The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

EFFECT OF EMULSIFIED REFINED COOKING OIL ON THE CARBONATION MITIGATION OF HIGH VOLUME MINERAL ADMIXTURE CONCRETE

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ABSTRACT

In this paper, tests are carried out to investigate experimentally the effect of emulsified refined waste cooking oil (ERCO) on the engineering properties and carbonation resistance of the concretes incorporating 30% of fly ash and 60% of blast furnace slag, respectively. ERCO was added to concrete ranged from 0% to 2% by mass of binder. Test results showed that the increase of ERCO dosage and contents in mineral admixture resulted in slight loss of the compressive strength. For carbonation resistance, it was found that, with an ERCO dosage of 1%, the carbonation depth of concrete incorporating 30% of fly ash and 60% of blast furnace slag had a level comparable to ordinary Portland concrete.

1. INTRODUCTION

Recently, multifold researches are being conducted all over the world to reduce the emission of greenhouse gas while protecting the national industries. In order to participate to this worldwide trend for the protection of the Earth, Korea enacted and promulgated the Framework Act on Low-Carbon Green Growth in 2011, which resulted in the implementation of research dedicated to the reduction of carbon dioxide (CO_2). One initiative taken by the construction industry to respond to this trend reduces the amount of cement in concrete by increasing the use of mineral admixtures like fly ash (FA) and blast furnace slag powder (BS) as substitute materials.

Concretes with large replacement ratios in mineral admixtures offer many advantages such as better fluidity, reduction of hydration heat, improvement of long-term strength, enhanced economic efficiency and reduction of carbon dioxide. However, such concretes experience also problems like the loss of early strength and the rapid

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progress of carbonation. Especially, since the rapid progress of carbonation is known to cause the loss of hydrogen ion concentration (pH) according to the reduction of the quantities of cement involved, the carbonation of concrete in reinforced concrete structures constitutes the most important factor determining the lifespan of the structure.

Measures have been proposed to prevent carbonation such as the application of a membrane on the surface of concrete to block physically the inflow of carbon dioxide inside concrete, and the method preventing the corrosion of the steel reinforcement by endowing alkalinity to the existing concrete that has lost its alkalinity (Aperador et al. 2009). However, these solutions are extremely costly and were reported to lack workability.

Besides, the authors found out that the autogenous shrinkage of high strength concrete could be mitigated by admixing refined cooking oil (Han and Song 2010). The admixing of refined cooking oil was seen to make the fatty acid constituents of the oil react with the calcium hydroxide generated in concrete (saponification reaction). The soap fines resulting from this reaction fill compactly the capillary pores inside concrete, which reduce the autogenous shrinkage of concrete. Accordingly, it can be presumed that the application of emulsified refined cooking oil (ERCO) in ordinary concrete would generate soap fines filling the capillary pores in concrete and provide an effective solution against the carbonation of concrete as well.

Therefore, this study investigates experimentally the effect of ERCO on the control of the carbonation of the high volume admixture concrete with 60% of water-to-binder ratio (W/B) under various dosages of ERCO.

2. THEORETICAL STUDY

2.1 Emulsified refined cooking oil (ERCO)

ERCO (Fig. 1) was manufactured to reduce the autogenous shrinkage of high strength concrete and improve the durability of ordinary concrete by filling the capillary pores inside concrete (Fig. 2). ERCO offers easy mixing with water. With a density of 0.98 g/cm^3, ERCO is composed of fats by 90 %, emulsifier by 9% and water by 1%.

Fig 1. ERCO

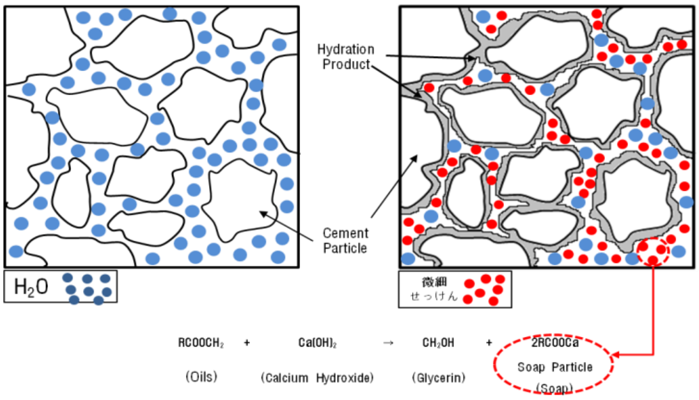

Fig 2. Filling mechanism of capillary pores

2.2 Saponification reaction of fatty acid by calcium hydroxide

The saponification reaction is the hydrolysis process of the fatty esters. The reaction of natural fats with a calcium hydroxide solution (alkaline aqueous solution) produces soap that is, higher fatty acid alkali-metal salt and glycerin. Expressing the fatty acid as RCOOCH, the filling mechanism of the capillary pores by the soap fines (fatty acid calcium salt) fabricated by the saponification reaction can be described by Fig 2.

