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# Activation of blast furnace slag by ettringite formation

Se-Hoon Jeon<sup>a,c</sup>, Seung-Min Kang<sup>b</sup>, Myong-Shin Song<sup>c,\*</sup> and Kyung-Nam Kim<sup>a,\*</sup>

<sup>a</sup>Department of Advanced Materials Engineering, Kangwon National University, Samcheok 25913, Korea <sup>b</sup>KC Green Materials Co., Ltd, Samcheok-ro 734, Samcheok, Korea <sup>c</sup>Research Center of Advanced Convergence Processing on Materials, Kangwon National University, Samcheok 25913, Korea

Blast furnace slag (BFS) can be characterized by latent hydraulic reactivity, with low early strength caused by a hydration delay. When BFS mixes with water, aluminosilicate glass is formed on the surface of the BFS. The aluminosilicate glass disturbs the ordinary hydration of BFS. Therefore, to activate the hydration of BFS, activator materials are usually added to the BFS. To break up the aluminosilicate glass layer and activate hydration, ettringite can be formed on the surface of the slag - the formation of ettringite was the focus of this study. The heat of hydration of the hardened blast furnace slag is less than half of that of Ordinary Portland Cement (OPC); however, the formed ettringite contributes greatly to initiating BFS hydration, and hardened BFS formed by this method exhibited compressive strengths of 83%, 58% and 54% of that of OPC, after 28 days. Properties of the hardened blast furnace slag were characterized by the heat of hydration and X-ray diffraction analysis of the hydrates.

Key words: Alkali activator, BFS, Cement hydrate, Calcium sulfoaluminate.

#### Introduction

Global warming due to greenhouse gas emissions is believed to be the cause of rapid climate change and abnormal weather patterns. To address this, the world has approached the problem on a global scale, as witnessed by the United Nations Framework Convention on Climate Change via the Kyoto Protocol and the regulation of CO<sub>2</sub> emissions in every industrial sector. Previous studies have found that approximately 870 kg of  $CO_2$  is emitted in the production of a single ton of Portland cement [1]. The overall CO<sub>2</sub> emissions of the cement industry accounts for approximately 7% of all industrial emissions. It is thus understandable that the cement industry is highly motivated to reduce the CO<sub>2</sub> emissions attributed to cement manufacturing. One method to meet emission regulations is to utilize fly ash or blast furnace slag as supplementary cementitious materials (SCMs). A typical by-product of the steel industry, BFS is generated during pig iron production. Molten BFS is a by-product of blast furnace technology that uses coke, iron ore and limestone. Vitreous BFS can be produced through rapid cooling by pressurized water.

Approximately 97% of the BFS is composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO. Due to the formation of an ASH<sub>6</sub> membrane, ion release upon mixing with water is inhibited, which in turn causes deficiencies in the initial hydration characteristics of hardened BFS's when mixed with cements. Efforts to mitigate this inhibition have motivated previous research [2]. To activate BFS's, a variety of methods have been proposed most of them have focused on utilizing BFS as an alternative or supplementary material to cements, through activation methods using strong alkalis and high curing temperatures. Studies on alkali activation have identified high shrinkage and weathering as some of the main problems [3]. The emission of  $CO_2$  and high energy consumption during the production of alkali activators are also considered significant drawbacks, because they can offset the advantages of BFS use [4]. To overcome these drawbacks, a number of studies have been conducted to replace alkali activators. Mun verified the development of superior strength and shrinkage compensation by adding BFS to limestone and anhydrite [5], similar to studies [6].

The present study was carried out in order to acceleration the early hydration and improve the physical properties of hardened BFS by combining it with gypsum and calcium aluminate compounds.

### **Experimental procedure**

The BFS used in this study was ground and granulated. Calcium sulfoaluminate (CSA) and calcium aluminate compounds (CAC), products of slag atomizing during the steel making process in Korea, were used as ettringite-forming additives. The mineral composition of CAC and CSA was determined by XRD pattern, and is presented in Figs. 1 and 2. Reagent grade

<sup>\*</sup>Corresponding author:

Tel:+82-33-570-6565 Fax: +82-33-570-6557

E-mail: knkim@kangwon.ac.kr, msong0422@kangwon.ac.kr



Fig. 1. XRD pattern of CAC powder.



Fig. 2. XRD pattern of CSA powder.

Table 1. Chemical composition of materials.

	Chemical composition (wt.%)							
	CaO	$SiO_2$	$Al_2O_3$	$SO_3$	MgO	${\rm TiO}_2$	$K_2O$	Fe <sub>2</sub> O <sub>3</sub>
BFS	38.02	35.23	15.73	5.15	4.26	0.47	0.35	0.25
OPC	61.5	20.6	5.39	2.17	0.15	0.34	1.04	2.91
CSA	44.8	1.40	37.8	13.2	0.291	0.039	0.101	0.357
CAC	50.6	9.28	26	2.69	7.65	0.344	0.0143	1.82

Table 2. Mixture proportions of activators.

