

Effect of temperature on the durability of class C fly ash belite cement in simulated radioactive liquid waste: Synergy of chloride and sulphate ions

A. Guerrero, S. Góñi, V.R. Allegro

Eduardo Torroja Institute for Construction Science (CSIC), C/Serrano Gábarche, 4, 28033 Madrid, Spain

ABSTRACT

The durability of class C fly ash belite cement (FABC-2-W) in simulated radioactive liquid waste (SRLW) rich in a mixed sodium chloride and sulphate solution is presented here. The effect of the temperature and potential synergic effect of chloride and sulfate ions are discussed. This study has been carried out according to the Koch-Steinberger test, at the temperature of 20 °C and 40 °C during a period of 180 days. The durability has been evaluated by the changes of the flexural strength of mortar, fabricated with this cement, immersed in a simulated radioactive liquid waste rich in sulfate (0.5 M), chloride (0.5 M) and sodium (1.5 M) ions - catalogued like severely aggressive for the traditional Portland cement - and demineralised water, which was used as reference. The reaction mechanism of sulphate, chloride and sodium 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 chloride binding and formation of Friedel's salt was inhibited by the presence of sulphate. Sulphate ion reacts preferentially with the calcium aluminate hydrates forming non-expansive ettringite which precipitated inside the pores; the microstructure was refined and the mechanical properties enhanced. This process was faster and more marked at 40 °C.

Keywords:

Fly ash belite cement
Durability
Synergy
Chloride + sulphate waste
Microstructure

1. Introduction

This work is in the durability research plan carried out in our laboratory on different cement-based materials, against the very concentrated salts that accompanied the simulated radioactive liquid waste (SRLW) of low level waste (LLW) and medium level waste (MLW). In particular, we presented here the effect of the temperature and potential synergic effect of chloride and sulphate ions on the durability of specific fly ash belite cement, here named (FABC-2-W), of low energy, low pH and low heat of hydration.

For Portland concrete, the degradation caused by external sulphate attack is based on chemical reactions, which produce the precipitation of expansive compounds such as: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot (\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$), thaumasite ($\text{Ca}_3[\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot (\text{SO}_4)_3$) or mixtures of these phases. Portlandite ($\text{Ca}(\text{OH})_2$) is the main source of Ca^{2+} ion, and hydrated monosulphate-calcium-aluminate ($[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot (\text{SO}_4) \cdot 2\text{H}_2\text{O}$) is the source of aluminate ions.

The aggressiveness of chloride is lower than that of sulphate ion, due to the chemical bounded compounds are not expansive. Chloride chemically reacts with the aluminate of hydrated phases of Portland concrete such as monosulphates ($\text{SO}_4\text{-AFIT}$) to form Friedel's salt: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$; chloro-sulfate AFm phase, called Kuzel's salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$). Another oxychloride compounds ($x\text{Ca}(\text{OH})_2 \cdot y\text{CaCl}_2 \cdot z\text{H}_2\text{O}$) can be also formed in the presence of concentrated chloride salts.

The chloride and sulphate synergy are known in the case Portland-based-concretes exposed to sea water environments: the presence of chloride limited the sulphate attack, due to the increase of solubility of portlandite ($\text{Ca}(\text{OH})_2$) and the formation of hydrated CaCl_2 compounds. Others authors noticed that the presence of sulphate decreased the binding capacity of chloride ion, inhibiting the formation of Friedel's salt.

Goni studied the durability of hydrated portland cement pastes containing up to a 30% of a Spanish ground copper slag (CuGS) in an aggressive solution ($\text{Cl}^- + \text{SO}_4^{2-}$). They pointed that the non-aggressiveness of sulphate in the presence of chloride ion is due to the preferential diffusion process of Cl^- and Na^+ ions versus sulphate ions. It seems that the high NaCl content in the pore solution activates the slag pozzolanic reactivity, leading to the formation of hydrated aluminates of layered structure, which are subsequently transformed into Friedel's salt via

OH/Cl ionic exchange inside the interlayer space. These processes decrease the porosity of the materials, thus increasing their flexural strengths.

