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A quantitative study of the influence of non-expansive sulfoaluminate cement on the corrosion of steel reinforcement

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Abstract

The corrosion resistance of steel reinforced mortar specimens made from non-expansive sulfoaluminate cement was investigated using Ordinary Portland Cement (OPC) specimens as reference. The specimens were prepared and exposed in three different environments, namely, continuous exposure in tap water, continuous exposure in 3.5% NaCl solution and intermittent exposure in 3.5% NaCl solution. The steel weight loss (WL) and the half cell potential (HCP) were measured vs. exposure time, up to the age of 12 months. Pore solution extraction and analysis and porosity determination were also performed. In continuous exposure in tap water, sulfoaluminate cement provided adequate protection against corrosion. In continuous exposure in 3.5% NaCl solution, a higher corrosion was observed. In the case of intermittent exposure in 3.5% NaCl solution, the simultaneous action of free chlorides and oxygen, as well as the low pH of the pore solution, resulted in the depassivation of steel reinforcement and led to severe corrosion effect. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfoaluminate; Mortar; Reinforcement; Corrosion; Pore solution

1. Introduction

Since the steep rise in the cost of energy, which began in 1973, efforts have increasingly been directed at reducing energy consumption in the production of cement [1]. A type of energy-saving cement that has been developed during the last 20 years is sulfoaluminate cement [2]. Its production requires a reduced input of fuel energy in comparison to Ordinary Portland cement (OPC), due to its lower burning temperature and lower proportion of calcium carbonate in the raw mix. Sulfoaluminate cement contains C_2S, $C_4A_3\bar{S}$, $C\bar{S}$ and C_4AF, and exhibits high early strength development, as well as exceptional high strengths at later ages [2,3].

Both expansive and non-expansive sulfoaluminate cements can be produced, depending mainly on the lime concentration of cement. When a CaO-deficient mixture is hydrated, most of the ettringite is formed before the full development of the skeletal structure and hardening of the paste, and therefore, no expansion is observed [4]. Also, a low-alkali content promotes the non-expansive properties of sulfoaluminate cement [5].

The results of a project aiming at the preparation and hydration study of sulfoaluminate cement with non-expansive behavior have been published elsewhere [6]. The purpose of the present investigation is the study of the corrosion resistance of steel reinforced mortar specimens made from non-expansive sulfoaluminate cement, using OPC specimens as reference. The averaged corrosion rate was measured by the direct method of weight loss (WL) of reinforcing bars of the specimens, and correlated to half cell potential (HCP) measurements, pore solution analysis, total chloride content measurements, and porosity determination. A similar study on the corrosion resistance of steel reinforcement in alinite cement mortars has also been conducted and published [7].

2. Experimental

Sulfoaluminate clinker was prepared in a laboratory electric furnace using the following industrial raw mate-

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Table 1
Sulfoaluminate and Portland cement chemical analysis and potential mineral composition

	Sulfoaluminate cement	Portland cement
Cement chemical analysis (%)		
SiO_2	15.52	19.81
Al_2O_3	13.08	4.99
Fe_2O_3	5.20	3.85
CaO	50.33	62.44
MgO	1.62	2.63
K_2O	0.05	0.53
Na_2O	0.03	0.34
Total Cl^-	0.007	0.008
Water-soluble Cl^-	0.005	
SO_3	14.21	2.66
CaO_{free}	0.14	1.96
Potential mineral composition (%)		
	C_2S 44.54	C_3S 49.04
	$C_4A_3\bar{S}$ 21.00	C_2S 19.80
	$C\bar{S}$ 19.83	C_4AF 11.72
	C_4AF 15.81	C_3A 6.71

rials: limestone (37.76%), bauxite (25.59%), siliceous earth (10.50%) and an iron-rich industrial by-product (0.75%). Also, 25.40% gypsum was added in the raw mix. The raw materials were mixed in such proportions as to obtain the desirable clinker composition and were ground to a fineness of R90 μm = 10.4%. The clinker was formed by burning the raw mix in the final burning temperature of 1280°C. Sulfoaluminate cement was prepared by grinding the clinker to a fineness of 2800 cm^2/g (Blaine), without any supplementary addition of gypsum [2]. As reference cement, an industrially produced OPC of fineness 3500 cm^2/g (Blaine) was used. The sulfoaluminate and Portland cement chemical analysis and potential mineral composition are shown in Table 1. The $C_4A_3\bar{S}$ content was calculated on the basis of the SO_3 content in the sulfoaluminate phase [8].

The mortar mixtures for both sulfoaluminate and Portland cement were obtained using the following proportions: aggregate/water/cement = 3/0.45/1. The reinforcing steel was ST37 type. The steel bars were cleaned and a part of them was isolated with Araldite as shown in Fig. 1a. Cylindrical mortar specimens with an axially embedded steel bar were cast (Fig. 1b). The preparation and cleaning of the bars and the casting procedure are described by Batis et al. [9]. The specimens remained for 24 h at 20 ± 1.5°C and RH >98%. After demoulding, the specimens were cured in water for 24 h and then allowed to dry for another 24 h. A wire was adjusted to the free edge of the steel bar, and finally, the steel that was not covered with cement, as well as the upper part of the concrete, was isolated with Araldite, as shown in Fig. 1b. The specimens were then exposed in the following environments, suspended from their wire, so that only their non-insulated part was remained immersed: (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) intermittent exposure in 3.5% NaCl solution. The water and the NaCl solutions were contained in basins which were installed in a room with T = 20 ± 1.5°C and RH >98%. For the intermittent exposure, the specimens were immersed in NaCl solution for 2 weeks, followed by 1 week in laboratory atmosphere.