	Mixture proportions (mol)				
	CSA	CAC	CaO	CaSO <sub>4</sub>	
A1	10		1.5	8.5	
A2		14.5		5.5	

CaO and  $CaSO_4$  were also used. The chemical properties of the materials are shown in Table 1.

Ettringite ( $3CaO \cdot Al_2O_33CaSO_432H_2O$ ) was generated via reactions of CAC, CSA, CaO and CaSO<sub>4</sub>. To achieve optimal conditions for ettringite formation for the given activators, the proportion of CaO and SO<sub>3</sub> with regard to  $Al_2O_3$  was calculated to find the appropriate proportion of CSA and CAC. Deficiencies in CaO and



Fig. 3. X-ray diffraction of the hardened activator A1.



Fig. 4. X-ray diffraction of the hardened activator A2.

 $SO_3$  were supplemented by adding reagent grade CaO and CaSO<sub>4</sub>. X-ray diffraction analysis (XRD) was used to verify the hydrates of the materials (denotedA1 and A2), after one day of curing. The results are shown in Figs. 3 and 4. Table 2 shows the mixing ratios of A1 and A2.

To assess the compressive strength of the hardened BFS influenced by the formation of ettringite, the cement compressive strength measurement test method was used. The ratios of water to cementitious materials, and the water-cementitious materials ratio is preformed the ratio of sand to binder (S/B) were 0.5 and 3.0, respectively. Table 3 shows the mixing ratios. The mixed mortar was prepared with a prismatic mold with dimensions of  $40 \times 40 \times 160$ mm, and the hardened specimen was taken out of the mold after 24 hrs. All specimens were sealed and cured at 21 °C prior to the test. Compressive strengths were measured after 1, 7, 14 and 28 days of curing.

In order to observe the effect of the BFS on early hydration according to the mix type, the heats of hydration were measured. BFS paste mixed with 0.5 water-binder ratio was prepared using a custom-built, insulated container and sealed, and the heat of

	W/B	S:B	BFS (wt.%)	Activator (wt.%)			
				OPC	A1	A2	
SC				20			
SA1	0.5	1:3	80		20		
SA2						20	
Table 4. Curing time of pastes.							
Sample type					Curing tim	e	
Activators				3 hr, 12 hr, 24 hr			
Blast furnace slag + Activators				3 hr, 6 hr, 12 hr, 18 hr, 1d, 3d, 7d			

Table 3. Mixture proportions of BFS mortar.

hydration was measured every 1s for 72 hrs using a 10bit data logger (Ucam- 60b, Kyowa Co., Japan).

The hydrates of the hardened BFS were analyzed by using a BFS paste with a water-binder ratio of 0.5. The admixed paste was cured while it was sealed in a circular plastic mold. Table 4 shows the curing time. To analyze the microstructure of the hydrates after each curing period, the hardened pastes were pulverized and immersed in acetone for 2 hrs. Then, the acetone was removed by drying in a dryer under 40 °C for 24 hrs, and the pastes were stored in a vacuum desiccator. Powder XRD analysis was performed under conditions of 20 (CuK $\alpha$  radiation) 5-80 ° and 4 °/min to assess the hydrates after each day of curing.

In order to measure the leaching concentration of ions as a function of reaction time in the early hydration process of the BFS activated by ettringite, the concentrations of Ca-, Si- and Al-ions were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ICP-AES used was an Australia Varian Vista-Pro. The measurement conditions are listed in Table 4. The paste was mixed with a L/S ratio of 2.0 for ICP analysis, and the water of reaction at each curing period was extracted using a disposable syringe, then filtered using a Whatman syringe filter ( $0.5 \mu m$ ). For ion leaching concentration measurement, the filtrated water was collected at 6, 12, 18, 22, 26 and 44 hrs according to the temperature rise observed in the hydration measurements.

#### **Results and Discussion**

The results of the compressive strength tests are shown in Fig. 5. The compressive strengths of SA1, SA2, and SC after 28 days of aging were approximately 83%, 58%, and 54%, compared to that of OPC. Compressive strengths after one day of aging were all similar for the hardened BFS, although the compressive strength of SA1 was the highest. Kim et al. reported that the addition of CaO to BFS may lead to higher strength than using Ca(OH)<sub>2</sub>, which has been widely used as an alkali activator [7]. Thus, the reason for the SA1



Fig. 5. Compressive strength of hardened BFS with activator and hardened OPC.



Fig. 6. Temperature of BFS paste with different activators.