However, the durability behaviour of belite-based-cements is different from the one of Portland cements. According to previous durability studies carried out on specific fly ash belite cement in simulated radioactive liquid waste, which was very rich in sodium sulphate (0.5 M), expansive effects were not evidenced; on the contrary, 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 10 times, which promoted an alkaline activation of cement and the densification of the microstructure.

The durability of FABC-2-W was also excellent in SRLW rich in NaCl (0.5 M). In this case, the ingress of chloride into the microstructure of the FABC-2-W cement mortar caused the formation of non-expansive Friedel's salt ($\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$), inside the pores, mainly at 40 °C. The mechanism of Friedel's salt formation was via ionic $2\text{Cl}^- / \text{SO}_4^{2-}$ exchange in the interlayer space of the monosulphate-AFm type.

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 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 μm) 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.

Nevertheless, the aforementioned conversion caused by the temperature of 40 °C disappeared when the FABC-2-W mortar samples were immersed in simulated radioactive liquid waste, which was very rich in sodium sulphate 0.5 M or in sodium chloride 0.5 M. That was due to the precipitation of ettringite, in the case of sulphate, or Friedel's salt, in the case of chloride ion, from the hydrated calcium-monosulpho-aluminate, which inhibited the formation of katoite.

The main aim of this work is to establish the chloride and sulphate potential synergy and how it would affect the previous durability results at the temperature of 20 °C and 40 °C. The same experimental methodology was applied: testing the flexural strength of mortar samples immersed at the temperature of 20 °C and 40 °C during a period of 180 days, in a simulated radioactive liquid waste rich in sulphate (0.5 M), chloride (0.5 M) and sodium (1.5 M) ions, and demineralised water, which was used as reference. The reaction mechanism of sulphate, chloride and sodium ions with the mortar was evaluated by scanning electron microscopy (SEM), porosity and pore-size distribution, and X-ray diffraction (XRD). The results were compared with those, previously published [8,9].

The pH of the pore solutions was estimated by dissolving 1 g of powdered sample in 4 mL of demineralised water. The mixture was maintained for 1 day at ambient temperature, after which time the solid was filtered and the liquid was analysed. The pH was measured with a combined electrode for the pH range 0-14.

2. Experimental

The FABC-2-W cement 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, cement and mortar characterization can be consulted in Refs.

The FABC-2-W cement mortar was prepared with sand (a-quartz) to cement ratio of 3 and demineralised water to cement ratio of 0.65. For workability reasons, an organic additive (com-

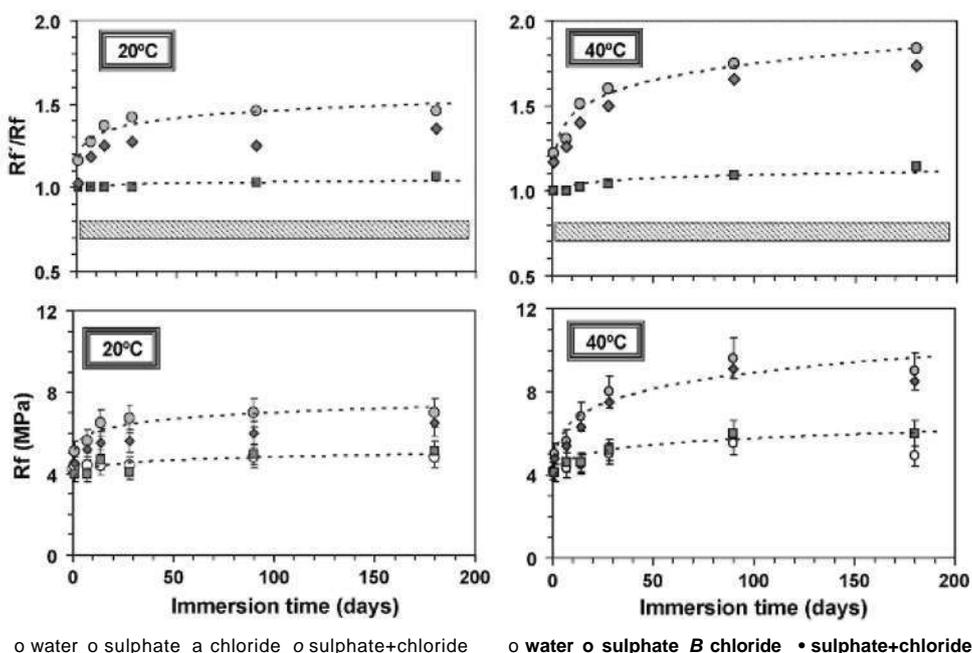


Fig. 1. Flexural strength and corrosion index (R_f/R_f) of mortar samples versus time, R_f = strength after immersion in the SRLW; R_f = strength after immersion in water.

