

# Manufacture of Cementitious Materials with Coal Combustion Bottom Ash and FGD gypsum

Kwang-suk You<sup>1</sup>, Nam-il UM<sup>1</sup>, Gi-Chun Han<sup>1</sup>, Hee Chan Cho<sup>2</sup> and Ji-Whan Ahn<sup>1</sup>

<sup>1</sup>Korea Institute of Geoscience & Mineral Resources, 92 Gwahango-no, Yuseong-gu, Daejeon, 305-350, KOREA; <sup>2</sup> School of Energy System Engineering, Seoul National University, San 56-1 Shinlim-dong, Kwanak-Gu, Seoul, KOREA

KEYWORDS: Coal Bottom ash, FGD Gypsum, Calcium aluminate, Hydration, Hydrates

## ABSTRACT

In this study, the manufacture of cementitious materials, such like calcium aluminate phases and calcium silicate phases, has been carried out by using coal combustion bottom ash and FGD gypsum which are by-products generated from Coal Power Plant. From the study, tetracalcium trialuminosulfate ( $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ ) and tricalcium aluminate ( $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ ) were formed from sintering at  $1200^\circ\text{C}$  to  $1350^\circ\text{C}$  as main calcium aluminate phases, together with calcium aluminosilicate ( $\text{CaOAl}_2\text{O}_3\text{SiO}_2$ ). These cementitious phases were melted at  $1400^\circ\text{C}$  of sintering temperature. The formation temperatures of those cementitious phases were relatively lower than that of theoretical formation temperature for them. The decreases of those formation temperatures are considered due to alkaline and iron component in bottom ash.

## 1. Introduction

The amount of coal usage in Korea is dramatically increasing very year in the power plants. The generation of coal ash in Korea enormously increases also with an increase in coal usage, and it was over 5.8 million tons in 2006, and the amount is expected as reaching 8 million tons by 2010. Coal ash can be divided by fly ash and bottom ash with generation position. Coal fly ash of them occupies about 80% by weight of all the ash and is reused in concrete and cement production and its recycling rate increases to reach 80% in 2003. But, coal bottom ash has nearly not been reused and disposed in ash pond. The recycling potential of coal bottom ash is determined by its physical properties such as gravity, particle size distribution, etc., while the reuse of coal fly ash affects by its chemical composition. At present, coal bottom ash is often used as a substitute for sand in the production of concrete blocks or sub-base materials in road construction [1-3].

But the chemical composition of coal bottom ash is also very similar to that of raw materials, such like  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Especially, the high  $\text{Al}_2\text{O}_3$  composition contained in coal bottom ash affects to form calcium aluminates cement, as coal bottom ash is used

as raw materials in cement. The calcium aluminate cements have many advantages during hydration compared to ordinary Portland cement. In general calcium aluminate cement such like calcium aluminate system and calcium sulfoaluminate system set about as quickly as those of ordinary Portland cement, but harden very rapidly; a high strength is reached in 24 hours. In this study, bottom ash was used as raw materials to manufacture calcium aluminate cement, and flue gas desulfurization gypsum which is generated from power plant, was mixed with it to support the composition of CaO and SO<sub>3</sub> so that calcium sulfoaluminate system is formed.

## 2. Experimental

The bottom ash and FGD gypsum which were generated from Boryong in South Korea, were used in the study. The manufacture temperature of sintering was controlled from 1200°C to 1400°C. And the mixing ratio between bottom ash and FGD gypsum initially was controlled at 50/37/13 of Al<sub>2</sub>O<sub>3</sub>/CaO/SO<sub>3</sub> in weight percent, of which the composite ration is calcium sulfoaluminate system; 4CaO·3Al<sub>2</sub>O<sub>3</sub>·SO<sub>3</sub>. Table 1 shows the chemical compositions of bottom ash and FGD gypsum which were used in the study. The bottom ash contains the amount of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and FGD gypsum is largely consist of SO<sub>3</sub> and CaO. And the minor chemical composition of coal bottom ash is shown in Table 2. In spite of alkaline content having very high, Cr content became low about 100 ppm. Figure 1 shows the X-ray diffraction pattern of FGD gypsum. As shown in this figure, FGD gypsum is CaSO<sub>4</sub>·2H<sub>2</sub>O. The X-ray diffraction patterns for coal bottom ash are shown in Fig. 2. It is confirmed that mullite, quartz, hematite, and labradorite exist as crystalline substance ash and glassy phases is presented from broad parts between 20° and 30° in coal bottom

