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COMPARATIVE INVESTIGATION OF CORROSION RESISTANCE OF STEEL REINFORCEMENT IN ALINITE AND PORTLAND CEMENT MORTARS

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ABSTRACT

The corrosion resistance of steel-reinforced mortar specimens made from alinite cement was investigated using ordinary Portland cement (OPC) specimens as reference. The specimens were prepared and exposed in three different environments: continuous exposure in tap water, interrupted exposure in tap water, and interrupted exposure in 3.5% NaCl solution. The steel weight loss and the half cell potential 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, alinite cement provided adequate protection against corrosion. In interrupted exposure in tap water, a higher corrosion was observed for alinite cement compared to OPC. In the case of interrupted exposure in 3.5% NaCl solution, the simultaneous action of free chlorides and oxygen resulted in the depassivation of steel reinforcing bars in alinite and Portland cement mortars, and led to severe corrosion effect. *© 1998 Elsevier Science Ltd*

Introduction

In the last few decades, efforts towards reducing energy consumption in the cement industry have led to the production of a new family of hydraulic materials, namely low-energy cements. Alinite cement is a low-energy cement that was originally developed twenty years ago in the Soviet Union (1), and that has been protected by patent since then (2). The technical specifications for its production were also adopted by the Ministry of Building Materials Industry of Soviet Union in 1983 (3).

Alinite cement is produced using calcium chloride in the mix of raw materials. A $CaCl_2$ content of 6–23% has been referred to in the literature (2,4,5). The chloride acts both as a mineralizer, promoting the formation of clinker compounds, as well as a flux, lowering the

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clinkering temperature (6). The main phase in this cement is alinite, a calciumsilicate phase which contains chloride, and its chemical formula may be represented by $Ca_{9.9}Mg_{0.8}\square_{0.3}[(SiO_4)_{3.4}(AlO_4)_{0.6}]O_{1.9}Cl_{1.0}$ ($\square$: lattice vacancy) (7). The formation of alinite phase is promoted by Cl^- ions, MgO addition (~3% in the clinker), and low alkali content (8,9). The other phases in alinite cement are β-C_2S, $C_{11}A_7{\cdot}CaCl_2$ and calcium ferrite. Alinite cement requires a lower w/c ratio than ordinary Portland cement (OPC), and it sets more quickly (10). The strength development of alinite cement is relatively low at early ages, but at later ages (after 28 days) its strength is comparable or even higher than that of OPC (9,11).

The saving in fuel energy in the production of alinite cement is achieved by reducing the proportion of calcium carbonate in the raw mix (LSF $\approx$ 80) and by lowering the burning temperature to 1200–1250°C. The activation energy for alinite phase formation is reported to be 120 kJ/mol lower than that of C_3S (12). In addition, the energy consumption for grinding alinite cement is lower, due to its better grindability (13). Consequently, the overall energy saving can be as high as 30% (13). Furthermore, it is possible to produce alinite cement using industrial wastes as raw materials (5,14).

Despite the benefits from energy savings in its production, alinite cement is possibly a material which promotes corrosion of steel reinforcement, due to its chloride content that may be released during hydration (13). Chlorides in concrete exist in three different conditions: a) chemically bound with the hydration products, b) physically bound on the surface of the gel pores, and c) free in the pore solution. It is only the concentration of free chlorides that are responsible for corrosion. A high free Cl^- content in the pore solution may have a catastrophic effect on the steel embedded in concrete. Consequently, this issue is of critical importance and should be examined thoroughly before alinite cement is considered for use as a building material.

The purpose of this investigation was to evaluate the corrosion effect of Cl^- ions on steel reinforced mortar specimens made from alinite cement, using OPC specimens as reference. The corrosion rate was measured by the direct method of weight loss of reinforcing bars of the specimens, and correlated to half cell potential measurements, pore solution analysis, and porosity determination.

Materials and Methods

Alinite cement clinker was prepared in a laboratory electric furnace using industrial raw materials. $CaCl_2$ and MgO were 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 $\mu m = 10\%$. The clinker was formed by burning the raw mix in the final burning temperature of 1230°C. Alinite cement was prepared by grinding the clinker with 6% gypsum, to a fineness of 3600 cm^2/g (Blaine). As a reference cement, an industrially produced OPC of fineness 3500 cm^2/g (Blaine) was used. The alinite and Portland cement chemical analysis, ratios, and mineral composition are shown in Table 1. The total Cl^- content of alinite cement was 1.92%, while the water-soluble Cl^- were maintained at a low level (0.4%).

