Journal of Ceramic Processing Research. Vol. 18, No. 3, pp. 177~182 (2017)

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

Characteristics of energetically modified fly ash (EMFa) blended cement

Sung Kwan Seo[a,b], Yong Sik Chu[a,]* and Kwang Bo Shim[b]
[a]*Energy & Environmental Division, Korea Institute of Ceramic Eng. & Tech., Jinju 660-031, Korea*
[b]*Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea*

Around 39% of domestic power is generated from coal-fired power plants, and coal ash is generated as a by-product. While the amount of domestic coal fly ash is about 8.35 million tons/year, about 80% of which is reported as fly ash (6.84 million tons) and 20% is bottom ash (1.51 million tons). Generally, fly ash is used for concrete admixture, subsidiary raw materials of cement fabrication process, etc. However, it is not used in large scale because of its low early-term strength and the problem of lowering the alkaline of concrete. Therefore, this study aims to increase early-term reactivity of fly ash and to increase cement substitution amount by fabricating the energetically modified fly ash (EMFa) through grinding of fly ash. Experimental results show that the EMFa is more effective in accelerating early-term hydration than when mixed with non-grinding fly ash. Also, when 20% of EMFa was substituted, it showed compressive strength equal to or higher than that of OPC, and the carbonation resistance was also increased in comparison with that of non-grinding fly ash.

Key words: Fly ash, Cement admixture, Energetically-modified material, Hydration reactivity, Carbonation resistance.

Introduction

Since the industrialization of the 19th century, energy usage has been sharply increased, and the fossil fuels also tend to be increased. In Korea, about 39% of total power generation is produced in coal-fired power plants, and coal ash is generated as a by-product. The fly ash is discharged from the boiler together with the flue gas after the coal combustion, and is largely classified into fly ash collected at the dust collector and bottom ash, which is the bottom accumulation residue of the boiler. The amount of coal fly ash by-product in Korea is about 8.35 million tons/year and it is reported that about 80% of that is reported as fly ash (6.84 million tons) and 20% is bottom ash (1.15 million tons) [1]. In addition, according to the 6th Basic Plan for Electricity Supply and Demand announced in 2014, around KRW 28,000 billion is planned to be spent as an invest for coal-fired power generation facility during the period (2013 ~ 2027). Of that, KRW 12,000 billion is planned to be used for the construction of new facilities, and therefore the amount of coal ash by-product is expected to increase.

Generally, fly ash is used for concrete admixture and subsidiary raw materials of cement fabrication process, and bottom ash is used for embankment, etc. In particular, when fly ash is substituted for cement, it is used for dams and mass concrete due to advantages such as fluidity improvement, long term strength improvement, and hydration heat reduction. But it is a situation that it has not been used in large scale due to low early-term strength and the problem of lowering the alkaline of concrete caused by consumption of calcium hydroxide ($Ca(OH)_2$) generated after cement hydration [2]. In other words, it is a situation that not only most bottom ash but also some fly ash is buried [3, 4]. In addition, the amount of coal ash is gradually increasing since the amount of coal ash exceeding the standard (more than 5% of unburned carbon) is increasing as the usage of low-grade coal increases, and the problem of processing coal ash that has not been recycled is expected to become even more visible [5].

Therefore, this study aims to increase early-term reactivity of fly ash and to increase cement substitution amount by fabricating the EMFa through grinding of fly ash. Mechanically activated fly ash was mixed with cement to produce EMFa blended cement, and the hydration and mortar characteristics were aimed to be investigated. When it comes to a method of examining hydration characteristics, crystalline analysis and microstructural observation were carried out by curing day. Also, the physical properties of EMFa blended cement mortar were investigated through the measurement of flow, compressive strength and length change rate. In addition, the carbonation resistance due to alkaline degradation was analyzed by reviewing the carbonation depth of EMFa blended cement mortar.

*Corresponding author:
Tel : +82-55-792-2463
Fax: +82-55-792-2458
E-mail: yschu@kicet.re.kr

Experimental Method

To investigate the characteristics of cement mortar

Table 1. Mortar mixing ratio.