Table 1. The major chemical composition of coal bottom ash and FGD gypsum [ % ]

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>
Bottom ash	19.77	47.72	5.81	15.03	1.99	-
FGD Gypsum	0.62	0.48	31.30	0.03	0.44	44.60

Table 2. The minor chemical composition of coal bottom ash [%]

	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO
Bottom ash	0.552	1.985	1.134	0.749	0.010	0.119

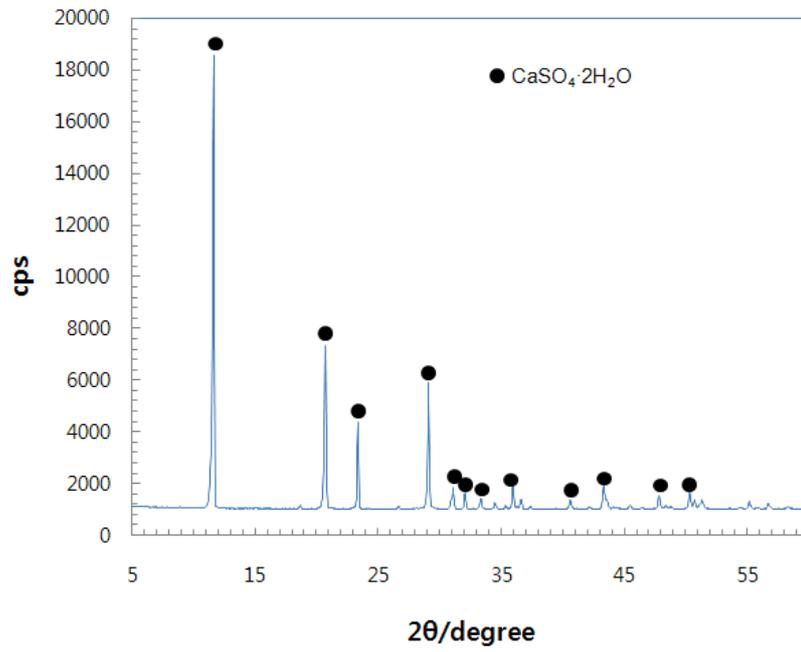


Figure 1. X-ray diffraction patterns of FGD gypsum

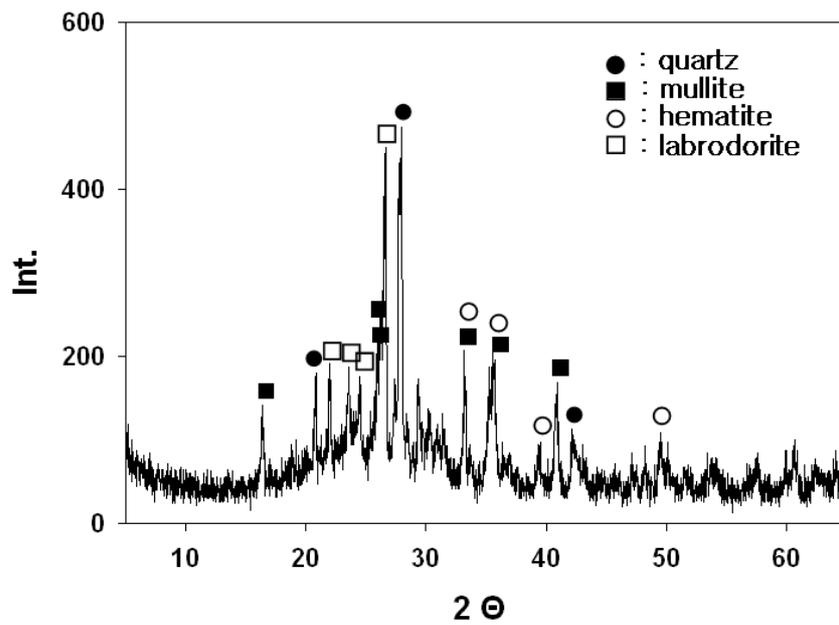


Figure 2. X-ray diffraction patterns of coal bottom ash.