The microstructural examination of alinite clinker was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy (OM). The XRD pattern of alinite clinker (Fig. 1) showed that all alinite clinker phases were formed: alinite, β-C_2S, $C_{11}A_7{\cdot}CaCl_2$, and C_2F. Small amounts of CF, CaO_f, periclase (MgO), C_3S, and γ-C_2S

TABLE 1
Alinite and Portland cement chemical analysis, ratios, and potential mineral composition.

	Alinite cement	Portland cement
	Cement chemical analysis (%)	
SiO_2	22.80	19.81
Al_2O_3	3.64	4.99
Fe_2O_3	3.53	3.85
CaO	60.16	62.44
MgO	3.04	2.63
K_2O	0.04	0.53
Na_2O	0.03	0.34
Total Cl^-	1.92	
Water-soluble Cl^-	0.40	
SO_3	3.05	2.66
CaO_{free}	1.39	1.96
	Cement ratios	
LSF[1]	83.3	97.8
SR	3.18	2.24
AR	1.03	1.30
	Potential mineral composition (%)	
	Alinite: 48.4	C_3S: 49.04
	β-C_2S: 37.0	β-C_2S: 19.80
	$C_{11}A_7 \cdot CaCl_2$: 4.9	C_4AF: 11.72
	C_2F: 5.7	C_3A: 6.71

[1] In the case of alinite clinker: LSF = 100 (C − 0.789Cl)/(2.80S + 1.18A + 0.65F)

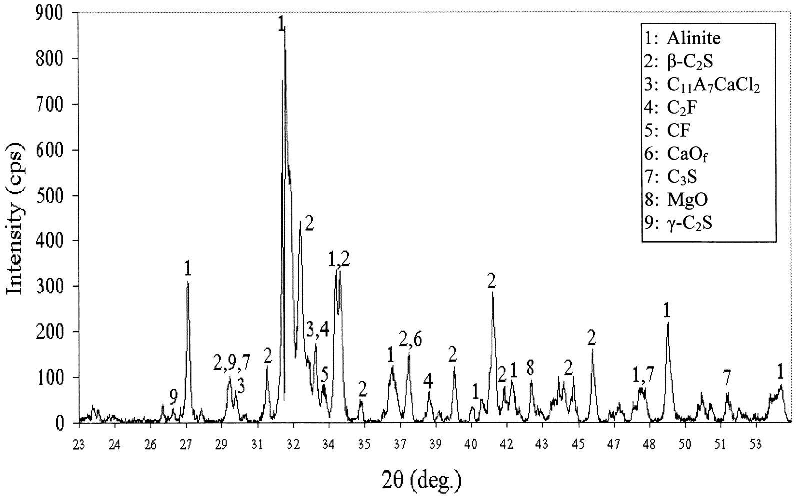

FIG. 1.
X-ray diffraction pattern of alinite clinker.

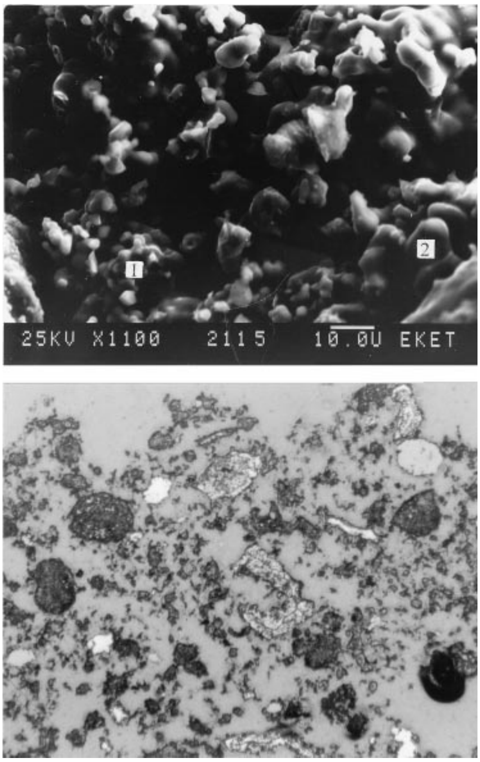

FIG. 2.
(*a*) SEM micrograph (×1100) and (*b*) OM micrograph (×100) of alinite clinker. 1: alinite, 2: β-C_2S.

were also present. In the SEM micrograph of Figure 2a, the phases of alinite and β-C_2S can be observed. Alinite clinker exhibits high porosity, as can be seen in the OM micrograph of Figure 2b.