Type	OPC (%)	FA (%)	GFA (%)
OPC	100	–	–
R10	90	10	–
R20	80	20	–
R30	70	30	–
GR10	90	–	10
GR20	80	–	20
GR30	70	–	30

※ OPC: Ordinary Portland Cement, FA: Non-grinding Fly Ash, GFA: Energetically Modified Fly Ash.

with EMFa blend, the fly ash from N coal-fired power plant in Korea was obtained and milled for 1 hr in a vibratory mill (WTVM, Woongbi Machinery, Korea). In vibratory mill, 10 mm steel balls were used as grinding media and the filling rate was controlled to 70%. Table 1 shows the mixing ratio of EMFa mixed cement. Fly ash was substituted with 10%, 20% and 30% of cement weight, and the EMFa was also tested under the same conditions.

Cement paste was prepared to investigate hydration characteristics of EMFa blended cement. In the manufacture of cement paste, mixed water content was fixed at 35% based on binder and the manufactured hydrate was cured in a 23 °C-90% RH thermo-hygrostat for 1 day and then was cured in 20 °C water bate until respective curing days (3 days and 7 days). Hydration heat analysis was performed for the hydrates which completed the curing for each curing period, and crystalline phases and microstructure were observed by using X-ray diffractometer (XRD, D / MAX-3000, Rigaku, JAPAN), and scanning electron microscope (SEM, SM300, Topcon, JAPAN).

And, mortar flow, compressive strength, length change rate and accelerated carbonation depth were measured to evaluate the characteristics of EMFa blended cement mortar. When manufacturing cement mortar specimens, the water/ binder ratio was fixed at 62% and the amount of using sand/ binder was fixed at 250%. In addition, flow and compressive strength of mortar specimens were measured respectively in accordance with KS L 5105 (Testing method for compressive strength of hydraulic cement mortar) and KS L ISO 679 (Methods of testing cement determination of strength). Also, the rate of change in length by age of mortar was tested according to KS F 2424 (Standard test method for length change of mortar and concrete) and after stored in the atmosphere for each curing period, the length was measured. In addition, to evaluate the carbonation resistance of cement mortar by carbon dioxide (CO_2), cement mortar specimens of 40 × 40 × 160 mm size were prepared and then they were cured in a water bath controlled at 20 °C for 4 weeks. For the specimen that was finished with the curing process in the water bath, the accelerated carbonation experiment was carried out for 4 weeks by using a carbonation test chamber (CC600, Woojin Precise, Korea) with temperature, relative humidity and CO_2 concentration controlled at 20 °C, 60% and 5%, respectively. The depth of carbonation was measured in accordance with KS F 2584 (Standard test method for accelerated carbonation of concrete) for the carbonated specimen.

Results and Discussion

Analysis of hydration characteristics of blended cement

The mixed water content was controlled to 35% based on the binder, and cement paste specimens were prepared by mixing the EMFa. The prepared specimens were cured in water for 3 days and 7 days in a water bath at 20 °C, and then crystalline phases and microstructure were analyzed.

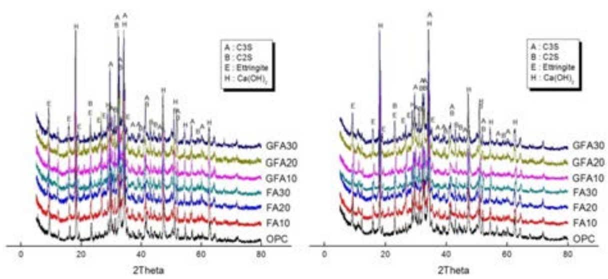
Fly ash is a typical pozzolanic substance and it is a substance that causes hydration reaction when mixed with cement as shown below (1), (2). However, it is known that the pozzolanic reaction of fly ash does not occur early in the general curing condition but occurs in long term hydration reaction. Therefore, various methods for promoting the pozzolanic reaction have been studied and among these methods, this study used the grinding technique.

$$Ca(OH)_2 + SiO_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \quad (1)$$

$$Ca(OH)_2 + Al_2O_3 \rightarrow 3CaO \cdot Al_2O_3 \cdot 3H_2O \quad (2)$$

As shown in Fig. 1, XRD pattern analysis of cement hydrates on the 3 day and 7 day showed that $Ca(OH)_2$ peak and ettringite peak were observed in all specimens. Also, unreacted C3S (alite) and unreacted C2S (belite) peaks were identified. These peaks are typical hydrates observed in OPC hydrates, and thus it can be assumed that fly ash mixed cements also exhibit similar hydration characteristics to OPC.