Table 1

Regression equations obtained at 20 °C and 40 °C for the flexural strength and corrosion index changes with time of the FABC-2-W mortar immersed in different SRLW.

Types of SRLW	20 °C		40 °C	
	Rf	Ic	Rf	Ic
Sulphate	$j/ = 5.2x^{0.066}$	$j/ = 1.2x^{0.047}$	$y = 4.8x^{0.13}$	$y = 1.2x^{0.084}$
Sulphate + chloride	$y = 4.5x^{0.067}$	$j/ = 1.1x^{0.048}$	$y = 4.6x^{0.13}$	$y = 1.1x^{0.081}$
Chloride	$j/ = 3.9x^{0.049}$	$j/ = 0.98x^{0.042}$	$j/ = 3.9x^{0.081}$	$y = 0.97x^{0.025}$

mercial 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 x 1 cm x 6 cm prismatic specimens and compacted by vibration. After 2 days at 100% of 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 suspended and immersed in the simulated radioactive liquid waste rich in sulphate (0.5 M), chloride (0.5 M) and sodium (1.5 M) ions. These samples were stored in sealed plastic bottles at 20 °C and 40 °C for periods of 1, 7, 14, 28, 90 and 180 days. The volume of SRLW was 800 ml per 6 samples. Similar groups of 6 samples were stored at two tempera-

tures in demineralised water (used as a reference). After each period of time and prior to make the characterization study, the samples were washed three times with demineralised water to eliminate the excess of SRLW on the surface of the samples.

X-ray diffraction patterns were recorded on a Philips PW-1730 diffractometer, which used a graphite monochromator and Cu K α 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 (JEOL Ltd., Tokyo, Japan) equipped with an Oxford ISIS model EDX spectroscopy module (Oxford University, Oxford, UK). The samples were covered with carbon by sputtering. SEM/EDX semiquantitative analyses were made with an accelerating voltage of 20 kV and a reference current of 300 μ A on powder samples for determining the alkaline, alkaline-earth, iron oxides, alumina, silica and sulphur content. The EDX microanalysis has been carried out in spot mode over each different crystalline phase from areas of approximately 300 nm, given the detection limit of 0.2%.

3. Results and discussion

Fig. 1 shows the changes in flexural strength caused by the immersion of FABC-2-W mortar samples in demineralised water

