



## Durability of class C fly ash belite cement in simulated sodium chloride radioactive liquid waste: Influence of temperature

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### ABSTRACT

This work is a continuation of a previous durability study of class C fly ash belite cement (FABC-2-W) in simulated radioactive liquid waste (SRLW) that is very rich in sulphate salts. The same experimental methodology was applied in the present case, but with a SRLW rich in sodium chloride. The study was carried out by testing the flexural strength of mortars immersed in simulated radioactive liquid waste that was rich in chloride (0.5 M), and demineralised water as a reference, at 20 and 40 °C over a period of 180 days. The reaction mechanism of chloride ions with the mortar was evaluated by scanning electron microscopy (SEM), porosity and pore-size distribution, and X-ray diffraction (XRD). The results showed that the FABC mortar was stable against simulated chloride radioactive liquid waste (SCRLW) attack at the two chosen temperatures. The enhancement of mechanical properties was a result of the formation of non-expansive Friedel's salt inside the pores; accordingly, the microstructure was refined.

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### 1. Introduction

This work is a part of an extensive investigation on the potential application of a specific fly ash belite cement, here named (FABC-2-W), of low energy, low pH and low heat of hydration to be used in radioactive waste disposal [1–5]. It is well known that the high pH values of the pore solution together with the portlandite ( $\text{Ca}(\text{OH})_2$ ) content and high heat of hydration of Portland-based cements are, among others, the factors that cause expansive reactions, such as the alkali-silica reaction (ASR) or the formation of destructive ettringite and/or gypsum in the case of a potential sulphate attack [6,7], and can even alter the properties of clay such as bentonite, which could be used together with concrete to seal an underground high level waste (HLW) repository. The use of pozzolanic additions to Portland cement is considered the best way for decreasing the pH of the pore solution (below 11), which is necessary for these applications [8–13].

Temperature is another important factor that also influences the cement properties of matrices used in radioactive waste disposal. The storage facility for LLW and MLW in Spain is located in “The Cabril” near the city of Cordoba, where the temperature can reach values of 40 °C. Thus, we were interested in studying the durability of FABC mortars at this temperature.

A previous study on the hydration of FABC-2-W cement at 40 °C and saturated humidity [3] showed a densification of the C–S–H gel, which favoured the formation of pores ~3 nm in diameter, leading to higher surface area value, compared with that of the C–S–H gel formed at 20 °C. The capillary porosity ( $>0.05 \mu\text{m}$ ) increased at later ages of hydration because of the conversion of low density hydration products, such as the hexagonal hydrated mono-sulphate-calcium-aluminate ( $\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), into higher density cubic katoite ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ). As a result, the compressive mechanical strength decreased. The temperature caused similar effects on the hydration of Portland cements [14–19].

Nevertheless, the aforementioned effects caused by the temperature of 40 °C disappeared when the FABC-2-W mortars were immersed in a specific simulated radioactive liquid waste (SRLW), which was very rich in sulphate (48,000 ppm) [2]. It was found that an enhancement of mechanical behaviour was produced by the ingress of sulphate and sodium ions into the microstructure. This ingress caused the formation of non-expansive ettringite ( $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ ) within pores via dissolution of the hydrated calcium-monosulpho-aluminate ( $\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ); the pH of the pore-solution increased by one order of magnitude, which promoted an alkaline activation of cement and the densification of the microstructure. Ettringite precipitation via dissolution of the hydrated calcium-monosulpho-aluminate inhibited the formation of katoite [2].

