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INFLUENCE OF SLAG CHEMISTRY AND COMPOSITION ON THE HYDRATION AND MECHANICAL PROPERTIES OF SUPERSULFATED CEMENT

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ABSTRACT

This research evaluates ways of improving early-age property of supersulfated cements. Mechanical performance of SSC was studied after optimizing the slag- calcium sulfate- alkali activator composition. This study was conducted using four slags of different chemical composition. The purpose was to find a correlation between slag composition and compressive strength and determine the influence of anhydrite content and alkali activator content on the hydration process of SSC. The results demonstrated that the compressive strength of mortars was strongly influenced by the Al_2O_3 content of the slag, which also influenced the optimum mix composition of the SSC mixtures. Mixtures containing slags with high Al_2O_3 required low amount of alkali activator in order to provide high strength values, while, increasing the activator content reduced the compressive strength. The heats of hydration of all the mixtures were also studied.

1. INTRODUCTION

Portland cement (PC) is the most common binder used in concrete for construction. However, its production contributes to 2–3% of global primary energy use and to approximately 5% of manmade CO_2 emissions (Juenger et al., 2011). In order to reduce energy use and greenhouse gas emissions associated with the production of Portland cement, the cement industry is presently seeking alternatives. Supersulfated cement (SSC) is potentially a more sustainable alternative to Portland cement for concrete applications as it is typically composed of 80 – 85% slag, 8 - 12% anhydrite, and less than 5% Portland cement (Lea, 1979). High Al_2O_3-content slags (13% and higher) are generally viewed as suitable for the production of SSC (Matschei et al., 2005). However, SSC is under-utilized due to its slow rate of early strength gain. Therefore, further research is required in order to evaluate ways to improve properties of this type of cement.

2. MATERIALS & METHODS

Four different slags were used to produce SSC, the chemical composition of the slags is provided in Table 1. To obtain anhydrite ($CaSO_4$) gypsum ($CaSO_4 \cdot 2H_2O$) was fired at 650°C for 1 hr. XRD analysis was done to confirm the results as provided in Figure 1. A wide range of mixtures was used to determine the influence of calcium sulfate and alkali activator (CSA Type GU cement) content on the strength development and heat of hydration of SSC. Calcium sulfate in the range of 5-20% and alkali activator ranging from 1-10% were used in all mixtures. A list of the mixtures studied is provided in Table 2.

Mortar cubes were cast according to ASTM C109, in order to determine the optimum slag- anhydrite- alkali activator content for all four slags, which would develop comparable strengths to those of Portland cement mortar cubes. The water content of the mix was adjusted to obtain a flow of 110±5. The samples were cured and then stored in limewater at 23°C. The compressive strengths were measured at 1, 3, 7, 28 and 90 days.

Calorimetric measurements were determined on 30 g of SSC paste samples with a w/c of 0.40 for 7 days at 23°C using the I-Cal8000 Isothermal Calorimeter. Heat of hydration was measured on all mixtures shown in Table 2.

Table 1: Slag Chemical Composition

Oxides	Slag A	Slag B	Slag C	Slag D
SO_3 (%)	5.31	3.62	3.32	2.8
SiO_2 (%)	31.78	32.55	35.14	38.85
Al_2O_3 (%)	13.34	11.79	10.94	7.43
TiO_2 (%)	0.49	0.49	1.03	0.4
P_2O_5 (%)	0.02	0.02	0.01	0.01
Fe_2O_3 (%)	0.71	0.86	0.78	0.41
CaO (%)	41.58	43.26	37.21	38.94
MgO (%)	4.38	4.95	11.19	10.26
Na_2O (%)	0.2	0.23	0.41	0.29
K_2O (%)	0.34	0.43	0.41	0.46
Mn_2O_3 (%)	0.29	0.2	0.52	0.61
SrO (%)	0.09	0.07	0.07	0.06
SO_3 (%)	5.09	3.6	3.3	2.74
BaO (%)	0.06	0.05	0.02	0.05
ZnO (%)	0	0	0	0
Cr_2O_3 (%)	0	0	0.01	0.01
$(CaO+MgO)/SiO_2$	1.4	1.5	1.4	1.3
Blaine (m^2/kg)	446	500	468	587