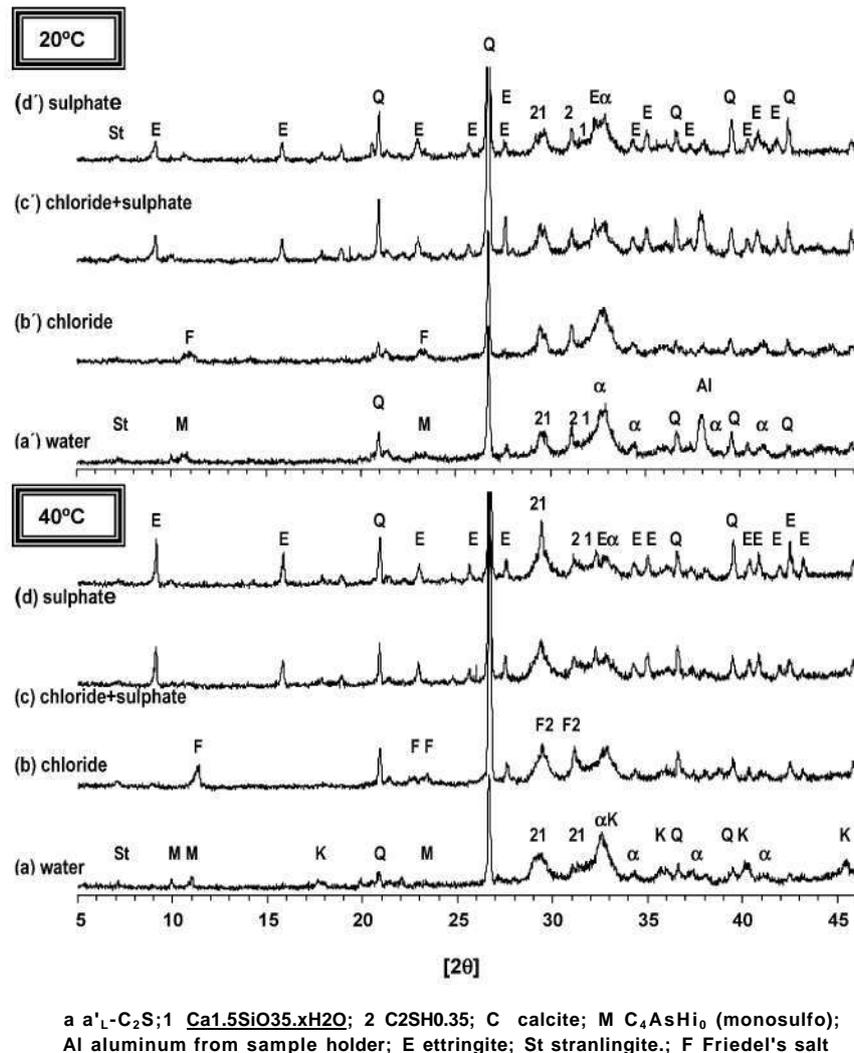


Fig. 2. XRD patterns of mortar samples after 180 days of immersion in different SRLW. Influence of temperature.

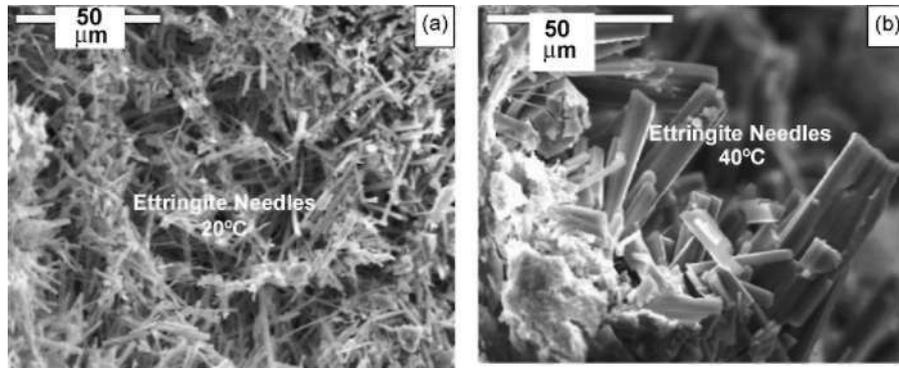


Fig. 3. SEM images of ettringite needles growing on the external coat covering the mortars after 180 days of immersion in sulphate + chloride SRLW at (a) 20 °C; (b)40°C.

and in SRLW solution (mixture of sodium chloride 0.5 M and sodium sulphate 0.5 M) at the two temperatures considered (20 °C and 40 °C). Previous published results corresponding to NaCl 0.5 M and Na₂SO₄ 0.5 M attack have been also included for comparison. Each value represents the average of six measurements, and the bars represent the standard deviation of the mean values. Time 0 in the figures correspond to samples cured for 7 days at 40°C in water, before starting the potential attack.

At 20°C, the flexural strength values of mortar immersed in the mixed NaCl + Na₂SO₄ SRLW are located between those of NaCl and Na₂SO₄; those of NaCl are the lowest and those of Na₂SO₄ the highest.

The influence of the temperature was manifested by faster and strong gain of strength; the difference between the values of the mixed NaCl + Na₂SO₄ and Na₂SO₄ SRLW almost disappeared. In fact, the mechanical strength of the mortar samples immersed in the SRLW solutions increased with time according to a potential function, where the exponent of the equation (related to the rate of gain of strength) was near two times higher respected to that of 20 °C (see Table 1).

