Journal of Ceramic Processing Research. Vol. 15, No. 4, pp. 212~215 (2014)

J O U R N A L O F
Ceramic Processing Research

Property Enhancement of Supercritically Carbonated Specimen by Particle-Size Separation of Fly Ash and Cement

Junyoung Park and Yootaek Kim*
[a]*Dept. of Advanced Materials Science and Engineering, Kyonggi University, Suwon 305-340, Korea*

The effects of supercritical carbonation on fly ash (FA) separated according to particle size and raw cement powder were investigated. ASTM Class C fly ash containing a high content of CaO produced from a fluidized bed-type boiler and normal portland cement were used as raw materials. This type of FA is used to carbonate mortar under supercritical conditions for CO_2 fixation because it cannot be recycled and simply reclaimed because the high CaO content may adversely affect environmental friendliness as a result of its volume expansibility. Specimens of various particle sizes of FA and cement (the particles were separated in steps that varied from as received to less than 45 μm in 4 steps), were prepared with distilled water, aged for 3, 7, and 28 days, and subsequently, carbonated in a supercritical CO_2 atmosphere at 80 kgf/cm^2 pressure and at 40 °C for 60 min. As a result, an improvement in the mechanical properties of the specimens was expected because $CaCO_3$ was produced in the specimens, which fills the cracks, leading to an enhancement in the mechanical strength. However, because the vacant sites were filled with the reaction products, the average particle size plays an important role in the final compressive strength of the specimen that was carbonated under the supercritical condition. This study investigates the relationship between the average particle size and the mechanical strength after carbonation.

Key words: Fly ash, Supercritical condition, Carbonation, Particle-size separation.

Introduction

The production process of Portland cement is currently undergoing a critical evaluation because it releases high amounts of CO_2 gas into the atmosphere. Attempts to increase the utilization of fly ash, which is a by-product of thermal power generation, by using it to partially replace cement in concrete are gathering momentum. However, most of the fly ash generated is currently dumped in landfills, creating a threat to the environment [1].

Ash from power plants is generally classified as bottom ash and fly ash. The fly ash is mainly generated in fluidized bed-type boilers- and contains high levels of CaO, which is used for the desulfurization of exhaust gases from the boiler. This type of fly ash, classified as ASTM Class C fly ash, cannot be recycled and reclaimed easily because of the presence of a high content of alkali-earth metal oxides such as CaO and MgO, which have a high volume expansibility that may adversely affect fly ash's eco-friendliness [2-4]. Therefore, a proper method for recycling this type of fly ash is required urgently, especially as the number of fluidized bed-type boilers in use in Korea increases [5].

Despite the presence of alkali-earth metal oxides such as CaO and MgO in fly ash, it is likely that this type of fly ash can be recycled for use as a construction material by subjecting it to a carbonation process. If the carbonation process is successful, it is hypothesized that the fly ash would possess a denser microstructure, better workability, greater long-term strength, and lower cost than that of other construction materials in similar applications.

Carbonation of spent concrete powder has been previously studied to determine its ability to store CO_2 in a stable form [6-7]. In the case of cement products, carbonation of $Ca(OH)_2$ with supercritical CO_2, which shows characteristics of both liquid and gaseous states, to form $CaCO_3$ has been studied. The supercritical CO_2 carbonation is fast and fills the cracks inside cement-based structures with the products of the carbonation reaction, leading to enhancements in mechanical strength and leaching resistance of the cement-based structures [8-9].

In this study, we investigate the mechanical properties of cement mortars containing fly ash that is an industrial by-product. The carbonation process under supercritical conditions was performed to control the volume expansion or expansibility of the CaO component of fly ash, which usually has an adverse effect on the mechanical strength of the fly ash-cement mortar. It is hypothesized that most of the CaO will react with CO_2 under the supercritical condition and that the products of this reaction will fill the existing voids and cracks in the non-cement mortar specimen. However, because the vacant sites are filled with the reaction products of the supercritical carbonation process, the average

*Corresponding author:
Tel : +82-31-249-9765
Fax: +82-31-249-9774
E-mail: ytkim@kgu.ac.kr

Table 1. Elemental compositions (wt%), expressed in oxide forms of fly ash.