This work is a continuation on that durability study. The same experimental methodology was applied: testing the flexural

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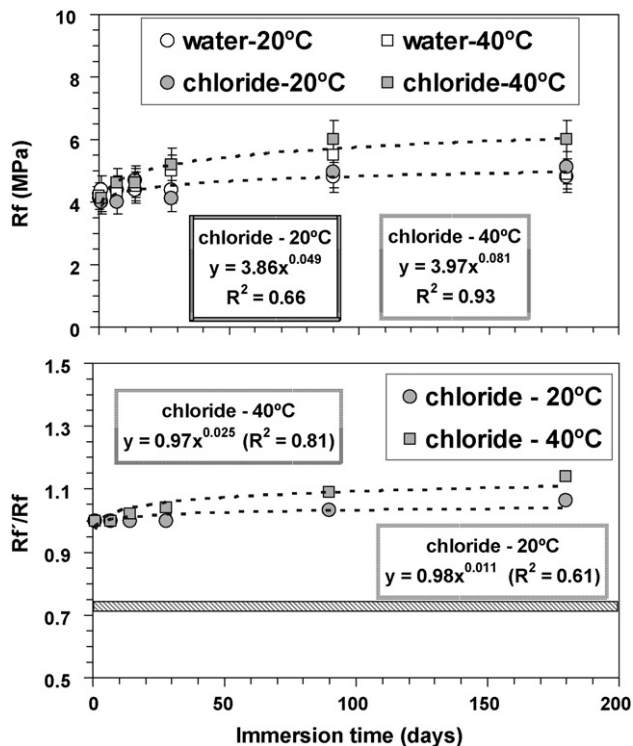


Fig. 1. Flexural strength and corrosion index ( $R_f/R_f$ ) of mortar samples versus time,  $R_f$  = strength after immersion in the SCRLW;  $R_f$  = strength after immersion in water.

strength of mortars immersed in simulated chloride radioactive liquid waste (SCRLW) that was rich in chloride (0.5 M), and demineralised water as a reference, at 20 and 40 °C over a period of 180 days. The reaction mechanism of chloride ions with the mortar was evaluated by scanning electron microscopy (SEM), porosity and pore-size distribution and X-ray diffraction (XRD).

## 2. Experimental

The FABC-2-W was synthesized by the hydrothermal-calcination route by using fly ash class C (from coal combustion) as secondary raw material. Details of the cement synthesis, fly ash, and cement and mortar characterization can be obtained in references [2–4].

The FABC-2-W cement mortar was prepared with a sand ( $\alpha$ -quartz) to cement ratio of 3, and demineralised water to cement ratio of 0.65. To improve workability, an organic additive (commercial name “Rheobuild-1000” Degussa Construction Chemicals, Barcelona, Spain) was introduced in a proportion of 2% (by weight of cement). After mixing, different portions were moulded into 1 cm  $\times$  1 cm  $\times$  6 cm prismatic specimens and compacted by vibration. After 2 days at 100% relative humidity (rh), samples were demoulded and cured by immersion in demineralised water at 40 °C for 7 days. The volume of liquid was 100 ml per 6 samples. After this curing period, groups of 6 samples were immersed and suspended in the SCRLW (concentration of chloride ion = 0.5 M). These samples were stored in sealed plastic bottles at 20 and 40 °C for periods of 1, 7, 14, 28, 90 and 180 days. The volume of SCRLW was 800 ml per 6 samples. Similar groups of 6 samples were stored at two temperatures in demineralised water (used as a reference). After each period of time, and prior to the characterization study, the samples were washed three times with demineralised water to eliminate the excess of SCRLW.

X-ray diffraction patterns were recorded on a Philips PW-1730 diffractometer, which used a graphite monochromator and Cu K $\alpha$ 1 radiation. Porosity and pore-size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics Auto Pore IV 9500 v1.05. SEM analysis was performed using a JEOL JSM 5400 microscope (Ltd., Tokyo, Japan) equipped with an Oxford ISIS model EDX spectroscopy module (Oxford University, Oxford, UK). Sputtering was used to cover the samples with carbon.

## 3. Results and discussion

The mechanical strength of mortars immersed in the SCRLW solution at 20 °C are quite similar to those obtained in water; at 40 °C the values are slightly higher, most notably after 180 days, when the decrease observed in water disappeared (Fig. 1). The gain of strength with time is adjusted to a potential function. At the temperature of 40 °C, the gain of strength (exponent of the equation) was nearly two times higher than that at 20 °C.