According to the Koch-Steinberger test [19], the criterion to classify a material as resistant or durable in a specific aggressive medium is that the corrosion index (Ic) (relative strength of aggressive-solution-stored samples (Fs') to water-stored ones (Fs)) must be higher than 0.7. As shown in Fig. 1, the corrosion index values increased with time, according to a potential function with the exponent about two times higher at 40 °C (see Table 1). These results suggest that the FABC-2-W can be classified as durable or resistant to the mixed sodium chloride and sodium sulphate SRLW attack, during the period of time and experimental conditions of this work.

The presence of sulphate in the mixed SRLW caused a positive synergy from the flexural strength point of view. In other words, sulphate promoted preferential microstructural changes

compared with those promoted by chloride ion, from which the gain of strength was produced. This was more appreciated at the temperature of 40°C.

In fact, the diffusion of chloride and sulphate ions into the mortars caused the preferential formation of ettringite (3CaO-AI₂O₃-3CaSO₄-32H₂O) within pores as observed through XRD (Fig. 2(c)) and SEM analyses (Figs. 3 and 4). The Friedel's salt (Ca₄[Al(OH)₆]2-Cl₂-5H₂O) peaks, which appeared mainly at 40 °C in the NaCl SRLW (Fig. 2(b)), are not present in diagram (c).

From these results one can deduce that the presence of sulphate inhibited the formation of Friedel's salt, as in the case of Portland cement. Chloride ions are mainly bounded as CaCl₂-2H₂O in the external coat formed on the surfaces of mortar samples together with calcite (CaCO₃) and ettringite, and also were retained in the paste, as the EDX analysis demonstrated (Fig. 5).

The main differences observed at 40°C were: (i) the inhibition of katoite (Ca₃Al₂(SiO₄)(OH)₈) (appeared in the samples immersed in water (Fig. 2(a))), (ii) the higher intensity of the ettringite and Friedel's salt XRD-peaks, which suggest higher amount of both ettringite and Friedel's salt (compare Fig. 2(b)-(d) with (b')-(d')); (iii) the precipitation of bigger crystals of ettringite (compare Fig. 3(a) and (b)). Details of the ettringite crystals growing inside pores after 180 days of immersion are given in Fig. 4(a)-(c).

Chloride and sodium ions are present mainly in the paste, as showed in Fig. 5, where the Al/Ca and Si/Ca atom ratios are plotted vs Cl/Na atom ratio. The corresponding microanalyses of ettringite needles growing inside pores are also included for comparison.

Another interesting effect caused by the ingress of the mixed chloride and sulphate SRLW is the increase of the pore-solution pH values (Fig. 6) compared with those of mortar samples immersed in water (from 11.2 to 12.5 at 20°C and from 11.5 to 12.6 at 40 °C). This increase was also produced in the case of NaCl and Na₂SO₄ SRLW and the same explanation could be given: the ettringite formation via dissolution of the hydrated calcium-monosulpho-

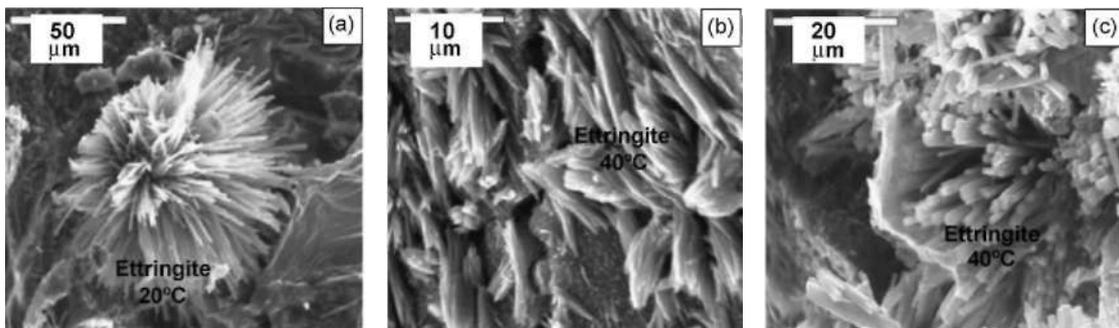


Fig. 4. SEM images of ettringite crystals of different morphologies growing inside pores after 180 days of immersion in sulphate* chloride SRLW.

