2nd International Symposium on Service Life Design for Infrastructure
4-6 October 2010, Delft, The Netherlands

REACTION EXPERIMENTAL STUDY ON CHLORIDE BINDING BEHAVIOR IN CEMENT COMPOSITION

In-Seok Yoon

Dept. of Construction Information Engineering, Induk University, Seoul, Korea

Abstract

Chloride binding capacity in cementitious materials is a crucial factor for service life prediction of marine concrete. Many researchers have dealt with experimental works and got experimental constants within the scope of Freundlich / Langmuir binding isotherm. However, the constants depend on mixing proportion properties of the cementitous materials and the degree of hydration. Thus, it is necessary to explore reasonable approach to integrate chloride binding behavior of cementitious materials and that is a good motivation of this study.

Firstly chloride binding isotherm of major cement hydrates is examined and then chloride binding isotherm is estimated from the chloride binding of these hydrates. The result shows that monosulfates and C-S-H phase have significant binding capacity and this is main mechanism of the binding capacity. The chloride binding by mosnosulfate hydrates is attributed to produce Friedel's salt. C-S-H hydrates also can lead to physic-chemical binding. Based on the experiment results, to develop integrated system for prediction of chloride binding behaviors is final goals.

1. INTRODUCTION

Chloride penetration is one of the main causes of the reinforcement corrosion in concrete. Among the governing factors of chloride penetration in concrete, chloride binding reduces the amount of movable chloride and then reduce the critical chloride content for reinforcement corrosion. The studies reporting chloride binding isotherm have involved the experimental measurement of the total chloride content and water soluble chloride content. However, there is no agreement on its value because the studies have tried to define chloride binding isotherm within the scope of their experimental concrete mix proportion at arbitrary time although chloride binding is influenced by many factors such as mixing proportion properties of concrete, type / amount of binder (cement and admixture), degree of hydration, and so on.

Chloride ions are existed in concrete as two forms: water soluble chloride ions (free chloride) in the aqua phase of cement paste, and bound chloride ions in the solid phase. Bound chlorides can be divided as; Friedel's salt by C_3A / C_4AF, bound chloride by C-S-H physically and chemically. Affecting factor of the bound chlorides is schematically shown in Figure 1. The mechanism of bound chloride is very complicated; Friedel's salt due to C_3A or C_4AF, Kuzel's salt, and bound chlorides by C-S-H.

The purpose of this study is to investigate and to quantify chloride binding capacity by means of reaction experiment. The contributions of C-S-H and AFm to produce bound chlorides are examined, based on main mechanism of chloride binding in cementitious materials.

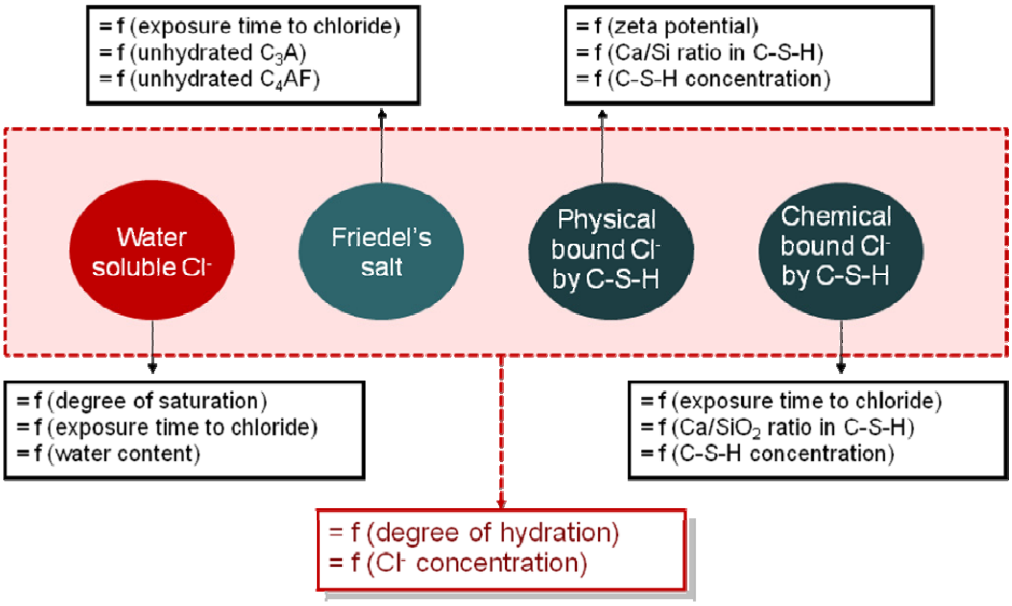

Figure 1: Affecting factors of chloride binding

2. EXPERIMENTAL DESIGN

2.1 Materials

AFm was synthesized as follows : C_3A, gypsum and water were mixed at molar ratios of 1:1:5 respectively, then seal-cured at 20^{o}C, then at 40 ^{o}C and again at 20^{o}C. The curing time was 3 days. C-S-H with 1.50 of Ca/Si ratio was synthesized by mizing C_3S with water at a water to solid ratio of 1:10 at 20^{o}C, and cured for 2 months under sealed condition.

