

Behaviors of CO₂ Solidification CFBC coal ash by accelerated carbonationSeong-Young Nam¹, Chun-sik Kim¹, Shin-Seok Seo¹, Yong-Kwang Cho¹,
Hyung-Woo Lee¹, Ji-Whan Ahn^{2*}

1. Technical Center, HANIL CEMENT Co.Ltd., 50 Daehwa-ro 52beonan-gil, Daedeok-gu, Daejeon, Korea.

2. Center for Carbon Mineralization, Korea Institute of Geosciences and Mineral Resources (KIGAM),
124 Gwahagno, Yuseong gu, Daejeon, Korea**Abstract**

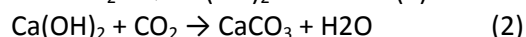
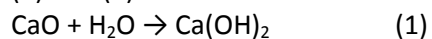
In this study, in order to stabilize the CaO component of CFBC coal ash through accelerated carbonation, optimum conditions were obtained a various conditions as liquid-solid-ratio, temperature, and CO₂ concentration, quantitative CO₂solidification amount and heavy metal release characteristics were evaluated. The results involved that the carbonation time increases with increasing liquid-solid-ratio, temperature, and decreasing CO₂ concentration. The CO₂ solidification rate of bottom ash, fly ash was 2.909%, 5.818% by carbonation, respectively. As a result, 29.09g of CO₂ in bottom ash, 58.18g of CO₂ in fly ash could be storage in 1kg of coal ash. Thus, theheavy metal of coal ash was stabilized by CO₂ solidification.

ACKNOWLEDGMENTS

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1. Introduction

As electric power demand for electric power consumption increases, the Korean government plans to establish 20 new coal-fired power plants according to the electricity supply and electric supply plan. The generation of coal ash from coal-fired power plants in 2010 is about 7.4 million tons per year, and the amount of coal ash generated is expected to increase 15 million tons in 2021. Domestic coal-fired power plants can be divided into Pulverized Coal (PC) type and Circulating Fluidized Bed Combustion (CFBC) type, and more than 80% of the fly ash generated from PC type coal-fired power plants is mixed with concrete and recycled as raw material in cement production. However, the coal ash generated from CFBC type coal-fired power plants does not comply with KS L 5405 and contains a relatively large amount of calcium oxide compound. The introduction of it as concrete admixture is able to bring about problems such as expansion of concrete and cracks etc. due to calcium oxide component, so it is necessary to develop new recycling technology. Meanwhile, various technologies have been developed to reduce greenhouse gas emissions due to the increase greenhouse gas emissions, and Carbon CaptureStorage (CCS) technologies have been developed to reduce them by methods such as underground storage, ocean storage, and mineral carbonation. Among them, mineral carbonation is a technology to reduce CO₂ by utilizing minerals or industrial by-products, and it is a technology that is able to store CO₂ as a stable state in the solid through precipitation reaction of carbonate. Accelerated carbonation is a technique for accelerating the precipitation reaction of carbonates. It has a mechanism such as weathering which occurs in nature. It reacts with substances such as monovalent sodium, potassium, divalent calcium and magnesium ions and produces carbonate which sequesters CO₂. Generally, the carbonation reaction means a reaction that produces CaCO₃ by the following equations (1) and (2).



Therefore, in order to stabilize the CaO component of CFBC coal ash through accelerated carbonation, optimum conditions were obtained under various accelerated carbonation conditions, quantitative CO₂ solidification amount and heavy metal release characteristics were evaluated. The carbonated ash of CFBC type coal-fired power plant was developed to utilize it for various recycling applications such as concrete admixture and mine filler material etc. in the future.

