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Studies of chloride binding in concrete exposed in a marine environment

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Abstract

The concentrations of "free" chloride and hydroxide ions in extracted pore solution from concrete exposed and submerged in a marine field station were studied by the pore solution expression method. In addition, the corresponding concentrations of total acid soluble chloride in the concrete was analyzed. The relationship between total and free chlorides was analyzed and compared with similar data from laboratory-exposed cement paste and concrete. Hydroxide ions were found to be transported away from the concrete at a rate similar to the penetration rate of chloride ions into the concrete. The amount of bound chlorides was found to increase as the concentration of hydroxide ions in the pore solution decreases. As a consequence, the relationship between free and total chlorides in concrete with a chloride and hydroxide ion gradient was found to be almost linear. It was suggested that the nonlinear chloride binding relationship observed in laboratory equilibrium tests is not relevant for submerged concrete with diffusion gradients of chloride and hydroxide. However, only limited information exists on the long-term chloride binding relationship reflecting the long-term situation when all alkali hydroxides have been leached to the sea. It was speculated that the chloride binding and the transport rate depend on the available amount of mobile alkali hydroxide and thus on the thickness of the concrete member.

Keywords: Chloride; Pore solution; Diffusion; Concrete

Relationships between total free and bound chloride ions in concrete are important for the development of models for service life predictions of reinforced concrete with respect to reinforcement corrosion. The binding of chlorides in hydrated cement paste affects both the transport rate of chlorides into concrete and the amount of chlorides necessary to initiate active corrosion.

1. Background

1.1. Literature data on equilibrium laboratory studies of chloride binding in hydrated cement paste

Equilibrium laboratory studies of chloride binding in hydrated cement paste normally results in a nonlinear relationship between free and bound chloride [1]. As a consequence of the nonlinear chloride binding, the relationship between free and total chloride is also nonlinear. Tang and Nilsson [1] studied the adsorption of chloride ions in crushed cement paste and mortar from a NaCl solution saturated with calcium hydroxide (Fig. 1A). The total acid-soluble chloride content and the available pore volume, defined as the dry porosity at 11% relative humidity, were analyzed while the free chloride concentration was assumed to be equal to that in the equilibrium solution.

Sandberg and Larsson [2] used a similar approach to study the effect of hydroxide ion concentration on chloride binding in cement paste disks exposed for 6 months in simulated pore solutions reflecting the composition of the pore solution in concrete (Fig. 1B). The total acid-soluble chloride content and the available pore volume were analyzed similarly as described previously [1], but the free chloride and hydroxide ion concentrations in the cement paste also were analyzed in extracted pore solution by the pore solution expression method [3]. It was found that the difference in free chloride and hydroxide ion concentrations measured in the surrounding simulated pore solution and in the extracted pore solution was less than 5%, showing that equilibrium had actually been reached.

1.2. Literature data on laboratory studies of the combined transport of chloride and hydroxide ions in cement paste

Laboratory studies of the transport of chloride and hydroxide ions in cement paste immersed in a saline solution indicated that the transport rates for chloride (ingress) and hydroxide (leaching) are about the same [4] (Fig. 2). The corresponding diffusivities for chloride and hydroxide ions

