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Communication

Relationship between free chloride and total chloride contents in concrete

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Abstract

Linear relationships between free chloride and total chloride contents in concrete are proposed based on the results of several long-term exposure tests under marine environment for various cements, such as ordinary portland cement (OPC), high early strength portland cement (HES), moderate heat portland cement (MH), calcium aluminate cement (AL), slag cements of Types A (SCA) and B (SCB), and fly ash cement of Type B (FACB). A high chloride-binding ability is found for AL as compared to the other cements. Replacing the OPC with slag reduces the chloride-binding ability. The proposed linear relationships show reasonably good agreement with field data obtained from the wharf structures.
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Keywords: Concrete; Chloride; Portland cement; Calcium aluminate cement; Blended cement

1. Introduction

Chloride-induced corrosion of steel bars in marine concrete structures is a major concern to the concrete professionals. The chloride occurs in concrete both in free or uncombined form as well as bound to cement hydration products through adsorption or chemical composition in the form of Friedel's salt. Although the free chloride is generally believed to be responsible for the initiation of corrosion, the chloride threshold value necessary to initiate corrosion of steel bars in concrete is mostly provided in terms of total chloride and only occasionally in terms of free chloride [1–4]. It is supposed due to the difficulties in evaluating free chloride contents in concrete. However, with the existence of reasonably accurate relationships between free and total chlorides, this problem can be solved. In recent technical literature, this matter was also pointed out [5,6]. Due to the lack of long-term exposure data, generally short-term exposure data are used to predict the relationship between total and free chloride contents in concrete. However, the authors realized that the relationship between free and total chloride contents in concrete is necessary to be established based on the results of long-term exposure tests under marine environment, where chlorides are allowed to diffuse into concrete naturally.

With the abovementioned background, relationships between free chloride and total chloride contents in concrete are proposed for various types of cements, such as ordinary portland cement (OPC), moderate heat portland cement (MH), high early strength portland cement (HES), calcium aluminate cement (AL), slag cements of Types A (SCA) and B (SCB), and fly ash cement of Type B (FACB). Irrespective of the cement type, the total chloride content is found to increase with an increase in the free chloride content. A higher chloride binding is observed for AL. Separate linear relationships are proposed for various types of cements. The results of this report should be very useful to the concrete professionals dealing with corrosion of steel bars in concrete.

2. Experimental method

The cements investigated in this study cover OPC, HES, MH, AL, blended cements such as SCA and SCB, and FACB. In SCA and SCB, the slag contents were 5–30%, and 30–60% of cement mass, respectively. In FACB, the fly ash content was 5–10% of cement mass.

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Table 1
Physical properties and chemical composition of seawater

Specific gravity	pH	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO_4 (ppm)	CO_3 (ppm)
1.022	7.77	9290	346	356	1167	17,087	2378	110

River sand and crushed granite coarse aggregate were used in most of the investigations. W/C ratios varied from 0.45 to 0.55 in most of the cases.

Chloride sampling was done from the cylinder specimens in most cases and from beam specimens in a few cases. The specimens were exposed to a tidal pool beside the sea. Seawater was automatically pumped in and drained out at 6-h intervals directly from the sea. The physical properties and chemical compositions of seawater are listed in Table 1. Concrete samples were collected from the surface to the inner region of the specimens at regular intervals using a diamond cutter. The age of the sampled specimens ranged from 10 to 30 years. Concrete samples were also collected from various wharves in Japan that ranged from 15 to 50 years in age.

Acid- and water-soluble chloride concentrations in concrete were measured as per JCI SC4 standard test method. The concrete samples from the specimens exposed to the tidal pool were analyzed by the authors. The samples collected from the wharf structures were analyzed at several other laboratories. Note that the water-soluble chloride concentration is defined here as the free chloride and acid-soluble chloride concentration as the total chloride.

