STUDY ON CHEMICAL AND PHYSICAL CHLORIDE BINDING OF SLAG BLENDED CEMENT WITH DIFFERENT REPLACEMENT RATIOS

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1. INTRODUCTION

Chloride ingress through pore solution to embedded steel is the reason for corrosion induction in reinforced concrete structures exposed to seawater and de-icer applied environment. As chloride ion ingress, some are bound physically by hydration products, and some bound chemically that are mainly in the form of Friedel's salt (FS), leading to the immobilization of those ions. The more chlorides are bound, the less free chlorides are available to cause corrosion.

The use of ground granulated blast furnaced slag (BFS) as a supplementary cementitious material has been known beneficial for chloride resistance because of their high alumina content and the refinement of pore structure. The replacement ratios of slag in cement are defined in standards, for example, JIS R5211(5-70%) and ENV 197-1 (36-95%). However, slag blended in Portland cement may exhibit different reactivity and characteristics of hydration product depending on chemical compositions, slag ratio, water-to-binder ratio (w/b), and curing temperature, which may lead to different chloride binding capacity. Past studies focusing on the influence of slag replacement ratio on chloride binding are still limited. In this research, experimental study on chemical and physical binding were carried out for slag blended cement with different slag replacement ratios.

2. EXPERIMENTAL PROGRAM

Slag was blended in OPC with four replacement ratios (0%, 20%, 50%, and 70%), two w/b ratios (0.3 and 0.5) and cured in two temperatures (20 and 40°C), respectively. The cement paste was cured to the ages of 186 days. The equilibrium method developed by Luping and Nilsson (1993) was applied for chloride binding test. After curing, the hardened cement paste was crushed into small pieces of approximately 5 mm, placed in a vacuum desiccator containing silica gel and soda lime, and dried for three days under low vacuum pressure to eliminate most of the excess water. Subsequently, the samples were stored for 14 days while maintaining a relative humidity of 11% using saturated lithium chloride. Under this relative humidity, only a monolayer of water was adsorbed onto C-S-H gels. The samples were then ground and sieved to obtain particles with sizes in the range of 150–300 µm. Distilled water pre-saturated with $Ca(OH)_2$, utilized to prevent leaching from the samples, was used to prepare NaCl solutions with concentrations of 0.1, 0.3, 0.5, 0.7, 1, 2, and 3 mol/L (M). The samples were placed in bottles and soaked in a NaCl solution with a liquid-to-solid ratio of 4 by weight. The temperature of the solutions was maintained at 20°C and 40°C, corresponding to the curing temperatures. Potentiometric titration against silver nitrate was performed to determine the concentration of chloride ions. When the equilibrium of binding was reached, bound chloride was determined by the reduction in chloride concentration from its initial value.

After the chloride binding test, the samples in the NaCl solution were reclaimed by filtering and washed with deionized water. They were then placed in a vacuum desiccator and dried at 20°C for 24 h. The samples were ground again using a mortar and pestle to obtain finer powder that was appropriate for thermogravimetric analysis (TGA). Approximately 50 mg of ground samples was analyzed by TGA, heated to 950°C at a rate of 10°C/min. According to Shi et al. (2017), the decomposition of FS in TGA occurred in two temperature ranges due to the loss of four interlayer water molecules and six main layer water molecules, respectively. The amount of FS in the cement paste was quantified for six main layers of water molecules in the temperature range of approximately 230–410°C as below

$$m_{fs} = \frac{M_{fs}}{6\times M_H} m_H \qquad (1)$$

where M_{fs} is the molar mass of FS with the chemical composition ($Ca_4Al_2(OH)_{12}Cl_2{\cdot}4H_2O$), $\boldsymbol{M}_H$ is the molar mass of H_2O, m_H is the measured mass loss from the differential curve of TGA (DTG) for the main layer of water in FS. Eq. 2 was adopted to calculate the amount of chemically bound chloride c_b^{FS} (mg/g of initial mass of raw materials) required for the formation of FS.

$$c_b^{FS} = 2M_{Cl}\frac{m_{fs}}{M_{fs}} \qquad (2)$$

where, M_{Cl} is the molar mass of chloride (35.45 g/mol) and the factor "2" is for 2 mol chloride per mol of FS.

3. RESULTS AND DISCUSSIONS

The isotherms of total chloride binding are shown in Fig. 1. It can be found that the addition of slag was beneficial in chloride binding than OPC and 50% slag ratio provided the highest values due to the high alumina content of slag. In slag blended cement, more alumina than OPC reacts with all available SO_4^{2-} to form AFm that was converted to more FS by combining Cl^-. Meanwhile, C-S-H from slag reaction adsorbed more Cl^- physically due to higher surface area and charge density. In addition, past studies have reported that the reaction degree of slag in blended cement generally decreased with

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increasing slag ratio. Therefore, low values at 70% slag ratio and lower w ratio /b correlated to the less hydration products, denser pore structure and the different properties of C-S-H. At high slag ratio, C-S-H become less positive, which cause the reduction of Cl^- adsorption. Meanwhile, less SO_4^{2-} is available from OPC, so the amount of AFm available for FS formation decreased.