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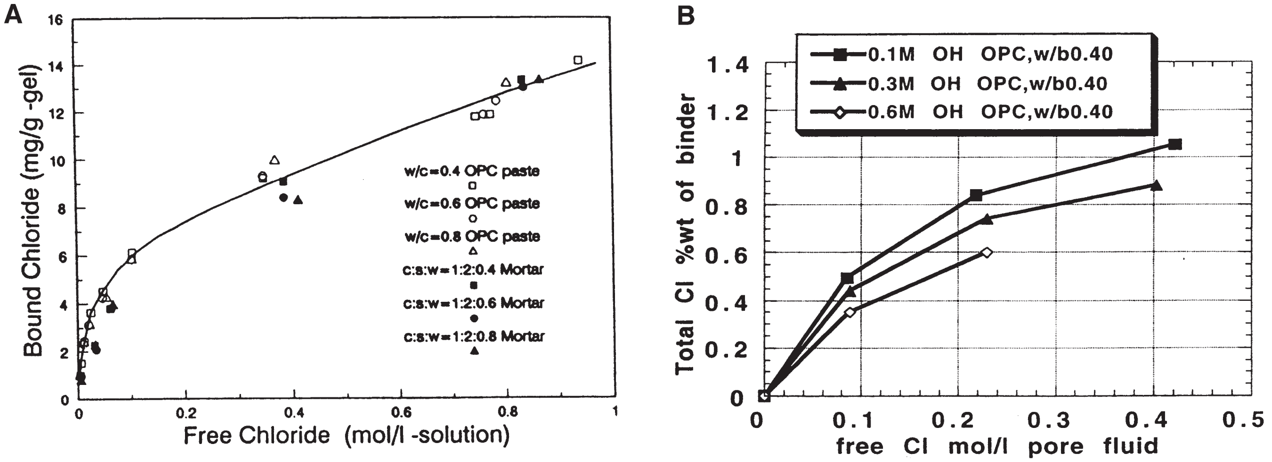

Fig. 1. (*A*) Chloride adsorption isotherms of ordinary Portland cement (OPC) pastes and mortars (per unit weight of CSH gel) (1). (*B*) Influence of hydroxide ion concentration on chloride adsorption [2]. w/c, water-to-cement ratio.

were calculated to 15 and 19 E-12 m^2/s, respectively, by fitting the measured profiles to a solution to Fick's second law of diffusion, assuming linear binding and a constant diffusion coefficient.

1.3. The relationship between free and bound chlorides in field-exposed concrete

The relationship between free and total chlorides shown in Fig. 1 is derived from equilibrium studies of thin cement paste or mortar specimens in saline solutions. Field-exposed concrete is not at equilibrium. In submerged concrete, the chloride concentration gradient is accompanied by a hydroxide concentration gradient, as indicated in Fig. 2. It therefore can be anticipated that the effect of hydroxide ion concentration on the chloride binding (Fig. 1) and the effect of the hydroxide gradient (Fig. 2) would increase the amount of bound chlorides in the surface of submerged field-exposed concrete. As a consequence, the relationship between free and total chlorides would become more linear in field-exposed concrete with a hydroxide gradient as compared to the relationships shown in Fig. 1. This was confirmed as shown in the following.

2. Experimental

Concrete slabs, height 100 cm, width 70 cm, thickness 10 cm, were cast according to Tables 1 and 2. They were moist cured for 10 days before marine exposure and mounted on a floating pontoon at Träslövsläge on the Swedish west coast. The bottom half of each slab was submerged in the sea.

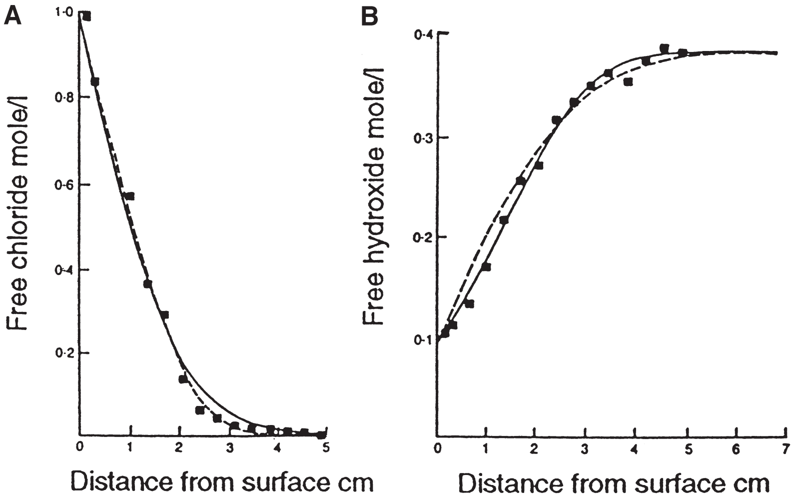

Fig. 2. Concentration profiles of chloride ion (*A*) and hydroxide ion (*B*) in expressed pore solution from a Portland cement paste, w/c = 0.50, immersed for 100 days in a 1.0M NaCl solution saturated with calcium hydroxide [4].