2. Materials and Methods

In this study, the CFBC coal ash was supplied by a Circulating fluidized bed combustion (CFBC) power plant located in the metropolitan area of Sam-Cheek in South Korea. In order to obtain samples that have not been through a weathering process, samples that had been stored for approximately a day were used in the experiments. Moisture content of CFBC fly ash and bottom ash were measured according to the standard test methods. The masses of the samples were measured prior to drying, and then measured again after 4 hours of drying at 105°C. The moisture content was calculated through the mass differences of the samples before and after drying. It was measured three times for each sample and the average was taken. The moisture content of CFBC fly ash and bottom ash were 17.15% and 8.64%, on average, respectively. The obtained samples were dried at 105°C for 3 days in a large dryer and then sealed from the external environment. The step mentioned above was taken to minimize errors in the experiments possibly induced by weathering when the samples are exposed to air. CFBC bottom ash is composed of materials with various particle sizes. Therefore, the bottom ash was separated through 6 standard sieves of +4.75, 2.36~4.75, 1.18~2.36, 0.6~1.18, 0.3~0.6, 0.15~0.3, -0.15 mm. Incineration fly ash is composed of fine particulates and it was separated using a 100 mesh. Accelerated carbonation was conducted to stabilize the high content of hazardous heavy metals in CFBC coal ash, and carbonation reactions experiments were conducted using a various condition with a liquid-solid-ratio, temperature, and CO₂ concentration. Figure 1 schematically illustrates the equipment used in the experiments. The detailed experiment conditions were conducted with a liquid-solid ratio as 10, 5, 3 dm³/kg, conducted with temperature as 20°C, 40°C, and 60°C, conducted CO₂ concentration as 10%, 100%. Other conditions of the experiments used here were injection at a rate of 1L/min, and stirring at 300rpm. The experiment of carbonation was terminated when the measured pH was below 7 and did not change any further.

3. Results and Discussion

3.1 Characteristics of CFBC coal ash

X-ray fluorescence (XRF, Rigaku, Primus 2) and X-ray diffraction (XRD, Rigaku, RU-200) were used in the analyses of the chemical compositions and crystalline structures of CFBC coal ash. Table 1 shows the chemical compositions of CFBC coal fly ash and bottom ash. The major components of CFBC fly ash are 37.0% of CaO, 19.1% of SiO₂, 12.5% of Fe₂O₃, 9.89% of Al₂O₃, and 9.14% of MgO. The major components of CFBC bottom ash are 31.6% of SiO₂, 30.6% of CaO, 12.8% of Fe₂O₃, 9.49% of Al₂O₃, and 6.28% of SO₃.

Table 1. Chemical compositions of CFBC coal ash

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	P ₂ O ₅	Na ₂ O	K ₂ O	I.g.-loss
CFBC fly ash	19.1	9.89	12.5	37.0	9.14	4.79	0.06	0.13	0.83	5.52
CFBC bottom ash	31.6	9.49	12.8	30.6	5.49	6.28	0.06	0.35	1.44	0.87

Figure 1 illustrates the XRD crystalline analysis results. From the analyses the major crystalline structures of CFBC fly ash are composed of Quartz (SiO₂), Periclase (MgO), Lime (CaO), Calcite (CaCO₃), and

Anhydrite(CaSO_4), and the major crystalline structures of CFBC bottom ash are composed of Quartz(SiO_2), Periclase(MgO), Lime(CaO), Anhydrite(CaSO_4), and Magnetite(Fe_2O_3).

