

Penetration of Chloride Ions into Cement Pastes and Concretes

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BECAUSE of their low cost, CaCl₂, NaCl, and KCl are the deicing agents most frequently used. These salts, in combination with freezing and thawing, are, however, the principal cause of surface deterioration on concrete highways and bridge decks.^{1,2} In addition, in the presence of oxygen Cl⁻ ion can corrode steel in reinforced concretes.

In the present work, penetration of CaCl₂ into cement pastes and concretes was studied. In particular, the effects of the type of cement used, the method of preparing the concrete, and the temperature of the environment on the penetration rate of the Cl⁻ ion were examined.

Portland cement (ASTM type II) and pozzolanic cement were used to prepare the pastes and concretes. The pozzolanic cement was obtained by mixing the portland cement with 35 wt% of Salone pozzolana. About 4.5 parts by weight of aggregate were used for 1 part of cement. Chemical analyses of all materials used and the particle size distribution of the aggregate (maximum size 12 mm) were described previously.³

Immediately after the cylindrical test samples were prepared, the pastes (water/cement ratio=0.4) were evacuated ($P=10$ cm Hg) for a few minutes to eliminate air bubbles; some of the concretes (those with the lower w/c ratios) were prepared by vibration. Both the pastes and the concretes (w/c=0.5 or 0.6) were cured at 25°C under wet sand for 2 months. After an additional month of air-curing, the test samples were put in contact with a CaCl₂ solution (30 g/kg water) using the method described in Ref. 3. The CaCl₂ solutions were renewed each week with freshly prepared solutions of the same concentration. The pastes were kept at 10°, 25°, and 40°C, the concretes at 25°C. Samples were removed periodically from the thermostated vessels and cut into slices perpendicular to the axis of the cylinder at distances of x cm from the surface moistened by the solution. The Cl⁻ ion concentration, C_x (Mg Cl⁻/g of paste), of each slice was determined by chemical analysis.

Isothermal adsorption of N₂ was measured for the paste samples, and pore-size distribution curves were calculated.⁴ Cumulative pore-size distribution curves were obtained for the same samples and for the concretes using an Hg porosimeter.⁴ Coarse aggregate in the concrete was removed.

The diffusion coefficient (D) of Cl⁻ ion in the pastes (Table I) was calculated from the equation $C_x/C_0 = 1 - \text{erf}(x/2\sqrt{Dt})$, which is the solution⁵ of Fick's second law under non-steady-state conditions for diffusion in a semi-infinite solid and for the boundary conditions $C_x=0$ at $t=0$, $0 < x < \infty$; $C_x=C_0$ at $x=0$, $0 < t < \infty$. The values of $\text{erf}(x/2\sqrt{Dt})$ vs $x/2\sqrt{Dt}$ are available in mathematical tables,⁶ so that when C_x , C_0 , x , and t are known, the diffusion coefficient, D , can be calculated. By extrapolating the curve of C_x vs x to $x=0$, values of C_0 and D were obtained.

At 25°C the order of magnitude of the diffusion coefficients for Cl⁻ ion in the cement pastes is 10^{-8} cm²/s, a value smaller than D for Cl⁻ ion diffusion in water (2.03×10^{-5} cm²/s) (Ref. 7) by a factor of 10^3 . The interaction between the surfaces of the pores and the diffusing ions could be responsible for lowering the diffusion coefficient of the Cl⁻ ion in the hydrated cement.

The pozzolanic cements offer a higher resistance to the flow of Cl⁻ ions than the portland cement pastes. At 25°C the value of D is ≈ 3 times larger in the portland cement. The total volume of the micropores (0.1 cm³/g of paste) and

Table I. Coefficients for Diffusion of Chloride Ion into Cement Pastes and Concretes

Sample	D (cm ² s ⁻¹ × 10 ⁹)	Temp. (°C)
Portland cement paste	1.23	10
" "	2.51	25
" "	4.85	40
Pozzolanic cement paste	0.83	10
" "	0.90	25
" "	0.97	40
Portland cement concrete (vibrated)	1.65	25
Portland cement concrete (nonvibrated)	3.24	25
Pozzolanic cement concrete (vibrated)	1.05	25
Pozzolanic cement concrete (nonvibrated)	2.26	25