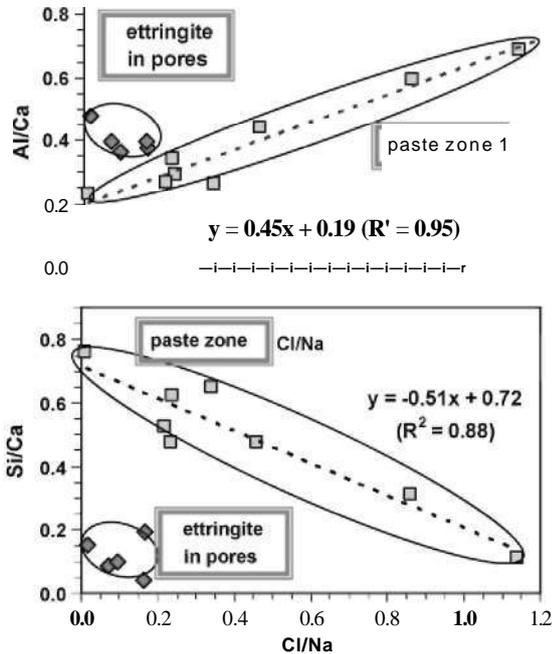


Fig. 5. Al/Ca and Si/Ca atom ratios versus Cl/Na atom ratio of paste zones and ettringite needles growing inside pores.

aluminate ($\text{Ca}_4[\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which liberated OH^- to the pore-solution [8]. The strong increase of the pH promoted an alkaline activation of cement hydration and subsequent densification of the microstructure.

In fact, the microstructure densification can be observed in Fig. 6, where the mean-pore-diameter of FABC-2-W mortars after 180 days of immersion in the different types of SRLW are given. The mean-pore-diameter values decreased near 50% - irrespective of the kind of SRLW - compared with the value of mortar immersed

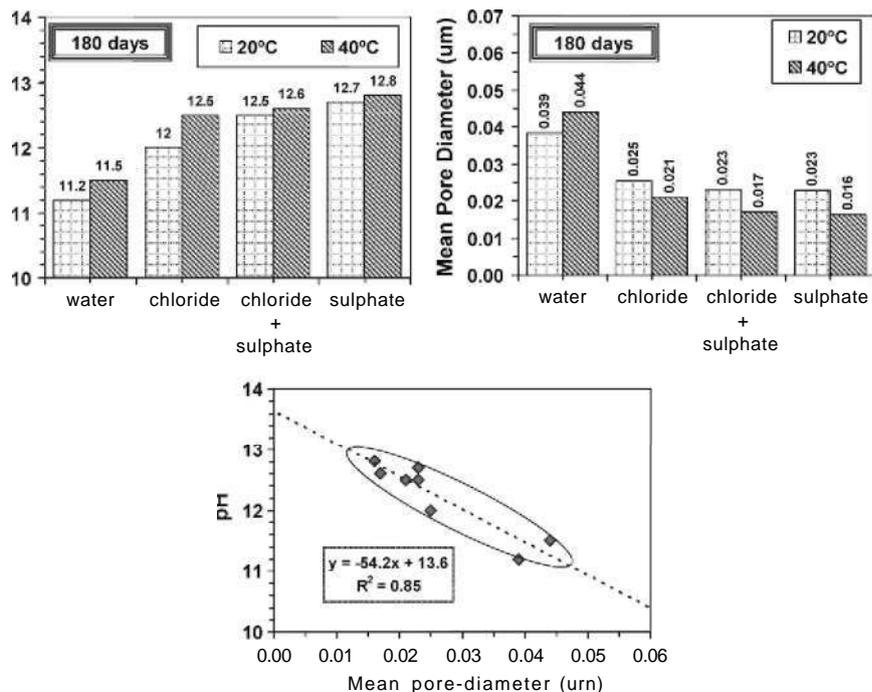


Fig. 6. Changes of the pH of the simulated pore solution and mean-pore-diameter of mortar samples after 180 days of immersion in demineralised water, chloride, chloride + sulphate and sulphate SRLW. Influence of the temperature and quantitative correlation.