In order to analyze the change of reactivity of cement hydrate with fly ash grinding, the main peak intensities and ratios of the cement paste main hydrates (ettringite, $Ca(OH)_2$, unreacted C3S) are shown in Table 2, based



(a) 3 days (b) 7days

Fig. 1. XRD pattern by fly ash mixing ratio.

Table 2. Comparison of main peak intensity on main hydrates.

	Ettringite		$Ca(OH)_2$		C3S		$Ca(OH)_2$/C3S	
	3days	7days	3days	7days	3days	7days	3days	7days
OPC	1391	2087	3570	7812	2154	4608	1.66	1.70
FA10	1246	1829	3583	6383	1954	2500	1.83	2.55
FA20	1492	2350	4813	8620	2688	3404	1.79	2.53
FA30	1458	1308	5133	3167	3742	1996	1.37	1.59
GFA10	1450	1813	4417	5258	1942	1704	2.27	3.09
GFA20	1533	1813	5516	5375	2858	2500	1.93	2.15
GFA30	1521	1992	5925	5233	4041	2896	1.47	1.81

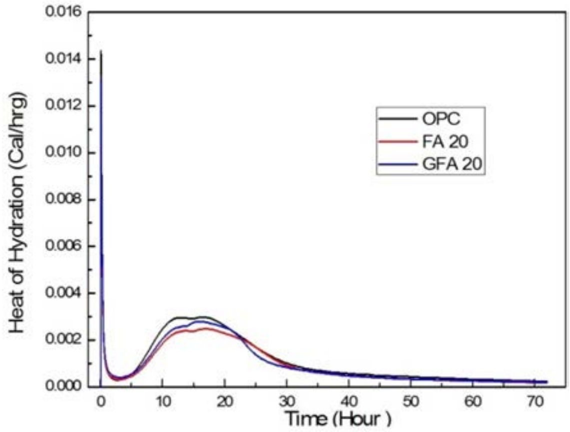


Fig. 2. Fly ash's hydration heat before and after activation (72 hours basis).

on the XRD pattern analysis result above.

When the main peak intensity of the hydrate is compared ($Ca(OH)_2$ / C3S), the amount of $Ca(OH)_2$ produced from unreacted C3S decreased (1.83 → 1.79 → 1.37, 2.27 → 1.93 → 1.47) as the amount of non-grinding and grinding fly ash increase. Also, when the EMFa was mixed, the amount of $Ca(OH)_2$ produced was higher compared to when using the same amount of non-grinding fly ash. In other words, it is considered that fly ash is mechanically activated through the grinding process and reacts relatively quickly with cement hydrate (pozzolanic reaction).

Fig. 2 is a hydration heat graph of OPC, 20% fly ash blended cement and EMFa 20% mixed cement. The first peak of hydration heat was slightly reduced compared to OPC depending on fly ash mixing before and after grinding and this indirectly demonstrates that the amount of ettringite produced in fly ash mixed cement is lower than in OPC. The first peak of fly ash mixture before and after grinding did not show any significant difference, but a difference at the second peak was seen after the induction period. The timing of the second peak of EMFa was slightly accelerated and in addition, a phenomenon that the secondary peak height also increases was observed. This phenomenon means that EMFa reacts with cement hydrate relatively fast, it was judged that the hydration promotion role of the activated powder has been in progress.

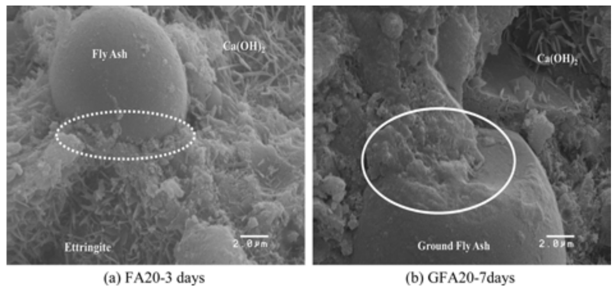


Fig. 3. Microstructure of fly ash blended cement (3days, 5kx).

