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Influence of Chemical Activators on Cement-Fly ash Paste and Strength Development of Concrete

Jong-Taek Song, Sung-Dae Yun, Jae-Young Kim and Chin-Yong Lee*

Department of Materials Science & Engineering, Dankook University, Cheonan 330-714, Korea
**Civil R & D Team, Dongah Construction Industrial Co., Ltd., Yongin 449-900, Korea*
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The effects of replacement level, curing method and chemical admixtures were investigated in the cement-fly ash paste. The strength of cement-fly ash paste is lower than that of controlled cement paste only and the differences increase with replacement level. However, in steam curing, strength of cement-fly ash pastes is improved, especially, at early ages. In order to improve early strength, the use of Na_2SO_4 in cement-fly ash paste increases the quality of concrete. In addition, improvement of strength of concrete including 30% of fly ash can be obtained and achieves the highest strength compared to other concrete mixtures.

Key words: Strength, Cement-paste, Early strength, Water curing, Steam curing, Chemical admixture

I. Introduction

Fly ash is the waste material from the combustion of electric power stations and it's use is very important in terms of conservation of clean environment and recycling of waste material. Many countries have investigated to facilitate fly ash as a construction material. For instance, the Canada has concentrated on use of high volume fly ash in concrete and in the U.K. cement has been substituted to pozzolanic materials(Fly Ash, Slag) up to about 50% of the total consumption of cement.[1] In Korea, about 2.6 million tons of fly ash has been produced in 1996, however only 15% in total production of fly ash has been used as a construction material. It is much less than that of industrial countries such as 60% -70% in Japan, U.S.A., Italy and Belgium. In the year of 2,000, the production of fly ash will be reached to 4 million tons in Korea. Therefore, technology guiding utility of fly ash should be developed to increase the consumption of fly ash.

Fly ash is mainly used as cement replacement material, fine aggregate in concrete and as other construction material such as subbase layer on road construction. But due to the lack of technology, the application of fly ash to construction works is very limited in Korea compared to other industrial countries.

In order to increase the consumption of fly ash up to the level of industrial countries, the characteristics of cement-fly ash paste should be evaluated and admixtures associated with higher early strength should be also developed. Therefore, this research is carried out for finding characteristics of cement-fly ash paste and developing activators which accelerate the cement-fly ash hydration and pozzolanic activity. It is also aimed to develop more economic and durable concrete containing fly ash which can be applied to the mainstream structural engineering.

II. Experimental Details

Tests including XRD, and heating method for quantifying $Ca(OH)_2$[2] are carried out to evaluate the characteristics of cement-fly ash paste with various admixtures. Many trial mixes of fly ash concrete have been performed to obtain the optimum mix proportion with varying replacement level of fly ash and their strength development are also analyzed. Water and steam curing are considered and the influence of chemical admixtures with respect to strength development is also taken into account.

1. Materials and Mix Proportions for Cement-fly ash Paste

1.1 Materials

Ordinary Portland Cement, meeting the requirements of

Table 1. Chemical Compositions and Physical Characteristics of Binder Materials

Sort \ Item	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Ig. loss (%)	Density (g/cm^3)	Specific surface (cm^2/g)
Cement	20.57	5.64	3.26	63.1	3.35	2.11	1.21	3.15	3,150
Fly ash	52.09	25.36	12.90	2.58	1.37	0.07	3.70	2.15	4,230

Table 2. Mix Proportions (cement-fly ash paste)

Sort of admixtures	Amounts of admixtures (%)	Curing method		Mix proportion	
		Water curing	Steam curing	OPC	FA
Na_2SO_4	2	○	○	70	30
	4	○	○		
$CaCl_2$	2	○	–		
	4	○	–		
$Ca(NO_3)_2$	2	○	–		
	4	○	–		
NaOH	2	○	○		
	4	○	○		

Korean Standard (KS L 5201) and low-calcium Fly Ash to KS L 5405 are used (Table 1). The chemical compositions are as follow.

1.2 Mix proportions

For finding the characteristics of cement-fly ash paste, the cement and fly ash are mixed with ratio of 70:30 and various chemical admixtures are added (Table 2).