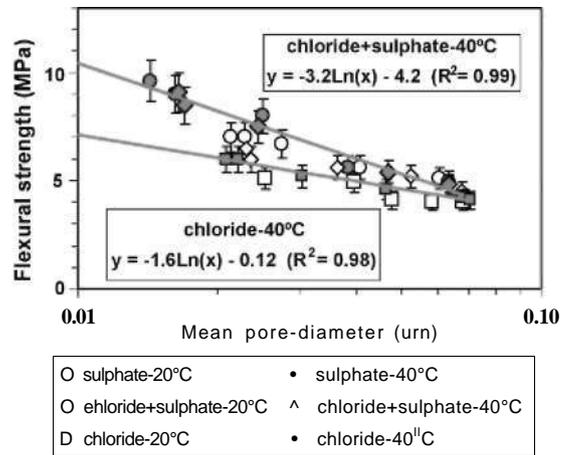


Fig. 7. Quantitative correlation between the flexural strength and mean pore-diameter of mortar samples immersed in chloride, chloride + sulphate and sulphate SRLW.

in water. This effect was produced at the two temperatures, 20 °C and 40°C.

The increase observed in water at 40°C was not observed in the rest of the SRLW, where the higher temperature caused the lower mean-pore-diameter values. These porosity results corroborated the hypothesis concerning that katoite formation, from the low-density paste constituents, increased the mean-pore-diameter. In the case of the SRLW, this was not produced because of the inhibition of katoite, which was promoted by the preferential reaction of calcium aluminates with sulphates to form ettringite, in the case of Na_2SO_4 and $\text{NaCl} + \text{Na}_2\text{SO}_4$ SRLW (Fig. 2(c) and (d)) or Friedel's salt formation in the case of NaCl SRLW (Fig. 2(b)).

The quantitative inverse linear correlation obtained between values of pH of pore-solution and mean pore-diameter (Fig. 6) corroborated the mechanism proposed.

Furthermore, the consequence of all microstructure changes is the increase of the mechanical strength. As a result, important quantitative correlation between values of the mean-pore-diameter and flexural strength are obtained (Fig. 7), which corroborates the modelling of the mechanism involved during the immersion of belite mortars in the mixed chloride and sulphate SRLW.

The higher slope of mixed chloride and sulphate SRLW (3.2) compared with that obtained without sulphate (1.6) clearly indicate the sulphate synergy, which was stronger at 40 °C. In other words, the porous microstructure changes, promoted by the presence of sulphates, caused an increase of two times the flexural strength values respect those obtained without sulphate.

4. Conclusions

- According to the Koch-Steinegger test, the FABC-2-W cement mortar can be catalogued as resistant against the mixed chloride and sulphate simulated radioactive liquid waste of the concentration and experimental conditions here considered.
- The ingress of chloride and sulphate ions into the microstructure of the FABC-2-W cement mortar caused the formation of non-expansive ettringite inside the pores, inhibiting the Friedel's salt formation.
- Chloride ions are bounded as $\text{CaCl}_2\text{-H}_2\text{O}$ mainly in the external coat of the mortars and retained in the paste without a defined morphology.
- The pH increase of the pore solution was associated to the ettringite formation via monosulfo dissolution, which inhibited 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 parameter as the mean-pore-diameter, pH of the pore-solution and macrostructural mechanical strength are found.
- The sulphate and chloride synergy are manifested by: (i) the inhibition of Friedel's salt formation; (ii) the porous microstructure changes, promoted by the presence of sulphates, caused an increase of two times the flexural strength values respect those obtained without sulphate.

Acknowledgements

Funding for the present research was provided by the Minister of Science and Technology under Project no. MAT 2002-04023-CO3.

The authors wish to thank the Thermal Station of Ceres (Catalonia) for the fly ash supplied.