Fig. 3 shows an example of three-day curing microstructure observation of 20% non-grinding fly ash blended cement and 20% EMFa blended cement. As a result of the microstructure observation, typical cement hydrates such as ettringite and $Ca(OH)_2$ could be found. In addition, it was confirmed that the fly ash present in the non-grinding fly ash blended hydrate showed little hydration reaction (Fig. 4(a) dot line). However, in EMFa blended cement hydrate, the hydration reaction proceeds in a certain amount and there were parts where it was difficult to accurately identify the fly ash interface as well (Fig. 4(b) solid line). In other words, cement hydrate and grinding fly ash particles participate in the reaction so that it was confirmed that a new hydration material was generated at the fly ash interface. These hydration characteristics were considered to be important factors in improving the early-term compressive strength of mortar.

Characterization analysis of blended cement mortar

To examine the characteristics of EMFa blended cement mortar, mortar flow, compressive strength, rate of change in length and carbonation depth were measured. The mortar flow produced according to each mixing ratio is shown in Fig. 4. Flow increased as the mixing ratio of non-grinding fly ash increases and at this time, all flow values were better than OPC. This suggests that the amount of cement that can contribute to early-term hydration is decreased. [6] Also, the EMFa (GFA 10 ~ 30) which is made by grinding fly ash showed an excellent flow characteristics compared to OPC and there was a trend that it increases by

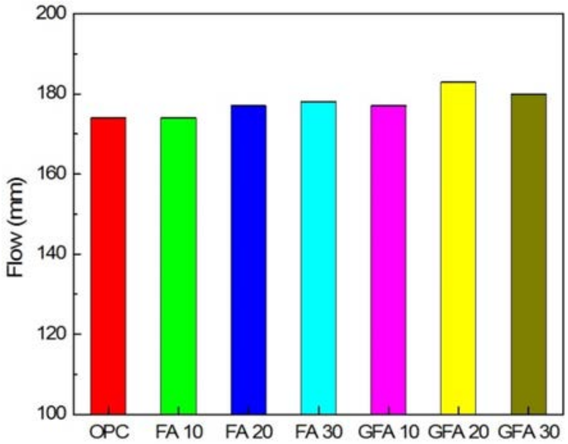


Fig. 4. Mortar flow of fly ash blended mortar.

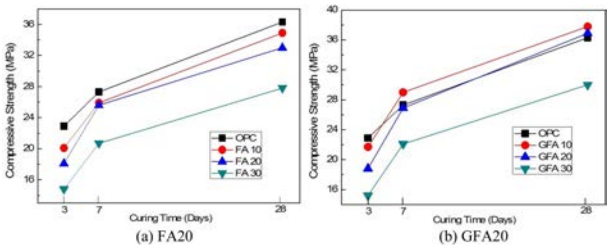


Fig. 5. Compressive strength of fly ash blended mortar.

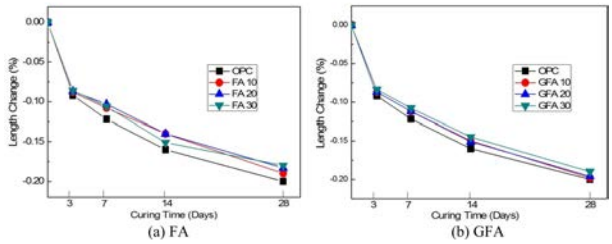


Fig. 6. Length change rate of fly ash blended mortar.

3 ~ 9 mm compared to OPC. And, the flow of EMFa showed a higher numerical flow value than non-grinding fly ash. This suggests that the EMFa can improve the workability of mortar and concrete.

The compressive strength of the fly ash blended mortar is shown in Fig. 5. When the non-grinding fly ash was blended, the compressive strength was lower than that of OPC in all specimens. In addition, the compressive strength decreased proportionally as the amount of fly ash was increased. Especially, the compressive strength at 28 day under 30% mixing condition was 77% compared to OPC. Compressive strength of ground fly ash blended cement also decreased with increasing amount of fly ash. However, the decrease in compressive strength with increasing mixing amount was greatly reduced and especially, a more definite tendency was observed regarding the 3 day and 7 day compressive strength up to 20% of grinding fly ash. The compressive strength at the 3 day was similar to that of OPC at 10% mixing and 82% at 20% mixing. The result that the compressive strength at 28 day was similar to or slightly increased from OPC at 10% and 20% was derived so that it was confirmed that fly ash was activated by vibration milling process. In other words, it means that the time required for fly ash to cause hydration (pozzolanic reaction) reaction through grinding process is faster than the condition with non-grinding.