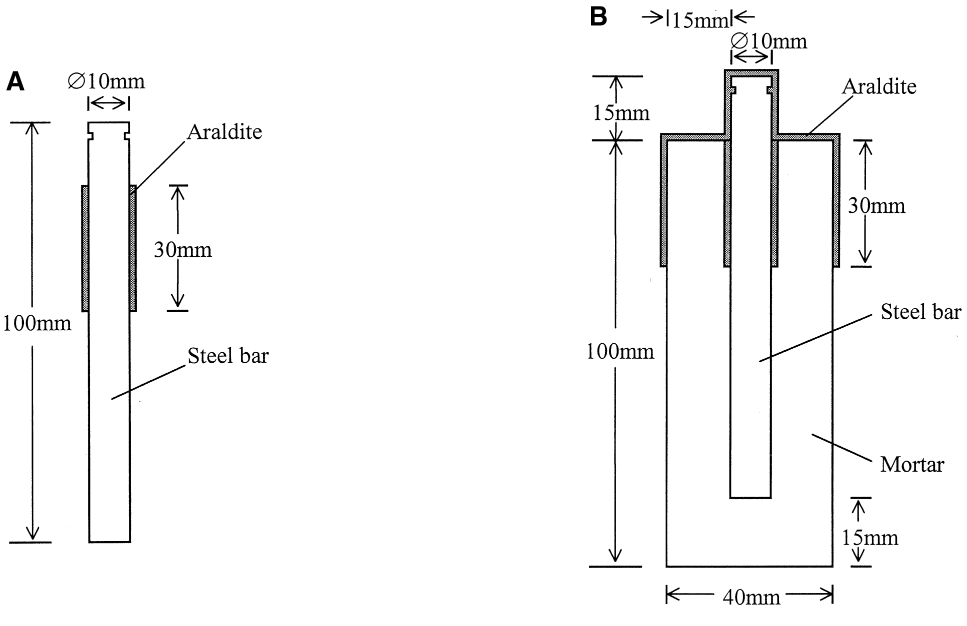

Fig. 1. (a) Steel bar partly isolated with Araldite. (b) Cylindrical mortar specimen with an axially embedded steel bar for tests on rebar corrosion (Araldite isolation is also shown).

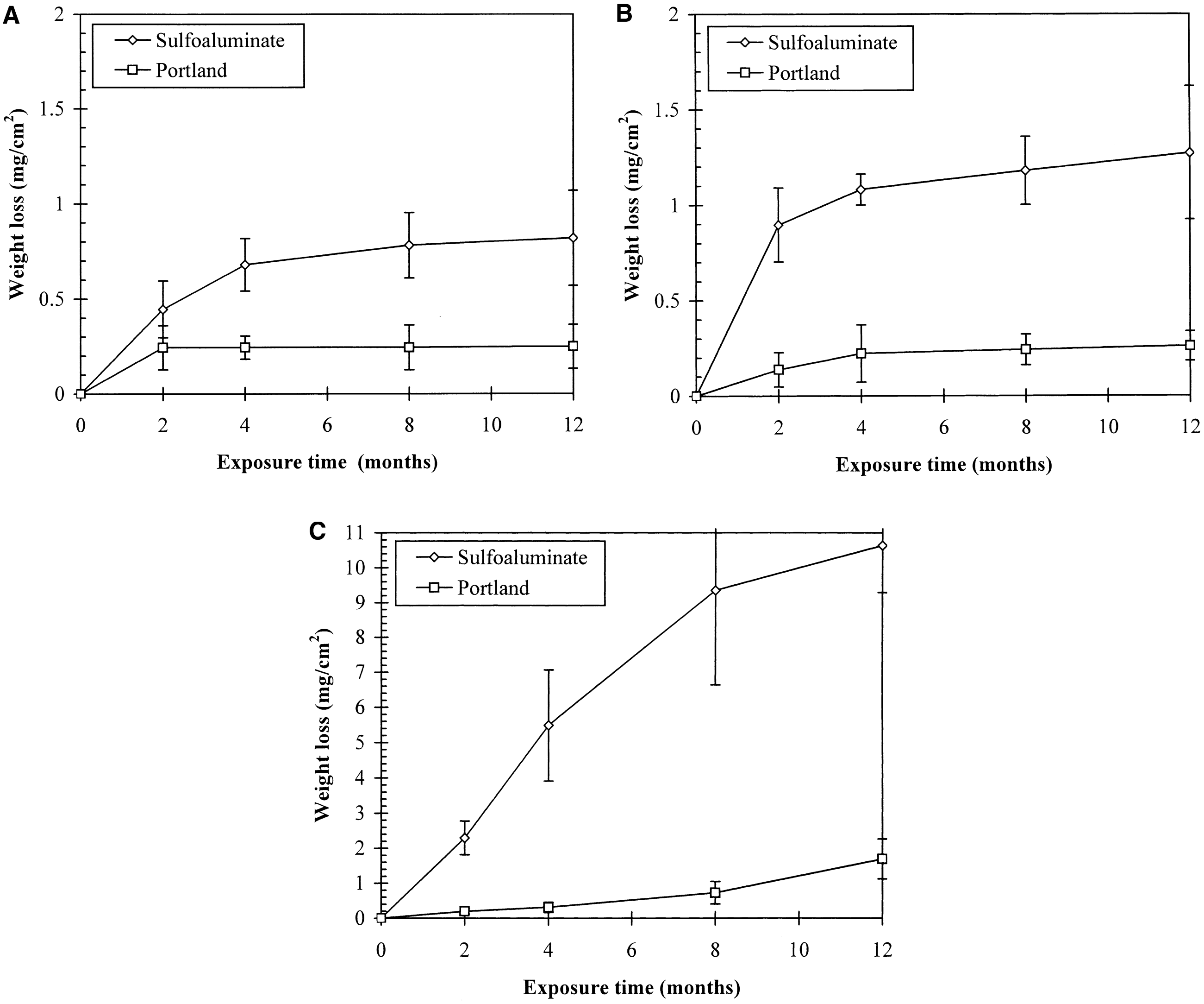

Fig. 2. Weight loss of steel bars embedded in sulfoaluminate and Portland cement mortars as a function of time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