1.3 Test methods for cement-fly ash paste

XRD (Shimadzu, XD-D1) using CuKα of 30 kV, 30 mA with a scan speed 4 deg/min is used to investigate hydration products and to clarify the physical properties of paste respectively. Heating method for quantifying $Ca(OH)_2$ is also introduced.

2. Materials and Mix Proportions for Fly ash Concrete

2.1 Materials

(1) Aggregate

The aggregates consisted of crushed rock (19 mm-5 mm) and crushed sand. The physical properties are shown in Table 3. A superplasticizer is also used to improve workability.

Table 3. Physical Characteristics of Aggregate

Sort	Density (g/cm^3)	Absorption (%)	Fine Modules	Bulk unit Weight (kg/m^3)
Fine aggregate	2.61	1.2	2.58	1,512
Coarse aggregate	2.64	0.3	7.42	1,552

(2) Mix Proportions

Initial control mix proportions for OPC (Ordinary Portland Cement) are designed according to Korean Concrete Specification and the mixes containing fly ash contents of 10, 30, 50% are also designed according to this method. Trial mixes are carried out until the design strength of 270 kg/cm^2 and the required slump (80±25 mm) are obtained. Considering the lower early strength of fly ash concrete, there is a increase in binder content and a decrease in W/C ratio with increasing fly ash content. Mix proportions used in this part of study are given in Table 4.

2.2. Test for concrete strength

The 20 cm×diameter 10 cm cylinder specimens are crushed in a Shimadzu compression machine in accordance with KS 2405 and tested at 3, 7, 28 days.

2.3 Curing

In order to achieve a better understanding of influences of temperature, standard and steam curing are considered;

- Standard curing: 21°C in water
- Steam curing: after casting, increasing temperature up to 85°C in 3 hours, sustaining temperature 85°C for 5 hours, and down to 21°C in 3 hours and then air curing

III. Results and Discussion

1. Cement-fly ash Paste

It is shown in Fig. 1 that the amount of $Ca(OH)_2$ produced

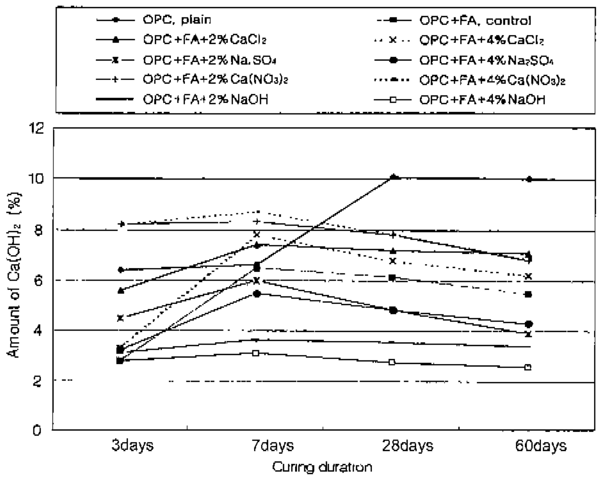

Fig. 1. Amount of $Ca(OH)_2$ according to chemical admixtures.

Table 4. Mix Proportions

Design strength (kg/cm^2)	Mixes	Mix proportions, kg/m^3						
		W/B	Water	Binder		Fine aggregate	Coarse aggregate	Admixture
				Cement	Fly ash			
270	FA 0%	0.50	200	400	0	733	983	-
	cfa 10%	0.47	195	373	41	709	991	-
	cfa 30%	0.39	190	341	146	657	956	1.242
	cfa 50%	0.36	185	257	257	620	941	3.598

Mix proportions having increase of cement content and decrease of W/C ratio to obtain the equal strength at 28 days are designated as cfa 10%, cfa 30% and cfa 50%.

