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## Study of the pore solution and the microstructure of mineral additions blended cement pastes

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### Abstract

In this paper, the influence of mineral additions on the microstructure and the chemical composition of the pore solution of cementitious materials is investigated. For this purpose, hardened cement pastes based on Portland cement CEM I are used. In order to study the influence of the cementitious materials composition on their microstructure and pore solution, a part of the cement is substituted by different mineral additions (limestone filler, fly ash, blast furnace slag and silica fumes). Experimental tests covered measurement of chloride diffusion coefficient by migration test and water and mercury porosimetry. Furthermore, pore solutions are extracted by pressing from cement pastes and analyzed by ionic chromatography. Results show that the substitution of cement by mineral addition modifies the total porosity and the pore sizes distribution of the blended cement pastes tested. Chemical analyses showed that all the tested pore solutions are mainly composed by sodium and potassium. A significant concentration of divalent ions, such as sulfates and calcium, is also noticed. The substitution of cement by mineral addition also significantly modifies the pore solution of cement pastes. In fact, a substitution of cement by 10% of silica fume decreases the alkalis concentrations and increases the sulfates and calcium ones. Thus, the divalent species ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) should be taken into account for the chloride diffusion modelling unlike the current models of the literature. Results of this chemical investigation could be used as initial and boundary conditions in the modeling of aggressive species transport through porous construction materials.

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*Keywords:* cement pastes, microstructure, pore solution, extraction, chemical analyses.

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## 1. Introduction

The durability of the reinforced concrete structures is conditioned by the mechanical behaviour of materials used as well as their physico-chemical one against aggressive species attacks. This latter concerns especially the transfer of these aggressive species in the material porosity such as the diffusion of marine salt, the carbonation, the external sulfates attack, etc... It is thus necessary to understand all the mechanisms which occur during the transfer of these species.

These transfer mechanisms depend on the physical and chemical interactions of aggressive species with the cementitious matrix and the other species in the pore solution. In order to well understand these transfer phenomena, a prior chemical investigation of the pore solution composition is necessary.

Among the important parameters describing the pore solution, one can distinguish the ionic strength, the pH, the concentration of each component and the redox potential to determine the oxidation state of the multivalent elements.

A study of the chemical composition of the pore solution, made by Andersson et al. [1], showed that the pore solution of the cementitious materials is influenced by the type of cement and the mineral addition used. For this purpose, they analyzed pore solutions extracted from seven different cement pastes with a W/B (Water/Binder) of 0.5. The extraction method firstly described by Longuet et al. [2] was used. The authors distinguished that the pore solution is composed mainly by sodium, potassium, calcium and sulfates. A significant difference is noticed between the pore solution extracted from paste 1 (containing Portland cement produced in Sweden), paste 2 (Portland cement produced in France) and paste 3 (Cement resistant to sulfates). The paste manufactured by cement rich in silica contains the weakest concentration of  $\text{Na}^+$  and  $\text{K}^+$  while the pastes manufactured by cement rich in aluminium and fly ash are very low in calcium. In fact, other researchers studied the influence of fly ash on the pore solution of cementitious material [3-6]. Results showed that the alkalinity of pore solution decreases as the silica content of fly ash increases, on the other hand, it increases as the calcium and the alkali content of fly ash increases.

Nevertheless, the studies on the chemical composition of the pore solution of cementitious materials are still relatively rare. In this context, the experimental work presented in this paper has two objectives. The first one is to study the effect of mineral addition on the microstructure of cement paste and the second one is to analyze the chemical composition of the pore solution of cement pastes

## 2. Experimental protocol

### 2.1. Materials

Ordinary Portland cement (CEM I 52.5 N in respect with European standard NF EN 197-1) is used. The fractions mass of the principal clinker phases provided by the manufacturer (Calcia, Bussac-France) are 65%  $\text{C}_3\text{S}$ , 13%  $\text{C}_2\text{S}$ , 7%  $\text{C}_3\text{A}$ , 13%  $\text{C}_4\text{AF}$  and 4.9% gypsum. The chemical composition of this cement is given in Table 1. Furthermore, Different mineral additions were chosen. They were used as substituent of the cement as follows: 30% of fly ash (FA30), 75% of blast furnace slag (S75), 25% limestone filler (LF25) and 10% silica fume (SF10). A reference cement paste with 100% Portland cement is also manufactured and is called (PC).

Table 1. Chemical composition of materials used.