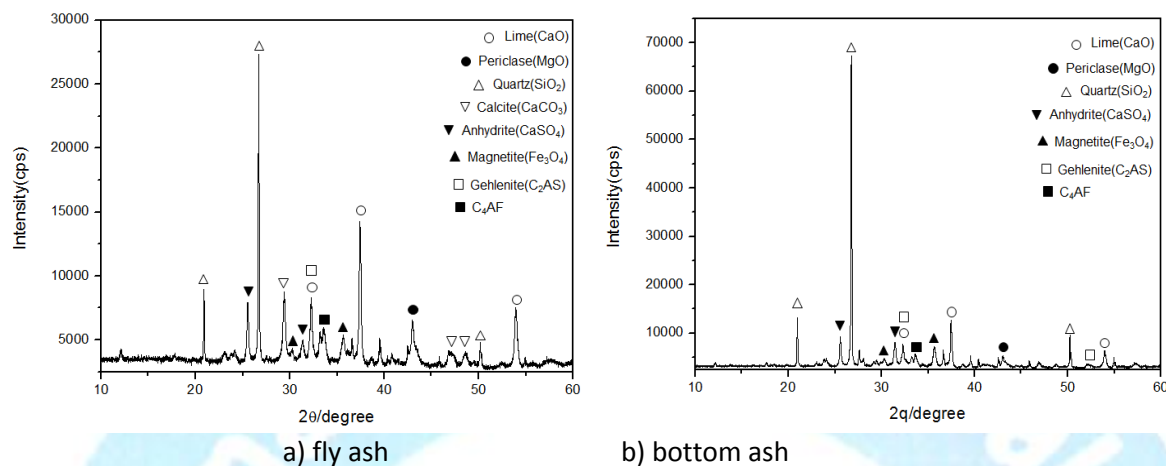


Figure 1. Crystalline structures of CFBC coal ash

Table 2 shows the particle size distribution of CFBC bottom ash presenting a regular distribution ratio of each particle size. The CFBC bottom ash was divided into several size fractions by standard sieves (+4.75 mm, 4.75~2.36 mm, 2.36~1.18 mm, 1.18~0.6mm, 0.6~0.3 mm, 0.3~0.15 mm, and -0.15 mm). Table 3 shows the particle size distribution of the CFBC bottom ash and flyash. Particles under 100 mesh particle size composed about 99% of the CFBC fly ash, and particles under 100 mesh particle size composed about 14% of the CFBC.

Table 2. Particle size distribution of CFBC bottom ash

	CFBC bottom ash						
Particle Size (mm)	+4.75	4.75~2.36	2.36~1.18	1.18~0.6	0.6~0.3	0.3~0.15	-0.15
Composition (wt%)	0.42	1.22	3.39	8.48	12.18	60.45	13.86

Table 3. Particle size distribution of CFBC fly ash, bottom ash separated $\pm 0.15\text{mm}$

	CFBC fly ash		CFBC bottom ash	
Particle Size (mm)	+0.15mm	-0.15mm	+0.15mm	-0.15mm
Composition (wt%)	1	99	86	14

In order to evaluate the environmental stability of CFBC coal ash, heavy metal content and leaching test were conducted. Heavy metal content test was pretreated by US EPA 6010 method and Heavy metal leaching test was pretreated by Korea leaching test method. The concentration was measured by Inductively Coupled Plasma (ICP-OES; Optima 8300, Perkin Elmer) analysis after pretreatment.

Table 4 shows a result of analyzing the heavy metal content of CFBC coal ash, the fly ash contains 9.0mg/kg of Pb, 32.3mg/kg of Cu, 7.5mg/kg of As, 5.6mg/kg of Cd, 31.1mg/kg of Cr, 0.589mg/kg of Hg.

The bottom ash contains 2.1mg/kg of Pb, 7.9mg/kg of Cu, 25.0g/kg of As, 4.8mg/kg of Cd, 30.7mg/kg of Cr, 0.007mg/kg of Hg.

Table 4. The heavy metal content of CFBC coal ash

	Pb	Cu	As	Cd	Cr	Hg
CFBC fly ash	9.0	32.3	7.5	5.6	31.1	0.589
CFBC bottom ash	2.1	7.9	25.0	4.8	30.7	0.007

Table 5 shows a results of analyzing the heavy metal leaching content of CFBC coal ash, the fly ash and bottom ash were not eluted as a whole, and the fly ash was 0.07mg/L of Cr. .

Table 5. The heavy metal leaching content of CFBC coal ash

	Pb	Cu	As	Cd	Cr	Hg
CFBC fly ash	N.d.	N.d.	N.d.	N.d.	0.07	N.d.
CFBC bottom ash	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.

3.2 CO₂ Solidification of CFBC coal ash

Figure 2 shows a result of crystalline structure of CFBC coal ash after carbonation, to explain the characteristics of the variation in the mineral phase of fly ash, bottom ash via a carbonation reaction, the mineral phase of fly ash, bottom ash obviously changed with accelerated carbonation reaction, as shown in Figure 2. In the case of calcite (CaCO₃), the peak in the carbonated fly ash, bottom ash increased with in the carbonation reaction. The decomposition of lime (CaO) with carbon dioxide assumed to involve the chemical reaction.