The mortar mixtures for both alinite 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 Figure 3a. Cylindrical mortar specimens with an axially embedded steel bar were cast (Fig. 3b). The preparation of the bars and the casting procedure are described by Batis et al. (15). The specimens were exposed in the following environments: a) continuous exposure in tap water, b) interrupted exposure in tap water and c) interrupted exposure in 3.5% NaCl solution. The water and the NaCl solutions were contained in basins which were installed in a room with $T = 20 \pm 1.5°C$ and $RH > 98\%$. For the interrupted exposure, the specimens were periodically immersed in tap water or NaCl solution for two weeks, followed by one week in laboratory atmosphere. The reinforced mortar specimens were used for the weight loss and half cell potential measurements. Specimens without reinforcement were prepared and exposed in the same environments, and used for the pore solution extraction and porosity determination. For every kind of exposure, type of cement and age of measurement, 5 specimens were prepared for the weight loss measurements and 2 specimens for the pore

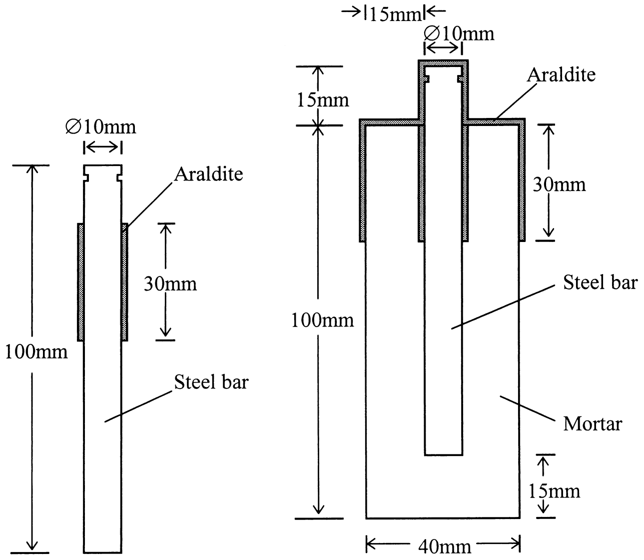

FIG. 3.
(*a*) Steel bar partly isolated with Araldite. (*b*) Cylindrical mortar specimen with an axially embedded steel bar for tests on rebar corrosion (Araldite isolation is also shown).

solution extraction and porosity determination. For the half cell potential measurements, 5 specimens were used for every kind of exposure and type of cement. In each case the mean value was calculated.

The weight loss 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. The bars were then cleaned from their rust by the same procedure used for their preparation. The mean value of 5 measurements, normalized for active (non-insulated) area, and the standard deviation were calculated.

The half cell potential measurement gives an indication of the corrosion risk of the steel (16). 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, and 38 days and 2, 4, and 8 months, using a pore solution expression device similar to that described by Tritthart (17). 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, and 28 days and 2, 4, and 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.

Results

Weight Loss (WL)

Figure 4 shows the weight loss of steel bars embedded in alinite and Portland cement mortars versus exposure time, in the three examined environments. The WL of steel bars in alinite cement mortars was greater than that in OPC mortars in all environments. However, in the case of continuous exposure in tap water, the measured values for both types of specimens did not represent significant corrosion up to 12 months, but they revealed a base-level of passive film creation and maintenance (18).

The WL values for alinite specimens of interrupted exposure in tap water were a little higher compared to those of continuous exposure. However, they remained almost constant above the age of 2 months, and they did not exceed the level of 1–1.5 mg/cm^2, which is considered to represent the WL of the passive film (18). The corresponding values for OPC specimens were very similar to those of continuous exposure.