3. Experimental results and discussion

Data for total chloride versus free chloride are plotted in Figs. 1–7 for OPC, HES, MH, AL, SCA, SCB, and FACB. Chloride data were obtained from the concrete specimens exposed to the marine environment for 10 to 30 years. The total chloride content was found to increase with increase in the free chloride content irrespective of the cement type. For some cements, such as MH, HES, AL, and SCA, relatively very little data were available as compared to the OPC, SCB, and FACB. Using the available data, the following

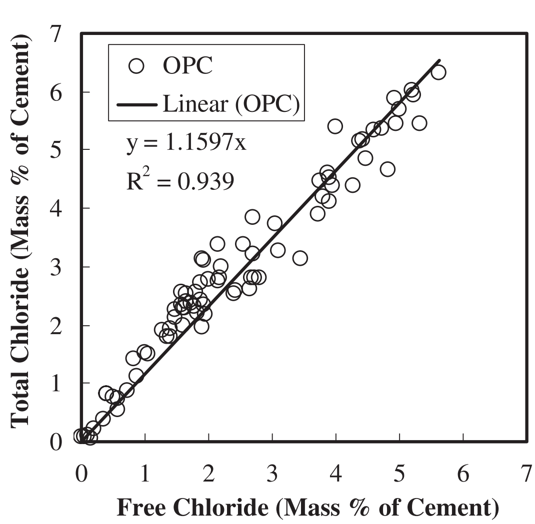

Fig. 1. Relationship between total chloride and free chloride—OPC.

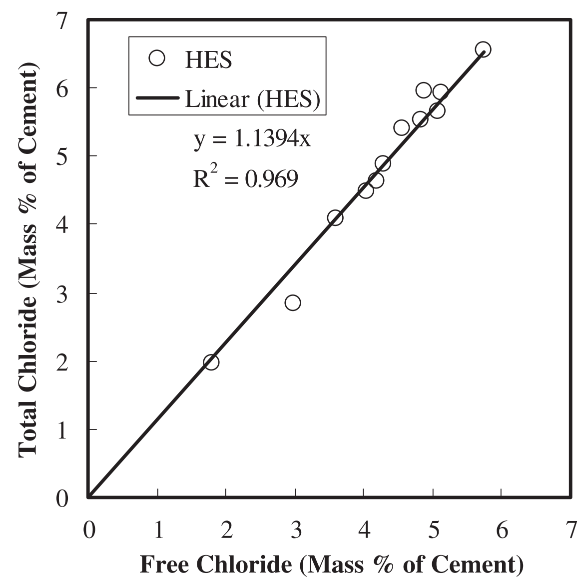

Fig. 2. Relationship between total chloride and free chloride—HES.

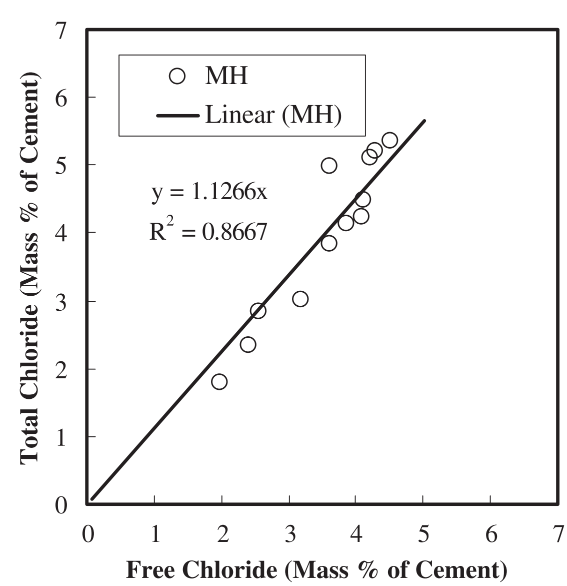

Fig. 3. Relationship between total chloride and free chloride—MH.