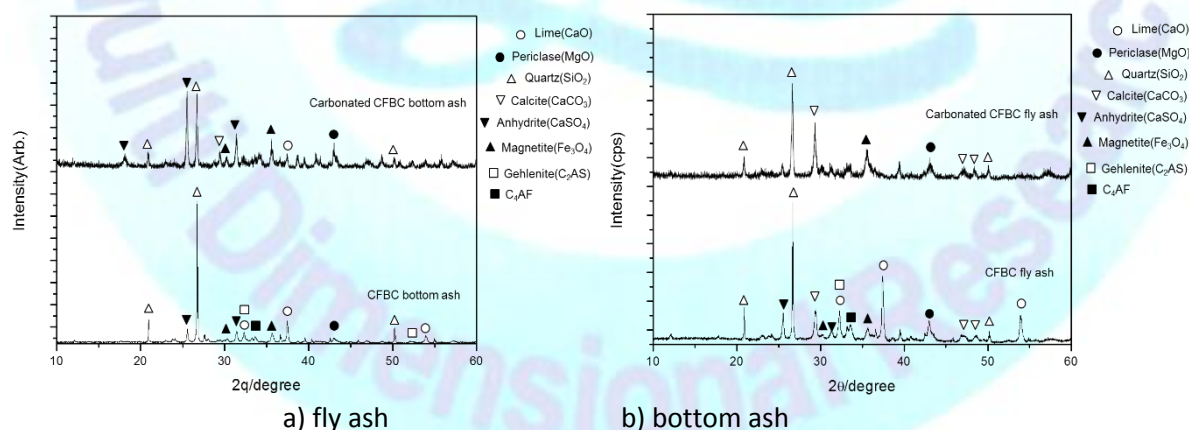


Figure 2. Crystalline structures of CFBC coal ash after carbonation

Figure 3 shows a result of behavior of CFBC coal ash by carbonation at liquid-solid-ratio. As a liquid-solid-ratio of fly ash increased, the carbonation reaction time increased, and bottom ash showed similar carbonation reaction time by liquid-solid-ratio. In results show that the reaction is terminated relatively quickly due to the relatively low content of alkaline components that can react with CO₂ in the bottom ash.

