-Oxfordian

COx particles are a smooth and fine powder, with a micrometer size. They belong to the ultrafine family of mineral particles with a size of less than 9 µm, which indicates that COx is a more reactive element and this property is necessary to improve the durability and mechanical properties of concrete.

The chemical composition of COx is given in the table below, by the X-ray fluorescence (XRF) technique, the result shows that the clay fraction contains significant amounts of SiO_2 (40.991%), and almost equal amounts of (MgO,Al_2O_3,Fe_2O_3). while the other elements are present with minor contents (Table 3).

MgO	7.635 %
Al_2O_3	7.392. %
SiO_2	40.991 %
P_2O_5	0.402 %
SO_3	1.261 %
K_2O	2.314 %
CaO	2.284 %
Fe_2O_3	6.973 %
Ti	0.456 %

Table 3: X-ray fluorescence analysis of COx.

5) Ion exchange resin

The ion exchange resin (IER) used in our work is in the form of a gel of the type PUROLITE NRW 37, and consists of an assembly of three particle sizes: the first is formed of grains with a diameter of less than 0.31 mm, the second is between 0.4 and 1.0 mm, and the third is greater than 1.25 mm. The water content of the IER used throughout this study is approximately 60%. The water content is an important factor in the formulation process and is measured periodically to keep the amount of water used in the preparation of the formulation stable. It is given by the following formula:

$$\boldsymbol{H}(\%) = \frac{\boldsymbol{M_H}-\boldsymbol{M_S}}{\boldsymbol{M_H}} \times \mathbf{100} \quad \text{(Equation 1)}$$

Where $\boldsymbol{M_H}$ and $\boldsymbol{M_S}$ are respectively the wet mass 1 Kg of IER and the mass of the dried resin, at a temperature of 105°C for 48 hours.

B. The rate of mixtures

From the described materials, six mixtures were prepared, the first one is of reference noted MC0 and four other mixtures noted MC1-MC2-MC3-MC4 and MC5 were formulated by partially replacing the sand with COx at different percentages between 2 to 10% with a step of 2% by weight.

Formulation	**COx** **%**	**Portland Cement %**	**Sand** **%**	**Resin** **%**	**Mixing Water %**
MC0	0	53	16.504	15	16.12
MC1	2	53	14.504	15	16.12
MC2	4	53	12.504	15	16.12
MC3	6	53	10.504	15	16.12
MC4	8	53	8.504	15	16.12
MC5	10	53	6.504	15	16.12

Table 4: Composition of the cement formulations with 15 % IER

C. Process for preparing cemented containment packages

For 60s, the IER with water is added, and the whole is mixed again at the same speed of 60s. The mixing is stopped for 2 min. and then resumed for 2 min. at high speed.

The dough is glued into molds, 8.4 cm high and 4.2 cm in diameter. To facilitate their demoulding the moulds are oiled with a release oil.

After 3 hours of hardening. The specimens are recovered and placed in a place chosen for curing under normal conditions of pressure and temperature.

The compressive strength of the specimens was determined after 7, 14, 21 and 90 days of curing. The same preparation technique was used for all the mortars.

3. RESULTS AND DISCUSSIONS

A. Properties of cemented IER packages

1) The mechanical resistance to compression

In order to ensure the safety and security of man and his environment against the harmful effects of radiation emitted by radioactive waste, the IER in our case, the latter must be well confined and cemented in a cask and have at the same time a good compressive strength to improve the durability of the casks conditioned in the phase of storage and final storage. Each specimen was regularly monitored for different ages up to 90 days.

	7 days	***14 days***	***21 days***	***28 days***	***90 days***
0%	12.7404	14.156	16.9872	19.8184	21.234
2%	15.5716	16.2794	18.4028	22.6496	24.0652
4%	15.5716	16.9872	17.695	19.8184	19.8184
6%	11.3248	12.7404	14.156	16.9872	19.8184
8%	11.3248	12.7404	12.7404	14.156	16.9872
10%	12.7404	14.156	14.8638	15.5716	16.9872

Table 5: Compressive strength results in MPa

To follow the evolution of the compressive strength in the medium term, tests were carried out on six samples, the results of the compressive strength are given as a function of the Callovo-Oxfordian content from 0 to 10% and the curing time which is from 7 to 90 days.