In the case of the interrupted exposure in NaCl solution, the corrosion rate of the rebars embedded in alinite specimens was higher than that of OPC specimens, for which it became significant after 8 months of exposure.

Half Cell Potential (HCP)

The half cell potentials of the specimens vs. exposure time, up to 13 months, are illustrated in Figure 5. For all three environments, the potentials of alinite specimens were always more negative than those of OPC ones. This result indicates a greater tendency for corrosion of the rebars in alinite specimens, and it is in accordance with the WL measurements.

In the case of interrupted exposures, in order to avoid the effect of dryness of the sample, the HCP measurement was performed one hour 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 measured values for alinite specimens exposed continuously in tap water were in the range of −300 to −500 mV, while those of interrupted exposure in tap water rose to −200 mV after 1 month of exposure, and constantly remained above that value after the age of 4 months. These results indicated a higher corrosion risk for continuous than for interrupted exposure. The opposite behavior was observed by the WL measurements, and an explanation of this contradiction will be given in the discussion. For both types of exposure in tap water, the measured values of OPC specimens indicated no risk of corrosion.

The HCP values for alinite specimens of interrupted exposure in NaCl solution were always lower than −300 mV, indicating high corrosion risk, in agreement with the high corrosion rate measured by WL. The measured values of OPC specimens became more negative than −200 mV after 4 months of interrupted exposure in NaCl solution, and reached −300 mV after 7 months of exposure. This result is also in agreement with the WL measurements.

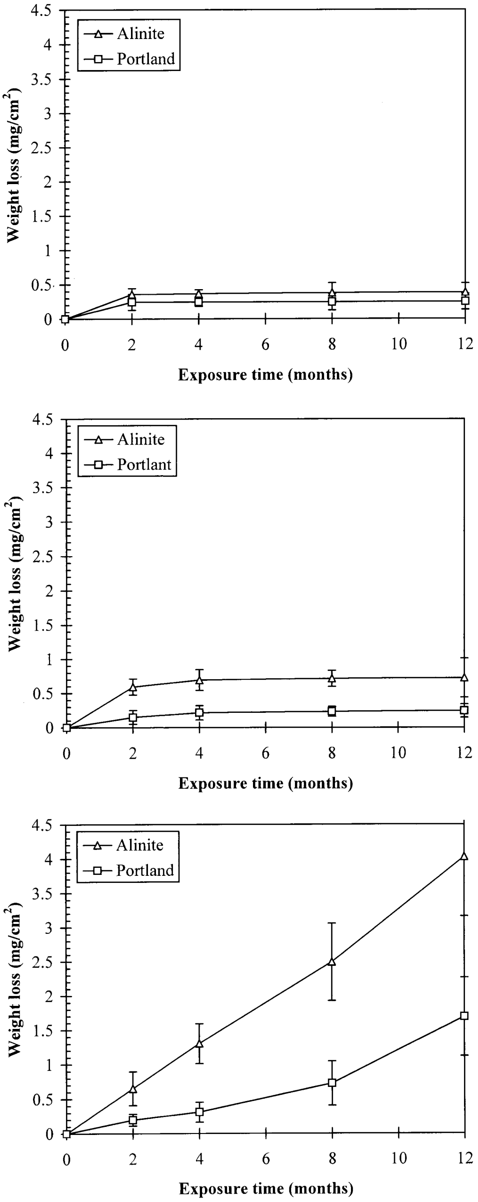

FIG. 4.

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

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 Figures 6 and 7, respectively. The Cl^-