Table 5. Strength Development of Cement-Fly ash Paste including Na_2SO_4

Sort	Curing	Compressive strength (kg/cm^3)			
		1d	3d	7d	28d
P1(FA0)	Water	-	234	292	357
P2(FA30)		-	172	221	256
P3(FA30-2%Na_2SO_4)		-	211	312	382
P4(FA30-4%N_2aSO_4)		-	233	305	401
P1(FA0)	Steam	209	321	321	335
P2(FA30)		166	192	252	261
P3(FA30-2%Na_2SO_4)		294	327	348	395
P4(FA30-4%Na_2SO_4)		242	293	307	388

during hydration is plotted with respect to time. In the beginning of hydration(up to 7 days), cement-fly ash pastes containing $Ca(NO)_3$ and $CaCl_2$ produce more $Ca(OH)_2$ than that of cement-fly ash paste only.[3, 4] It is suggested that the dissociation of these calcium compounds accelerate the formation of $Ca(OH)_2$ at initial stage of hydration. But paste containing Na_2SO_4 exhibited higher compressive strength shows less amount of $Ca(OH)_2$ because $Ca(OH)_2$ is partially consumed for the production of ettringite. It is also indicated that $Ca(OH)_2$ in plain cement paste is gradually increased up to 28 days and then saturated. Unlike this plain cement paste, the cement-fly ash paste slowly reduces $Ca(OH)_2$ beyond 7 days due to pozzolanic activity.

The compressive strength of cement-fly ash pastes containing various chemical admixtures is tested at 1, 3, 7, 28 days and found that Na_2SO_4 is superior to other corresponding results. It is also shown under steam curing that the paste with Na_2SO_4 has much higher strength at early ages and in these mixes the paste incorporating 2% of Na_2SO_4 has better performance than that containing 4% of Na_2SO_4 (Table 5).

Test equipment of XRD is utilized for obtaining the influence of Na_2SO_4 on cement-fly ash paste. Fig. 2 shows test result of XRD. It is indicated that generally $Ca(OH)_2$, C-S-H and calcite are main products, and residual C_3S and β-C_2S, and ettringite are partially exhibited and existing calcite is due to the carbonation of $Ca(OH)_2$. Cement-fly ash paste containing 2% of Na_2SO_4 have more ettringite than that of cement-fly ash paste only. But hydrates of paste without chemical admixtures has lower early strength due to relatively slower reaction of hydration.

High temperature in steam curing stimulates the hydration of cement-fly ash paste and produces more C-S-H and Ca $(OH)_2$ in comparison with that cured in water. It is also shown that hydrates at 1 day under steam curing is equivalent to that under water curing at 3 days.

2. Fly ash and Concrete

For achieving the target slump (80±25 mm) a superplasticizer is used to compensate the offset of slump due to the reduction of W/C ratio.

2.1 Strength development of fly ash concrete cured in water

A pozzolanic material is siliceous(fly ash) material which itself possesses little or no cementitious properties but which, in the presence of moisture, chemically reacts at ordinary temperature to form compounds possessing cementitious properties. When this material is present with cement, it cause the reduction of early strength due to the slow reaction of hydration. Many previous researchers agreed to this result.[5, 6] In this project, it is also found in Table 6 that strength is dramatically decreased with increasing fly ash content and is mostly dependant on binder content and W/C ratio. To overcome lower early strength, the cement and fly ash are added and W/C ratio is reduced on the basis of equal 28day strength(cfa 10%, cfa 30%, cfa 50%). In com-