Fig. 6 shows the rate of change in length of fly ash blended mortar by age. The shrinkage rate increased with increasing mortar curing period and the shrinkage rate varied with the type of mixing material. The shrinkage rate was the largest in OPC mortar and the lowest value in the non-grinding fly ash. Also, the grinding fly ash blended mortar exhibited a similar shrinkage to OPC and it is assumed that the grinding fly ash hydrates more quickly than the non-grinding fly ash. In other words, the high specific surface area of the grinding fly ash improves the pozzolanic reactivity so that it accelerated the consumption of $Ca(OH)_2$ and affects the expansion of the hydrate.

Fig. 7 shows the results of carbonation resistance measurement of fly ash blended mortar according to phenolphthalein spraying method. In general, factors affecting carbonation of cement mortar can be divided into material factor and chemical factor. Material factors can be divided into physical factors such as porosity and maximum pore diameter, and chemical factors such as pore solution and total amount of calcium hydroxide ($Ca(OH)_2$) in the mortar. In other words, the higher the water-cement ratio, the greater the drying shrinkage occurs largely and the porosity of the mortar and the amount of the pore solution become large. This increase in porosity facilitates the inflow of CO_2 gas so that it promotes the carbonation of the mortar [7]. Therefore, the larger the W / B, the more mortar becomes vulnerable to carbonation by increasing porosity and pore solution. And, when it comes to carbonation, carbonation occurs when CO_2 gas enters the mortar and reacts with the surrounding alkaline substance and the alkaline substance is exhausted. But in case of mortar mixed with fly ash, since the amount of calcium hydroxide becomes small, the carbonation reaction proceeds rapidly so that it is known that it progresses more rapidly in the movement of carbonated surface compared to OPC [8, 9].

The results of the 4-week carbonation depth measurements were 2.25 → 3.30 → 4.45 → 5.19 mm for OPC and 3.01 → 5.42 → 6.14 → 8.18 mm for the FA10 specimen mixed with 10%. And, in the case of 30% mixed fly ash (FA30), it was 7.61 → 11.79 → 14.41 → 18.12 mm, and for the EMFa 30% mixed specimen (GFA30), it was 6.22 → 9.90 → 12.74 → 15.59 mm. In other words, cement mortar is carbonated as accelerated carbonation test goes and as the amount of fly ash is increased, carbonation proceeds more

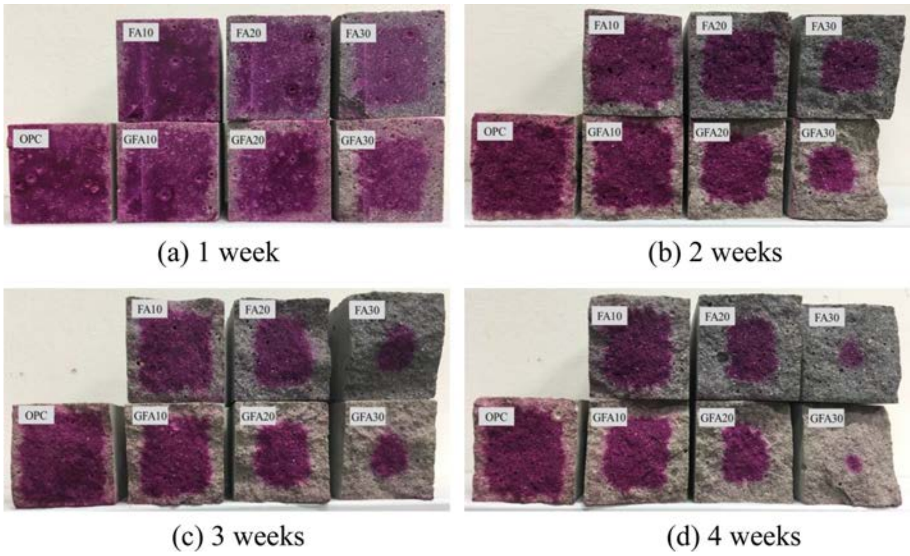


Fig. 7. Carbonation resistance of fly ash blended mortar.

