

Effect of blast furnace slag and silica fumes on the composition of the pore solution of cementitious materials.

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Abstract This paper presents the effect of the cement substitution by blast furnace slag and silica fumes in “green concretes” on the chemical composition of their pore solution. The latter is necessary to provide ionic transfer models with input data. Three types of hardened cement pastes were tested. Because of the lack of data in the literature dealing with the chemical composition of cementitious materials containing mineral addition, these pastes were manufactured using a Portland cement (CEMI) and two mineral additions (blast furnace slag and silica fumes). The results of the chemical analyses of the pore solutions obtained by ionic chromatography show a significative content of divalent ions (Calcium and sulfates). The reference cement paste contains 1,8 mmol/l of calcium and 1,6 mmol/l of sulfates. We have observed that the use of mineral addition significantly modifies the pore solution chemistry. Indeed, the substitution of the Portland cement by 10% of silica fumes increase the content of calcium to 12,2mmol/l and sulfates to 6,7 mmol/l. This chemical composition change causes modifications in pH and ionic strength that must be considered in the multispecies transfer and the thermodynamic equilibrium models.

Keyword Cementitious materials, Mineral additions, pore solution, chemical composition, durability.

I. INTRODUCTION

Despite the complexity of transfer phenomena of aggressive species in cementitious materials, several studies were conducted in order to better understand and predict their effects. Chloride ions, from seawater or de-icing salts, have an important impact on the durability of structures. The latter penetrate the concrete under a concentration gradient. Once the concrete rebars reached by these species with a critical concentration, they lose their passivation and the corrosion begins. This phenomenon was widely studied during the last decades in the world because of the high cost of maintenance caused by chlorides damage and the related economic issues [1, 2].

More recently, multispecies transfer modelling including the portlandite dissolution and the precipitation of Friedel’s and Kugel’s salts during chloride transfer were proposed [3]. Nevertheless, non-negligible differences between the experimental and numerical results were often observed. These differences are mainly due to the lack of data regarding the chemical composition of pore solutions of cementitious materials. Consequently, the models cannot be supplied correctly with input data. The most interesting study was conducted by Anderson *et al.* [4]. They analyzed pore solutions of seven cement pastes containing Portland cement and slag. However, their study targeted a limited number of monovalent and divalent ions.

This paper presents a chemical investigation of three cement pastes pore solutions using ionic chromatography technique. The studied cement pastes were manufactured with Ordinary Portland cement (CEMI) paste (named PCI with W/B ratio of 0.5), blast furnace slag (substitution of 75% of the CEMI: named S75 with W/B ratio of 0.44) and silica fumes (substitution of 10% of the CEMI: named S10 with W/B ratio of 0.47). The mineral addition substitution rates are taken at these values in order to be the most efficient regarding the materials properties. The pastes

compositions are obtained from concrete ones (equivalent performances approach) by removing the aggregate phase. The difference between the W/B ratios of the three pastes is due to the considering of the chemical activity of each addition in the paste formulation. The results of the chemical compositions allow: (i) to calculate the ionic strength of the pore solutions and, (ii) to better provide the multispecies transfer models with input data (Initial and boundary conditions).

II. TESTS AND PROCEDURES

A. Water and mercury porosimetry

Water porosimetry was measured by an under vacuum saturation and hydrostatic weighting following the French standard NFP 18-459.

The critical pore diameter and the pore size distribution were determined by mercury intrusion porosimetry (MIP). The tests were performed using an Autopore V9620 from Micromeritics®. This device allows the detection of pore diameters ranging between 0.003 μm and 360 μm .

B. Diffusion coefficient of chlorides

The effective diffusion coefficient of chlorides was determined by a migration test in steady state [5]. Its calculation is based on the chlorides flux through the sample, which the determination is based on the chloride concentration at the downstream of the sample.

C. Extraction and analysis of the pore solution

The pore solution extraction from the materials tested was performed with an OpiCAD® press device. For this purpose, a sample with a volume of 137cm³, was placed in a cylindrical chamber within the device. A piston was placed above the sample and allows applying the pressure, by means of a compression machine, necessary for the pore solution extraction. The best method to get the best yield consists of a loading by application of successive steps: 15 minutes loading step at a velocity of 0.02 MPa.s⁻¹ followed by a 5 minutes idle step [6,7] (to reach a strength around 150 MPa). Then, the obtained solutions were analyzed by ionic chromatography.

III. RESULTS AND DISCUSSION

A. Intrinsic properties of the materials studied

The results of the water porosity and the chlorides diffusion coefficient for the three hardened cement pastes tested are presented in Table 1. These results show that the total porosity of the PCI is higher than the other two pastes. The latter is mainly due to the W/B ratio, which is slightly higher for PCI than S75 and SF10. Furthermore, the results show that S75 has the smallest diffusion coefficient, which is due to the use of slag that refines the porosity [8] and decreases the pores critical diameter (0.008 μm), as shown in figure 1. This figure shows also monomodal pore size distributions obtained by MIP for the cement pastes tested. In addition, the use of slag increases the chemical and physical bounding of chlorides in the C-S-H layers and, thus, slows down the chloride diffusivity [9]. The critical pore diameters of the cement pastes tested are in accordance with the values of the diffusion coefficient presented in Table 1.

