Carbonation of Circulating Fluidized Bed Combustion Fly Ash with Hybrid Reaction

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ABSTRACT

This paper investigates the reaction rate of CO₂ storing carbonation hybrid reaction by comparing the behavior of carbonation between Ca(OH)₂ and fly ash with that of CFBC (Circulating Fluidized Bed Combustion) containing plenty of Free-CaO. Because fly ash with CFBC contains a lot of unreacted CaO, it cannot be used as a raw material for concrete admixtures and its usages are limited. To reuse such material, we stabilized unreacted CaO by carbonation and investigated the carbonation rate. We used a pH meter and a thermometer to check the rate of the carbonization. Also, we set the contents of fly ash with CFBC, Ca(OH)₂, flow and fluid of CO₂, respectively, to 100 g, 50 g, 100 ~ 1000 cc/min and 400 g based on the content of Free-CaO. We used carbonated water instead of water, and added an alkaline activator to promote the carbonation rate. As a result, the addition of the alkaline activator and carbonated water promoted the rate of carbonation via a hybrid reaction.

Key words : Alkaline earth oxides, Powders, Hybrid reaction, Carbonation, CFBC fly ash

1. Introduction

Methods of generating energy using coal in power plants include the pulverized coal combustion (PCC) method and circulating fluidized bed combustion (CFBC) method. The CFBC method can effectively burn high sulfur and low grade coal, and recently there has been increasing interest in this method as a power generation technology due to the outstanding economic feasibility and environmental impact of the equipment related to the method.¹⁾ CFBC has a long bituminous coal combustion duration, which can lead to in-furnace desulfurization, and the combustion temperature is low, minimizing the production of NO_x and reducing the production of particulate matter. However, since this method leads to in-furnace desulfurization, Ca of approximately 2 ~ 2.5 times the amount of sulfur in the fuel is necessary. So, a large amount of limestone is added, resulting in significant amounts of unreacted CaO and anhydrous gypsum in the coal ash. This SiO₂ content does not meet the KS standard (KS L 5405); thus, the coal ash cannot be recycled and the entire amount is buried.²⁾ Also, Korea is currently ranked 7th in the world (for the year 2015) for greenhouse gas emissions. For greenhouse gas emissions to continue to improve, research on carbon capture and storage (CCS) is actively being pursued in order to fulfill the mandatory reduction requirements according to the Kyoto Protocol.^{3,4)}

Therefore, the recycling of fluidized bed coal ash requires

mineral carbonation for the stabilization of unreacted CaO; this area is a part of CCS research.

Domestic research carried out by Byeon *et al.*⁵⁾ verified the carbonation process of raw materials through carbonation using steel slag, which is an industrial by-product; Ahn *et al.*⁶⁾ showed the applicability of accelerated carbonation technology using carbon dioxide reduction through wet carbonation of waste concrete powder. Moreover, Lee *et al.*^{7,8)} conducted research on the carbonation reaction rate and carried out experiments to observe the carbonation behavior using fluidized bed coal ash; they attempted to determine whether carbonation is possible and how much solid is produced.⁹⁾ Additionally, Ahn *et al.*¹⁰⁾ performed carbonation experimentation by fabricating a suspension using Ca(OH)₂ as the main ingredient; its reaction rate was determined, and was found to increase linearly with increases of the solid amount and of the temperature. Lee^{11,12)} used additives to waste cement and investigated their impact on the carbonation reaction.

However, research on the carbonation behavior and recycling of fluidized bed coal ash is lacking and, especially, carbonation research on large amounts of fluidized bed coal ash does not yet exist, severely restricting the recycling of fluidized bed coal ash.

Therefore, in this study, to investigate various ways of recycling concrete admixtures, a large amount of fluidized bed coal ash was carbonated and converted to an environmentally and chemically stable material. A preceding study⁸⁾ used the dissolution reaction of Ca²⁺ ions produced by the hydration of the CaO component, which is a rate limiting reaction of the carbonation reaction, and determined the carbonation behavior according to the solid content.

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Experimentation using the dissolution reaction of CO_2 to an aqueous solution state, which is another rate limiting reaction in the carbonation process, was performed to compare the carbonation behaviors of unreacted CaO , which is significantly included in the fluidized bed coal ash and $\text{Ca}(\text{OH})_2$. An alkali additive was used to investigate the hybrid carbonation mechanism of fluidized bed coal ash through the carbonation reaction rate and temperature.