According to the Koch-Steinegger test [20] the criterion to classify a material as durable in a specific aggressive medium is that the corrosion index [relative strength of aggressive solution-stored ( $F_s'$ ) samples to water-stored ones ( $F_s$ )] must be higher than 0.7. As shown in Fig. 1, the corrosion index values increased with time according to a potential function, with a exponent nearly two times higher in the case of the temperature of 40 °C. Therefore, the FABC-2-W can be classified as durable, or resistant to the SCRLW attack, during the period of time and experimental conditions here studied.

The diffusion of chloride ions into the mortars caused the formation of Friedel's salt ( $\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ ), as can be seen in Fig. 2.

Friedel's salt formation is the result of chlorides reacting with hydrated phases such as monosulphate:  $\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Both Friedel's salt and monosulphate belong to the same structural lamellar family (named AFm type), with the unique difference that negative sulphate or chloride are inside the basal space to balance the positive charge of the layers:  $[\text{Ca}_2\text{Al}(\text{OH})_6]^{+}$  [6]. As shown in Fig. 2, the basal XRD peak of the  $\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (appearing at 10.8  $2\theta$  angular zone) (Fig. 2(a) and (b)), shifted to higher  $2\theta$  angular zone (11.35) after 180 days of immersion in the SCRLW (Fig. 2(c) and (d)). This shift was more evident at 40 °C (Fig. 2(d)).

The proposed mechanisms for Friedel's salt formation are dissolution/precipitation and ionic exchange from monosulphates

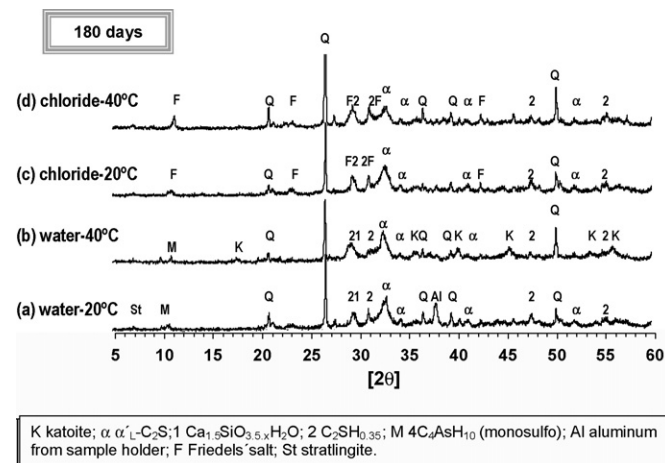


Fig. 2. XRD patterns of mortar samples after 180 days of immersion in de-ionized water and simulated chloride radioactive liquid waste (SCRLW) at the temperatures of 20 and 40 °C.

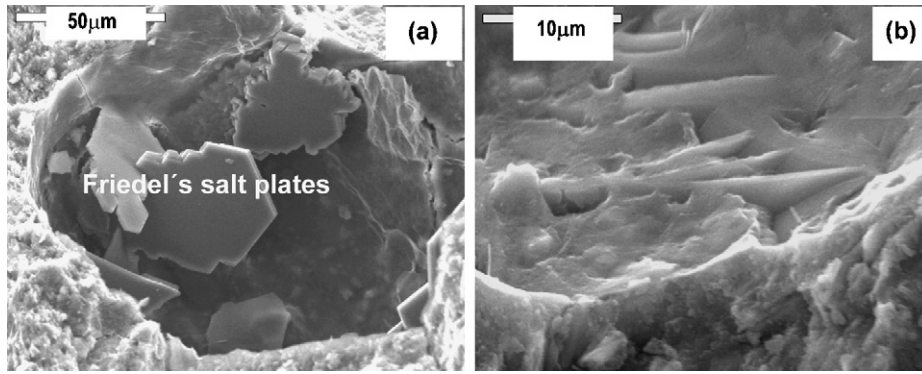


Fig. 3. SEM images of Friedel's salt growing inside the pores of mortar samples after 180 days of immersion at 40 °C in simulated chloride radioactive liquid waste (SCRLW).