### 3. Results and discussion

Figure 3 shows X-ray diffraction patterns of products formed as the designed mixture is sintered at 1200, 1250, 1300, 1350 and 1400°C of temperature. The products formed were shown such like tricalcium aluminate, calcium aluminosilicate phases and calcium sulfoaluminate phases, made from coal combustion bottom ash and FGD gypsum. In particular, tetracalcium trialuminosulfate ( $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ ) and tricalcium aluminate ( $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ ) were formed from sintering at 1200°C to 1350°C as main calcium aluminate phases, together with calcium aluminosilicate ( $\text{CaOAl}_2\text{O}_3\text{SiO}_2$ ). These cementitious phases were melted at 1400°C of sintering temperature. The formation temperatures of those cementitious phases were relatively lower than that of theoretical formation temperature for them. The decreases of those formation temperatures are considered due to alkaline and iron component in bottom ash.

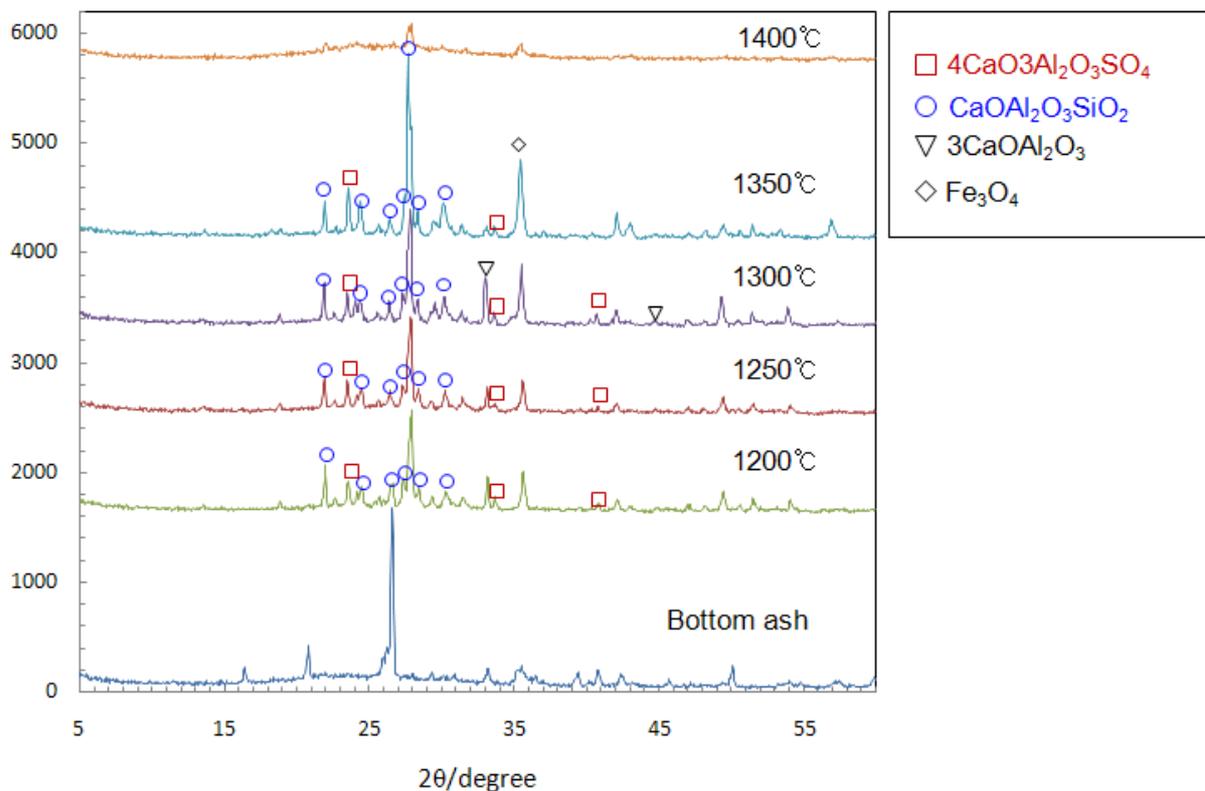


Figure 3. X-ray diffraction patterns of products as sintering temperature.