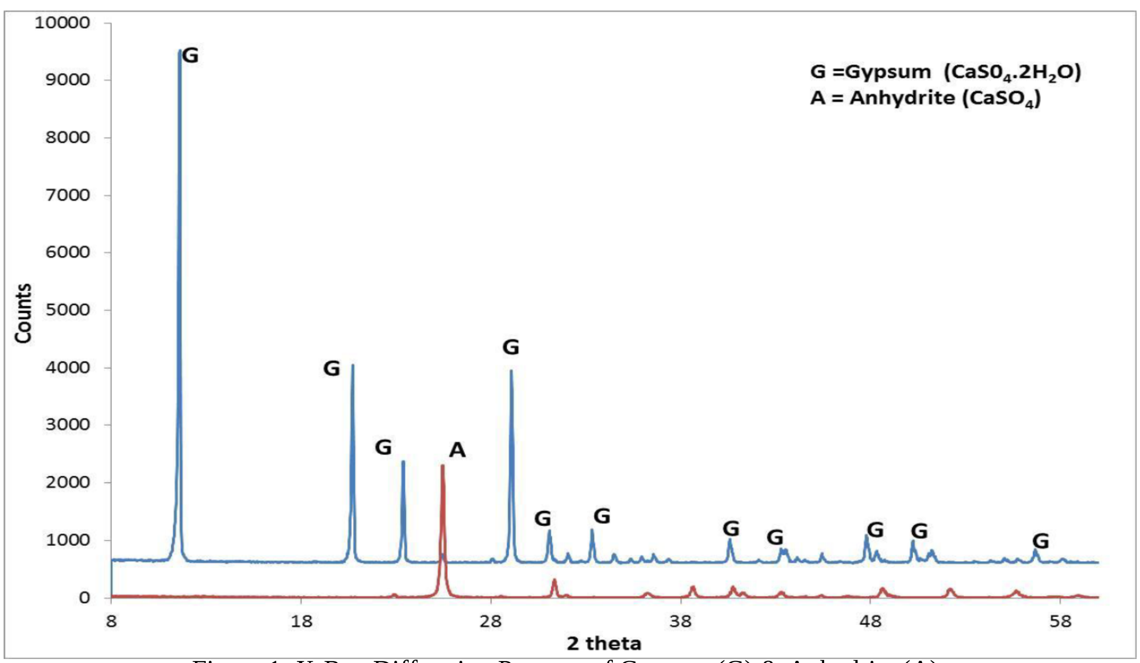

Figure 1: X-Ray Diffraction Patterns of Gypsum (G) & Anhydrite (A)

Table 2: SSC Mixture Compositions

MIX I.D.	Slag	Anhydrite	GU Cement
85.5.10	85%	5%	10%
80.10.10	80%	10%	10%
75.15.10	75%	15%	10%
70.20.10	70%	20%	10%
87.5.8	87%	5%	8%
82.10.8	82%	10%	8%
77.15.8	77%	15%	8%
72.20.8	72%	20%	8%
90.5.5	90%	5%	5%
85.10.5	85%	10%	5%
80.15.5	80%	15%	5%
75.20.5	75%	20%	5%
93.5.2	93%	5%	2%
88.10.2	88%	10%	2%
83.15.2	83%	15%	2%
78.20.2	78%	20%	2%
94.5.1	94%	5%	1%
89.10.1	89%	10%	1%
84.15.1	84%	15%	1%
89.10.1	89%	10%	1%
84.15.1	84%	15%	1%
79.20.1	79%	20%	1%

3. RESULTS & DISCUSSION

3.1 Compressive Strength Results

Based on the compressive strength results it was found that the Al_2O_3 content of the slag plays a significant role in strength development of SSC mixtures and it highly influenced the optimal mixture composition of SSC. All SSC mortar mixes were compared to a reference mix of 100% Portland cement.

Mixes containing slag with a high content of Al_2O_3 (above 13%) exhibited higher compressive strength at all ages compared to slags with lower Al_2O_3 contents (approx. 7%). As shown in Figures 2-5 Mixes with slag A demonstrated higher compressive strength at all ages and compositions compared to Slags B, C and D. For slag A SSC mixes as shown in Figure 2 as the amount of alkali activator content decreases, the compressive strength increases. The optimum composition for slag A, SSC mix was found at 79% slag 20% anhydrite and 1% GU cement.