**Table 5.** Heat of hydration of BFS paste; time to achieve highest temperature and the highest temperature.

	The time to highest temperature (hr)	Highest temperature (°C)
OPC	14	95.6
SA1	16	44.3
SA2	14	37.0
SC	28	46.9
BFS only	84	23.0

having the highest compressive strength after a single day of aging was likely the alkali activation due to the added CaO, along with CSA. Specimen SA2 exhibited low compressive strength for 14 days of aging, but a rapid development in compressive strength was observed after that time. The low compressive strength during early hydration was related to the weak generation of Ca(OH)<sub>2</sub>. The rapid development of compressive strength after 14 days of aging was caused by the dominance of the calcium aluminate compound (CAC) added to the BFS forming-activator, while rapid strength development was achieved due to its acceleration of hydration after 14 days. The specimen SC showed similar strength development to that of SA1 after a day of aging, but the compressive strength development was reduced after 7 days. This is because the amount of OPC contributing to the development of compressive strength was as small as 20 wt.%. It was also because only the hydration of BFS contributes to the development of compressive strength. This can also be explained by the reduction in  $Ca(OH)_2$  up to 7 days of aging, also revealed by XRD.

Fig. 6 and Table 5 show the results of the simple measurement of the heat of hydration of the hardened BFS mixed with CAC. The specimen SA1 exhibited two different heats of hydration: the first seen in the first 2 hrs was due to the reaction of the added CaO, while the second at 44.3 °C after approximately 16 hrs was due to ettringite generation. Specimen SA2 showed the lowest temperature of 37 °C among the hardened BFS after approximately 14 hrs. Ordinary Portland cement showed the highest heat after approximately 14 hrs, whereas SC had a low temperature of 46.9 °C after 28 hrs. The hydration of BFS alone did not occur to agent extent, as compared to the temperature of the OPC. The hardened BFS with CAC as an activator showed a relatively low overall temperature, compared to that of OPC. The BFS did not show any hydration even after some time, whereas the hardened BFS with CAC as the activator did.

CSA forms ettringite and monosulfate mainly by the hydration reaction, whereas CA forms ettringite in the presence of SO<sub>3</sub> [8, 9]. The XRD results of the hydrates of the activator shown in Figs. 3 and 4 revealed that both A1 and A2 formed ettringite and monosulfate within 3 hrs. The XRD results for the hardened, activator-mixed BFS are shown in Fig. 7. As seen, SA1 and SA2 formed ettringite within 3 hrs and a peak of the remaining gypsum was verified. The gypsum peak was due to the reaction of the remaining anhydrite after forming ettringite upon mixing with water. In SC, a weak peak of ettringite was observed after 6 hrs, which was due to the forming effect of OPC a peak of ettringite can be clearly seen after 12 hrs of hydration. A peak for monosulfate, which was observed only in the activator-mixed hydrates, was not found in the hardened BFS, including each of the activators. A possible reason for this is that the gypsum used as a pulverizing agent during BFS pulverization, present in the hardened BFS, was not consumed completely so that a transition from ettringite to monosulfate did not occur.

Fig. 8 shows the XRD results of the hardened BFS after curing for 1, 3, and 7 days. As hydration continued, the intensity counts of the peaks for SA1, SA2, and anhydrite tended to decrease. This was due to the reduction in the anhydrite peak caused by the continuous generation of ettringite due to reactions with  $SO_3$ , CSA and CAC in the hardened BFS. A relatively low anhydrite peak intensity was observed in the case of SC which used OPC. This was possibly



Fig.7. X-ray diffraction of hardened BFS after each curing time.



**Fig. 8.** X-ray diffraction of hardened BFS after curing for 1, 3 and 7 days.

caused by a small amount of gypsum contained in the processing of the BFS. The anhydrite peak was not



Fig. 9. Concentration of ions in hydrated GGBFS activated by ettringite.

observed after 3 days of aging.

Fig. 9 shows the amount of ions leached as a function of the curing time of BFS through hydration, activated by ettringite formed from CAC and CSA. Figs. 9(a-c) indicate the amount of Ca-, Si- and Al-ions leached from the activated, hardened BFS. Fig. 9(a) shows the leaching characteristics of Ca-ions and verifies that Ca-ions exhibited significantly higher leaching concentrations than those of other ions. It is also seen that SA1, SA2 and SC show similar concentrations of Ca-ions at the curing time of 44 hrs. Particularly, Ca-ions are leached in high concentration

during the initial hydration from SA1 and SC, because SC is affected by OPC, as shown in Table 3, and SA1 by CaO through A1, as shown in Table 2. Moreover, the Ca-ions of SA2 are leached from pure calcium aluminate. Fig. 9(b) shows the leaching concentration of Si-ions and confirms that a greater amount of Si-ions are leached from SA1 than from SC and SC2.

# Conclusions

The method developed in this study enhances the hydration of BFS, which is typically delayed by the formation of aluminosilicate glass, by using calcium aluminate compounds instead of alkali activators such as NaOH to form ettringite. The results of this study verify that ettringite is formed during the initial hydration of BFS. It is proposed that this disturbs the formation of aluminosilicate glass on the surface of the BFS, thereby increasing the hydration of BFS. The BFS mortar studied in this work, which contained calcium aluminate compounds, had comparable or better physical properties than those of the OPC mortar.

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