References

- A. Guerrero, M^oS. Hernandez, S. Goni, Durability of cement-based materials in simulated radioactive liquid waste: effects of phosphate, sulphate and chloride ions, *J. Mater. Res.* 13 (8) (1998) 2151-2160.
- A. Guerrero, M^oS. Hernandez, S. Goni, The role of the fly ash pozzolanic activity in simulated sulphate radioactive liquid waste, *Waste Manage.* 20 (2000) 51-58.
- A. Guerrero, S. Goni, M^oS. Hernandez, Thermodynamic solubility constant of Ca(OH)_2 in simulated radioactive sulfate liquid waste, *J. Am. Ceram. Soc.* 83 (4) (2000) 882-888.
- A. Guerrero, M^oS. Hernandez, S. Goni, Effect of simulated radioactive liquid waste on the microstructure of cementitious materials: Portlandite orientation and saturation factors in the pore solution, *J. Am. Ceram. Soc.* 83 (11) (2000) 2803-2808.
- S. Goni, A. Guerrero, M^oS. Hernandez, Spanish LLW and MLW disposal: durability of cemented materials in (Na, K)Cl simulated radioactive liquid waste, *Waste Manage.* 21(2001)69-77.
- A. Guerrero, S. Goni, Efficiency of a blast furnace slag cement for immobilizing simulated borate radioactive liquid waste, *Waste Manage.* 22 (2002) 831-836.
- S. Goni, A. Guerrero, Efficiency of fly ash belite cement and zeolite matrices for immobilizing caesium, *J. Hazard. Mater. B137* (2006) 1608-1617.
- A. Guerrero, S. Goni, V.R. Allegro, Resistance of class C fly ash belite cement in simulated sodium sulphate radioactive liquid waste attack, *J. Hazard. Mater.* 161(2009)1250-1254.
- A. Guerrero, S. Goni, V.R. Allegro, Durability of class C fly ash belite cement in simulated sodium chloride radioactive liquid waste: influence of the temperature, *J. Hazard. Mater.* 162 (2009) 1099-1102.
- FP. Glasser, J. Marchand, E. Samson, Durability of concrete—degradation phenomena involving detrimental chemical reactions, *Cem. Concr. Res.* 38 (2008) 226-246.
- Q. Yuan, C. Shi, G. De Schutter, K. Audenaert, D. Deng, Chloride binding of cement-based materials subjected to external chloride environment—a review, *Constr. Build Mater.* 23 (2009) 1-13.
- K. Byfors, Chloride binding in cement paste, *Nordic Concr. Res.* 5 (1986) 27-38.
- O. Wowra, M.J. Setzer, in: M.J. Setzer, R. Auberg (Eds.), Sorption of Chlorides on Hydrated Cements and C_3S Pastes, Frost Resistance of Concrete, E&FN Spon, London, 1997, pp. 147-153.
- W.R. Holden, C.L. Page, N.R. Short, in: A.P. Crane (Ed.), The Influence of Chlorides and Sulphates on Durability, Corrosion of Reinforcement in Concrete Construction, Ellis Horwood Ltd., Chichester, 1983, pp. 143-150.
- S. Goni, M2P. Lorenzo, J.L. Sagrera, Durability of hydrated Portland cement with copper slag addition in $\text{NaCl} + \text{NaSO}_4$ medium, *Cem. Concr. Res.* 24 (8) (1994) 1403-1412.
- S. Goni, A. Guerrero, Modifications of the C-S-H gel by hydration at 40 °C of two types of fly ash belite cements, *J. Am. Ceram. Soc.* 91 (1) (2008) 209-214.
- S. Goni, A. Guerrero, SEM/EDX characterization of the hydration products of belite cements from coal fly ash class C, *J. Am. Ceram. Soc.* 90 (12) (2007) 3915-3922.
- A. Guerrero, S. Goni, I. Campillo, A. Moragues, Belite cement clinker from coal fly ash of high Ca content, optimization of synthesis parameters, *Environ. Sci. Technol.* 38(12) (2004) 3209-3213.
- A. Koch, H. Steinegger, A rapid test for cements for their behaviour under sulphated attack, *Zement-Kalk-Gips* 7 (1960) 317-324.