The opposite trend was observed in the case of mixtures containing slag with low Al_2O_3 content (below 13%); as the alkali activator content increased, the compressive strength also increased as shown in Figures 3 and 5. However, this did not apply to Slag C that has an Al_2O_3 content of roughly 11%, as shown in Figure 4. This may suggest that other factors than the Al_2O_3 content of the slag may influence the compressive strength results, and further research is required. For Slags B and D, the optimum mixture composition was found at 87% slag 5% Anhydrite and 8% GU cement and 70% slag 20% Anhydrite and 10% GU cement respectively. For slag D mixes at 12% GU content were also performed to determine if higher level of activator replacement has any major influence. As shown in Figure 5 the compressive strength results did not change significantly between 10% and 12% replacement levels. In addition, for Slag D the 1-day compressive measurement was not performed, as the mixes were too weak to be tested. For Slag C the optimum mix was found at 94% slag and 5% anhydrite and 1% GU cement as shown in Figure 4. Therefore, there is a wide range of formulation in terms of what is considered to be the optimum mixture composition for SSC depending on the chemistry of the slag used. In all four slags, the alkali activator content significantly influenced the compressive strength results and the anhydrite content did not play a significant role in the mechanical performance of SSC.

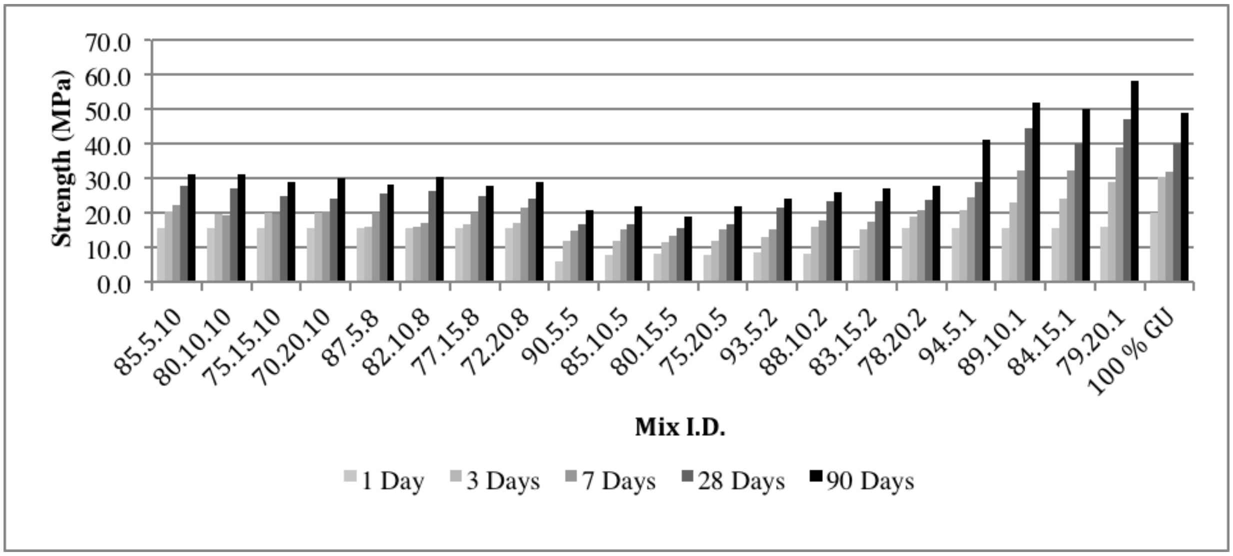

Figure 2: Slag A Compressive Strength (13.07% Al_2O_3)