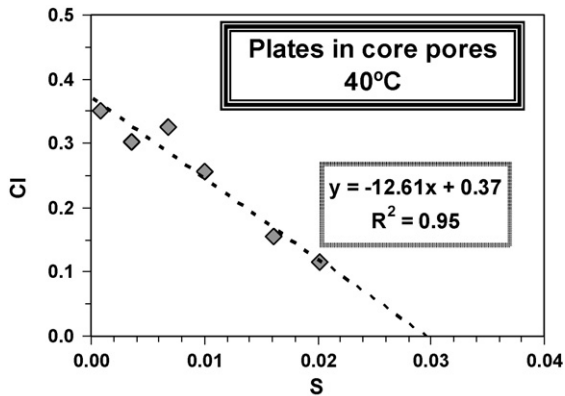


Fig. 4. Cl versus S atom ratio from spot X-ray microanalyses of plates formed in pores at 40 °C.

(SO<sub>4</sub>-AFm) or hydroxy-AFm). Both mechanisms can take place simultaneously, and the relative importance of each one depends on the chloride concentration in the pore solution [7]. In the case of ionic exchange from hydroxy-AFm, the release of one mol of OH<sup>-</sup> is produced by each mol of Cl<sup>-</sup> exchanged; in the case of the monosulphate-AFm, the release of one mol of SO<sub>4</sub><sup>2-</sup> is produced by every two moles of Cl<sup>-</sup> exchanged.

Friedel's salt appeared as hexagonal plates growing inside the pores, as can be observed through SEM analyses (Fig. 3). The X-ray microanalyses of S and Cl (carried out in the spot mode) in the plates seems to indicate that the mechanism of Friedel's salt is via ionic/exchange of Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup>. In fact, an

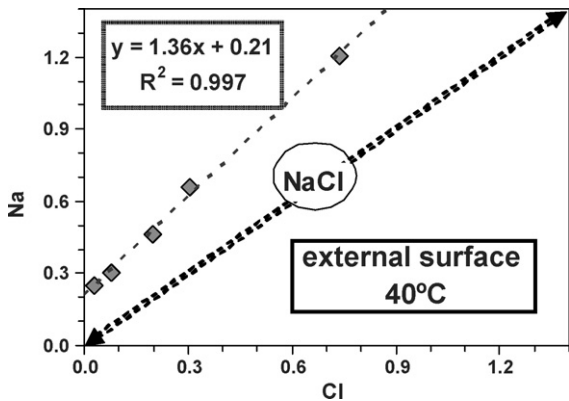


Fig. 5. Na versus Cl atom ratio from spot X-ray microanalyses of external surface at 40 °C.

inverse linear correlation is obtained when Cl is plotted versus S (Fig. 4).

The X-ray microanalyses of Na and Cl carried out in the interface with the SCRLW (Fig. 5) are located over the diagonal line. That means that there is an excess of Na to respect Cl probably because of the combination of chloride as Friedel's salt. The excess of Na<sup>+</sup> is balanced with OH<sup>-</sup> as revealed by the high pH of the pore-solution (pH 12.5) compared with the pH of the pore-solution of mortars immersed in demineralised water (pH 11).