The 2-week wet–1-week dry intervals were regularly repeated in a cyclic manner. Reinforced mortar specimens were used for WL and HCP measurements. Mortar specimens without reinforcement were prepared and exposed in the above environments, and used for pore solution extraction and porosity determination. For every kind of exposure, type of cement and age of measurement, five specimens were prepared for the WL and total chloride measurements and two specimens for the pore solution extraction and porosity determination. For the HCP measurements, five specimens were used for every kind of exposure and type of cement. In each case, the mean value was calculated.

The WL of steel rebars embedded in mortar specimens is a direct method for the determination of corrosion. Measurements at the ages of 2, 4, 8, and 12 months were performed. At each of the predetermined ages, the specimens were removed from the environment and the mortar was broken by axial loading on a hydraulic compressive apparatus to reveal the steel bars. In those cases where corrosion of the steel occurred, the formation of rust was nearly uniform. The bars were cleaned by the same procedure used for their preparation. The mean value of five measurements, normalized for active (non-insulated) area and the standard deviation were calculated.

The HCP measurement gives an indication of the corrosion risk of the steel [10]. The measurement is linked by empirical comparisons to the probability of corrosion. The measurements were performed in small time intervals up to 13 months using a silver/silver-chloride (Ag/AgCl) electrode.

The pore solution of the non-reinforced specimens was extracted at 0, 4, 7, 13, 20, 38 days and 2, 4, 8 months, using a pore solution expression device. The method was first reported by Longuet et al. [11] and

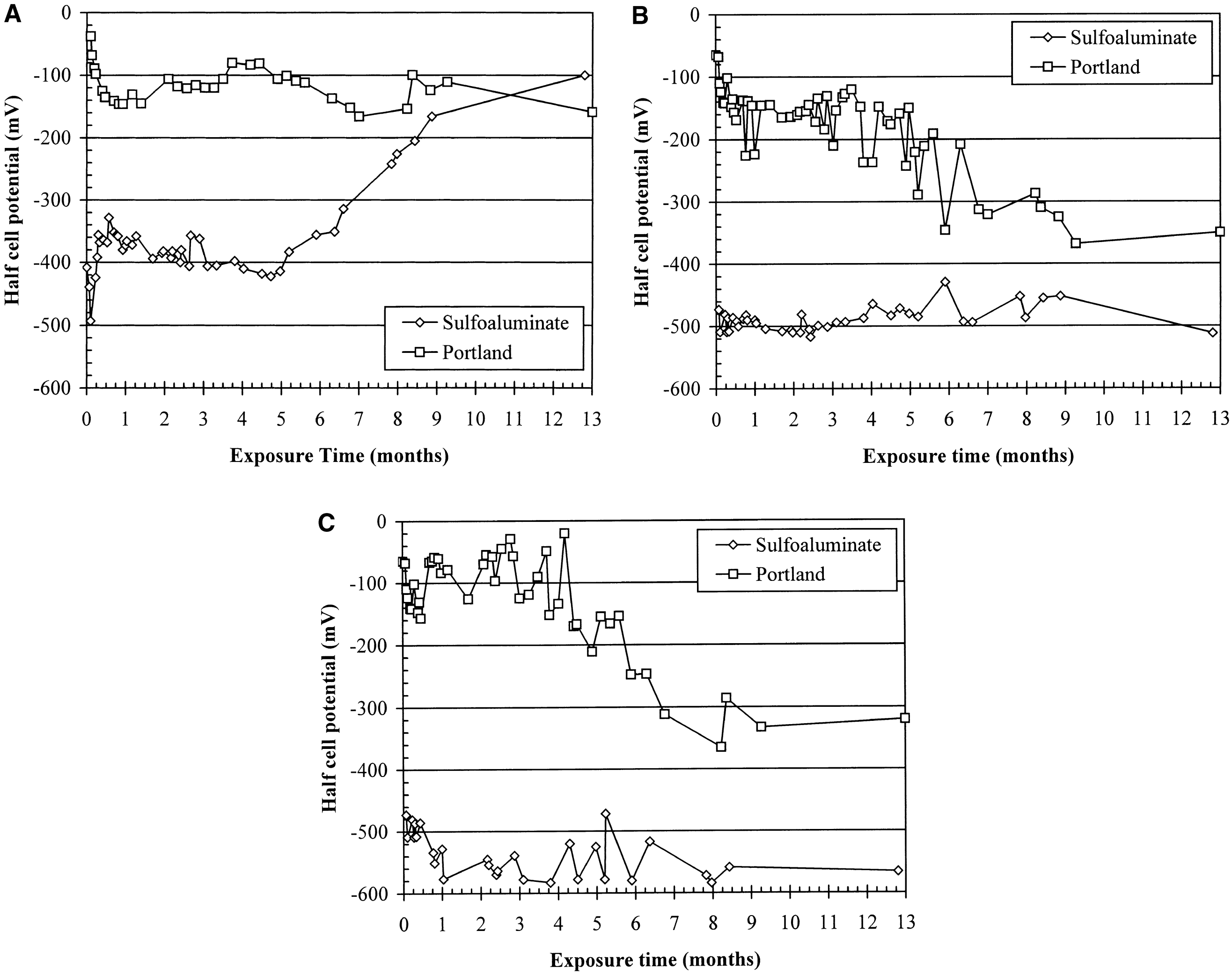

Fig. 3. Half cell potentials of steel reinforcement in sulfoaluminate and Portland cement mortars as a function of time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