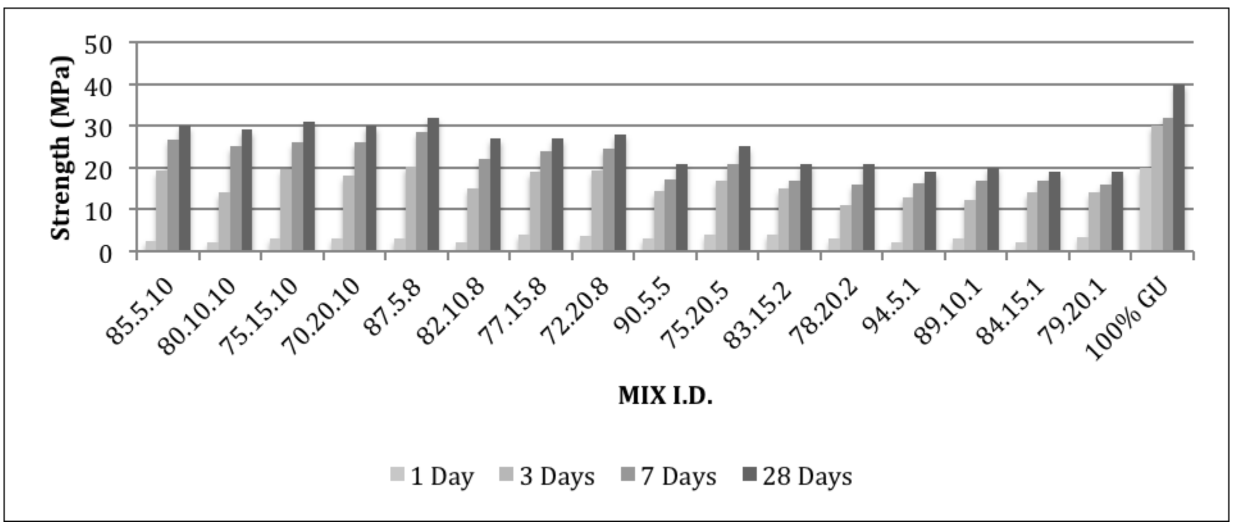

Figure 3: Slag B Compressive Strength (11.79% Al_2O_3)

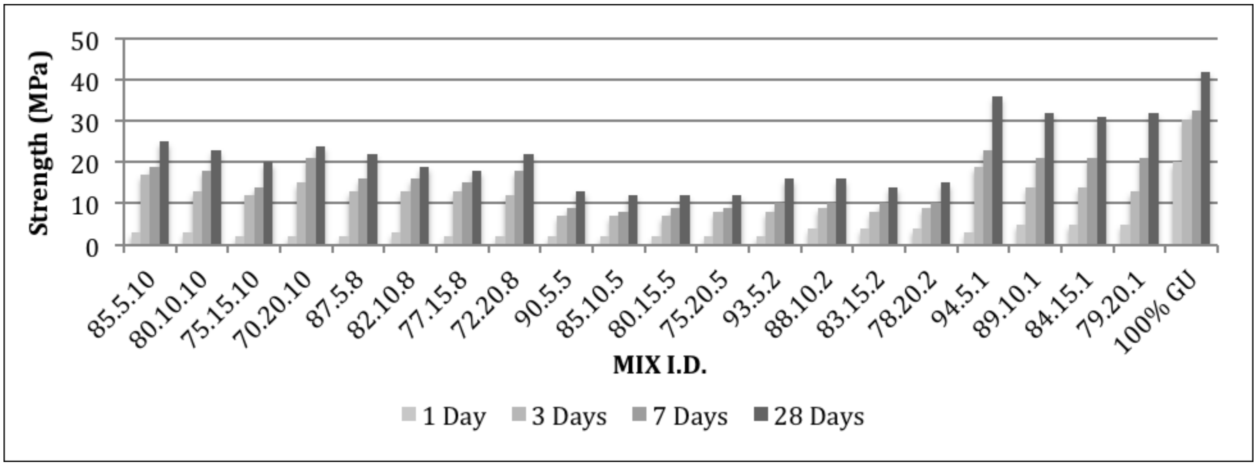

Figure 4: Slag C Compressive Strength (10.94% Al_2O_3)