2. Experimental Procedure

2.1. Carbonation According to the CO_2 Flow Rate

Experiments were carried out to examine the carbonation behavior when the CO_2 flow rate was increased to increase the reaction surface areas of CO_2 and water. The precipitated calcium carbonate fabrication method of injecting CO_2 gas (99% purity) into the suspension prepared by mixing water and fluidized bed coal ash containing high amounts of CaO , which is the main component of carbon storage, was employed at room temperature. In a plastic beaker of 2000 ml container volume, the fluidized bed coal ash and water mixed suspension was injected with CO_2 to induce carbonation. A magnetic stirrer was used to stir the suspension. After determining that the solid-liquid ratio indicated sufficient stirring of the CO_2 , experimentation was conducted to determine the reaction rate of the conversion of the CaO component integrated with CO_2 to CaCO_3 crystalline phase. In order to identify the carbonation reaction behavior of the fluidized bed coal ash, a suspension was prepared with $\text{Ca}(\text{OH})_2$ as the primary ingredient, so that only the CaO component, and not other components among the ingredients, was converted to CaCO_3 crystalline phase; the experiment was conducted by increasing the CO_2 flow rate. The carbonation experiment used conditions of 50 g $\text{Ca}(\text{OH})_2$ mass, solid-liquid ratio of 1 : 3, and 5 stage CO_2 flow rate between 100 cc/min ~ 1000 cc/min. After the carbonation reaction, a pH meter (pH-230SD, Lutron, Taiwan) was used to measure the pH change at 2 second intervals and a thermometer (MTM-380SD, Lutron, Taiwan) was used to measure the temperature change in 2 minute intervals to determine the temperature increase due to the exothermic reaction.

2.2. Carbonation using Carbonated Water

For the experiment conducted to determine that the CO_2 dissolution rate is a rate limiting reaction, a $\text{Ca}(\text{OH})_2$ suspension was prepared. Before suspension preparation, CO_2 was injected in advance into the fabricated carbonated water; then, the ingredients were added to carry out the carbonation reaction and examine the effect of the rate limiting CO_2 reaction. For the experiment conditions, the time dura-

tion of CO_2 early injection was set to 2 and 3 h, while the solid amount was 50 g, solid-liquid ratio was 1 : 3, and the CO_2 flow rate was set to the optimal condition of 700 cc/min obtained in the above experiment for the carbonation reaction. In order to determine the carbonation reaction rate, the pH meter was used to identify the neutralization reaction of the OH^- ions produced during the hydration of CaO . The pH meter and thermometer were used to obtain the data for reaction rate determination.

2.3. Carbonation using Alkali Additives

Alkali additives were used when fabricating the suspension, and carbonation was conducted to investigate the effect of the CO_2 rate limiting reaction, with its dissolution of alkali components (Na^+ , Ca^{2+} , etc.), on the carbonation reaction rate of the fluidized bed fly ash. The fluidized bed coal ash (Y domestic power plant) used in the experiment had the chemical composition shown in Table 1, where the CaO and S components were 38.41% and 10.15%, respectively, showing that there were significant amounts of unreacted CaO and gypsum. The fluidized bed coal ash was the same as that used in the experiment conducted by Lee,⁸⁾ in which the coal ash contained approximately 22% of unreacted CaO . For the experiment conditions, 3 types of alkali additives, at 2 wt% each, were used: NaOH , Na_2CO_3 , and NaHCO_3 . A solid amount of 100 g and solid-liquid ratio of 1 : 4 were used for the carbonation reaction. In order to determine the carbonation reaction rate, the pH meter was used to identify the neutralization reaction of the OH^- ions produced during the hydration of CaO . The pH meter and thermometer were used to obtain the data for reaction rate determination.

3. Results and Discussion

Unreacted CaO existing within the fluidized bed coal ash hydrates to become solid $\text{Ca}(\text{OH})_2$ (Eq. (1) in Table 2 and Reaction (1) in Fig. 1) and ionizes to Ca^{++} and OH^- by dissociation (Reaction (2) in Table 2), resulting in the provision of Ca^{++} to the solution and simultaneously increasing the solution pH due to the OH^- ions. This reaction is an endothermic reaction and the carbonation reaction becomes the rate limiting reaction. In order to increase the reaction rate by increasing the Ca^{++} solubility, the reaction can be carried out at low temperature and an ion exchange reaction with Na^+ can be induced. However, the low temperatures that increase the solubility of the Ca^{++} in water lead to increased process costs; thus, it was determined that the ion exchange reaction with Na^+ was possible.