developed by others [12–15]. The extraction was performed on the whole cylinder, immediately after it was removed from the environment at which it was exposed. It has been stated that it is valid to use the pore solution expression device to determine the free chloride content of cement, since the chloride concentration of the expressed solution is the same as that in the pore fluid [16]. The pH of the pore solution was measured using very sensitive pH-meter papers immediately after extraction, to avoid errors due to carbonation. The pore solution was analyzed using a chloride ion selective electrode to determine the Cl^- concentration.

The porosity measurements were carried out at the ages of 0, 2, 7, 28 days and 2, 4, 8 months. Prior to the measurements, hydration was stopped by means of acetone and ether extraction. The total porosity and pore size distribution were determined by mercury porosimetry, using a Carlo Erba Porosimeter 4000.

3. Results and discussion

3.1. Weight loss

Fig. 2 shows the WL of steel bars embedded in sulfoaluminate and Portland cement mortars vs. exposure time. The WL of steel bars in sulfoaluminate cement mortars was greater than that in OPC mortars in all environments. However, in the case of continuous exposure in tap water (Fig. 2a), the measured WL values for both types of specimens did not represent significant corrosion. The values remained almost constant above the age of 4 months, and they did not exceed the level of 1–1.5 mg/cm^2, which is considered to represent the WL expected when the steel is protected by a passive film [17]. Also, the visual observation of the bars' surface did not reveal the formation of rust.

The averaged corrosion rate for sulfoaluminate specimens of continuous exposure in NaCl solution (Fig. 2b)

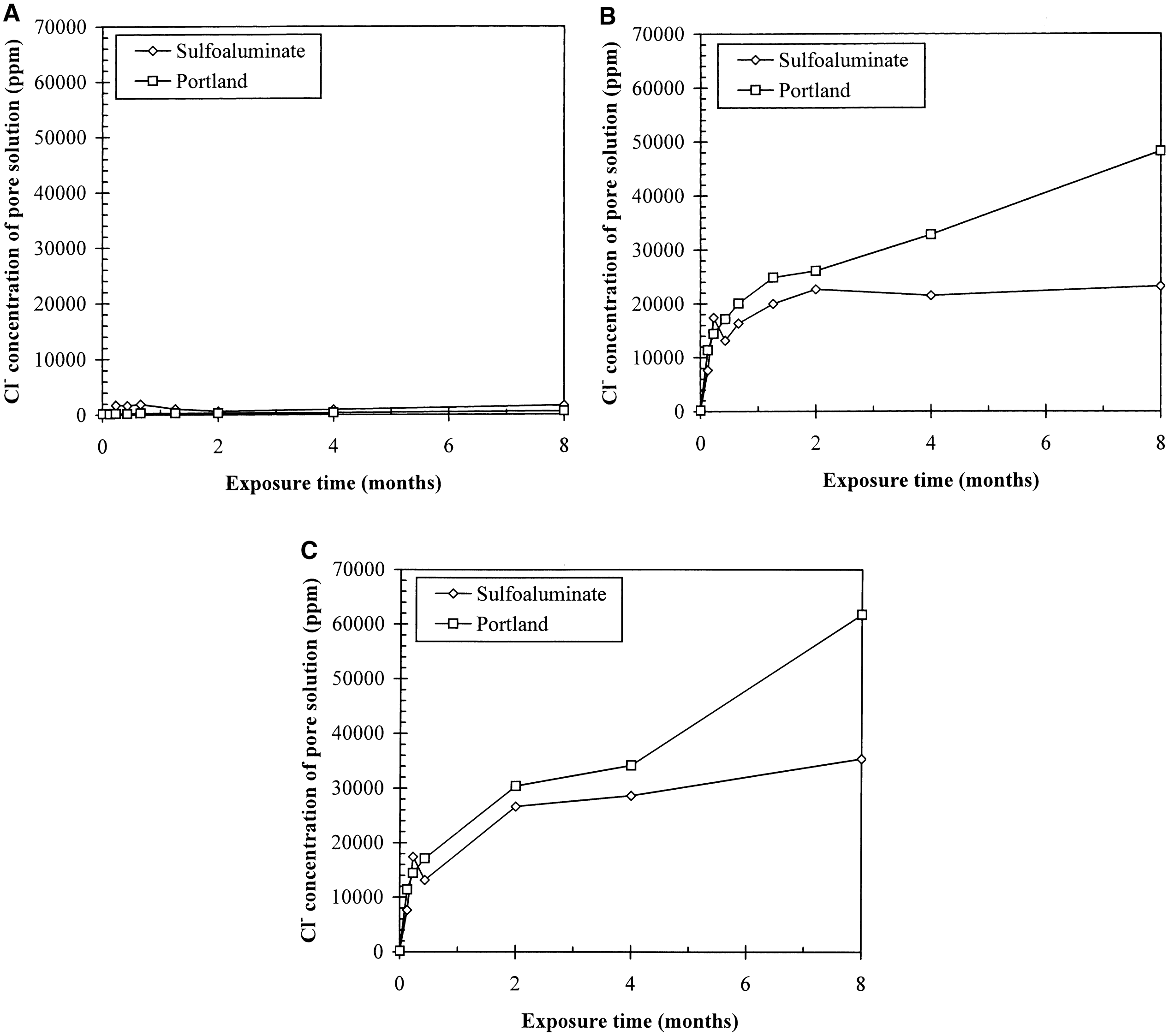

Fig. 4. Cl⁻ concentration of pore solution vs. time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