Composition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Chlorides	Density	Blaine fineness (m <sup>2</sup> /kg)
CEM I(wt.%)	64.20	20.50	5.00	3.90	2.50	0.29	0.05	1.40	3.80	405
LF (wt.%)	98.80	0.30	-	-	0.01	0.01	0.001	0.001	2.70	498
FA (wt.%)	5.10		85.53		0.59	2.00	1.95	0.013	2.21	405
Slag (wt.%)	41.50	33.30	12.50	0.40	0.50	-	-	-	2.89	450
SF (wt.%)	1.00	89.00	-	-	2.00	-	1.00	0.10	2.24	-

The objectives of the choice of these additions are:

75% of the slag bring major modifications to the pore solution of cementitious materials, particularly the physical

fixation of chloride ions at the walls of the pores and the layers of C-S-H during migration tests [7].

Fraay et al. [8] showed that in the case of use of 30% fly ash, only 50% of the amount used react at the end of the first year.

According to Perraton et al. [9], the use of silica fume is from 5 to 10% of substitution in mass of cement. With more than 10% the replacement is useless and the performance of the material decreases.

Cement pastes with a medium W/B are chosen for this work in order to facilitate the pore solution extraction. A performance-based approach [10] was used in order to determine the amount of substitution for each mineral addition. This method takes into account the pozzolanic index of each addition. The compositions of the cement pastes used are given in Table 2.

Table 2. Composition of cement pastes used.

Component (kg/m <sup>3</sup> )	PC	FA30	S75	LF25	SF10
A/C	0.00	0.43	3.00	0.35	0.11
W/B	0.50	0.40	0.44	0.38	0.47

## 2.2. Tests and procedures

### 2.2.1. Water and mercury porosimetry

Water porosity is determined on discs of 65mm diameter and 10mm thick, following a hydrostatic weighing according to the French standard NFP 18-459. This method is very simple and practicable on a wide variety of materials.

Mercury intrusion porosimetry (MIP) performed on cubes of about 1cm<sup>3</sup> samples, allows the measurement of pore sizes distribution leading to the critical pore diameter. This test is based on the physical principle that a non-wetting liquid is injected in opened pores under a controlled pressure. The method is based on the Laplace law linking the mercury injection pressure to the diameter of the pore. Considering the pores as cylindrical, the diameter is calculated Washburn law [11].

### 2.2.2. Migration test

The objective of this test is to determine the effective diffusion coefficient at steady state regime. The chloride diffusion is accelerated by applying an electric field of 300 V/m between the two faces of the sample (disc of 65mm diameter and 10 mm thick, surrounded by an epoxy resin ring) A more detailed description of the method used is given by Amiri et al. [12].

### 2.2.3. Extraction of pore solution and ionic chromatography

To extract the pore solution from the cement pastes, a device from OpiCAD<sup>®</sup> was used. For this purpose, a press piston is inserted above the cement paste sample (50mm diameter and 70mm height) placed in the cylindrical chamber which volume is of about 137.375 ml. The pressure necessary to extract the pore solution is applied using a hydraulic press.

The solution from the pores is collected through a channel located at the bottom of the device using a syringe to avoid any contact of the solution with air. The solution is kept at the refrigerator in a sealed flask

Analyse of pore solutions is performed by ionic chromatography at latest 24 hours after their extraction in order to avoid a possible carbonation. A dilution of 300 times is necessary to dose the sodium and potassium. However, to dose calcium and sulfates, the solutions are diluted 10 and 70 times respectively.

## 3. Results and discussion

### 3.1. Microstructure and chloride diffusion coefficient

Fig 1 shows the results of total porosity and chloride diffusion coefficient of each sample at the age of 9 months. The chloride diffusion coefficient is based on the chloride ion flux measured at the downstream of the sample. The effective chloride diffusion coefficient  $D_{\text{eff}}$  (m<sup>2</sup>/s) was calculated from (Eq.1) [13]

