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MEASURING CHLORIDE DIFFUSION COEFFICIENTS FROM NON-STEADY STATE DIFFUSION TESTS

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ABSTRACT

This study presents a reliable method for evaluating chloride-effective diffusivity in cementitous materials. Four types of mortars with various w/c ratios and admixtures were investigated. Binding capacities of mortars were measured by solution immersion tests in order to respect non-linearity of binding in solving Fick's diffusion equation. Total chloride profiles were precisely measured after diffusion tests at various times of exposure. Then free chloride profiles were evaluated, with full knowledge of isotherms and physical properties. From total and free chloride profiles, it was possible to calculate the evolution of chloride diffusivity over the whole range of chloride concentration. Diffusivity was found to decrease while free chloride concentration increases, but the influence is significant only for very low concentrations. *© 1998 Elsevier Science Ltd*

Introduction

Chloride-induced corrosion is a major cause of deterioration for structures exposed to a marine environment or to deicing salt. Therefore, the development of reliable methods to predict chloride ingress into concrete is essential for durability design.

The first step towards a better prediction is a quantitative study of chloride motion in saturated materials. Unfortunately, steady-state diffusion tests as commonly used do not provide essential information about the interactions between chloride and hydrated cement pastes or about the influence of chloride concentration upon the effective diffusivity, which has been the subject of discussion for a number of years (1).

To provide a few answers, chloride diffusion in non-steady state was studied by following chloride profiles in the materials and taking into account the non-linearity of chloride binding.

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TABLE 1
Compositions and properties of cements.

	Oxydes (%)				Bogue (%)				Properties	
	CaO	SiO_2	Al_2O_3	Fe_2O_3	C_3S	C_2S	C_3A	C_4AF	Fineness m^2/kg	Density
CEM I, 52.5 HTS	67.0	22.8	2.8	2.1	67.2	16.4	6.5	4.5	317	3.18
CEM I, 52.5	65.0	20.9	5.0	1.9	58.9	14.7	11.3	6.6	290	3.14

Materials

Two types of Portland cement were used in this study. Their chemical composition and physical properties are given in Table 1.

Four compositions of mortar were studied. Their compositions and properties are given in Table 2. Physical properties of mortars were measured after 1 year using mercury porosimetry. Specimens were molded in Ø 120 × 240 mm PVC cylinders and stored at 100% RH and 20°C for 1 day. Then specimens were demoulded and kept in water at 20°C for at least 1 year so that hydration processes could not interfere.

Chloride-Binding Isotherms

To determine the binding capacity of mortars, mortar samples were immersed into basic solutions (NaOH: 1 g/L, KOH: 4.65 g/L) with various NaCl concentrations (1).

After curing, the central regions of mortar cylinders were extracted and crushed into 0–2 mm particles. These particles were then vacuum-dried in a desiccator with silica gel at 20°C for 3 days and stored at 11% RH in a desiccator with saturated LiCl solution for 1 week, so that only a monolayer of water was adsorbed on the pore walls (2).

About $M = 50$ g of particles were then immersed into 100 mL of a known initial chloride solution (c_i). The containers were sealed and stored at 20°C for 21 days so that binding equilibrium was fully reached, as previous measurements (7) showed no clear evolution after 1 day of exposure. Then the whole solution was extracted by filtration and titrated (c_f). The amount of bound chloride was given by the difference between initial and final concentrations of the solution, assuming that chloride concentration in porewater is equal to that of the solution. All concentrations were measured by potentiometric titration using $AgNO_3$ with a METROHM 736 titrator.

TABLE 2
Compositions and physical properties of mortars.

	Cement	W/C	S/C	Dolomite filler	Silica Fume	Porosity	Apparent density	Specific. area m^2/kg
M1N	52.5 HTS	0.5	3	/	/	0.13	2.22	7500
M1	52.5 HTS	0.64	4.75	33% C	/	0.15	2.24	11800
M2N	52.5	0.5	3	/	/	0.12	2.21	9100
M2	52.5	0.48	3.9	18% C	9% C	0.14	2.28	15400

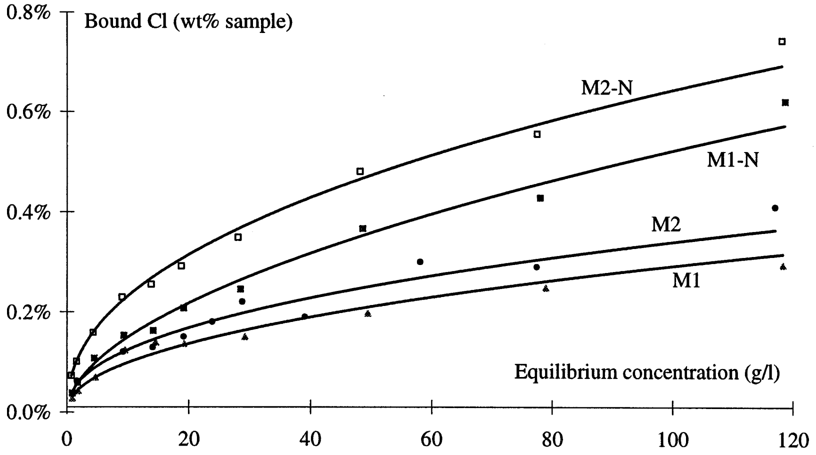

FIG. 1.
Chloride-binding isotherms of mortars.

$$\text{Bound Cl}^- = 0.1\,\frac{c_i - c_f}{M}\ \text{in weight \% of dry material}$$

The results of bound Cl^- as a function of equilibrium concentration are shown in Figure 1. Experimental curves were fitted by Freundlich isotherms (Table 3) with correlation coefficients higher than 0.96.