was higher compared to that of continuous exposure in tap water. The WL continued to increase at a low rate above the age of 2 months, but remained below the level of 1–1.5 mg/cm^2, up to the age of 12 months. However, traces of rust were visible by inspecting the steel's surface after long exposures (above 4 months). Therefore, no certain evidence exists whether the steel remains passive in mortar specimens exposed in NaCl solution. The corresponding values for OPC specimens were very similar to those of continuous exposure in tap water and no rust was observed on the bars' surface.

In the case of the intermittent exposure in NaCl solution (Fig. 2c), the averaged corrosion rate of the rebars embedded in sulfoaluminate specimens was very high compared to that of OPC specimens, for which it became significant after 8 months of exposure.

3.2. Half cell potential

The HCPs of the specimens vs. exposure time, up to 13 months, are illustrated in Fig. 3. For all three environments, the potentials of sulfoaluminate specimens were always more negative than those of OPC specimens. This result indicates a greater tendency for corrosion of the rebars in sulfoaluminate specimens than in OPC ones, and it is in accordance with the WL measurements.

In the case of intermittent exposure, in order to avoid the effect of dryness of the sample, the HCP measurement was performed 1 h after rewetting of the specimens. However, the values measured at the end of each "dry" period were always more positive than those measured at the end of each "wet" period. The HCP values for sulfoaluminate specimens of intermittent

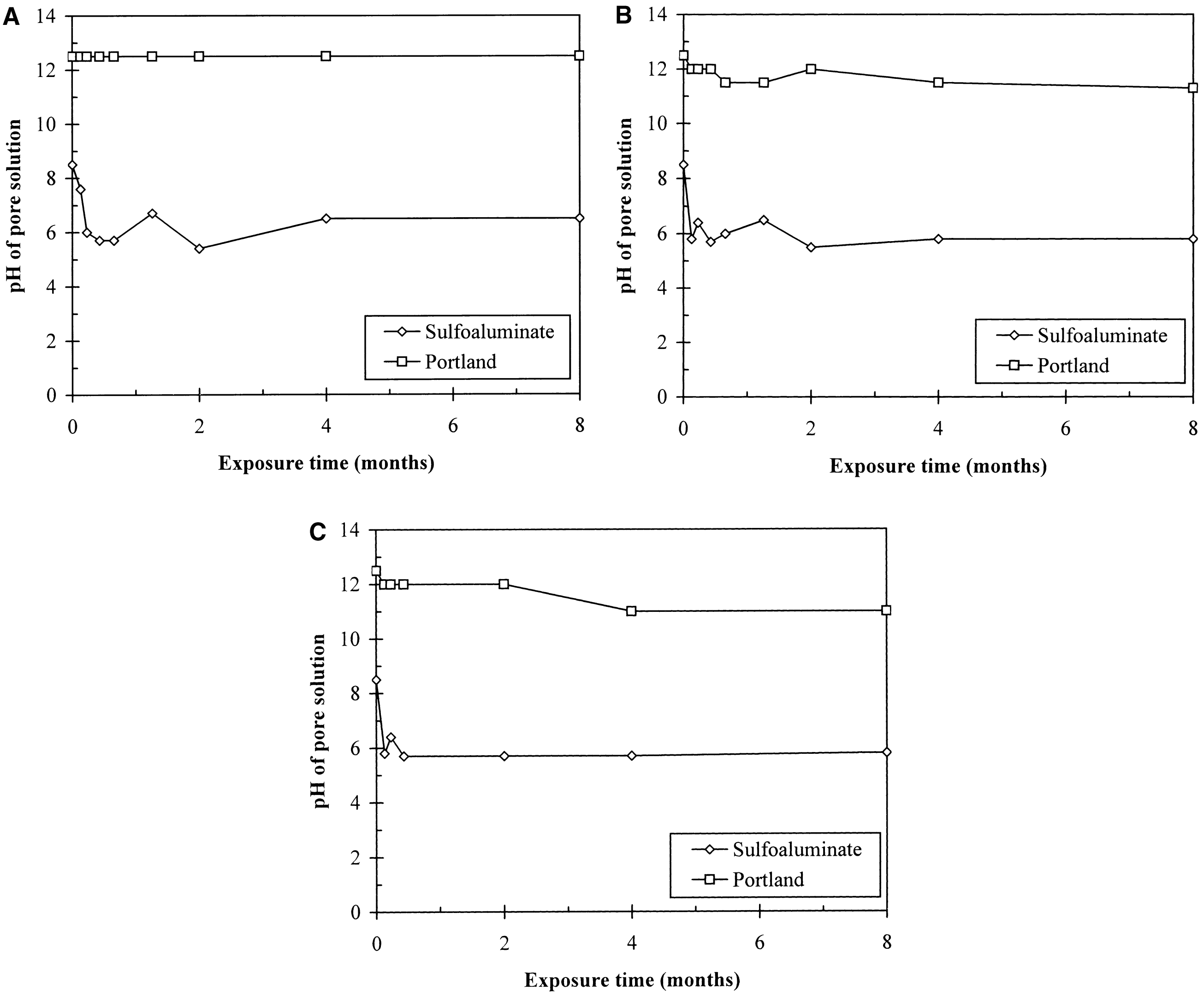

Fig. 5. pH of pore solution vs. time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

exposure in NaCl solution were in the range of −500 to −600 mV, indicating high corrosion risk, in agreement with the high averaged corrosion rate measured by WL. The measured values of OPC specimens became more negative than −200 mV, after 4 months of intermittent exposure in NaCl solution, and reached −300 mV after 7 months of exposure. This result is also in agreement with the WL measurements.