	Ig. Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	P_2O_5	Cr_2O_3	MnO	SO_3	Total
FA	1.94	29.32	5.34	9.46	41.25	7.33	0.16	0.84	0.50					3.81	100

Table 2. Mixture proportions of mortars.

Specimen	Fly Ash	Cement	Flow (Water)
Plain	120 g	480 g	150~160 mm
75 μm ↑			
75 ~ 45 μm			
45 μm ↓			

particle size plays an important role in the final compressive strength of the specimen that was carbonated under the supercritical condition. This study investigates the relationship between the average particle size and the mechanical strength after carbonation.

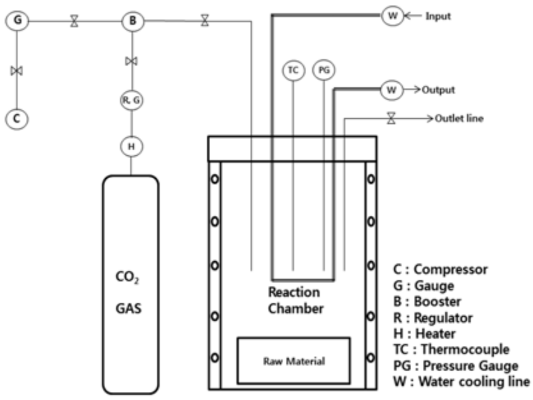

Fig. 1. Schematic diagram of autoclave apparatus for carbonation.

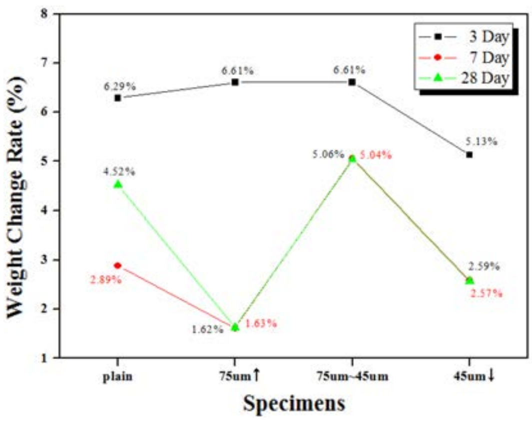

Fig. 2. Weight change rate of the particle-size separated mortars after carbonation under the supercritical condition (80 kgf/cm^2 and 40°C-60min).

Experimental Procedures

Materials

Three different particle size distributions (under 45 μm, between 45 and 75 μm, and over 75 μm) obtained by sieving of domestic ordinary Portland cement and fly ash were used in this study. Fly ash was produced at Y-power plant in Korea and can be classified as ASTM C type fly ash, whose chemical composition is shown in Table 1. As seen from Table 1, fly ash mainly consists of CaO and SiO_2, (45.40 wt% and 21.94 wt%, respectively). As the fly ash used in this study is obtained from the fluidized bed-type boiler, it contains a higher CaO content compared to the fly ash obtained from a pulverized coal (PC) boiler. Therefore, this type of fly ash is better suited as a raw material for carbonation. The fly ash and the cement were separated by 75 μm and 45 μm sieves in order to confirm the carbonation efficiency for each particle size.

Mixture ratios and experimental methods

The mixture ratio and experimental conditions are shown in Table 2. The mixture ratio of cement to fly ash is 8:2 as shown in Table 2. The flow of water to binder was set at 150-160 mm for all specimens.

Mortar mixture was filled in a cubic mold (50 × 50 × 50 mm^3) and then tapped and pressed 20-30 times with a compaction tool for removing voids and air in the mixture. After aging for 24 hrs in the mold, the specimens were removed from the mold and then aged for 3, 14, and 28 days at room temperature in air. After aging, specimens were carbonated for 60 min at the supercritical condition, under a pressure of 80 kgf/cm^2 at 40 °C in an autoclave system shown in Fig. 1.