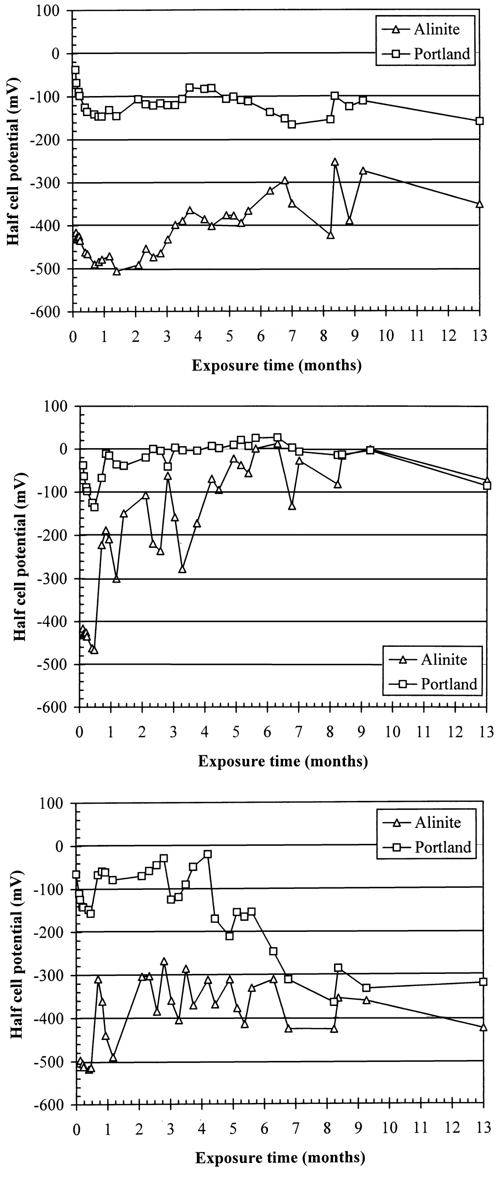

FIG. 5.

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

concentration of the pore solution of alinite cement mortars was higher than that of OPC, as expected, because Cl^- ions were included in the structure of the alinite clinker.

A continuous decrease of Cl^- concentration in the pore solution of alinite mortars exposed in tap water was observed, which was interrupted by an increase at 7 days. At the age of 8 months the Cl^- concentration increased slightly. At that age, however, the extraction of pore

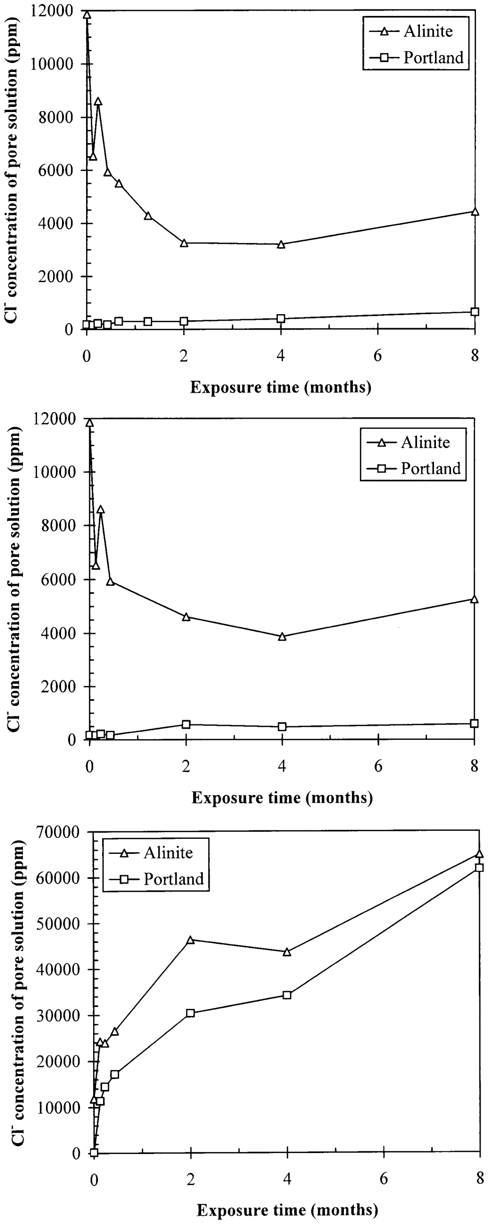

FIG. 6.

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

solution yielded lower volume, and thus the high pressure was sustained longer. This possibly resulted in the dissolution of bound chlorides. The pore solution extracted from the OPC mortars of continuous or interrupted exposure in tap water had a low and almost constant level of Cl^- concentration.