Table 1
Concrete mixture proportions

Materials (dry kg/m^3)	SRPC (w/c 0.45)	SRPC (w/c 0.50)	OPC (w/c 0.50)	SRPC 5% silica fume (w/c 0.50)	SRPC (w/c 0.75)	SRPC 5% silica fume (w/c 0.75)
Cement	400	370	390	351	240	233
Silica fume	—	—	—	19	—	12
Sand 0–8 mm	850	876	853	840	1013	966
Gravel 8–16 mm	788	808	787	840	796	823
Air content (%)	6	6	6	6	6	6
f′c 28d (MPa)	47	41	43	45	21	21

OPC, ordinary Portland cement; SRPC, sulfate-resisting Portland cement.

Concrete with high water-to-cement (w/c) ratios was studied for the following reasons:

1. The pore solution expression method is relatively easy to perform on concrete with w/c ratio >0.45. The amount of expressible pore solution is high, which improves the accuracy of the method.
2. The chloride penetration, the hydroxide leaching, and the cement hydration proceed faster the higher the w/c ratio. A shorter field exposure time for concrete with a high w/c ratio may simulate the situation in concrete with a low w/c ratio after a much longer field exposure time.

After 7, 14, and 24 months of field exposure, cores with diameter 100 mm were drilled from the submerged and splash zone parts of the slabs. Immediately after drilling, the cores were split parallel to the exposed surface into 10- to 15-mm-thick disks. Each disk was immediately sealed into an airtight plastic bag before transport to the laboratory, where the outermost 10 mm closest to the sawn surface of each disk was removed. The remaining part of each disk was analyzed for total acid-soluble chloride content by weight of binder and for the concentration of free chloride and hydroxide ions in expressed pore solution. The total acid-soluble chloride content and the binder content were analyzed as described by Fredericsen [5], whereas the free

Table 2
Details of cementitious materials

	Sulfate-resisting Portland cement	Ordinary Portland cement	Silica fume
Fineness (percent passing)			
45 µm	85.9	97.4	100
20 µm	51.3	64.0	
10 µm	33.1	41.7	
5 µm	19.5	26.0	
1 µm	3.8	5.4	
Specific surface (m^2/kg)			
Blaine	300	360	
BET			23000
Specific gravity	3.15	3.11	2.22
Compressive strength EN196 (MPa)			
1 day	10.1	18.9	
7 days	35.6	45.2	
28 days	56.2	55.2	
Chemical analysis (%)			
CaO	63.8	62.5	0.4
SiO_2	22.8	19.6	94.2*
Al_2O_3	3.48	4.17	0.62
Fe_2O_3	4.74	2.17	0.95
MgO	0.80	3.45	0.65
SO_3	1.98	3.29	0.33
K_2O	0.55	1.29	0.5
Na_2O	0.06	0.26	0.2
Bogue potential compounds (%)			
C_3S	51.5	61.4	
C_2S	25.5	9.9	
C_3A	1.3	7.6	
C_4AF	14.3	6.6	

*Amorphous silica content.

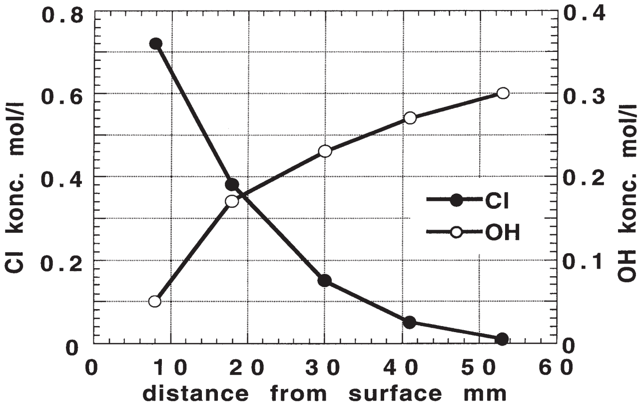

Fig. 3. Concentration profiles of hydroxide and chloride ions measured in expressed concrete pore solution for w/c = 0.50 and 14 months of exposure in the submerged zone.