Table II. Porosity in Concretes Wetted for 5 Months as Measured by Hg Porosimetry

Concrete	w/c	Porosity (cm ³ /g of dry sample × 10 ³)
Portland cement vibrated concrete	0.5	52.3
Portland cement nonvibrated concrete	.6	71.4
Pozzolanic cement vibrated concrete	.5	62.7
Pozzolanic cement nonvibrated concrete	.6	81.4

the pore-size distribution (10 to 300 Å) are essentially the same in the two types of cement paste. The pozzolanic cement paste has a slightly larger pore volume in the macropore range (0.01 to 10 μm). In paste samples wetted for 5 months at 25°C, the cumulative volume of macropores at a pore diameter of 0.01 μm is 0.21 and 0.23 cm³/g of paste for the portland and pozzolanic cement pastes, respectively. Similar results were obtained for other curing times.

The greater resistance offered by the pozzolanic cement paste to the diffusion of Cl⁻ ions cannot therefore be ascribed to a less porous hydrated product or to a product with the same total porosity but smaller pores. It seems reasonable then to assume that this difference in the diffusion coefficients arises from different types of interactions between the Cl⁻ ions and the pore surfaces of the materials studied. The difference in the diffusion coefficients could also be ascribed to a differing mobility of the water molecules present in the gel pores resulting from differences in the nature of the pore surfaces in the two cases.

The activation energy calculated from the temperature dependence of the diffusion coefficient is ≈ 8.5 kcal/mol for the portland cement paste and 1.0 kcal/mol for the pozzolanic cement paste. This result is of considerable practical interest because it shows that the difference in the rate of pene-

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tration of the Cl^- ion through the cement pastes is more pronounced during summer.

In Table I results are also shown for penetration of Cl^- ions into concrete samples. These data confirm those obtained using pastes; the addition of pozzolana causes a decrease in the rate of penetration of Cl^- ion. For the same type of cement, the concretes which had not been vibrated were less resistant to penetration of Cl^- ion than those vibrated and prepared with less water. Comparison of the macropore volumes (Table II) shows that, for the same type of cement, nonvibrated concretes are more porous than vibrated ones. These results confirm those of Ost and Monfore,⁶ i.e. when porosity (as deduced from the w/c ratio) is the only variable, its increase produces an increase in the penetration rate of Cl^- ions. However, for the same w/c ratio and same vibration treatment, the concretes prepared with pozzolanic cement, although more porous, are less permeable to Cl^- ions than those containing portland cement. This result supports the hypothesis that the differing nature of the surfaces of the pores formed in the presence of pozzolana plays a vital role in

affecting the behavior of the cement structures during the penetration of Cl^- ions.

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² M. Jack Snyder, "Protective Coatings to Prevent Deterioration of Concrete by Deicing Chemicals," National Cooperative Highway Research Program, Rept. No. 18, pp. 1-21 (1965).

³ Mario Collepardi, Aldo Marcialis, and Renato Turriziani, "Kinetics of Penetration of Chloride Ions in Concrete," *Ind. Ital. Cem.*, 4, 157-64 (1970).

⁴ Mario Collepardi, Giulio Rossi, and M. C. Spiga, "Influence of Calcium Chloride in Paste Hydration of Tricalcium Silicate," *Rend. Accad. Naz.* 40 [*Quaranta*], 18, 1-12 (1968).

⁵ J. Crank, *Mathematics of Diffusion*. Clarendon Press, Oxford, 1956.

⁶ *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*; p. 295. Edited by Milton Abramowitz and I. A. Stegun. Applied Mathematics Series, No. 55, National Bureau of Standards, Washington, D. C., 1965.

⁷ I. M. Kolthoff and J. J. Lingane; p. 52 in *Polarography*, Vol. 1, 2d ed. Interscience Publishers, Inc., N. Y., 1952.

⁸ Borje Ost and G. E. Monfore, "Penetration of Chloride into Concrete," *J. PCA Res. Develop. Lab.*, 8 [1] 46-52 (1966).