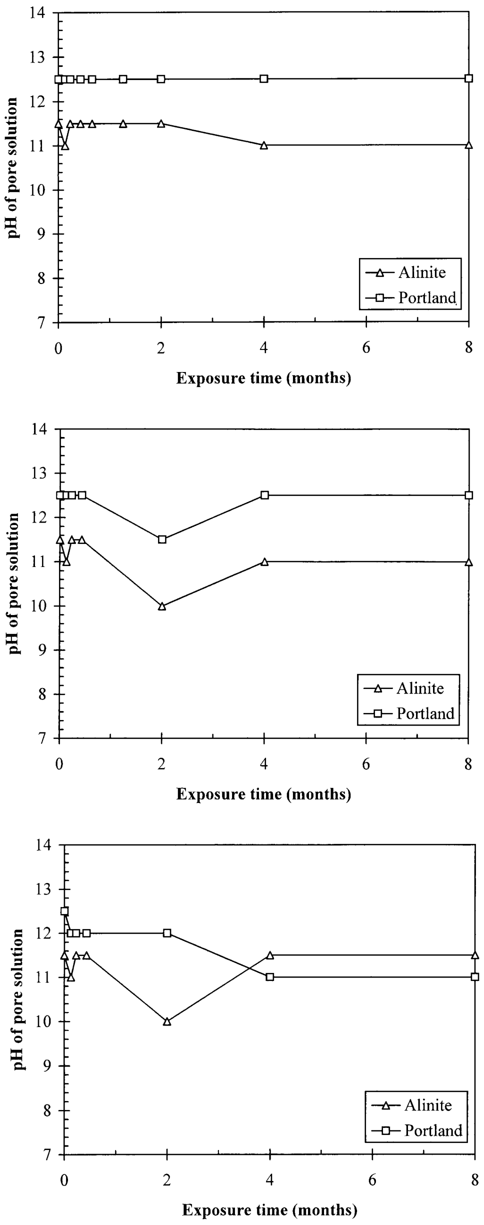

FIG. 7.

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

For both cements, the interrupted exposure in NaCl solution resulted in high values of Cl^- concentration, which increased with time, and showed a more steep increase above the age of 4 months.

The results of the pH measurements (Fig. 7) showed lower pH values (in the range

11–11.5) for alinite cement mortars in compison to OPC mortars, for all three environments. This is due to the different composition of alinite cement in respect to OPC, that results in lower $Ca(OH)_2$ production during alinite cement hydration (9,11). For interrupted exposure in NaCl solution, the pH of the OPC pore solution decreased from 12.5 to 11 by the age of 4 months.

Porosity

The evolution of total porosity of alinite and Portland cement mortars as a function of exposure time is illustrated in Figure 8, for the three environments. In all cases, the porosity decreased with time up to the age of 2 months, and remained almost stable thereafter. The curves are rather similar between alinite and Portland cement, and no significant differences are observed. A comparative examination of the pore size distribution, though, reveals that the average pore diameters in the case of alinite cement mortars (Fig. 9) lay at a considerably lower level than that of OPC mortars (Fig. 10). Thus, the structure of the pore system for alinite cement does not seem to contribute to the observed higher corrosion rates.

Discussion

Continuous Exposure in Tap Water

The HPC measurements of alinite cement specimens indicated a high corrosion risk, although the corrosion rate was low. The reason for this is the absence of sufficient oxygen near the steel surface, as the specimens remained constantly immersed in water. The very negative HCP values could be explained by the lack of oxygen access to the cathode, which increases the cathodic polarization (19). Another reason for the limited corrosion of steel rebars in alinite cement mortars may be the observed reduction of Cl^- concentration in the pore solution (free Cl^-) with time, thus diminishing the corrosion risk.

The decrease of free Cl^- at the early hydration stage (0–4 days) is due to chloride binding by the formation of Friedel's salt, $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ (9,11). The increased Cl^- concentration observed at the age of 7 days is attributed to the hydration of alinite phase, leading to the release of Cl^- ions in the solution. The constant decrease that followed, resulted from the diffusion of Cl^- ions towards the surface of the specimen, due to the concentration gradient which was established between the pore solution and the water of the curing bath.

Interrupted Exposure in Tap Water

In the case of interrupted exposure of alinite specimens in tap water, the WL measurements and the Cl^- concentration of pore solution were a little higher compared to the corresponding values of continuous exposure. However, the HCP measurements did not indicate a high corrosion risk, in agreement with the direct corrosion rate measurements. The observed tendency of the HCP values to move to less negative levels during the first 2 months, corresponded to the concurrent decrease of Cl^- concentration of pore solution, thus reducing the corrosion risk.