Fig.2 (a) shows a typical result of DTG for samples with the w/b of 0.3 and the temperature of 20°C after chloride binding in 3M NaCl solution. It can be seen that FS peak increased up to 50% slag ratio and around 1/3 chloride were bound chemically due to formation of FS (Fig.2 (b)). The trend of binding was different from total binding and effectively all slag ratios provided high values than OPC. Physically bound chloride was determined by subtracting chemically bound from total bound (Fig.3). Chemically bound chloride increased up to 50% slag ratio irrespective of w/b ratio even 70% slag ratio showed high values than OPC, whereas the reduction of total binding for 70% slag ratio than OPC in case of 0.3 w/b was due to prominent negative effect of physical binding.

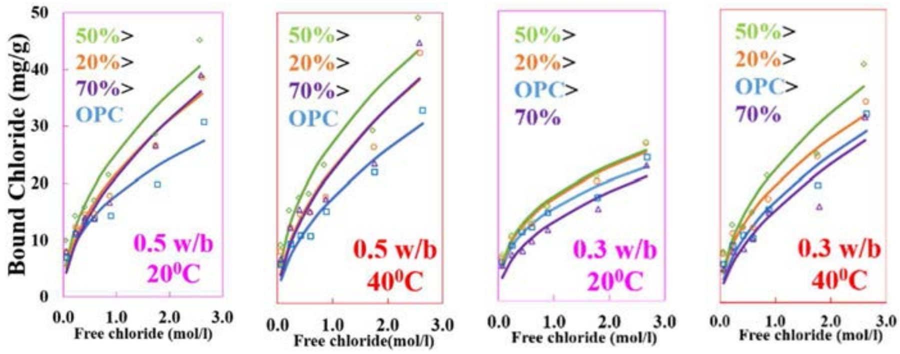
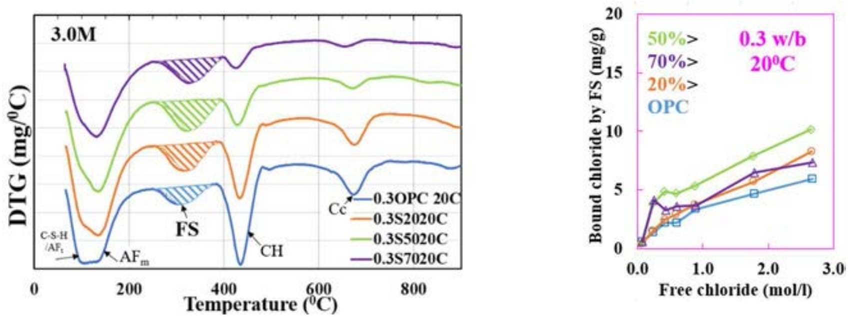


Fig.1 Total chloride binding isotherm



(a)FS decomposition peak in DTG plot (b)Bound chloride by FS

Fig.2 Chemically bound chloride due to FS formation

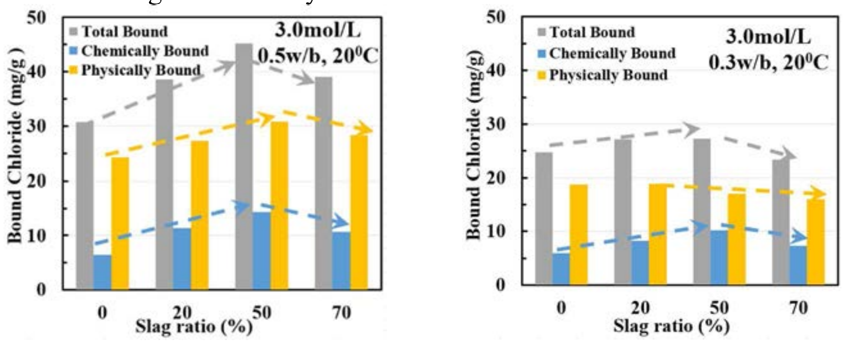


Fig.3 Relationship of the total, chemically and physically bound chloride

4. CONCLUSIONS

Chloride binding of slag blended cement were related to slag replacement ratio, which is considered to be intrinsically related to the properties of hydration products and the reaction degree of slag. 50% slag provided highest values for chloride binding at later age. In addition, the effectiveness of slag blends in chloride binding than OPC is because of prevalent chemical binding.

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