2.2 Adsorption-reaction experiment

Synthesized AFm, C-S-H were added to chloride solution with various concentrations. The apparatus was sealed with rubber cap in order to prevent decreasing of pH due to carbonation. The adsorption-reaction experiment was carried out for 10 days at 20 ^{o}C.

For the duration of the experiment, synthesized products were reacted with chloride solution and this leads to chloride binding. Before measurement of chloride concentration, the solution was stirred for enough time.

Ion chromatography method was used to measure the amount of chloride solution. The difference between initial chloride concentration before and after reaction experiments was regarded as the amount of adsorbed chemically or physically chloride in solid phase because of AFm or C-S-H.

3. RESULT AND DISCUSSION

Figure 2 shows the amount of bound chloride adsorbed by AFm. The amount of bound chloride adsorbed by AFm increases, with the increase of chloride concentration in liquid phase. In order to express the relationship between chloride content in aqua phase and bound chloride content adsorbed by AFm, it is thought that Langmuir isotherm is more suitable than Freundlich isotherm. The bound chloride content at chloride concentration of 1 mol is only 0.44 mol per 1 mol of AFm. This value is significantly lower than 2 mol of stoichiometrical value.

Figure 3 represents the chloride binding capacity of C-S-H. C-S-H has a large surface area this leads physical adsorption of chloride by Van der Waals' force. Like AFm, the amount of bound chloride increases with the increase of chloride concentration in aqua phase. The binding isotherm shows a perfect fit for the regression curve of Langmuir isotherm. 1 g of C-S-H can bind chloride with 0.45 mMol at the chloride concentration of 1 Mol/L. Thus, the contribution of C-S-H is significant for chloride binding capacity of concrete. Physical and chemical properties of C-S-H depend on Ca/Si ratio. It is necessary to examine the Ca/Si ratio of C-S-H on chloride binding.

Finally, behavior of chloride binding can be expressed by Eq. (1) and Eq. (2). Eq. (1) is a contribution of AFm, while Eq. (2) is a contribution of C-S-H.

$$[Cl^-(s)](AFm) = \frac{1.081\,[Cl^-(aq)]}{1 + 1.456[Cl^-(aq)]} \tag{1}$$

$$[Cl^-(s)](CSH) = \frac{1.079\,[Cl^-(aq)]}{1 + 1.395\,[Cl^-(aq)]} \tag{2}$$

Common trend of two binding isotherms, Langmuir & Freundlich, is decreasing with increase of chloride concentration in aqua phase. By chloride concentration with 1.0 mol/L in aqua phase, the value of Langmuir isotherm is higher than that of Freundlich isotherm. However, the trend is reverse after the concentration. Bound chloride content is significantly decreased with increase of chloride concentration in aqua phase and Langmuir binding isotherm has good agreement with the trend consequently.

This study is the first step of experiment for investigation to quantify the amount of bound chloride in cementitious materials. Based on the result of this study, new model to predict chloride binding will be suggested. AFm and C-S-H are generated by hydration of cementitious materials, such as Portland cement, fly ash, granulated blast furnace slag, and developed with elapsed time. Developments of AFm and C-S-H will be coupled with the chloride binding isotherm of this study, as shown in Figure 4.