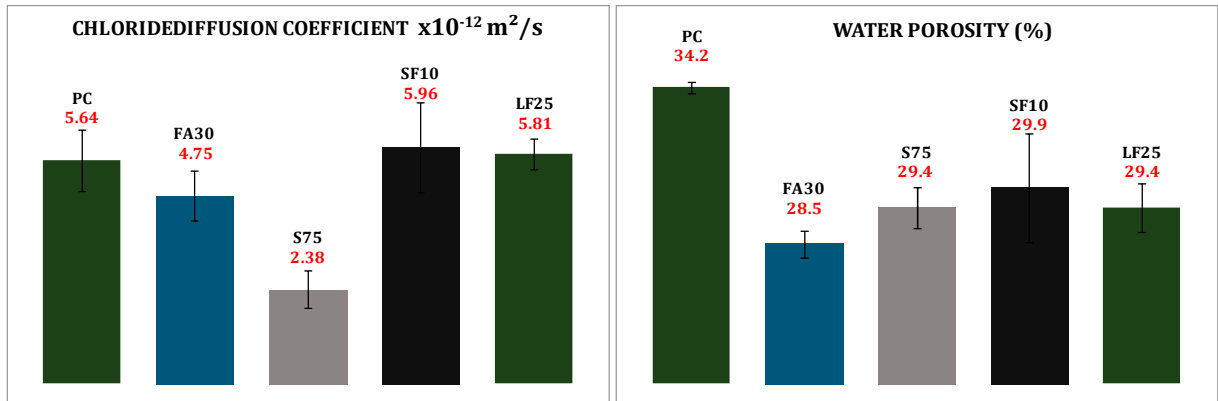


Fig. 1. Properties of the cement pastes tested.

$$D_{eff} = \frac{RT}{z_{Cl^-} F} \frac{L \Delta C}{E \Delta t} \frac{V_a}{AC_0} \left( 1 - e^{-\frac{z_{Cl^-} FE}{RT}} \right) \quad (1)$$

Where  $V_a$  ( $\text{m}^3$ ) is the volume of the downstream solution;  $\Delta C$  ( $\text{mol}/\text{m}^3$ ) is the increase of the chloride concentration in the downstream compartment during a migration time  $\Delta t$ ;  $A$  ( $\text{m}^2$ ) is the section of the sample.  $L$  ( $\text{m}$ ) is the thickness of the sample;  $C_0=500(\text{mol}/\text{m}^3)$  is the concentration of chloride ions in the upstream solution;  $E(V)$  is the potential difference applied at the sample terminals;  $F$ ,  $z_{Cl^-}$ ,  $R$  and  $T$  represent the Faraday constant, the valence of chlorides, the perfect gas constant and the absolute temperature (K).

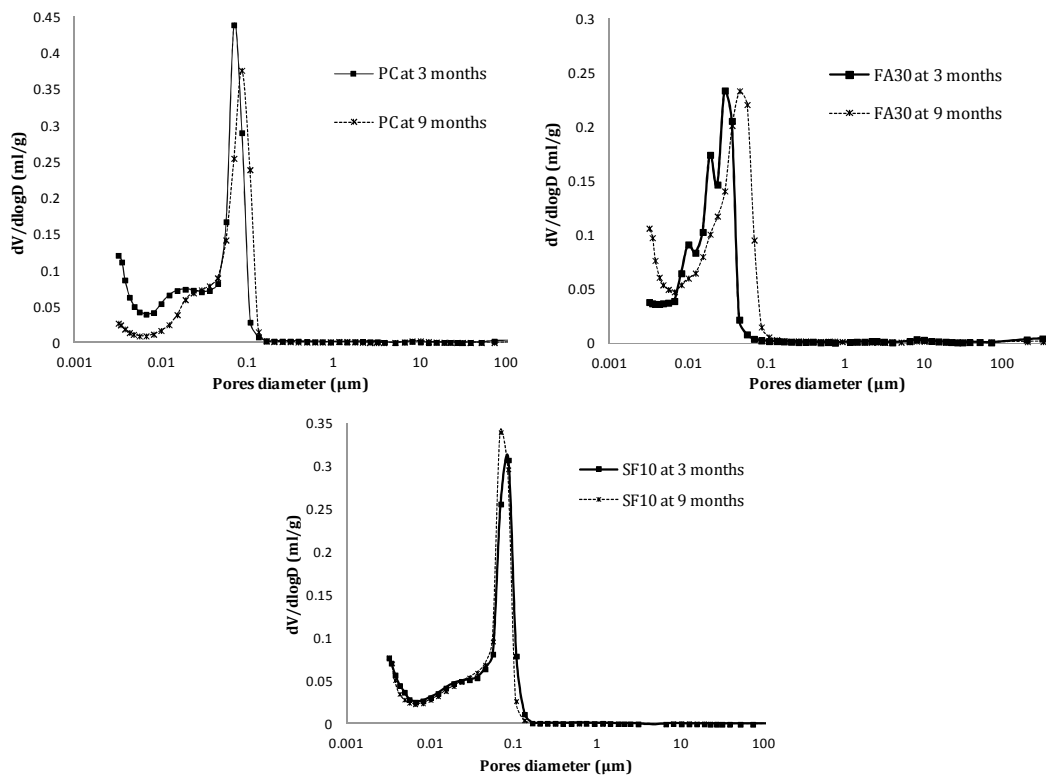


Fig. 2. Influence of mineral addition on the pore sizes distribution of the cement pastes tested.

