Effect of bound chloride on extraction of water soluble chloride in cement-based materials exposed to a chloride salt solution

Fuqiang He [a,b,c,*], Ruipan Wang [a,b], Caijun Shi [d], Runxiao Zhang [e], Zhenguo Shi [f,*], Duo Zhang [e]

[a] *School of Civil Engineering and Architecture, Xiamen University of Technology, Xiamen 361024, China*
[b] *Key Laboratory for Green Building Materials of the Education Department of Fujian Province, Xiamen 361024, China*
[c] *Fujian Provincial Key Laboratory of Fire Retardant Materials, Xiamen 361005, China*
[d] *School of Civil Engineering, Hunan University, Changsha 410082, China*
[e] *Department of Civil Engineering, University of Toronto, Toronto, ON M5S1A4, Canada*
[f] *Laboratory for Concrete & Construction Chemistry, Swiss Federal Laboratories for Materials Science and Technology (Empa), 8600 Dübendorf, Switzerland*

HIGHLIGHTS

- Water extraction method.
- Calculation of water extracted chloride concentration.
- Effect of release of bound chloride on water extracted chloride.
- Electrical double layer model.

ARTICLE INFO

ABSTRACT

In this study, chloride ion concentration in the water extracted solution was measured. For comparison, it was also calculated based on the electrical double layer model under extraction equilibrium. The results indicated that the release of physically bound chloride can result in 1–7 times higher water extracted chloride ion concentration than free chloride ion concentration. With increase of fineness of powder, the chloride ion concentration in the water extracted solution increased. When powder fineness was higher than 1 μm, a very small amount of water could completely extract the water soluble chloride under extraction equilibrium. With increase of water/solid ratio and water temperature, release of chemically bound chloride led to a higher concentration of chloride ions in water extracted solution. The calculation is very helpful for discussing the effects of physically and chemically bound chlorides on extraction of water soluble chloride. Finally, suggestions for improvement of water extraction method were proposed by taking into account the experimental parameters influencing the release of bound chloride.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The durability of reinforced concrete exposed to chloride environments is directly controlled by the ingress of the chloride ions. The chloride ions in concrete are present in Friedel's salt $(Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O)$, or in the diffuse layer between pores and the calcium-silicate-hydrate (C—S—H) phase, which are often referred to as chemically and physically bound chloride, respectively [1].The remaining chloride ions are present in the pore solution, i.e., as free chloride. Among these chloride ions, free chloride

is generally believed to be responsible for the initiation of steel corrosion in reinforced concrete [2]. Moreover, the linear relationship between total chloride (Cl_{total}) and free chloride (Cl_{free}) contents with a ratio of Cl_{total}/Cl_{free} slightly higher than 1 indicated that free chloride maybe represent large fraction of the total chloride content [2], and relatively low contribution of chloride from Friedel's salt and C—S—H phase [3].

The concentration of the free chloride ions has been widely determined using the pore solution expression method [4–6] and the water extraction method [7–15]. However, the chloride ion concentration measured by the water extraction method may overestimate the chloride ion concentration of the pore solution, since chemically and physically bound chloride ions may be released when cement-based materials are exposed to large

fraction of water [15–17]. Chaussadent et al. [15] showed that chemically bound chloride has been partially dissolved after being added to water for more than 3 min. Thus, they suggested an extraction time of 3 min for the water extraction method. Destabilization of Friedel's salt due to exposure to large fraction of solution was also reported by others [18–19], which was ascribed to the lowering of pH below 12 [18]. These observations reflected the fact that the water extracted chloride ion concentration measured by most researchers was larger than the free chloride ion concentration determined by pore solution expression method [11] or equilibrium method [20]. Especially in the case of low free chloride ion concentration, the concentration of the water extracted chloride can be over 7-fold higher [7].

2. Calculation of the chloride ion concentration in the water extracted solution

Based on discussion in Section 1, it has been known that chemically and physically bound will be released into water when powdered cement-based materials containing chloride is added to water. Extraction equilibrium will be obtained after sufficient extraction time, and at the same time a stable electrical double layer (EDL_e) will be formed closed to surface of the powdered cement-based materials. Under this equilibrium condition, the chloride ion concentration of the extracted solution can be calculated using Eq. (1) according to the EDL theory, and more details about the derivation of this equation are given in Appendix A.