An O-ring type autoclave was used for the carbonation process. Weight changes before and after carbonation were measured for an approximate analysis of the carbonation rate. Depth of carbonation was determined by spraying a 1% phenolphthalein solution on the fractured surface of the samples and observing the color change in them. The mechanical properties of the samples were analyzed by measuring their compressive strength. Accurate carbonation rates were obtained by TG/DTA analysis.

Results and Discussions

Weight change

The rate of weight change of specimens of fly ash and cement powder separated according to the particle size is shown in Fig. 2. As observed from Fig. 2, a greater rate of weight change was observed in the case of the 3-day aged specimens because of decreased evaporation of water, which results in a higher carbonation reaction compared to the specimens aged for longer. The specimens fabricated with particle size between 75-45 mm showed the highest rate of weight

Fig. 3. Carbonation depth of the specimens according to the particle-size separation after carbonation under the supercritical condition.

change. The weight change rate of the virgin specimen (raw material before separation) showed approximately the value similar to the average of the rates obtained from the three other particle-size separated specimens, which can be inferred theoretically. The weight change was observed in all the specimens and this is indirect evidence that all the specimens treated under the supercritical condition were carbonated to a certain extent.

The degree of carbonation was observed by spraying 1% phenolphthalein solution on the fracture surface of specimens as shown in Fig. 3. The colorless phenolphthalein solution usually reacts with alkaline components such as $Ca(OH)_2$, and turns purple. If the carbonation process occurred completely, no color change would be observed. As seen in Fig. 3, the area of color change decreased with an increase in the aging time. In addition, the purple color of the specimen fabricated with the 45-75 μm particles was lighter compared to the other specimens, indicating a greater extent of carbonation. These results are in good agreement with the results shown in Fig. 2.

Compressive strength

Fig. 4. shows the compressive strength of the specimens according to the particle-size separation of fly ash and cement, aging time, and carbonation conditions. For all specimens with different aging time, the compressive strength increased with an increase in curing time. For the specimens made with particles larger than 75 μm and with particles 45-75 μm in size, the compressive strength of the supercritically carbonated specimen is higher than that of the ambient specimen as shown in Fig. 4. The carbonation process under the supercritical condition was performed to

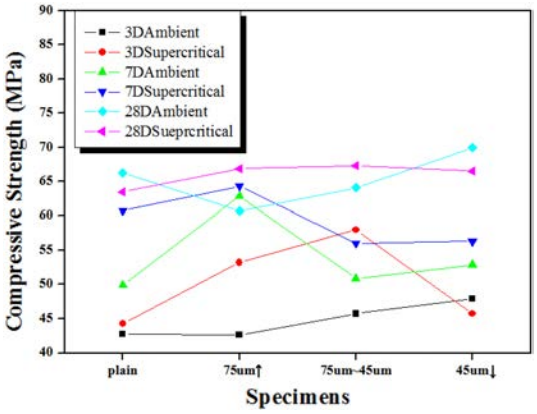

Fig. 4. Compressive strength of the particle-size separated mortars before and after carbonation. Here, 3D ambient in the inlet means aged for 3 days under ambient conditions and 3D Supercritical means aged for 3 days under ambient conditions and then carbonated supercritically (80 kgf/cm^2 and 40 ^{o}C- 60 min).