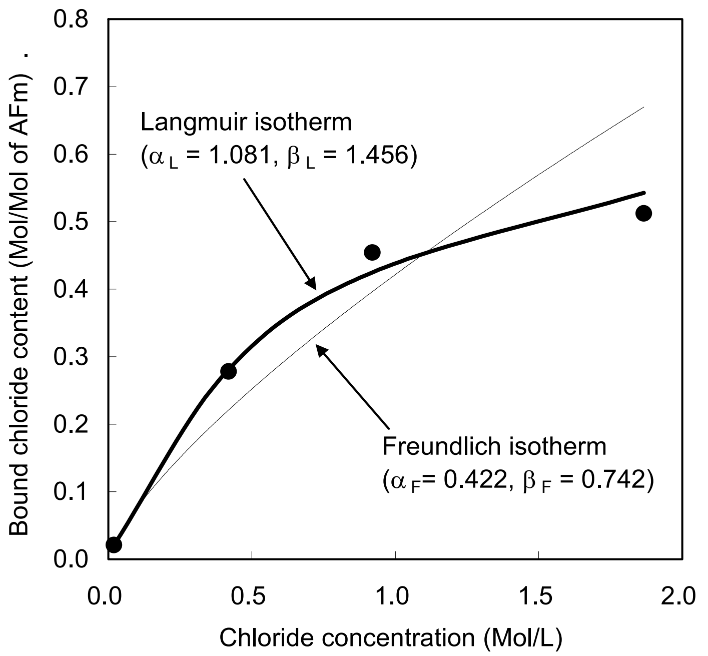

Figure 2: Chloride binding behavior by AFm

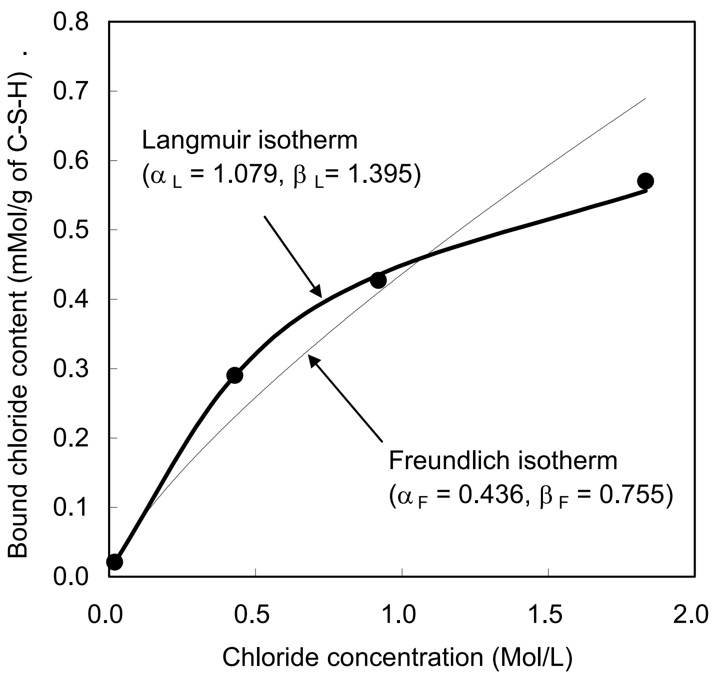

Figure 3: Chloride binding behavior by C-S-H

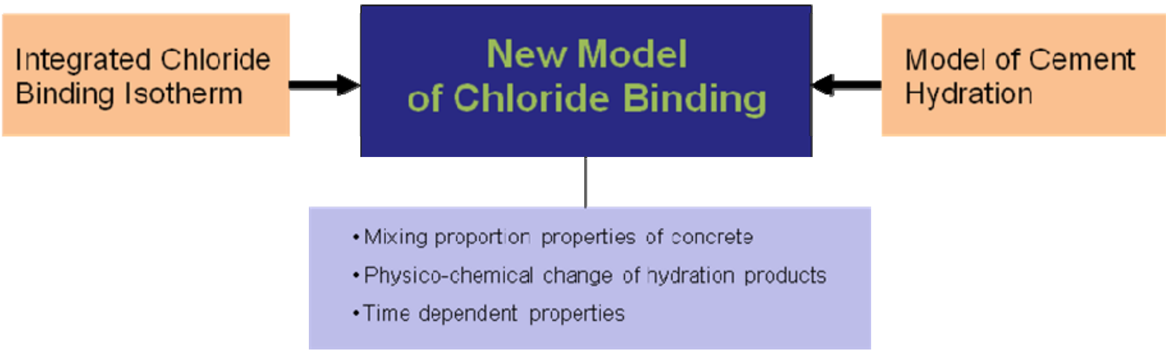

Figure 4: Strategy to develop new chloride binding model

4. CONCLUSIONS

- Langmuir binding isotherm is reasonable for chloride binding by AFm. The bound chloride content at chloride concentration of 1 mol is only 0.44 mol per 1 mol of AFm.
- For chloride binding by C-S-H, the binding isotherm shows a perfect fit for the regression curve of Langmuir isotherm. 1 g of C-S-H can bind chloride with 0.45 mMol at the chloride concentration of 1 Mol/L.
- Based on the result of this study, ongoing developments of hydration products will be coupled with the chloride binding isotherm of this study.

ACKNOWLEDGEMENTS

The author acknowledges the financial support of NRF, National Research Foundation, 2010-0005732, Korea.

REFERENCES

[1] Hirao, H., Yamada, K., Tarahashi, and H. Zibara H., 'Chloride Binding of Cement Estimated by Binding Isotherms of Hydrates,' *Journal of Advanced Concrete Technology*. **3** (1) (2005) 77-84.
[2] Suzuki, K., Nishikawa, T., and Ito N., 'Formation and Carbonation of C-S-H in Water,' *Cement and Concrete Research*. **15** (1985) 212-224.
[3] Saeki, T., and Sasaki, K., 'Hydration Model for Cementitious Materials Containing Mineral Admixtures,' *2nd International RILEM Workshop on Concrete Durability and Service Life Planning – ConcreteLife'09*, Haifa, Israel, September, 2009, 466-473.
[4] Zibara, H., 'Binding of External Chlorides by Cement Paste,' PhD Thesis, University of Toronto (2001)