For a given age, the compressive strength is maximum for the MC1 mix. At 90 days, we record an increase of almost 14% compared to the reference mix. This increase can be explained by the increase in the density of the mix by adding the COx.

The fines brought by the COx fill the inter-granular voids and thus increase the compactness. For MC4 and MC5, the compressive strength decreases compared to MC0, in fact, the higher fraction of Callovo-Oxfordian causes a discontinuity in the granular curve of the mixture. The mixture becomes less homogeneous and therefore less resistant, moreover it can be shown that the results of the compressive strength of the concretes of 6% of COx at 90 days leads to a better increase compared to the reference package of about 75%.

2) *The porosity*

The COx argillite is a sedimentary rock deposited 155 million years ago, its textural properties give it a low permeability throughout its thickness [27] of about (k=10-20m2,)[28],[29],[30], this permeability is due to a very small pore size of the rock and interactions between water and minerals [31].

Knowledge of the permeability properties of COx is of great importance for the design of the

The knowledge of the permeability properties of COx is of great importance for the design of the storage device, so the low permeability presents one of the important factors for a better strength and durability of the concretes.

COx (%)	Porosity (%)
0	32.08
2	31.76
4	33.64
6	34.15
8	34.50
10	36.18

Table 6 : Variation of porosity as a function of COx content in %.

The study of the variation of porosity with different percentages of Callovo-Oxfordian, shows that after the addition of the latter we observe a positive impact on the permeability of water, related to a small decrease in porosity of about 1% compared to the reference mortar, this decrease due to the precipitation of calcite, which itself comes from the dissolution of portlandite [32], and associated with a high content of carbonate minerals.

The strong correlation between the sensitivity to water of the COx clay and its mineralogical composition [34], [35], contribute to the increase in porosity which tends towards 36% for a rate of 10% of the clay, as other authors [36], [37], have linked this increase by the precipitation of C-S-H in the altered argillite zone in contact with the cement paste, their studies also show that there is a neoformation of C-S-H at the interface, following the diffusion of silicon from the argillite to the cement paste. Thus another study by [38] showed that this increase is the result of damage and swelling of the material during its saturation. The COx plays an important role in this variation of porosity being that a rock that presents a contrast of porosity, thus, the sensitivity to water increases when the proportion of argillite minerals increases.

B. *Chemical composition of cemented IER packages*

COx (%)	CaO	SiO_2	SO_3	Al_2O_3	Fe_2O_3	MgO	K_2O
0	48.21	25.84	1.72	5.04	4.17	1.09	0.45
2	46.57	26.36	1.60	5.20	4.48	0.96	0.42
4	48.20	25.15	1.73	4.52	3.89	0.76	0.82
6	49.90	25.30	2.14	4.37	4.15	0.74	0.65
8	50.04	24.04	2.32	4.23	3.86	0.81	0.74
10	51.3	22.18	3.54	4.17	3.69	0.68	0.67

Table 7: The chemical composition of cemented IER packages

The table above shows the chemical element contents given by the XRF analysis after 90 days of curing.
For a rate of 2% of COx, we observe a large proportion of silica, also for aluminum accompanied by a decrease in lime (CaO), This decrease is the result of the consumption of part of the portlandite to form by pozzolanic reaction, hydrates C-S-H ([39], [40]). The hydration of the cement leads to the formation of a greater proportion of C-S-H, denser, at the expense of the portlandite (which should theoretically be totally consumed). However, C-S-H has a

microstructure with very fine pores. The addition of COx clay therefore leads to a very fine microstructure of the concrete, while the SO_3 content is very low in the same COx content (2%).

4. CONCLUSION

This study shows the feasibility of partial substitution of silica sand by Callovo-Oxfordian clay powder in the composition of ordinary concrete.

In this work, we demonstrated the effect of the addition of Callovo-Oxfordian clay on the mechanical performance of the ion exchange resin (IER) confining matrix.

Indeed, the addition of COx has an effect on the compressive strength of the cementitious matrix, however, we noticed a significant improvement of the strength in the formulations: MC1, MC2, MC3, then a decrease in MC4, MC5 compared to the reference one.

Thus, it was shown that COx is an important factor in the variation of porosity being that it presents a contrast of porosity.

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