3.3. Pore solution analysis

In the pore solution extracted from the mortar specimens, the Cl^- concentration and the pH were measured, and the results are presented in Figs. 4 and 5, respectively. The values of Cl^- concentration and pH are average values over the entire sample, since the extraction was performed on the whole cylinder. The Cl^- concentration of the pore solution of continuous exposure in tap water remained low and at an almost constant level for both cements. For continuous and intermittent exposure in NaCl solution, the Cl^- concentration increased with exposure time. The intermittent exposure resulted to relatively higher values. The Cl^- concentration was a little lower for sulfoaluminate specimens, compared to OPC specimens, even though the former exhibited larger pores, as will be discussed in Section 3.4. The reason for this is probably because of a different chloride-binding behavior between the two cements.

The results of the pH measurements (Fig. 5) showed lower pH values (around 6, after a few days of exposure) for sulfoaluminate cement mortars, in comparison to OPC mortars, for all three environments. This is due to the different composition of sulfoaluminate cement in respect to OPC, that results in lower $Ca(OH)_2$ production during its hydration [6]. The low-alkali

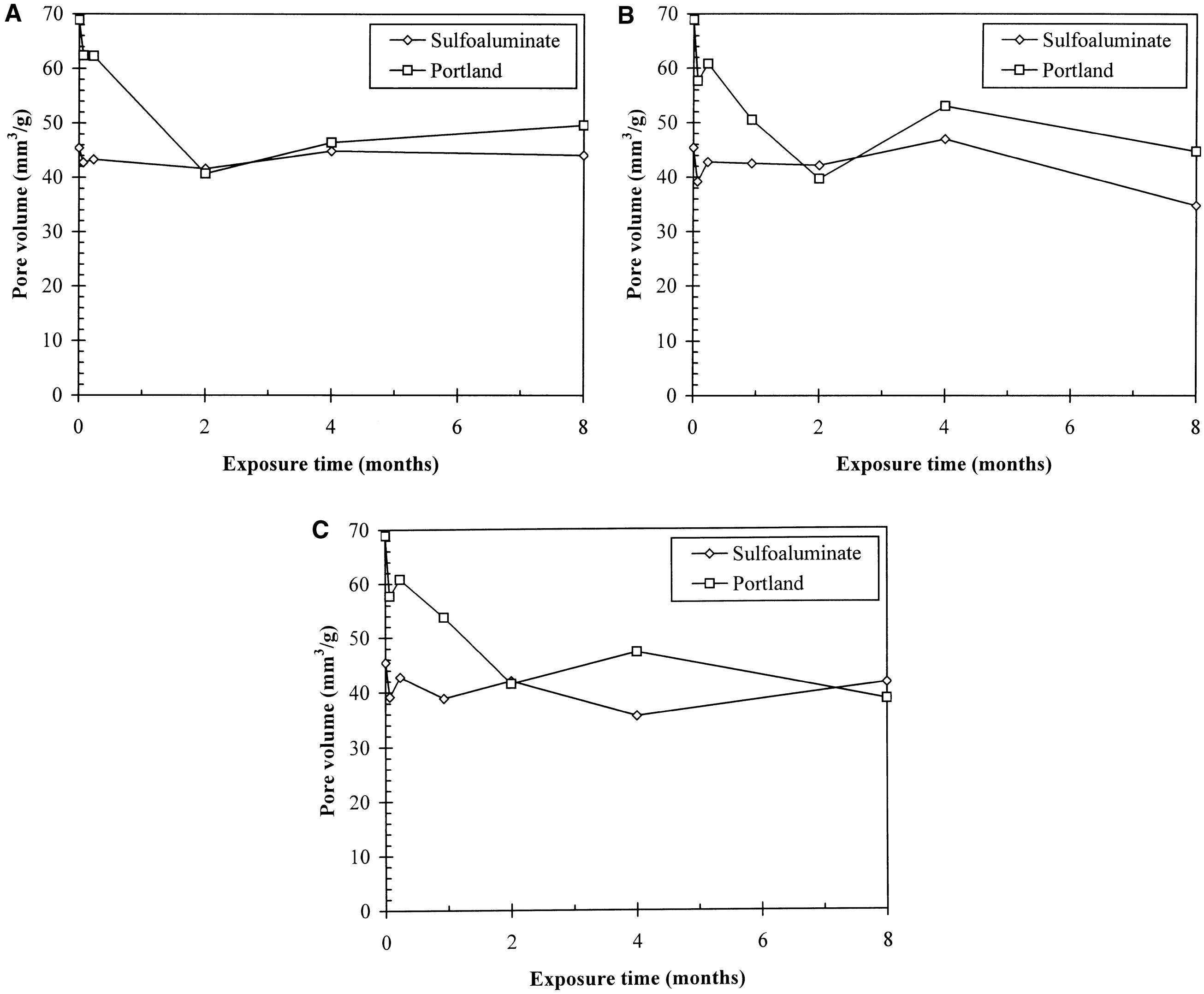

Fig. 6. Total porosity of sulfoaluminate and Portland cement mortars as a function of time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

content of sulfoaluminate cement also contributes to the low pH values of its pore solution. The passivation of the steel is lost in conditions of low pH, and when free chlorides and oxygen are also present near the steel surface, high averaged corrosion rates occur, as in the case of intermittent exposure in NaCl solution.