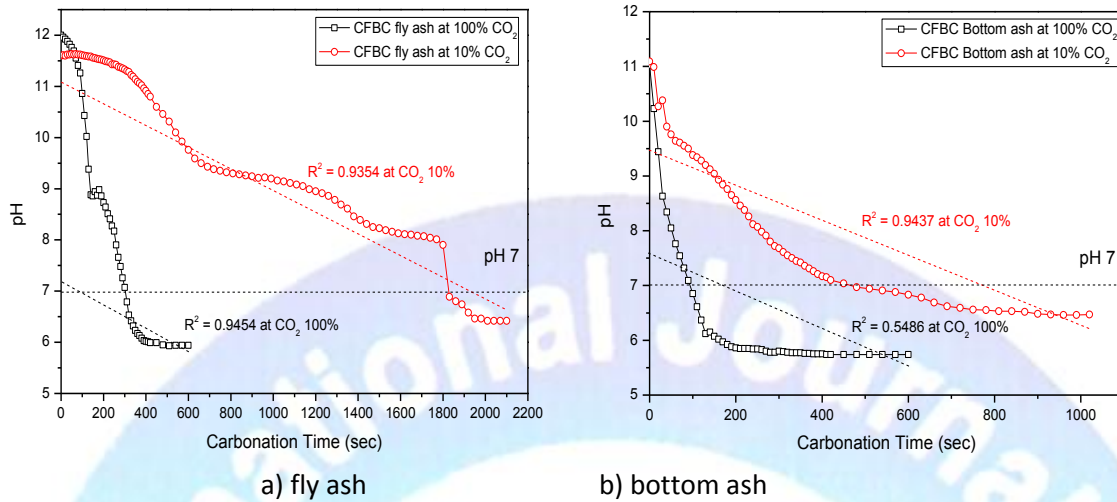


Figure 5. Behavior of CFBC coal ash by carbonation at CO₂ concentration

Figure 5 shows a result of quantitative evaluation of CFBC coal ash by Thermogravimetric-Differential Thermal Analyzer (DTG-60H, Shimadzu). The bottom ash mass decreased by 0.025wt% before carbonation, and after carbonation it decreased by 2.934wt%. As a result, CO₂ solidification rate was 2.909% by carbonation, and 29.09g of CO₂ could be storage in 1kg of bottom ash. The fly ash mass decreased by 2.286wt% before carbonation, and after carbonation it decreased by 8.104wt%. As a result, CO₂ solidification rate was 5.818% by carbonation, and 58.18g of CO₂ could be storage in 1kg of fly ash.

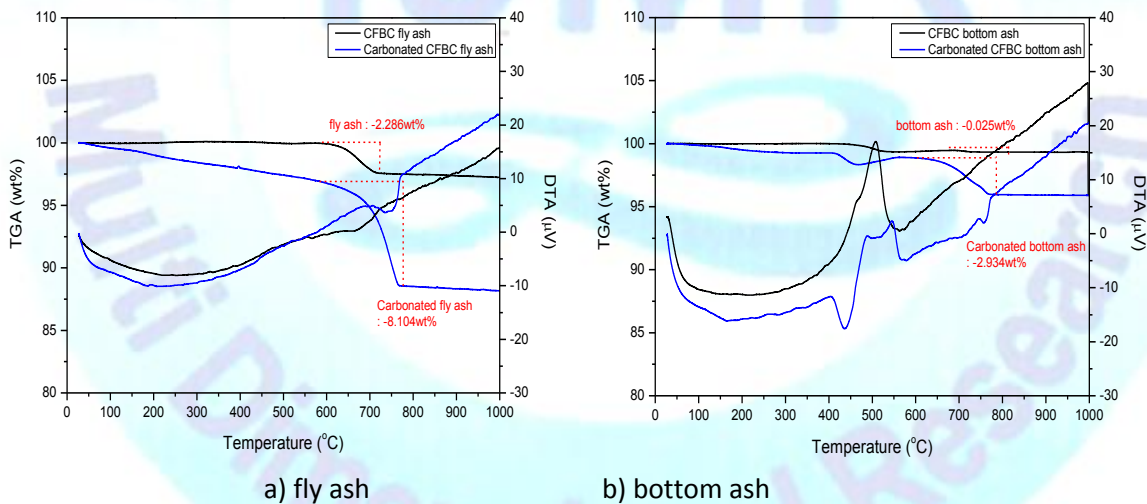


Figure 6. Quantitative evaluation of CO₂ solidification CFBC coal ash by TG/DTA

Table 6 shows a results of analyzing the heavy metal leaching content of carbonated CFBC coal ash, theCr of fly ash was stabilized by CO₂ solidification. In In general, the solubility of heavy metals such as Cu, Pb, and Cr in the neutral pH is relatively lower than that in the alkali pH. Therefore, the solubility of heavy metals in a coal ash stabilized at pH below 7 by CO₂solidification. In addition, the formed calcite on the surface of coal ash particles by CO₂solidification, the dissolution of heavy metals can be suppressed by capsulation effect.

Table 6. The heavy metal leaching content of CFBC coal ash after carbonation

		Pb	Cu	As	Cd	Cr	Hg
CFBC fly ash	Raw	N.d.	N.d.	N.d.	N.d.	0.07	N.d.
	Carbonation	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.
CFBC bottom ash	Raw	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.
	Carbonation	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.

4. Conclusion

This research focused on the behaviors of a liquid-solid-ratio, temperature, and CO₂ concentration on accelerated carbonation of CFBC coal ash for CO₂ solidification. The results involved that the carbonation time increases with increasing liquid-solid-ratio, temperature, and decreasing CO₂ concentration. The CO₂ solidification rate of bottom ash, fly ash was 2.909%, 5.818% by carbonation, respectively. As a result, 29.09g of CO₂ in bottom ash, 58.18g of CO₂ in fly ash could be storage in 1kg of coal ash. Thus, the heavy metal of coal ash was stabilized by CO₂ solidification.

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