$$C_{ews} = \left(\frac{3\left(\frac{4\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}{1-\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)} - \frac{4\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}{e-\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}\right)\sqrt{\frac{RT\varepsilon}{2}}}{2rQ_{v\,F}} + \frac{\sqrt{\frac{9\left(\frac{4\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}{1-\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)} - \frac{4\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}{e-\tanh\left(\frac{F}{4RT}\delta\psi_{0e}\right)}\right)^2 RT\varepsilon}{2r^2F^2} + 4Q_{mhbox v}(M_{CB} + N_t V_p C_{bCl^-})}}{2Q_v} \right)^2 \quad (1)$$

Despite of the overestimation of the free chloride ion concentration by measuring the concentration of the water soluble chloride, the water extraction method is still widely used for measuring the free chloride ion concentration in cement-based materials as a result of its operational convenience. Many countries and organizations have legislated their own technological specifications or codes for the water extraction method [21–33]. However, these specifications or codes employed completely different experimental parameters [34]. Arya et al. [7,9,10,34] reported that water extracted chloride amount were influenced by the fineness of powder, extraction temperature, stirring time, water/solid ratio and exposure time for cement-based materials under similar conditions such as methods for introducing chloride, cations of chloride salt, free chloride ion concentration and binder types. The results indicated that water extracted chloride concentrations obtained from different specifications or codes may not be comparable. Furthermore, many studies have used free chloride ion concentration to evaluate the initiation of the chloride-induced steel corrosion. For this purpose, some studies [35–39] have established a relationship between water soluble and free chloride ion concentrations, and they used this relationship to estimate the free chloride ion concentration. Unfortunately, it is anticipated that such estimation may not be reliable for evaluation of the actual risk of chloride-induced steel corrosion due to uncompared water soluble chloride concentration.

Based on the aforementioned discussion, one key problem needs to be solved for a proper application of the water extraction method, i.e., how release of physically and chemically bound chloride influence the amount of water extracted chloride when changing the experimental parameters. Understanding of the role of physically and chemically bound chloride can be beneficial for accurate determination of the water extracted chloride through which we can work out the free chloride. A calculation of water extracted chloride (including free and bound chloride) can be useful to understand or even accurate determination of free chloride. Therefore, this study aims to distinguish the role of physically and chemically bound chloride during the extraction of water soluble chloride by considering different experimental parameters based on the calculation of chloride ion concentration in the extracted solution. Finally, an improved procedure for extraction of water soluble chloride using water extraction method was suggested in the present study.

Based on mass conservation, the water extracted chloride ion concentration can be expressed as the ratio between the amount of water extracted chloride to the volume of pore solution in the sample (C_{pws}), which can be calculated according to Eq. (2):

$$C_{pws} = \frac{Q_v C_{ews}}{V_p} \quad (2)$$

where C_{ews} is chloride ion concentration in the extracted solution, mol/L; Q_v is the ratio of water to solid ratio by volume; V_p is the volume fraction of water per unit volume of sample before grinding, %; r is the fineness (i.e., radius) of powdered sample, m; $\delta\psi_{0e}$ is the relative OHP potential of the EDL_e between powders and solution, V; ε is the dielectric constant of the extracted solution, F/m; C_{bCl^-} is the ion concentration in the bulk solution of the cement-based material sample, mol/L; R is the gas constant; T is the temperature of extracted solution, K; F is the Faraday constant; and N_t is the concentration coefficient of transportable chloride ions in the sample. Above parameters were determined following the methods described in previous study [20]. M_{CB} is the amount of chemically bound chloride released into the extracted solution, mol; and C_{pws} is ratio of water extracted chloride amount to the pore solution volume in the sample, mol/L.

Due to presence of EDL between powders and water solution, water soluble chlorides which were released from cement-based materials will exist both in diffuse layer of the EDL and water solution. Therefore, tested chloride in the extracted solution (C_{ews}) is part of water soluble chloride. Depending upon fineness of powder and water/solid ratio, the amount of chloride ion in the EDL can be ignored in some cases, and thus C_{ews} can be assumed to equal to water soluble chloride ion concentration in these situations (see Section 4.2).

3. Experimental

3.1. Materials

Portland cement (P.I type according to Chinese code, GB175), silica fume (specified in Chinese code, GB/T27690) were used for preparation of the paste samples. Their chemical compositions determined by XRF method are shown in Table 1. The Na_2O_{eq} and free lime of the cement is 0.057% and 0.76%, respectively. The specific surface area of the cement is 347 m²/kg. The distilled water, analytical grade NaCl and $AgNO_3$ and a type of Polycarboxylate water reducing agent with 20% solid content were used in this study.