3.4. Porosity

The evolution of total porosity of sulfoaluminate and Portland cement mortars as a function of exposure time is illustrated in Fig. 6, for the three environments. No significant differences were observed between the curves for sulfoaluminate and Portland cement after the age of 2 months. The porosity of sulfoaluminate cement did not vary significantly in the whole examined time period. For OPC, the porosity was higher during the first 2 months of exposure.

A comparative examination of the pore size distribution reveals that the average pore diameters in the case of sulfoaluminate cement mortars (Fig. 7) lay at a considerably higher level than that of OPC mortars (Fig. 8), namely 400–600 and 100–150 Å, respectively, after 8 months of exposure. Thus, the structure of the pore system for sulfoaluminate cement seems to contribute to the observed higher averaged corrosion rates.

4. Conclusions

The low pH values (around 6) of the pore solution and the higher, compared to OPC, average pore diameters (400–600 Å) of sulfoaluminate cement mortars of this study exposed the reinforcing steel to a high corrosion risk, as revealed by the half cell potential measurements. However, other factors, like the concen-

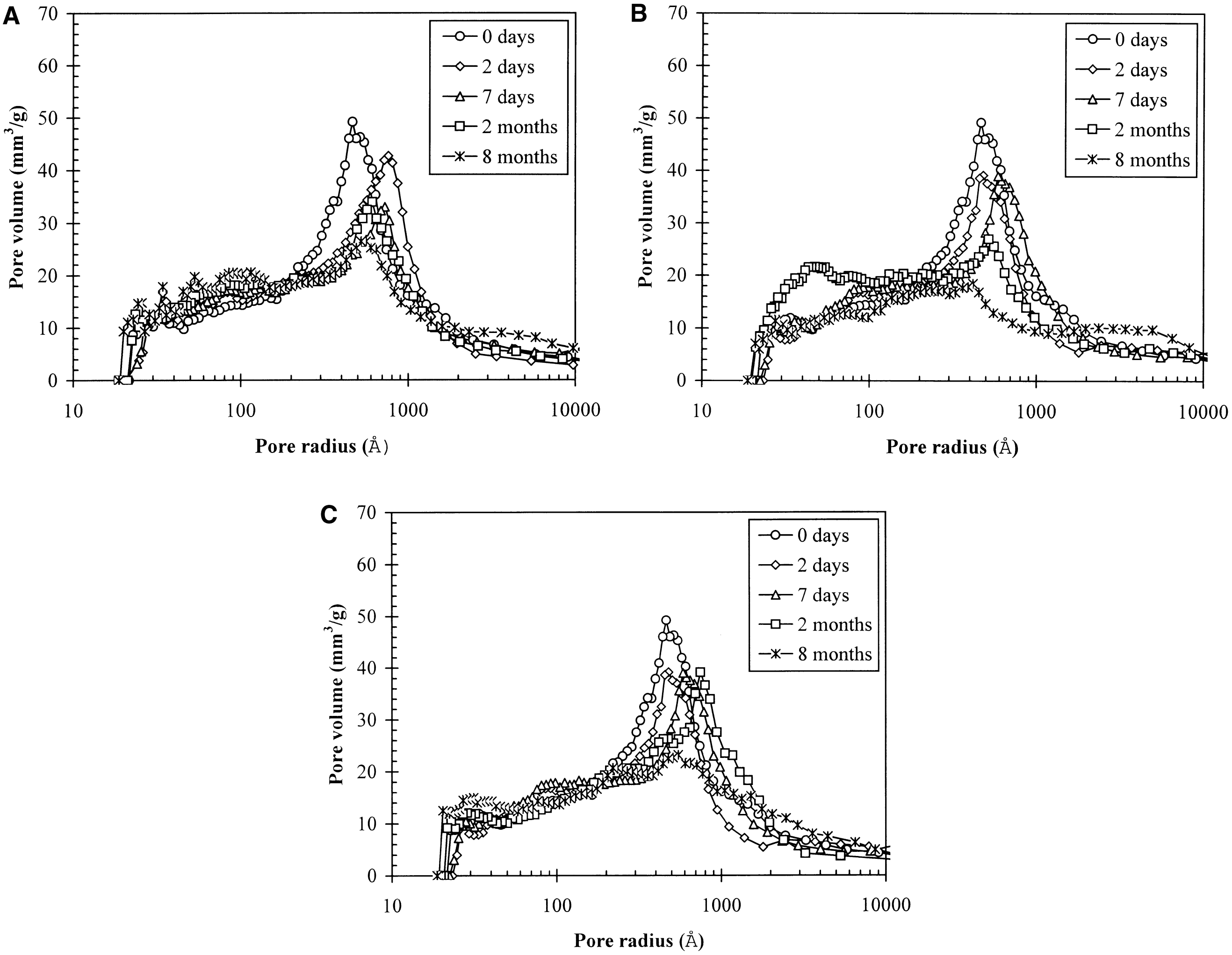

Fig. 7. Pore size distribution of sulfoaluminate cement mortars vs. time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

tration of free chlorides in the pore solution, the oxygen access to the steel surface and the total porosity also contributed to the observed averaged corrosion rate.