rapidly. It is considered that this is a result of decrease of calcium hydroxide production due to increase of fly ash content. Also, it is also found that when the fly ash is ground and mixed, the carbonation resistance is increased compared to the case of mixing the non-grinding fly ash. It is considered that the average particle size becomes smaller when the fly ash is crushed and the porosity of the mortar is decreased due to the pozzolanic reaction of the smaller fly ash particles so that it has created conditions in which carbonation is difficult to occur. [10]

Conclusions

In this study, the energetically modified fly ash (EMFa) was produced through vibration milling of fly ash to increase early-term reactivity and substitution amount of fly ash. In order to investigate the early-term reactivity, the hydration characteristics of EMFa blended cement were analyzed through crystalline phases and microstructure observation. In addition, the physical properties of mortar were analyzed by examining flow, compressive strength and length variation of mixed fly ash blended mortar. Also, the carbonation resistance was analyzed by measuring the depth of carbonation and the following conclusions were drawn.

1) The analysis results of C3S and $Ca(OH)_2$ main peaks have shown that it was confirmed that the amount of $Ca(OH)_2$ production decreased as the amount of fly ash increased, compared to C3S. Also, the amount of $Ca(OH)_2$ produced is higher when mixing EMFa than when mixing the same amount of non-grinding fly ash and it was found that the fly ash was activated through the grinding process and the early-term reactivity was increased.

2) The hydration heat measurement result of cement has shown that it was confirmed that the production amount of ettringite showed the highest in OPC. In addition, it was confirmed that the EMFa reacts with cement hydrate relatively more rapidly than the non-grinding fly ash and it was found that the EMFa has been promoted to hydrate.

3) The compressive strength measurement result of blended cement mortar has shown that compressive strength values were lower than OPC and as the amount of fly ash is increased, the compressive strength decreases proportionally. However, in case of compressive strength at 28 day on EMFa blended cement mortar, a result similar to or slightly higher than that of the OPC is obtained so that it was found that the fly ash was activated through the vibration milling process.

4) The carbonation resistance measurement result of fly ash blended mortar which is according to the phenolphthalein spraying method has shown that as the amount of fly ash increased, carbonation proceeded faster. Also, it was confirmed that the carbonation resistance was increased when the fly ash was ground and mixed, as compared with the case where the non-grinding fly ash was mixed.

Acknowledgments

The present study was carried out with the support of research fund from the Land, Infrastructure and Transport Technology Regional Specialization Project (15RDRPB103390-03), the Korea Ministry of Land, Infrastructure, and Transport. We would like to extend our sincere gratitude for the support.

References

1. J.H. Maeng, T.Y. Kim, and D.H. Seo, Korea Environment Inst. (2014) 87-88.
2. K.R. Hwang, J. Korea Concr. Inst. 14 (2002) 96-103.

3. O. Sengul, and M.A. Tasdemir, J. Mater. Civil Engineer. 21 (2009) 494-501.
4. C.C. Wiles, J. Hazard. Mater. 47 (1996) 325-344.
5. K.J. Bae, Korea Inst. Sci. Tech. 3 (2013) 15-16.
6. V.M. Malhotra, Cement and Concrete Composites 12 (1990) 271-277.
7. V.G. Papadakis, C.G. Vayenas and M.N. Fardis, J. ACI Mater. 88 (1996) 186-196.
8. A. Younsi, P. Turcry, E. Roziere, A. Ait-Mokhtar and A. Loukili, Cement and Concrete Composites 33 (2011) 993-1000.
9. H.W. Song, C.H. Lee, K.C. Lee, J.H. Kim and K.Y. Ann, J. Korea Concr. Inst. 20 (2008) 439-449.
10. P. Chindaprasirt, C. Jaturapitakkul and T. Sinsiri, Constr. Build. Mater. 21 (2007) 1534-1541.