Another endothermic reaction of the carbonation reaction is Eq. (3) in Table 2 (Reaction (3) in Fig. 1). Low tempera-

Table 1. Chemical Compositions of CFBC Fly Ash(%)

	ig-Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	C	S	Total
FA	1.05	24.73	10.33	4.95	38.42	4.54	4.03	0.84	0.51	0.13	0.00	0.32	10.15	100

Table 2. Carbonation reaction of Fly Ash

Chemical reaction equation	ΔG° (KJmole ⁻¹)	
$CaO(s) + H_2O(l) \Rightarrow Ca(OH)_2(s)$	-57.83 KJmole ⁻¹	(1)
$Ca(OH)_2(s) + H_2O(l) \Rightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2O(l)$	30.42 KJmole ⁻¹	(2)
$CO_2(g) + H_2O(l) \Rightarrow CO_2(aq) + H_2O(l)$	8.38 KJmole ⁻¹	(3)
$CO_2(aq) + OH^-(aq) \Rightarrow HCO_3^-(aq)$	-43.55 KJmole ⁻¹	(4)
$HCO_3^-(aq) + OH^-(aq) \Rightarrow H_2O(l) + CO_3^{2-}(aq)$	-20.92 KJmole ⁻¹	(5)
$Ca^{2+}(aq) + CO_3^{2-}(aq) \Rightarrow CaCO_3(s)$	-47.40 KJmole ⁻¹	(6)

Fig. 1. Schematic process of carbonation in water.⁸⁾

tures and high pH environments are advantageous to increase the solubility of CO₂; however, low temperatures are costly, and thus it was determined that increasing the pH through alkali addition was advantageous.

Therefore, the CO₂ flow rate was increased to catalyze the carbonation of fluidized bed coal ash, and carbonated water or alkali promoters were used to carry out the carbonation experiments.

3.1. Carbonation Experiment According to CO₂ Flow Rate Variation

Carbonation experiments were conducted by fabricating suspensions with a solid-liquid ratio of 1 : 3 between Ca(OH)₂ and water and with 5 stages for the CO₂ flow rate between 100 ~ 1000 cc/min. Fig. 2 shows the pH data results for the carbonation experiment according to the CO₂ flow rate change. Fig. 3 shows the temperature variation graph for the exothermic reaction in the carbonation process. The carbonation results show that the carbonation reaction rate completion time (the time until the pH becomes neutral, when the OH⁻ ions of the CaO component are removed and converted to CaCO₃) decreased as the CO₂ flow rate increased. As the CO₂ flow rate increased, the reaction surface area of CO₂ and water increased, increasing the CO₂

Fig. 2. Variation of pH of Ca(OH)₂ carbonation reaction with flow rate of CO₂.

aqueous solution state in the suspension and accelerating Eq. (3) to change CO₂ to an ionization state. As the CO₂ flow rate increases, the carbonation reaction rate increases but by comparing the values at 700 cc/min and 1000 cc/min, it was found that there was no further increase after 700 cc/min. It can be deduced that, because there is a limit to the solubility of CO₂, a surface area limit existed for the reaction between water and CO₂.

Fig. 3. Temperature variation of Ca(OH)₂ carbonation reaction with flow rate of CO₂.

Figure 3 shows that the times until the maximum temperature was reached were essentially the same. This reveals that the exothermic reaction occurred at the same time and the temperature increased as the reaction was made more active through the increase of CO₂ flow rate. Also, the temperature did not increase further when the CO₂ solubility limit was reached at 700 cc/min. Through this, the carbonation behavior was identified for times when the reaction surface areas of CO₂ and water were increased.

3.2. Effect of Carbonated Water on Carbonation

Carbonation was carried out for the conditions of 1 : 3 solid-liquid ratio between Ca(OH)₂ and water and fixed CO₂ flow rate of 700 cc/min. Carbonation was also carried out using carbonated water fabricated by feeding CO₂ in advance for 2 and 3 h. Fig. 4 shows the carbonation pH data for the case of advanced CO₂ feeding; Fig. 5 provides a temperature variation graph for the exothermic reaction in the carbonation process.

The pH data revealed that the reaction rate increased with early CO₂ feeding for the carbonated water fabrication case. This increased reaction rate result was thought to be due to the hybrid reaction used in the conversion of the CO₂ directly to the aqueous solution state by adding activation energy (Eqs. (4) and (5) of Table 2) to the slurry through an early reaction of water and CO₂. Moreover, the lack of difference between the reaction rates for the 2 h and 3 h cases was considered to be due to the CO₂ solubility limit.

The temperature graph shows that the times until maximum temperature in both Figs. 3 and 5 were almost the same. This reveals that the time that the exothermic reactions take are the same, and the carbonated water fabrication reaction produced a greater activation energy and activated the reaction, resulting in the elevated temperature within the suspension. Additionally, the solubility limit of CO₂ is thought to be the cause behind the identical reaction completion times for the 2 h and 3 h cases.

Fig. 4. Variation of pH of Ca(OH)₂ carbonation reaction according to whether or not reaction comes ahead of CO₂ injection.

Fig. 5. Temperature variation of Ca(OH)₂ carbonation reaction according to whether or not reaction comes ahead of CO₂ injection.

3.3. Effect of Alkali Promoters on Carbonation Reaction

Alkali promoters not only enhance the solubility of Ca⁺⁺ through ion exchange with Ca⁺⁺, but can also increase the solubility of CO₂. Carbonation occurs through the following reaction for alkali promoters.¹⁾

According to the above equations, NaOH, Na₂CO₃, and NaHCO₃ were used as the alkali promoters.

