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Discussion

A discussion of the paper "Relationship between the free and total chloride diffusivity in concrete" by Xinying Lu, Cuiling Li, and Haixia Zhang☆

T.U. Mohammed*, H. Hamada

Materials Division, Port and Airport Research Institute, Independent Administrative Institution, Yokosuka, 3-1-1 Nagase 239-0826, Japan

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Thanks to the authors for discussing an important matter in their recently published paper in *Cement and Concrete Research* journal. We were also thinking of summarizing a report based on our experimental data on free chloride and total chloride contents in concrete. We are still doing some experimental works on 30-year-old concrete specimens and we hope that we will be able to summarize the data in the near future. It is important to note that we have data from 10- to 30-year-old marine concrete specimens, which were exposed in a tidal pool near the sea, utilizing seawater directly from the sea. Some data were also randomly reported [1]. We have also data on the several wharves in Japan exposed to the marine environment from 2 to 55 years. The chloride contents were analyzed as per JCI SC4. After reading the authors' report on total and free chloride contents in concrete, we want to discuss with the authors the following three points:

> *Point 1:* The total chloride diffusivity is about 2.2 to 3.4 times than that of the free chloride in concrete.

Unfortunately, we cannot agree with these results based on our data observed in several long-term experimental programs. For reference, free and total chloride contents of 15-year-old concrete specimens made with ordinary portland, slag, and fly ash cements are given in Fig. 1. Here, two kinds of slag cement were used, such as slag cement of Types A and B. The slag contents were 5–30% and 30–60% in slag cement of Types A and B, respectively. In the case of fly ash cement, only fly ash cement of Type B was used, in which the fly ash content was 5–10% of cement mass. These cements are classified in the Japanese Industrial Standard. Remarkably, the total chloride content is not as high as the authors reported in their paper.

Three months of immersion in 3.5% NaCl solution may not provide the representative results as the concrete structures are made for more than 30 years of service life under marine environment. In addition, if the authors are going to check the data in future, perhaps a completely different conclusion can be found. At the very beginning stage of exposure, the amount of bound chloride may be higher due to the free calcium aluminate hydrate in the matrix as the bound chloride is strongly influenced by the tricalcium aluminate content of cement [2]. Based on the reported data in Fig. 1, the free chloride (C_f) and total chloride (C_t) for the different cements can be correlated with the following linear relations:

$$\text{OPC}: \; C_t = 1.16C_f, \; R^2 = 0.939 \quad (1)$$

$$\text{SCA}: \; C_t = 1.15C_f, \; R^2 = 0.942 \quad (2)$$

$$\text{SCB}: \; C_t = 1.11C_f, \; R^2 = 0.966 \quad (3)$$

$$\text{FACB}: \; C_t = 1.16C_f, R^2 = 0.934 \quad (4)$$

Subtracting the free chloride (C_f) from both sides of the above equations, it is possible to calculate the amount of bound chloride [total chloride (C_t) – free chloride (C_f)] as 0.16, 0.15, 0.11, and 0.16 times of free chloride for OPC, SCA, SCB, and FACB, respectively. These values are significantly different from that noted by the author in their paper. If the design engineers considered the total chloride diffusion coefficient as mentioned in the paper, the corrosion initiation time will be overestimated. It is expected that the short period of the authors' experimental program caused this kind of conclusion. After a long exposure period, it is expected that the situation will be changed with the availability of more free chloride.

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* Corresponding author. Tel.: +81-468-44-5061; fax: +81-468-44-0255.
E-mail address: tarek@pari.go.jp (T.U. Mohammed).

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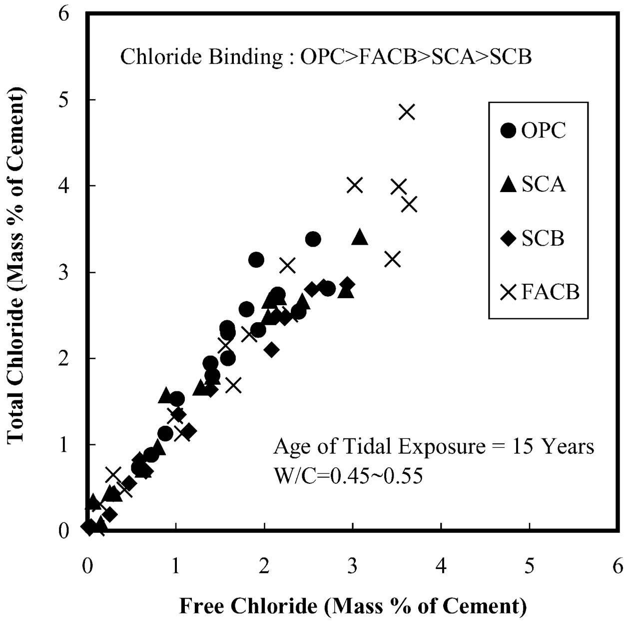

Fig. 1. Free chloride and total chloride contents in concrete.

> *Point 2:* The mineral admixtures, like fly ash, ground blast furnace slag, and silica fume, cannot only decrease the permeability of concrete, but also decrease the free chloride and increase the bound chloride content in concrete.

The reason behind the abovementioned discussion is unclear. Based on the reported data on Fig. 1, a tendency of having higher chloride-binding ability of ordinary portland cement is found compared to the other blended cements, especially slag cement. Recently, we are also investigating 30-year-old concrete specimens made with ordinary portland cement, slag cement of Type B, moderate-heat portland cement, high early-strength portland cement, and alumina cement. We clearly found that the chloride-binding ability of alumina cement is much higher than other cements due to the higher tricalcium aluminate content in the cement. In this cement, the bound chloride is about 0.5 times that of the free chloride. Based on these data, we did not find bound chloride as high as that noted by the authors in their paper.

> *Point 3:* In Fig. 7, the relation between the total and free chloride diffusivity is noted as follows:

$$D_t = 2.8211 D_f + 0.0046 \quad (\times 10^{-18}\ \mathrm{cm^2/s}) \tag{5}$$

It indicated that when the free chloride diffusivity is zero, the total chloride diffusivity has some value. We do not understand the physical meaning of this value.

The author’s comments on our pointed issues will be highly appreciated, which we hope would be very useful in summarizing our data in the near future. We would like to express again our sincere thanks to the authors for their publication on free chloride and total chloride contents in concrete.

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