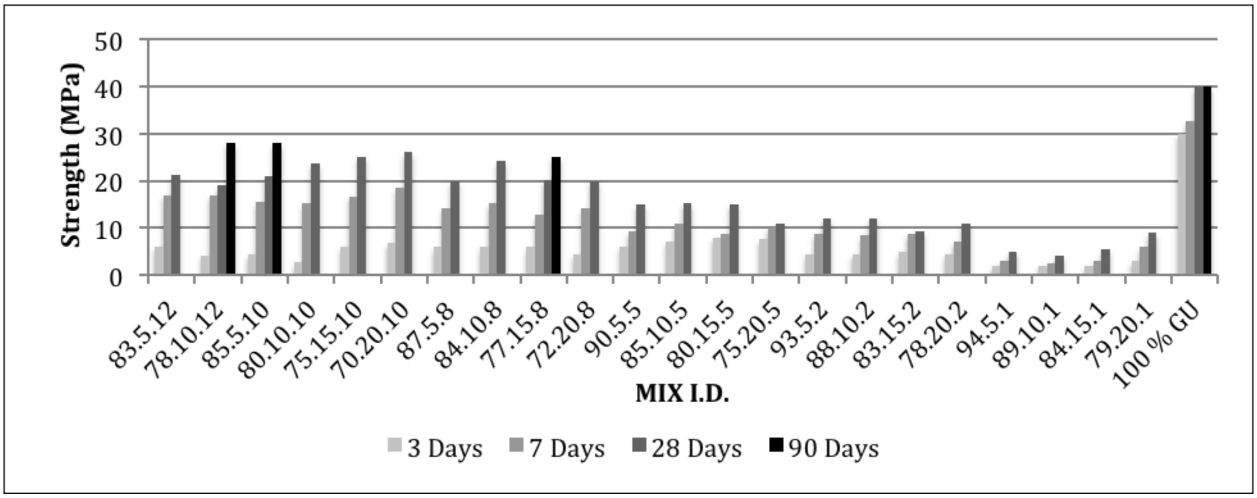

Figure 5: Slag D Compressive Strength (7.43% Al_2O_3)

3.2. Heat of Hydration

Isothermal calorimetry was performed on SSC mixes made using Slag A and Slag D. The two slags were chosen as Slag A had the highest Al_2O_3 content and performed the best of all four slags, and Slag D had the lowest Al_2O_3 content and had very poor performance. To determine the influence of anhydrite content and activator content on the heat of hydration the compositions previously mentioned in Table 2 were studied. The test was performed for 7 days at a w/c of 0.40.

Paste mixtures made with Slag A (13% Al_2O_3) had a short dormant period and an intense hydration peak between 10-23 hrs as demonstrated in Figure 6. While Slag D (7% Al_2O_3) had a wider hydration peak that was not as intense as Slag A as shown in Figure 7. For both slag mixtures the GU cement content influenced the heat flow rate and total heat more than the anhydrite and slag content. For Slag D, the higher the alkali activator content, the higher the total heat release, which correlates with the compressive strength, results. However, the opposite trend was observed for Slag A. As shown in Figure 6, as the alkali activator content increased the heat of hydration decreased but for the SSC mix containing 70% Slag A, 20% anhydrite and 10% GU cement, the total heat release is the highest and this may be explained by the hydration of cement and hydration of anhydrite which both release heat, but which may not be necessarily contributing to the compressive strength of the mixture.

