STUDY OF HYDRATION AND CHLORIDE BINDING PROPERTIES OF SLAG-BLENDED CEMENT WITH DIFFERENT BLENDING RATIOS

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1. INTRODUCTION

Blast furnace slag (BFS) is a non-ironic material waste left over from iron making. From the viewpoint of environmental and economic benefit, the use of slag as partially replacement of Portland cement is increasing to large volume. According to JIS R5211, 5% to 70% replacement of slag could be applied in cement. Slag has different reaction property from Portland cement, which depends on its physical & chemical composition, slag ratio, curing conditions, etc.

Corrosion initiates when penetrated chloride ions destroy passive film around steel reinforcing bars. As chloride ions ingress, however, some ions are bound in concrete physically by calcium silicate hydrate (C-S-H) and some chemically by aluminate compound to form Friedel's salt. More chlorides are bound, less free chlorides are available for corrosion. It is generally regarded that slag blended cement tends to bind more chloride chemically because of the high aluminum content of the slag. On the other hand, past researches indicated that the reaction degree of slag tended to decrease with the increasing ratio, which may lead to a less amount of hydration product and influence the effect of physically binding.

In this study, for the use of BFS blended cement, the degree of reaction of slag, the strength of mortar, and chloride binding capacity at different blending ratios were studied experimentally. Accordingly, the relationship among strength, degree of reaction of slag, and chloride binding (physically and chemically bound) are discussed.

2. EXPERIMENTAL PROGRAM

2.1 Sample Preparation

Slag powder with a specific surface area of 4,070 cm^2/g and Ordinary Portland Cement (OPC) of JIS R5210 were used. The blending ratios of slag as partial replacement of OPC were 0%, 20%, 50%, and 70%; water-to-binder (w/b) ratios were 0.3 and 0.5; and curing temperatures were 20°C and 40°C. Paste sample were prepared by mixing OPC and slag with water and pouring it into plastic cup. Samples were stored for 28 days under different curing temperatures. At the end of curing, the samples were crushed into ±5mm size and immersed into capped bottle with isopropanol for 7 days to stop hydration. Then, the crushed samples were vacuum-dried for 24 hours and powdered to obtain 250 to 630 µm particles for the selective dissolution and thermogravimetric analysis (TGA), and 0.075 to 2mm for chloride immersion. Mortar samples were prepared by mixing OPC, slag, and sand with different w/b ratios and casted into 50 x 100 mm cylindrical molds. The mortar specimens were cured to the test ages under different curing temperatures in water, 7 days and 28 days, respectively.

2.2 Selective Dissolution

The reaction degree of slag was determined by the extraction method from Villagran-Zaccardi et al. (2018). Ethylene diamine tetraacetic acid (EDTA), Na_2CO_3, and triethanolamine were mixed and used to dissolve 0.25g powdered sample. The mixture was then filtrated by filter paper after being stirred automatically under 300 rpm for 120 ± 5 min. The hydration product and unhydrated cement were dissolved, leaving unreacted slag remained. Pure slag and OPC were also dissolved and measured for the correction of the calculation.

2.3 Thermogravimetric Analysis (TGA)

TGA was conducted to identify the decomposition of $Ca(OH)_2$ and Friedel's salt. About 30 mg of powdered paste sample was heated up to 950°C with the rate of 10°C/min. $Ca(OH)_2$ decomposes between 400-500°C, while Friedel's salt between 230 -410°C for the samples after chloride binding.

2.4 Chloride Binding

The equilibrium method developed by Luping and Nilsson (1993) was applied for chloride binding. Different concentrations of NaCl solution, 0.1, 0.3, and 0.5mol/L, were used to immerse the powdered samples until the equilibrium after one month. The concentration change of the solution was then determined by titration with 0.01mol/L $AgNO_3$ solution. The immersed sample was then vacuum dried, powdered, and tested by TGA to determine the Friedel's salt, following the method proposed by Shi et al. (2017).

3. RESULTS AND DISCUSSIONS

It can be seen that, in general, the degree of reaction of slag in the paste samples at 28 days increased with increasing w/b ratio, curing temperature, and decreasing slag ratio (Fig.1). Relatively significant values were obtained in case of 0.5w/b and 40°C that varied from 48.8% to 39.2% for 20% to 70% slag ratios. Consumption of $Ca(OH)_2$ indicates indirectly the