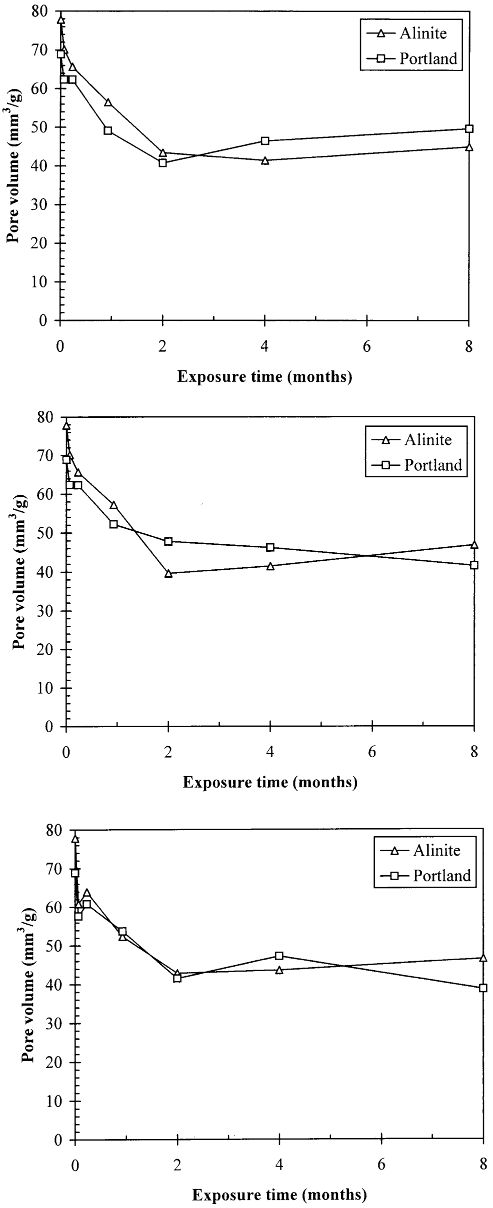

FIG. 8.

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

Interrupted Exposure in 3.5% NaCl Solution

When the specimens are exposed to alternating wetting and drying by a NaCl solution, a progressive ingress of chlorides occurs (20). When it is immersed in the NaCl solution, the

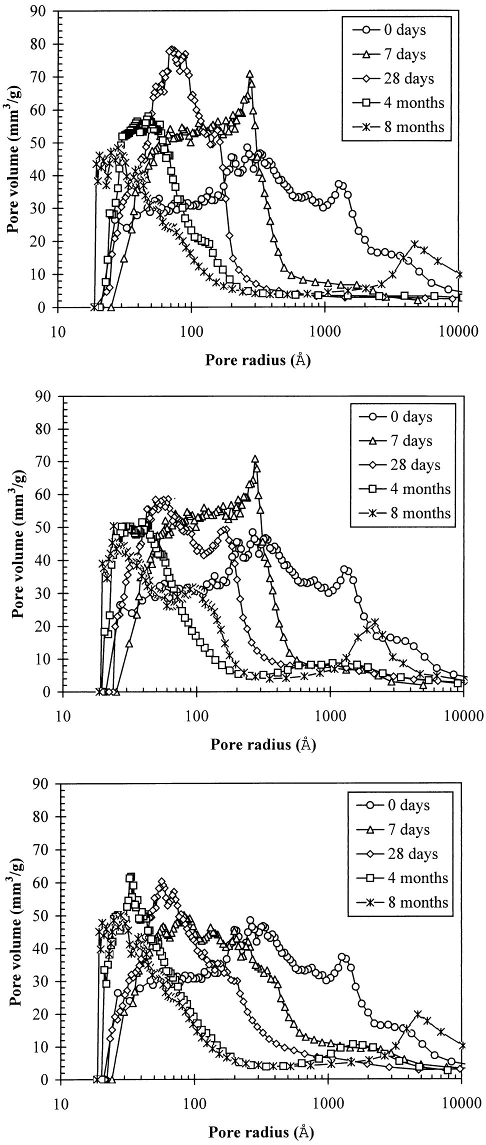

FIG. 9.