TABLE 1. Intrinsic properties obtained at the age of 1 year for the cement pastes studied

Materials	PCI	S75	SF10
Water porosity (%)	34.2 ± 0.2	29.4 ± 0.5	29.9 ± 1.3
D_{eff} (m ² /s) x10 ⁻¹²	5.64±0.78	2.38±0.47	5.96±1.13

Nevertheless, the substitution of the Portland Cement by 10% of silica fumes is expected to reduce the porosity and the critical pore diameter compared to PCI. However, the results obtained show that the critical diameter of PCI and SF10 are quite similar. This result can be explained by the way that the pastes are manufactured (without the use of plasticizer or vibration) leading to a non-optimized microstructure for the paste SF10.

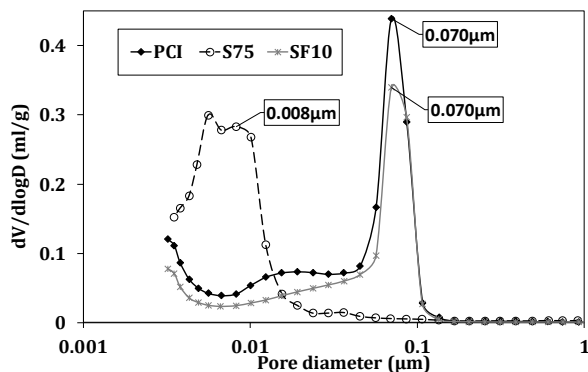


FIGURE 1. Pore size distribution measured by MIP at the age of 1 year for the cement pastes studied.

B. Chemical composition of the extracted pore solutions

Results obtained by ionic chromatography show that the sodium concentration of the pore solutions of PCI and S75 are close. However, the potassium concentration of S75 is lower than that of PCI (See figure 2). This difference is due to the chemical composition of the blast furnace slag, which is poor in potassium. Furthermore, a concentration decrease of about 5 times for the sodium and 11 times for the potassium is observed for SF10 compared to PCI. These differences are in good accordance, on the one hand, with the chemistry of the silica fumes that is mainly composed by silica and alkalis and, on the other hand, with the pozzolanic reaction of the silica fumes during which the silica dissolves in solutions with a high pH and forms negative charges. The latter are then neutralized by alkalis to form an alkali-silicate gel [10]. That is why the silicate ions in the pore solution are not analyzed. Their concentration is very low and does not affect the aggressive species transfer through the porosity.

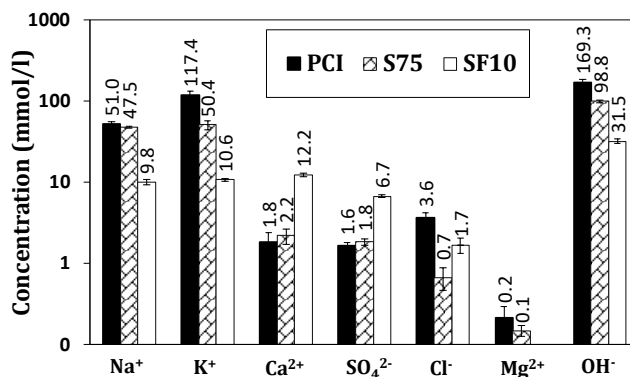


FIGURE 2. Ions concentrations in the cement pastes pore solutions at the age of 1 year.

An important concentration of calcium and sulfates were observed, especially for SF10 (12.2 mmol/l and 6.7 mmol/l, respectively). Even if the pozzolanic reaction of the silica fumes consume the calcium to form C-S-H, Andersson *et al.* [4] demonstrated that the concentration of calcium in cement pastes with silica fumes is higher than paste with only Portland cement or slag. Moreover, the high concentration of sulfates in SF10 can be explained, on the one hand, by the chemical

composition of the silica fumes rich with sulfates and on the other hand, by the hydration mechanisms of the silica fumes. Indeed, Lobo and Cohen [11] demonstrated that during the hydration of cement pastes with silica fumes, the ettringite formation is accelerated. After 48 hours, the alkalis content decreases and the ettringite formation slows down despite the presence of sulfates in the pore solution.

CONCLUSION

The study presented in this paper leads to the following conclusions:

For materials containing silica fumes (SF10), alkalis are absorbed at the silica surfaces and the concentrations of sodium and potassium in the pore solution are reduced by 5 and 11 times, respectively, compared to an ordinary Portland cement paste (PCI).

Divalent ions concentrations of the cement paste with silica fumes (SF10) are high: 12.2 mmol/l of calcium and 6.7 mmol/l of sulfates.

The blast furnace slag did not contain potassium; its concentration for S75 is lower (2 times) compared to PCI.

It is necessary to consider the effect of silica fumes and blast furnace slag on the pore solution for: (i) the cure solutions to avoid leaching and, (ii) the input data for the transfer modelling.

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