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reaction degree of slag, because $Ca(OH)_2$ activated the slag to cause its latent hydraulic property. Fig.2 indicates that for all considered w/b ratios and curing temperatures, $Ca(OH)_2$ amount decreased with increasing slag ratio because of less production from OPC and more consumption by slag. Higher curing temperature and w/b ratio increased the degree of reaction of slag, because the activation energy was increased and more water was available, respectively. For higher slag ratio, the degree of reaction became lower, which is probably related to the lower alkaline active environment in pastes. Development of compressive strength from Fig.3 indicates that almost in all cases slag blend specimens showed lower values than OPC at 7 days due to low reaction. It is important to note that, however, the slag blended cases showed more development in strength due to the latent hydration at 28 days. For some cases, for example, at 40°C with 20%, 50% and 70% slag ratios, the strength values were even higher than that of OPC at 28 days. This effect was more significant at w/b 0.3 than 0.5.
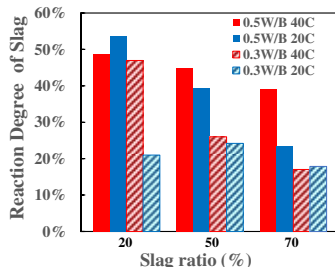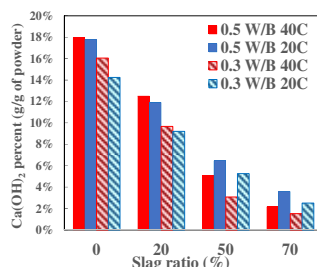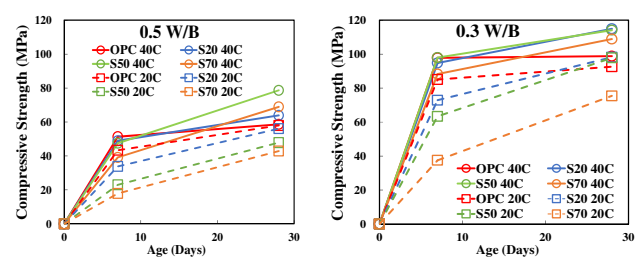

| Fig.1: Reaction degree of slag | Fig.2: $Ca(OH)_2$ amount | Fig.3: The compressive strength of mortar |

For chloride binding, only the cases of w/b 0.5 and 20°C are discussed in here. According to Fig.4, total bound chloride content at equilibrium increased with increasing slag blending ratio and free chloride concentration. By subtracting chemically bound chloride which were obtained by TGA from total bound, physically bound were calculated and also shown in Fig. 5. Chemically bound, which was Friedel's salt, were found to increase with increasing slag ratio. This may be because of the higher aluminum content in slag than OPC. Furthermore, for 0.1mol/L chloride solution, around 25-30% chloride were bound chemically, whereas this portion increased as the concentration increased, showing about 30-50% in 0.5mol/L solution. For physically bound chloride, it can be found that, for all the concentrations, the amount increased only slightly as slag ratio increased from 0% to 50%, but tended to decrease at 70%. The reason may be attributed to the decreased degree of reaction of slag with increasing slag ratio, resulting in a less amount of C-S-H for physically binding.
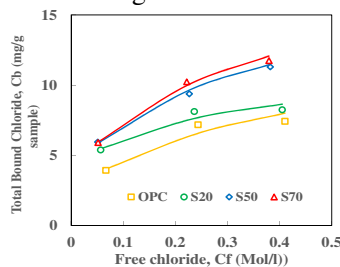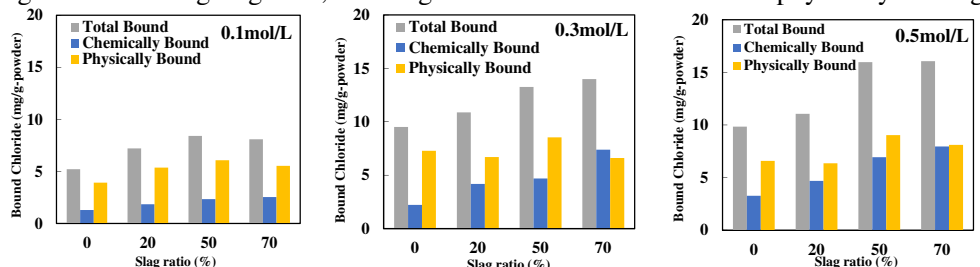

Fig.4: Chloride binding isotherm
(w/b 0.5 & 20°C)

Fig.5: Bound chloride that were immersed in 0.1, 0.3, and 0.5 mol/L chloride solutions

4. CONCLUSIONS

In this study, after investigating several factors, it can be concluded that slag that is blended in Portland cement shows different degree of reaction under different blending ratios, w/b, and curing temperatures, influencing the strength development and chloride binding capacity. The degree of reaction tends to decrease as the blending ratio increases, contributing to the low strength at early age under 20°C curing. It can be compensated by increasing curing temperature. Slag blend performance up to 70% are good in case of 0.5w/b and 40°C, with quite near strength to OPC at early age. Among all, 20% and 50% slag blend perform better at 40°C curing temperature irrespective of w/b ratio. Regarding to chloride binding, at w/b 0.5, the capacity of slag blend is higher than OPC, but does not increase proportionally with increasing slag ratio. At higher slag ratio, chemically bound chloride tends to increase more significantly than physically bound. This is probably because of the aluminum in slag. The physically bound chloride, on the other side, tends to decrease above the slag ratio 50%, probably because of the low degree of reaction and less amount of C-S-H.

5. REFERENCES

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