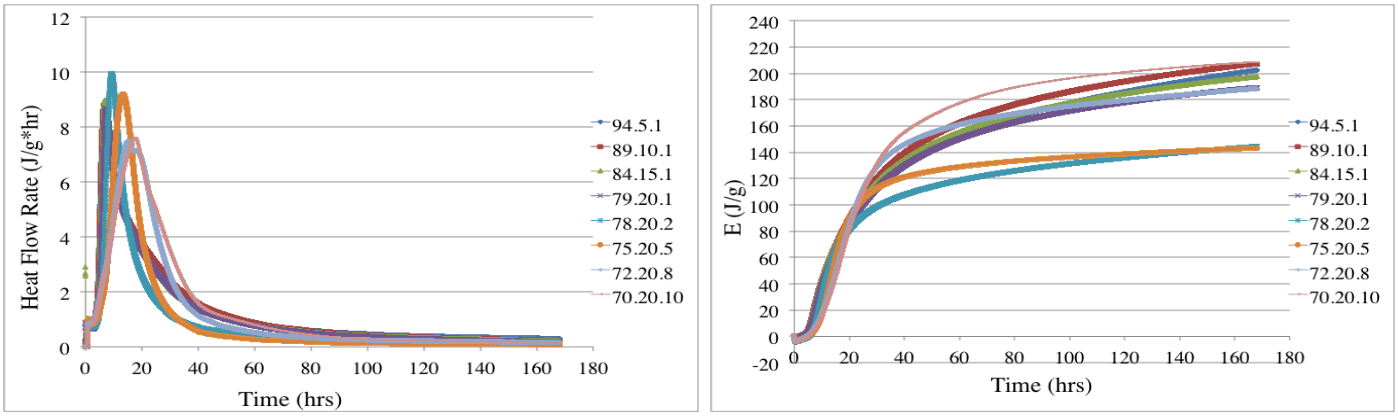

Figure 6: Slag A- Heat of Hydration

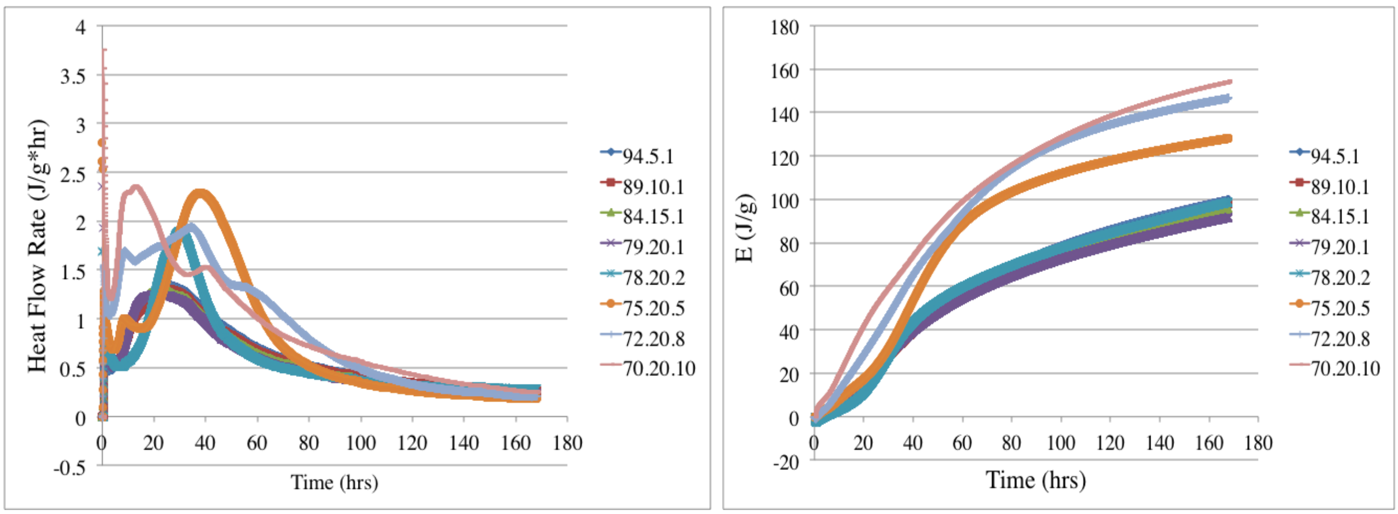

Figure 7: Slag D- Heat of Hydration

4. CONCLUSION

The chemical composition of the slag significantly influences the slag-anhydrite-alkali activator composition and the properties of the obtained supersulfated cement. Slag A which is classified as high Al_2O_3 Slag (13%) exhibit a higher compressive strength at all ages and mixture compositions compared to slags B, C and D.

The optimized mix for the high Al_2O_3 content Slag A provided high compressive strength (48 MPa at 28 days). As the alkali activator content decreased the compressive strength increased for this particular slag. The higher heat of hydration was consistent with the high compressive strength results.

Slags B, C and D had lower Al_2O_3 contents and the performance of these slags compared to the Portland cement control mix was very poor. For slag B at 28 days, strength of 30 MPa was achieved, while the optimized SSC mixes for Slags C and D provided compressive strengths of 31 and 25 MPa at 28 days respectively. For SSC mixtures using Slags B and D, as the alkali activator content increased, the compressive strength also increased but compared to the Portland cement control mix the performance was very poor at all ages. For Slag C, the opposite trend was observed; as the alkali activator content decreased, the compressive strength increased. Therefore, there needs to be further study to determine what other factors than the Al_2O_3 content of the slag influence the mechanical performance and composition of SSC. For all mixtures, the alkali activator content significantly influenced both heat of hydration and the compressive strength results while, the anhydrite content did not have a major effect.

The slag chemistry highly influences the mixture composition and properties of SSC. To further understand the differences in the reactivity of the slags with high and low Al_2O_3 contents, further studies such as pore solution analysis and X-ray diffraction must be carried out to examine the difference in the dissolution rate, and formation of hydrates for the slags of different chemical compositions.

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