Two main conclusions can be drawn out from these results. First, as many authors have observed (2), there is no proportionality between the amount of bound chloride and the free chloride concentration. Also the difference in bound chloride between M1N and M2N shows the influence of aluminates content upon chloride binding (4).

Diffusion Experiments

In order to reduce the testing time and to check chloride binding isotherms, we chose to analyze chloride diffusion by following chloride profiles in mortars in a non-steady state.

The samples were thin cylinders (Ø 120 × 2 cm) drawn out from central regions of initial specimens and then placed in diffusion cells. Upstream cells were filled with NaOH, KOH solutions with [Cl] = 20 g/L. Downstream cells only contained NaOH, KOH solutions. After at least 7 days of exposure, samples were removed and chloride profiles were measured using a Profile Grinder GERMANN INSTs (5) which draws powder (<80 μm) from the sample over a 73-mm disk and allows a 0.5-mm penetration increment.

TABLE 3
Freundlich isotherms.

M1N	$0.00042c_f^{0.55}$
M1	$0.00033c_f^{0.47}$
M2N	$0.00083c_f^{0.45}$
M2	$0.00045c_f^{0.44}$

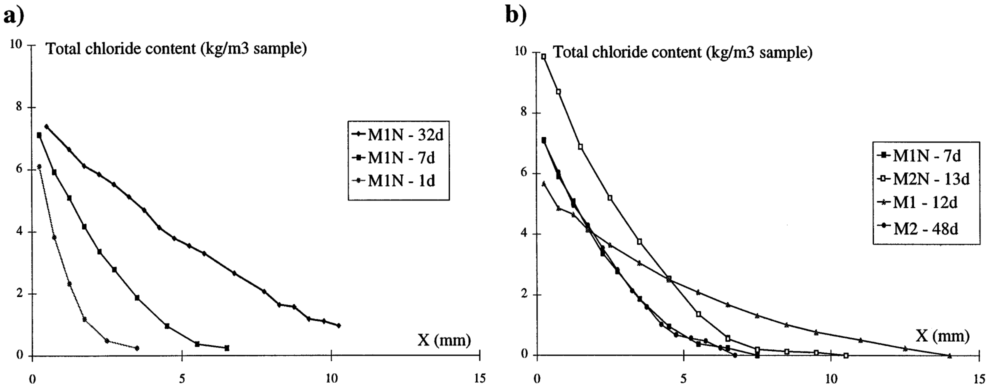

FIG. 2.
Total chloride profiles during diffusion tests.

The determination of total chloride content was performed on M ≈ 3 g of powder put in 10 mL of demineralized water with 3 ml of pure HNO_3 for 10 min. Then 50 mL of water was added and the solution heated at 80°C for 30 min. Then this solution was filtrated and up to 250 mL water was added. The concentration of the final solution was measured by potentiometric titration using 0.01 N $AgNO_3$. The total chloride content is given by:

$$m_{\mathrm{Cl}} = \frac{0.25\,c}{M}\,\rho_{\mathrm{H}}$$

where m_{Cl} is the total chloride content, kg/m^3 sample; c is the filtrated solution concentration, g/L; M is the weight of mortar powder, g; and ρ_{H} is the saturated mortar specific weight, kg/m^3.

Figure 2 shows total chloride profiles obtained for each material at various times of exposure.

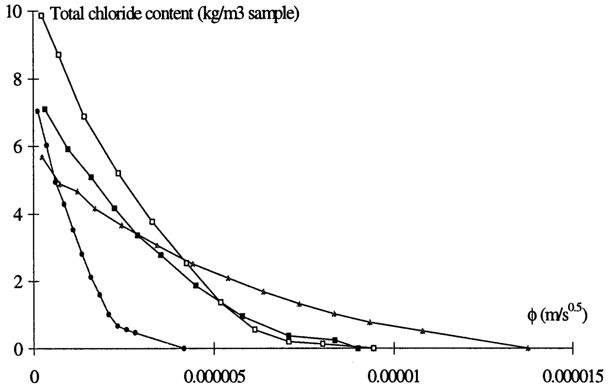

FIG. 3.
Total chloride content as a function of Boltzmann's variable.