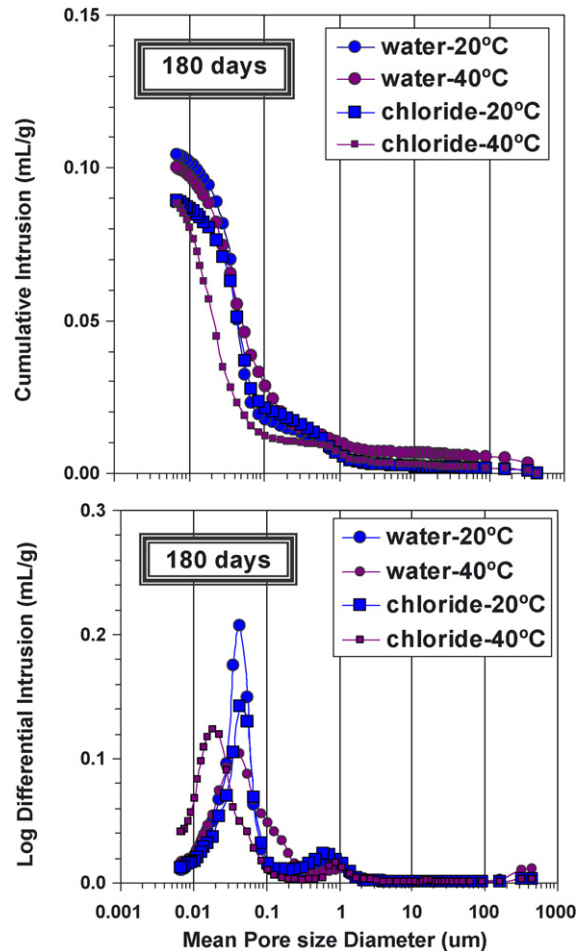


Fig. 6. Pore-size distribution curves of mortars samples after 180 days of immersion in de-ionized water and simulated chloride radioactive liquid waste (SCRLW) at the temperatures of 20 and 40 °C.

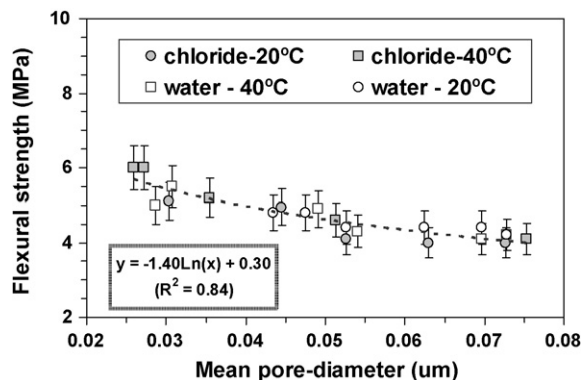


Fig. 7. Quantitative correlation between the flexural strength and mean pore-diameter.

Another important fact that derived from the proposed reaction mechanism is that katoite ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ) formation is inhibited. Katoite is detected in the mortar immersed in water at 40 °C (see Fig. 2(b)).

The formation of Friedel's salt within pores provoked a refinement of the porous microstructure, mainly at 40 °C, as can be seen in Fig. 6. The porosities of the belite mortars decreased after 180 days of immersion in the SCRLW solution, and the pore-size distribution shifted to lower pore-diameter values compared to those of specimens immersed in water for the same duration. The temperature of 40 °C caused an increase of pores in the range of 0.1–1 µm in diameter for the samples immersed in water.

This effect of the temperature is in agreement with that observed in a previous work [3] and similar mechanisms can be applied in this case: (i) the formation of katoite from low-density paste constituents (compare Fig. 2(a) and (b)) and (ii) the polymerization of C–S–H gel, which converge in the formation of larger capillary pores, resulting in the decrease of flexural strength detected in Fig. 1.

Finally, Fig. 7 presents an important quantitative correlation between the mean pore diameter and the flexural strength for mortars immersed in water and the SCRLW at 20 and 40 °C, which corroborate the modelling of the mechanism involved during the immersion of the belite mortars in the SCRLW.

#### 4. Conclusions

- According to the Koch–Steinegger test, the FABC-2-W cement mortar can be catalogued as resistant against the simulated chloride radioactive liquid waste at the concentration and experimental conditions here studied.
- The ingress of chloride into the microstructure of the FABC-2-W cement mortar caused the formation of non-expansive Friedel's salt inside the pores, mainly at 40 °C.
- The mechanism of Friedel's salt formation is via ionic  $2\text{Cl}^-/\text{SO}_4^{2-}$ -exchange in the basal space of the monosulphate-AFm type, inhibiting the formation of katoite.
- As a consequence, the porous microstructure was denser and the flexural strength increased. This effect was faster at the temperature of 40 °C.

- Important quantitative correlations between microstructural parameters, such as the mean pore diameter, and macrostructural mechanical strength are found.

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