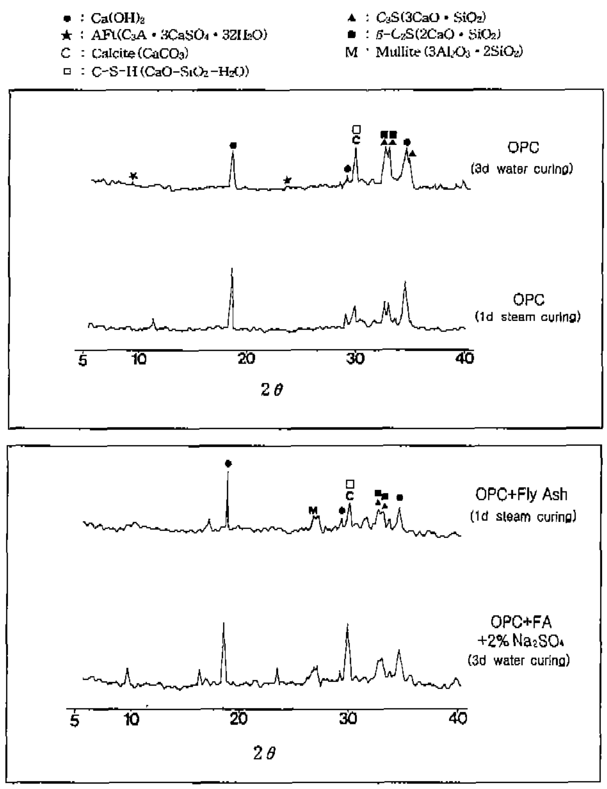

Fig. 2. XRD analysis of cement and fly ash pastes

Table 6. Strength Development of Fly ash Concretes in Water Curing

Duration \ Mixproportion	FA 0%	FA 10%	FA 30%	FA 50%	cfa 10%	cfa 30%	cfa 50%
3 days	168.0	162.0	129.0	66.0	174.0	150.0	110.0
7 days	246.0	242.0	215.0	122.0	257.0	228.0	190.0
28 days	342.0	335.0	297.0	190.0	340.0	336.0	335.0

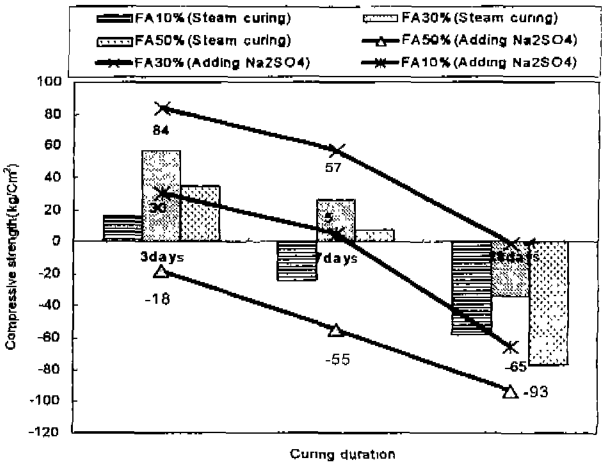

Fig. 3. Strength development of fly ash concrete with respect to concrete cured in water.

parison of two sets of mixes namely, FA10, 30, 50% and cfa 10%, cfa 30%, cfa 50%, the latter mixes show higher early strength than the former, such as 12, 21, 44kg/cm^2 higher, respectively (Table 6). In other words, the reduction of W/C ratio accelerates hydration and increases early strength, although concrete incorporates with high volume of fly ash.[7]

2.2 Strength development of concrete cured in steam

Steam curing is commonly adapted in concrete manufactory producing precast concrete for achieving early removal of formwork. In this study, the chemical admixture under steam curing is introduced to accelerate the pozzolanic activity and to overcome lower early strength of fly ash concrete as a results. Fig. 3 indicate that strength of fly ash concrete is increased at early days (3, 7 days) in comparison with that of OPC concrete, but the strength is decreased at 28 days. It is because reduction of C_3S and voids of circumference of cement may increase cracks and decreases concrete strength.[8-10] It is also found in a comparison between fly ash concrete and fly ash concrete containing Na_2SO_4 that the latter has higher strength than the former, and the differences are in a range of 0 to 84 kg/cm^2. It is suggested that the reaction of sulfate with calcium which produce ettringite, accelerate early strength development. Particularly, FA 30% is superior to other fly ash concrete mixes at 3, 7, 28 days.[3,4] But concrete containing 50% of fly ash reduces rather compressive strength regardless test ages.

IV. Conclusion

This study is carried out to increase the consumption of fly ash and following conclusions are drawn:

1. In cement paste, the hydration products [$Ca(OH)_2$ and C-S-H] increase with increasing time up to 28 days, however, in fly ash paste, $Ca(OH)_2$ is reduced between 7 to 28 days.
2. High curing temperature stimulates the reaction of hydration and produce a greater number of $Ca(OH)_2$ accelerating pozzolanic activity of fly ash at early ages.
3. Chemical admixture(Na_2SO_4) produces the ettringite at early ages(up to 7 days) and improves the strength of fly ash concrete, but at 28 days, it hardly affects to strength.

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