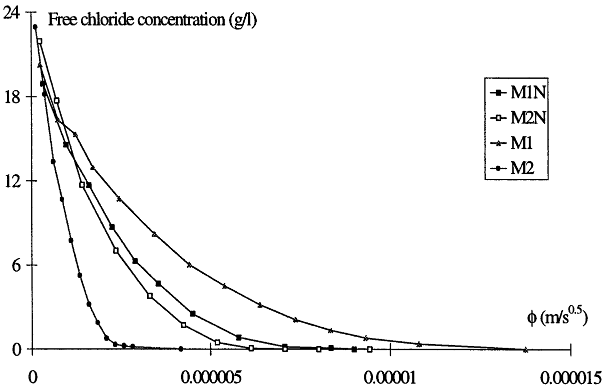

FIG. 4.
Free chloride concentration as a function of Boltzmann's variable.

Chloride Diffusivity Measurements

Figure 2a shows that the total amount of chloride close to upstream surface has already reached its equilibrium value after 1 day of exposure. Assuming then that chloride binding occurs almost instantaneously compared to the diffusion process, the free chloride concentration C (g/L) in porewater complies with the following equation:

$$m_{\mathrm{Cl}} = \tau \cdot C + \rho_S \cdot a \cdot C^{\gamma}$$

where τ is the porosity; a, γ are coefficients of Freundlich isotherm; and ρ_S: dry mortar specific weight, kg/m^3.

Chloride transport in porous media is governed by Fick's second law:

$$\frac{\partial m_{\mathrm{Cl}}}{\partial t} = \frac{\partial}{\partial X}\left[D(C) \cdot \frac{\partial C}{\partial X}\right]$$

if the diffusivity tensor D varies with the free chloride concentration.

To solve this equation in the case of unidimensional flow, we can introduce the Boltzmann's variable: $\phi = X/\sqrt{\pm}$.

The increase between *0* and t of total chloride content beyond X can be expressed as:

$$m(X, t) = \int_{x}^{\infty} m_{\mathrm{Cl}}(\xi, t) \cdot d\xi$$

The chloride flux at X, t can be calculated, assuming that infinite flux remains equal to *0*:

$$J(X, t) = \frac{\partial m}{\partial t} = \int_{x}^{\infty} \frac{\partial m_{\mathrm{Cl}}}{\partial t} \cdot d\xi \overset{\phi = X/\sqrt{t}}{=} \frac{1}{2\sqrt{t}} \int_{0}^{m_{\mathrm{Cl}}(X,t)} \phi \cdot d\xi$$

Moreover, from Fick's first law, J can be expressed as:

$$J(X, t) = -D(C) \cdot \frac{\partial C}{\partial X} \overset{\phi = X/\sqrt{t}}{=} -D(C) \cdot \frac{1}{\sqrt{t}} \cdot \frac{\partial C}{\partial \phi}$$

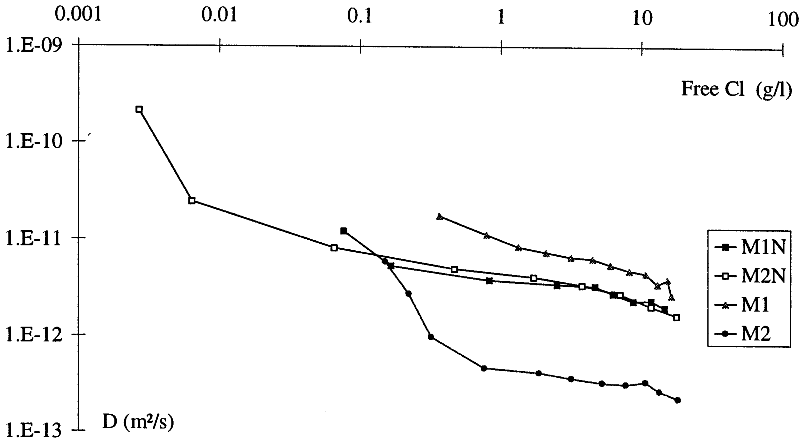

FIG. 5.
Chloride diffusivity as a function of free chloride concentration.

To finally obtain:

$$D(C) = -\frac{1}{2\frac{\partial C}{\partial \phi}} \int_0^{m_{\mathrm{Cl}}} \phi \cdot d\xi$$

So D can be readily obtained from the total chloride and free chloride concentration profiles.

Figures 3 and 4 show respectively the changes in total chloride content and free chloride concentration as a function of ϕ (Boltzmann's profiles).

Discussion

The calculation of chloride diffusivities (Fig. 5) clearly demonstrates the influence of mortar composition on diffusion processes. The two mortars with w/c ratio 0.5 have similar diffusivities despite their different binding capacities. Mortar M1, which has the highest w/c ratio, presents the highest permeability to chloride ions. Mortar M2 shows the influence of silica fume upon transfer properties by reducing pore size and connectivity.

It appears that chloride diffusivity decreases as porewater concentration increases, as predicted by certain authors (6). But the influence of concentration becomes predominant only for very low concentrations. Moreover, we must be aware that this influence could be nothing but the visible effect of various phenomena such as a decrease in connected porosity with the penetration depth and a concentration dependency of chloride-binding kinetics (3) that cannot occur instantly (7).

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