Results show that the PC has the much higher water porosity compared to the other cement pastes tested. This is due to the W/B ratios of PC (0.5) that is higher than one of LF25, FA30, S75 and SF10 (0.38, 0.40, 0.44 and 0.47, respectively). The use of 75% of blast furnace slag decreases the critical diameter of the cement paste used [7]. This increases the fixation of chlorides in the layers of C-S-H, therefore, the chloride diffusion coefficient decreases.

Fig. 3 presents the evolution with time of the pore sizes distribution of each material. For this study, PC, FA30 and SF10 have been used. The materials were tested at two ages (3 and 9 months). Results show that the pore sizes distributions of cement pastes tested are globally monomodal. The critical diameters of cement pastes tested are relatively constant. We notice that between 3 months and 9 months, the hydration influences slightly the evolution of the pore sizes distribution mainly for FA30. This is due the pozzolanic reaction of fly ash and silica fume with Portland cement which generates dissolution of portlandite to form more C-S-H and modifies the microstructure of materials[14].

Compared to the volume of the pore solution extracted (7.886 ml, 8.045 ml and 9.194 for PC, FA30 and SF10) mentioned in the following section and the microstructure of the cement pastes (porosity, and pore sizes distribution), it should be underlined that these properties are not sufficient to estimate the yield of the extraction. More information is necessary such as tortuosity and constrictivity [15].

### 3.2. Chemical composition of the pore solution of the cement pastes tested.

In order to study the chemical composition of the pore solution, three materials were used (PC, FA30 and SF10). The solution was obtained by pressing and then analyzed using ion chromatography as previously mentioned. The obtained results are shown in Table 3. The pore solutions of the studied cementitious materials contain mainly sodium and potassium. A significant concentration of divalent ions such as sulfates and calcium was also observed. However, the magnesium concentration remains very low. The  $\text{OH}^-$  concentration was calculated by the electroneutrality equation. Results show that the substitution of cement by mineral additions decreases the calcium concentration because of the pozzolanic reaction which causes the dissolution of portlandite and the formation of more C-S-H [14]. Sodium and potassium concentrations of SF10 pore solution are the much lower. For this purpose, Urhan [16] showed that the pozzolanic reaction between silica fume and Portland cement is initiated by the attack of the microsilica surfaces by  $\text{OH}^-$  ions released in the pore solution. This leads to the adsorption of alkalis on the surfaces of silanol groups formed as consequence of the attack of the silica by  $\text{OH}^-$ . This is in accordance with  $\text{OH}^-$  concentration and pH value of SF10 that is lower than those of PC and FA30. Pore solutions of cement pastes tested contain chlorides, taking into count to the chlorides concentration in tap water, chloride amount provided by anhydrous components of the binder can be deduced.

Table 1. Chemical composition of pore solution of cement pastes tested.

	Na(mg/l)	K(mg/l)	Ca(mg/l)	SO4(mg/l)	Cl(mg/l)	Mg(mg/l)	OH(mg/l)	pH
<b>PC</b>	1173.974	4591.904	72.846	155.375	126.558	5.100	2818.942	12.830
<b>FA30</b>	984.551	4657.484	81.499	175.812	37.351	23.458	2775.980	12.600
<b>SF10</b>	226.312	413.537	488.597	639.473	58.644	-	507.380	12.330
<b>Tap water</b>	276.743	45.632	2124.957	42.739	28.467	-	-	-

## 4. Conclusion

In this paper, microstructure and pore solution of cement pastes blended with mineral addition are studied. Conclusions are summarized in the following:

Substitution of cement by mineral additions modifies the microstructure of the cement pastes. Furthermore, the

water porosity and the pore sizes distribution of materials are not sufficient to connect the global porosity and the critical diameter of the cementitious material to the fluid flow through porous media (permeability) and the pore solution extraction yield. More information are needed such as tortuosity and constrictivity.

The chemical composition of the pore solution was studied. It contains mainly sodium and potassium. Large differences were found between the pore fluid of the SF10 and the other hardened cement pastes used because of the pozzolanic reaction between silica fume and Portland cement initiated since the first hours of mixing as well as the chemical adsorption of alkalis on the negatively charged silanol groups.

The pore solution contains a significant sulfates and calcium concentration. These two species cannot be neglected in multispecies ionic transport models, unlike models of the literatures which are only based on the monovalent ions.

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