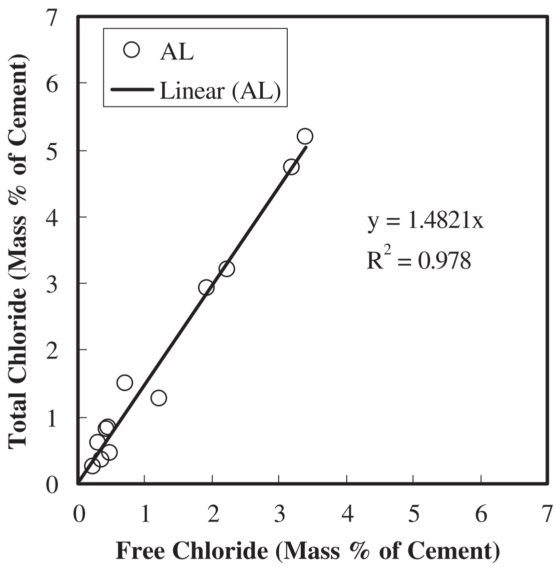

Fig. 4. Relationship between total chloride and free chloride—AL.

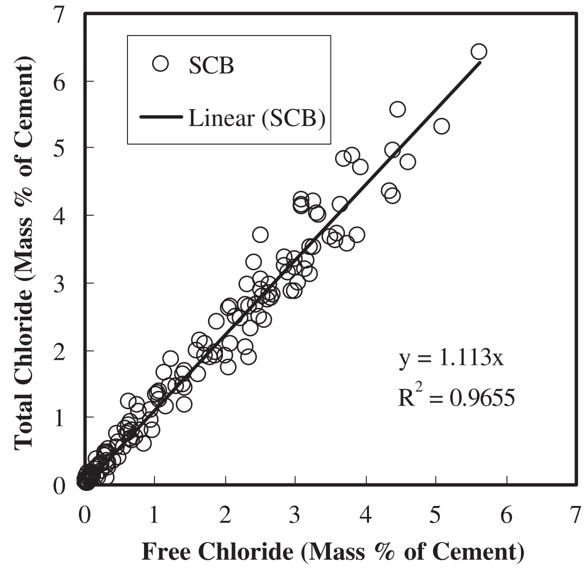

Fig. 6. Relationship between total chloride and free chloride—SCB.

linear relationships are proposed for various types of cements tested in this study:

$$\text{OPC}: \; C_t = 1.1597C_f, \qquad R^2 = 0.94 \tag{1}$$

$$\text{HES}: \; C_t = 1.139C_f, \qquad R^2 = 0.97 \tag{2}$$

$$\text{MH}: \; C_t = 1.1266C_f, \qquad R^2 = 0.87 \tag{3}$$

$$\text{AL}: \; C_t = 1.4821C_f, \qquad R^2 = 0.98 \tag{4}$$

$$\text{SCA}: \; C_t = 1.1533C_f, \qquad R^2 = 0.94 \tag{5}$$

$$\text{SCB}: \; C_t = 1.113C_f, \qquad R^2 = 0.97 \tag{6}$$

$$\text{FACB}: \; C_t = 1.221C_f, \qquad R^2 = 0.95 \tag{7}$$

where C_t is the total chloride content in concrete and C_f is the free chloride content in concrete. By subtracting the amount of free chloride from both sides of the above-mentioned equations, the amount of bound chloride ($C_t - C_f$) can be calculated. The amounts of bound chloride are 0.1597, 0.139, 0.1266, 0.4821, 0.1533, 0.113, and 0.221 times of free chloride for OPC, HES, MH, AL, SCA, SCB, and FACB, respectively. It can be easily recognized that the chloride-binding ability of AL is much higher than that of the other cements. No significant variation in chloride binding is found for OPC, HES, MH, and SCA. For SCB, the binding ability is lower than the SCA. It is to be expected due to a higher replacement of ordinary portland cement by slag in SCB.