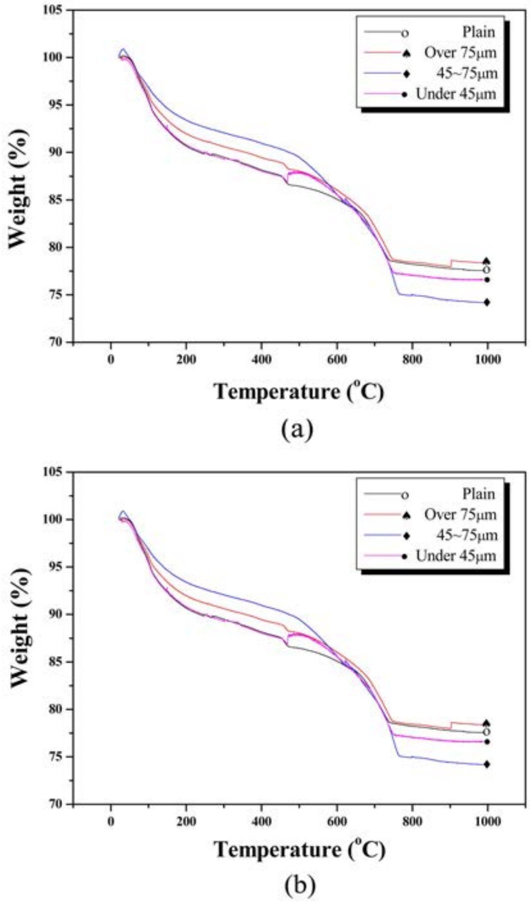

Fig. 5. (a) TGA and (b) DTA analysis of specimens according to the particle-size separation of fly ash and cement after carbonation under the supercritical condition and aging for 28 days.

enhance the mechanical property of specimens by filling the voids and cracks existing inside the cement specimen with $CaCO_3$ reactants. However, the compressive strength of the mortar specimen made with particles smaller than 45 μm, which consist of fine particles, decreased after carbonation under the supercritical condition. The fine particles in these specimens form a very high-density solid matrix. It is speculated that the products formed in the carbonation process under the supercritical condition may act to increase internal stress by over-growth within the cracks and voids in the specimen, which results in the degradation of compressive strength.

TG/DTA

Fig. 5. Shows the TG/DTA analysis of the specimens based on the separation by particle-size of fly ash and cement after carbonation and aging for 28 days. Generally, the gasification temperature of CO_2 is about 800 °C and the gasification temperature of the water of crystallization is about 550 °C. In the case of the mortar specimen made with particles between 45-75 μm, a high rate of weight reduction and an endothermic reaction at 800 °C (carbon dioxide gasification temperature) were observed. However, in the case of the specimen made with particles smaller than 45 μm, because the carbon dioxide was unable to penetrate due to the solid high density, the endothermic reaction occurred at a higher wt%. These results are in good agreement with those in Fig. 2.

Conclusions

The CaO component in the cement and fly ash reacts with the carbon dioxide and undergoes carbonation. In this study, it was confirmed that the carbonation reaction occurred for all the specimens using the rate of weight change and the phenolphthalein test. However, in case of the specimen made with particles under 45 μm, the carbonation reaction under the supercritical condition acts to increase internal stress because of the increase in matrix density and over-growth of products. Therefore, it is speculated that particle-size control may be an important factor affecting the mortar strength, with the highest compressive strength of the mortar obtained when the particle size of both fly ash and cement was controlled between 4-75 μm in diameter.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant number NRF-2013R1A2A2A04014978).

References

1. H.J. Kang, G.S. Ryu, K.T. Koh, and S.T. Kang, J. Kor. Resources Recycling Ins. 18 [2] (2009) 39-50.
2. S.H. Hong, B.D. Lee, and S.H. Han, J. Kor. Concrete Ins. 20 [1] (2008) 701-704.
3. N.S. Ahn, J.H. Lee, and Y.H. Lee, J. Kor. Building Construction Ins. 11 [6] (2011) 547-556.
4. J.S. Sim, K.G. Lee, Y.T. Kim, and S.K. Kang, J. Kor. Ceramic Soc. 49 [2] (2012) 185-190.
5. W.S. Kim, T.K. Kang, M.S. Paik, S.S. Kim, and S.J. Jung, J. Kor. Architectural Ins. 23 [1] (2003) 207-210.
6. N.R. Short, P. Purnell, and C.L. Page, J. Material Science 36 [1] (2001) 35-41.
7. I.T. Kim, H.Y. Kim, G.I. Park, J.H. Yoo, and J.H. Kim, Applied Chemistry 5 [1] (2001) 60-63.
8. T. Hartmann, J.B. Rubin, and P. Paviet-Hartmann, Waste Management 19 [5] (1999) 355-361.