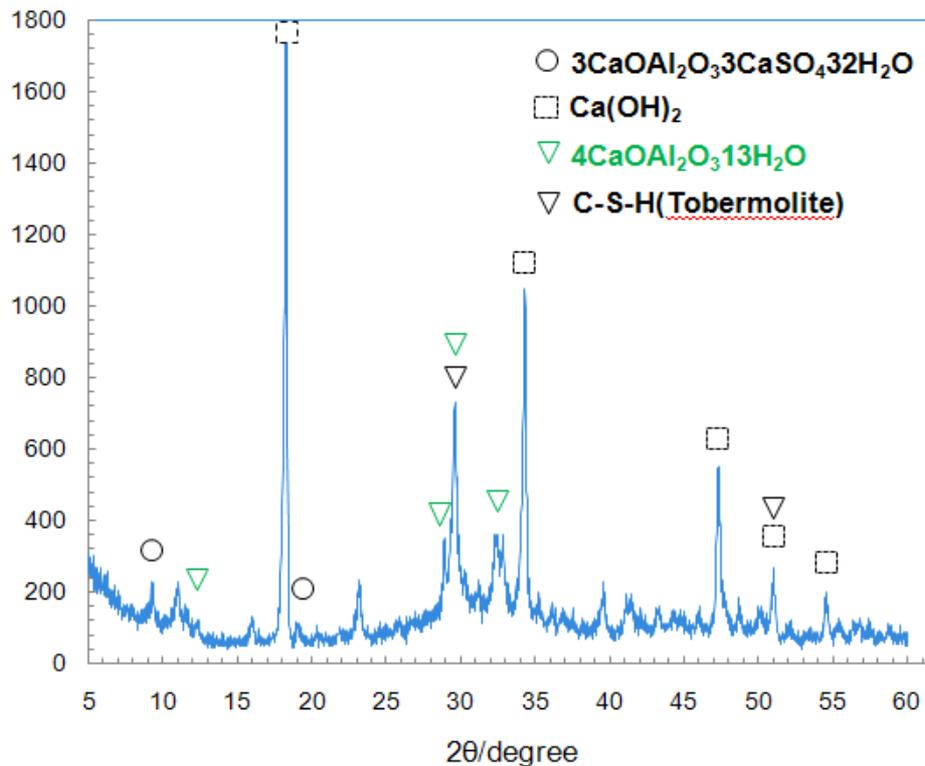


Figure 4. X-ray diffraction of products formed by the hydration of cementitious phases sintered at  $1350^\circ\text{C}$ .

Figure 4 shows the result of X-ray diffraction measurement for cementitious phase obtained by sintering at  $1350^\circ\text{C}$ . The hydration products were confirmed as ettringite;  $3\text{CaOAl}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ , and calcium hydroxide;  $\text{Ca}(\text{OH})_2$ , hydrogarnet;  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ , Calcium silicate hydrates (tobermorite); C-S-H. It is believed that Ettringite and hydrogarnet were formed by hydration of calcium aluminate phases such like tricalcium aluminate and tetracalcium trialuminosulfate which were formed by sintering mixture at  $1305^\circ\text{C}$ . And calcium hydroxide and tobermorite are expected to form during the hydration of calcium aluminosilicate.

#### 4. Conclusions

Tetracalcium trialuminosulfate ( $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ ) and tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) were formed by using coal bottom ash and FGD gypsum which are by-products generated from Coal Power Plant through sintering process from  $1200^\circ\text{C}$  to

1350°C together with calcium aluminosilicate( $\text{CaOAl}_2\text{O}_3\text{SiO}_2$ ). The cementitious phase obtained by sintering at 1350°C form various hydrates as ettringite, and calcium and hydrogarnet.

#### REFERENCES

- [1] N. Ghgafoori, Y. Cai, ACI Mater Journal 95 (2) 1998, pp. 121–130
- [2] N. Ghgafoori, Y. Cai : ACI Mater Journal 95 (3) 1998, pp. 244-251
- [3] Dj.M. Maric, and S.K. Estreicher, Mater. Sci. Forum Vol. 83-87,1992, pp. 119