For the suspension, the solid-liquid ratio between the fluidized bed coal ash and water was 1 : 4, the CO₂ flow rate was fixed at 700 cc/min, and the alkali activators NaHCO₃,

Fig. 6. Variation of pH of Fly ash carbonation reaction with various alkali compounds.

Fig. 7. Temperature variation of Fly ash carbonation reaction with various alkali compounds.

Na₂CO₃, and NaOH were each added at 2 wt% for carbonation. Fig. 6 shows the pH data graph for the carbonation experiment results using alkali promoters in the suspension. The hybrid reaction catalyzing the carbonation reaction was observed for the alkali activator added carbonation results.

The alkali ion addition case showed an initial slight increase in pH. The alkali ion addition accelerated the ion exchange to produce more OH⁻ and, as a result, promoted the dissolution of CO₂ and accelerated the production of CO₃²⁻. Consequently, the reaction rate was found to increase. Furthermore, when NaHCO₃ was added, the reaction rate acceleration reached its highest value. This result was determined to be due to the effect of the HCO₃⁻ ions, produced through the dissolution of the additive and acting as seeds, on the reaction rate.

Figure 7 provides a temperature graph for this reaction and, similarly, the exothermic reactions were found to finish at almost the same times. Not only that, the maximum temperature was so low that it was possible to carry out the car-

Fig. 9. Temperature variation of Fly ash carbonation reaction with NaHCO₃ alkali compound mass.

bonation reaction at an accelerated pace. This result was determined to be due to the additive reducing the reaction indicated by Eq. (4) in Table 2 and decreasing the heat generation.

Figure 8 shows the carbonation reaction according to the NaHCO₃ additive amount; this case showed the greatest increase of reaction rate. It was observed that the carbonation reaction was accelerated as the additive amount increased. This result was similarly due to ion exchange facilitated by the additive; the reaction accelerated as the additive amount increased. Also, when more than 1 wt% was added, the carbonation reaction did not increase further, revealing the existence of a reaction limit. The temperature graph in Fig. 9 shows that the maximum temperature decreased as the reaction became more active; this was determined to be due to the decreased of the reaction indicated in Eq. (4) in Table 2 and to more HCO₃⁻ acting as a seed to reduce heat generation.

4. Conclusions

CO₂ flow rate, carbonated water preparation, and alkali additives were used to carry out carbonation experiments in order to investigate the carbonation reaction behavior of the CaO component using fluidized bed coal ash and Ca(OH)₂. Carbonated water preparation and alkali additives were used to induce reactions other than the main reaction (CO₂ flow rate) to control the activation energy; the hybrid reaction combining the two reactions was used to control the carbonation reaction rate.

The following 3 experiments were conducted to control, among the carbonation reactions, the conversion reaction from CO₂ to an aqueous state.

1. Experiment to investigate the reaction surface areas of CO₂ and water

Through the reaction of water and CO₂, increasing the

Fig. 8. Variation of pH of Fly ash carbonation reaction with NaHCO₃ alkali compound mass.

CO₂ flow rate to 100 ~ 1000 cc/min resulted in an active reaction and saturation solubility was obtained when the CO₂ flow rate was 700 cc/min. In the case of the temperature, the times at which the maximum temperature was reached were almost the same, leading to the conclusion that the exothermic reaction occurred at the same time.

2. Carbonation reaction through fabrication of carbonated water by early feeding of CO₂

The reaction rate was found to increase when water and CO₂ were reacted before the carbonation reaction to create activation energy within the slurry for use in the conversion reaction from CO₂ to an aqueous state (Reaction (3)). Through this result, it was determined that the process water of the carbonation reaction can increase the reaction rate.

3. Carbonation using alkali additive

When the carbonation reaction was conducted using alkali additives to promote ion exchange, dissolution of CO₂ was accelerated to induce the active production of CO₃²⁻ and to catalyze the carbonation reaction via the seed role of HCO₃⁻. Also, in the case of temperature, the rate of Reaction (4) decreased along with heat generation, resulting in decreased temperatures. The NaHCO₃ additive showed the greatest acceleration of the carbonation reaction due to the sufficient seed role played by the production of HCO₃⁻ ions.

Through this, the carbonation reaction rate of the carbon storage fluidized bed coal ash containing the CaO component was determined and the CO₂ reaction was controlled using the activation energy produced by carbonated water and the alkali additive. As a result, it was possible to predict the reaction rate of the wet carbonation reaction and its behavior. In conclusion, to stabilize unreacted CaO and allow this material to be recycled for use in various construction fields, CO₂ can be stored in the CaO component in waste produced from thermal power plants.

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