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

specimen imbibes salt water by absorption. If a drying period follows, the direction of movement of water is reversed and water evaporates from the surface. Thus, the concentration of Cl^- ions in the pore solution increases near the surface of the specimen. The established concentration gradient causes the movement of Cl^- ions towards the interior of the specimen. A subsequent wetting of the specimen in the salt water brings more chlorides

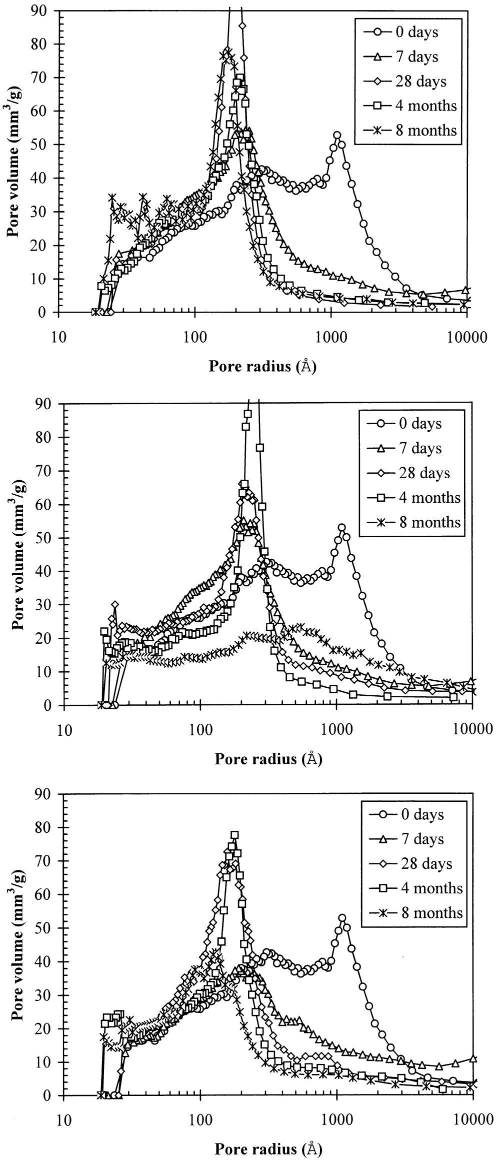

FIG. 10.
Pore size distribution of OPC mortars vs. time for (*a*) continuous exposure in tap water, (*b*) interrupted exposure in tap water, and (*c*) interrupted exposure in 3.5% NaCl solution.

into the pores, and so forth. The progressive ingress of chlorides towards the reinforcing steel may lead to a maximum chloride ion content in the pore solution, even in excess of the concentration of the surrounding NaCl solution (20).

The corrosion rate of steel rebars embedded in alinite or Portland cement mortars was high, under alternating wetting and drying by a NaCl solution, due to the simultaneous action of Cl^- ions at a high concentration, and oxygen. In the case of alinite cement a greater corrosion was induced compared to OPC, since a more aggressive environment existed near the steel bar. This was indicated by the constantly very negative half cell potentials measured, as well as by the high free Cl^- concentration, which was higher than that in the pore solution of OPC mortars.

Conclusions

In continuous exposure in tap water, alinite cement provided adequate protection against corrosion to steel reinforcement up to 12 months of exposure. The chlorides that remained unbound constituted a small percentage of the total chlorides present, and there was a rapid reduction of the concentration of Cl^- ions in the pore solution with time. Moreover, a limited access of oxygen occurred near the steel surface, as the specimens remained constantly immersed in water.

In interrupted exposure in tap water, the simultaneous action of chlorides and oxygen resulted in higher measured values of weight loss for alinite specimens compared to OPC ones. However, the magnitude of these values did not indicate significant corrosion, and remained almost constant at a very low level, due to the decrease of total porosity and the reduction of free chloride content.

In interrupted exposure in 3.5% NaCl solution, a high corrosion rate of steel reinforcement was observed for both alinite and Portland cement mortars. The corrosion was more pronounced in the case of alinite cement, due to its higher free chloride content. 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.

Acknowledgments

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