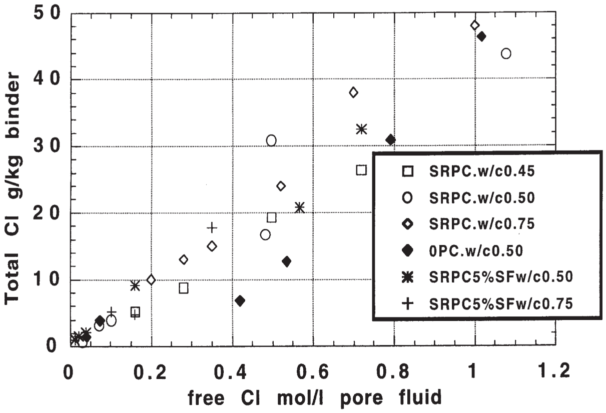

Fig. 4. Relationship between free and total chlorides in expressed pore solution from concrete exposed and submerged in seawater or in the splash zone.

chloride and hydroxide ions in expressed pore solution were analyzed as described by Byfors [6].

3. Results

A typical set of concentration profiles of hydroxide and chloride ions measured in expressed concrete pore solution for w/c ratio = 0.50 and 14 months of exposure is shown in Fig. 3. The relationship between measured total chloride content by weight of binder and the measured concentration of chloride ions in expressed pore solution for all disks analyzed is shown in Fig. 4.

4. Discussion

The relationship between free and total chlorides measured in field-exposed concrete was found to be more linear as compared to the corresponding relationship measured in equilibrium experiments without gradients of free chloride and hydroxide ions in the sample. The increased chloride binding at lower free hydroxide concentrations found in laboratory equilibrium experiments seems to explain, at least in part, the more linear relationship found in field-exposed concrete with concentration gradients of free chloride and hydroxide in the concrete pore solution.

The pore solution expression method is known to be more inaccurate when used on concrete as compared to cement paste; however, the scatter of the results shown in Fig. 4 indicates that the error is small enough to validate the use of the pore solution expression method on concrete. The data points at higher chloride concentrations correspond to measurements in concrete close to the exposed surface, e.g., concrete with low hydroxide ion concentrations in the expressed pore solution.

It would be anticipated that a difference in the exposure temperature and the laboratory temperature at which the pore solution expression is carried out would affect the chloride binding. The concrete temperature when sampled at the field station was approximately +15°C, +7°C and +4 °C after 7, 14, and 24 months of exposure, respectively. The concrete temperature was measured by thermocouples at relevant positions on parallel concrete slabs. The disk temperature was approximately +20 °C when subjected to the pore solution expression in the laboratory. The difference in chloride binding at such small temperature differences probably is not very large, as shown by Tritthart [7] for laboratory-exposed cement paste. Furthermore, any temperature “error” should have the same relative size at low and high chloride concentrations; therefore, the degree of linearity in Fig. 3 should not change.

The results from this field study suggest that the nonlinear chloride binding relationship observed in laboratory equilibrium tests is not relevant for concrete with diffusion gradients of chloride and hydroxide. It is suggested that most, if not all, chloride penetration in concrete before corrosion initiation in ordinary steel reinforcement takes place in concrete with a hydroxide concentration gradient as indicated in Figs. 2 and 3.

The transport rate of hydroxide ions appears very similar to the transport rate of chloride ions in concrete. However, the source of chloride ions in submerged concrete is unlimited, whereas the amount of alkali hydroxide depends on the cement type and content and is limited as compared to the source of chloride ions. The chloride ion diffusion rate in a thick concrete member would be affected by a continuous counter diffusion of hydroxide ions from the alkali hydroxide in the interior concrete for a relatively long time, but in a thin concrete member the reservoir of alkali hydroxides would be removed more quickly. As the hydroxide ion concentration drops, the chloride binding and the solubility of calcium hydroxide increases. It is possible that the net effect would be a chloride binding and chloride penetration rate that are dependent on the exposure zone and the thickness of the concrete member.

The almost linear relationship found between free and total chlorides in field-exposed concrete implies that solutions to Fick's second law of diffusion based on linear chloride binding can be used for simple prediction of chloride ingress in concrete.

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