In continuous exposure in tap water, sulfoaluminate cement seemed to provide adequate protection against corrosion to steel reinforcement, up to 12 months of exposure. The concentration of free chlorides was almost negligible, and the access of oxygen near the steel surface was limited, since the specimens remained constantly immersed in water. No rust formation was observed and the weight loss values remained below the level of 1–1.5 mg/cm^2, which is considered to represent the weight loss expected when the steel is protected by a passive film.

In continuous exposure in 3.5% NaCl solution, the action of free chlorides resulted in higher measured values of weight loss for sulfoaluminate specimens. Although these values remained below the level of 1–1.5 mg/cm^2, it is uncertain that the steel remains passive, since traces of rust were visible by inspecting the bars' surface after long exposures (above 4 months).

In intermittent exposure in 3.5% NaCl solution, a high averaged corrosion rate of steel reinforcement was observed for sulfoaluminate cement mortars. The concentration of Cl^- in the pore solution was constantly increasing as a progressive ingress of chlorides from the surrounding salt water into the specimen took place, while oxygen was able to reach the steel surface during drying periods. These factors, as well as the low OH^- concentration of the pore solution, resulted in the depassivation of the steel reinforcement, and led to severe corrosion effect.

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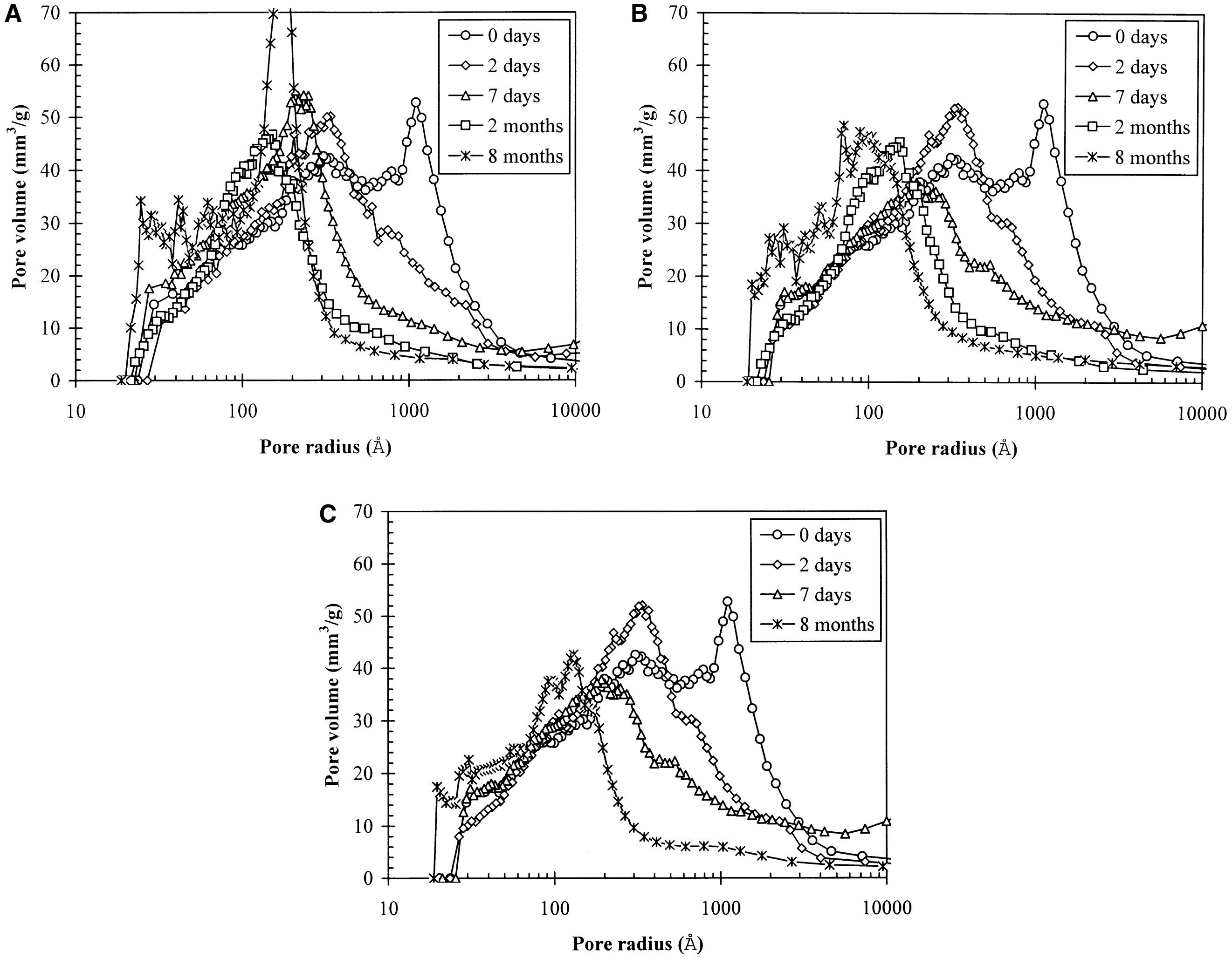

Fig. 8. Pore size distribution of OPC mortars vs. time for (a) continuous exposure in tap water, (b) continuous exposure in 3.5% NaCl solution and (c) interrupted exposure in 3.5% NaCl solution.

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