The water- and acid-soluble chloride concentrations in concrete obtained from 15- to 50-year-old wharves in Japan are presented in Fig. 8. These data are related to OPC. As

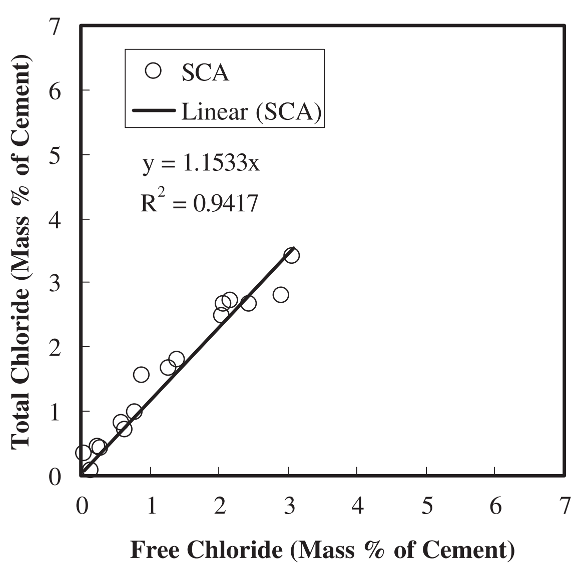

Fig. 5. Relationship between total chloride and free chloride—SCA.

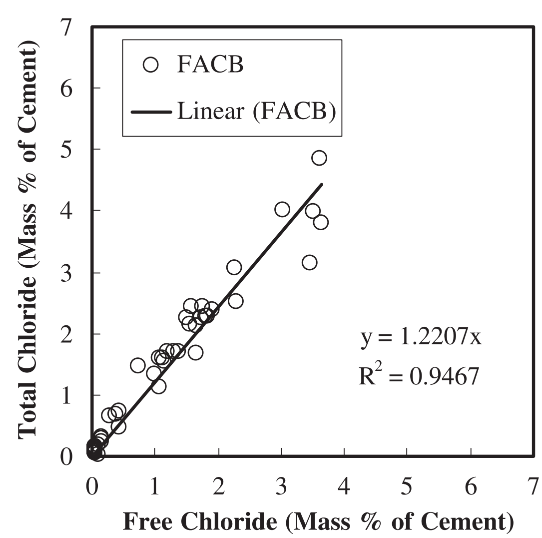

Fig. 7. Relationship between total chloride and free chloride—FACB.

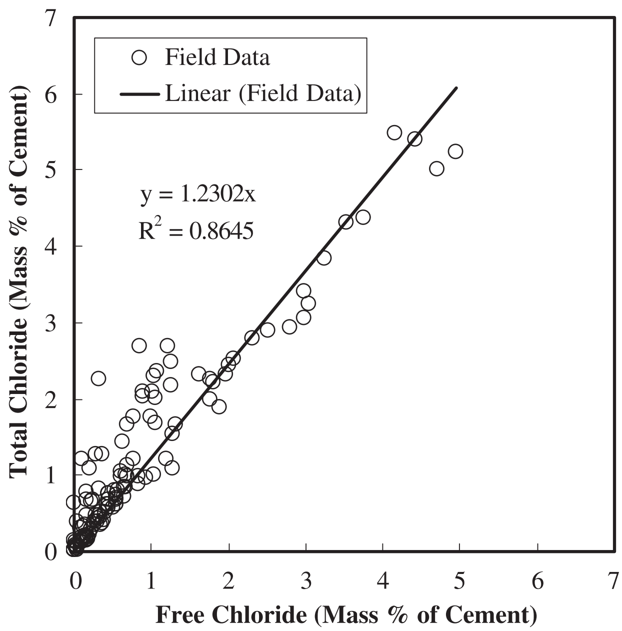

Fig. 8. Relationship between total chloride and free chloride—field data.

before, total chloride concentration increases with an increase in free chloride concentration. The following linear relationship between the free and total chloride is found:

$$C_t = 1.23C_f, \quad R^2 = 0.86 \tag{8}$$

The plot shows a rather large scattering of data particularly at low chloride levels. This may be due to factors such as the testing at other laboratories, sample collection by different people, etc. Still the relationship is in reasonable agreement with the proposed relationship for OPC before.

4. Conclusions

Based on the results of several long-term tests, linear relationships between free and total chloride concentrations are proposed for various types of cements, such as OPC, HES, MH, AL, SCA and SCB, and FACB. The chloride-binding ability of AL was found to be much higher than those of other cements. In slag cements, increased replacement of cement by slag cement caused a decrease in the chloride-binding ability.

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