3. EXPERIMENTAL PLAN AND METHOD

3.1 Experimental plan

Table 1 arranges the experimental plan of this study. Table 2 shows the mixture proportions of the concretes incorporating ERCO. A plain mix using only OPC (ordinary Portland cement) was considered with a W/B of 60%. Three levels of binder composition were planned using respectively fly ash (FA) with a replacement ratio of 30% and blast furnace slag powder (BS) with a replacement ratio of 60%. Here, three different mass ratios of ERCO to unit mass of binder (0, 1, 2%) were considered for the mixes. The mix design was conducted to satisfy a target slump of 150±10 mm and target air content of 4.5±1.5% for the plain mix. This design was identically applied to the other mixes. The slump and air content were planned to be measured on fresh concrete and, the compressive strength with age and penetration depth of carbonation to be measured on hardened concrete.

Table 1. Experimental Plan

Factors		Levels	
Mixture	W/B (%)	1	· 60
	Target slump (mm)		· 150 ± 10
	Target air contents (%)		· 4.5 ± 1.5
	Binder composition (%)[2)]	3	· OPC · FA30 · BS60
	ERCO replacement ratio (%)	3	· 0[1)] · 1 · 2
Experiment	Fresh concrete	2	· Slump · Air contents
	Hardened concrete	2	· Compressive strength (7, 14, 28, 56 days) · Carbonation resistance (1, 4, 8, 13 weeks) · Porosity by MIP (28 days)

1) Plain; 2) OPC = OPC 100, FA30 = OPC 70+FA 30, BS60 = OPC 40+BS 60

Table 2. Mixture proportions of the concretes

Type	W/B (%)	S/a (%)	ERCO replacement ratio (%)	W (kg/m^3)	SP/B (%)	AE/B (%)	Unit weight (kg/m^3)				
							C	S	G	FA	BS
Plain	60	47	0	175	0.70	0.008	292	843	940	0	0
Plain			1	172.1	0.60	0.019	292	843	940	0	0
Plain			2	169.2	0.60	0.010	292	843	940	0	0
FA30			0	175	0.70	0.008	204	826	921	88	0
FA30			1	172.1	0.60	0.019	204	826	921	88	0
FA30			2	169.2	0.60	0.010	204	826	921	88	0
BS60			0	175	0.70	0.008	117	837	933	0	175
BS60			1	172.1	0.60	0.019	117	837	933	0	175
BS60			2	169.2	0.60	0.010	117	837	933	0	175

3.2 Materials

Type 1 OPC produced by company A in Korea is used with the physical and chemical properties of Table 3. The aggregates are originated from Korea and present the physical properties listed in Table 4. The fine aggregates are a 6:4 mix of river sand and crushed sand. For the admixtures, type 2 FA from the thermoelectric power plant B in Korea and type 3 BS from company H with the physical and chemical properties arranged in Tables 5 and 6 are adopted.

In addition, superplasticizer (SP) and air-entraining (AE) agent as well as ERCO and emulsion produced by company D in Korea are used. The physical and chemical properties of these admixtures are listed in Tables 7 and 8.

Table 3. Physical properties of cement

Density (g/cm^3)	Blaine (cm^2/g)	Soundness (%)	Setting time (min)		Compressive strength (MPa)		
			Initial time	Final time	3 days	7 days	28 days
3.15	3 390	0.05	230	345	24.8	39.3	56.9

Table 4. Physical properties of aggregates

Type	Density (g/cm^3)	FM	Water absorption (%)	Passing amount through 0.08 mm sieve (%)
Natural fine aggregates	2.50	2.85	0.46	2.87
Crushed fine aggregates	2.63	2.54	0.46	3.00
Coarse aggregates	2.68	6.55	0.58	-

Table 5. Physical and chemical properties of FA

Density (g/cm^3)	Blaine (cm^2/g)	L.O.I (%)	SiO_2 (%)	Moisture content (%)
2.21	3 520	4.60	52.3	0.13

Table 6. Physical and chemical properties of BS

Density (g/cm^3)	Blaine (cm^2/g)	L.O.I (%)	Moisture content (%)	Chemical composition (%)				
				MgO	SO_3	Cl	SiO_2	CaO
2.90	4254	1.91	0.23	5.26	1.95	0.002	34.20	42.50

Table 7. Physical properties of agent

Admixture	Main property	Shape	Color	Density (g/cm^3)
Superplasticizer	Polycarboxylate	Liquid	Dark brown	1.05
Air-entraining agent	Naphthalene	Liquid	White	1.04

Table 8. Physical properties of ERCO

Admixture	Density (g/cm^3)	Main component (%)				Viscosity (cP)
		Saturated acid	Multi-unsaturated acid	Omega-3 Acids	Simple saturation	
ERCO	0.98	15	54	8	23	25

3.3 Test method

Concrete was mixed using a forced fan-type mixer.

For fresh concrete, the slump and air content were measured in compliance with the test methods regulated in KS F 2402 and KS F 2421, respectively.

For hardened concrete, compressive strength test and carbonation resistance test were conducted according to the methods specified in KS F 2405 and KS F 2584, respectively.

4. TEST RESULTS AND DISCUSSION

4.1 Characteristics of fresh concrete

Fig. 3 compares the values of the slump according to the mix ratio of ERCO. For the ERCO mix ratio of 0%, the mixes OPC, FA30 and BS60 satisfied the target slump of 150±10 mm with respective values of 155 mm, 160 mm and 150 mm, but the fluidity degraded with larger mix ratios. Concretely, for the ERCO mix ratio of 1%, the slumps of mixes OPC, FA30 and BS60 are respectively 145 mm, 150 mm and 130 mm, representing a degradation of the fluidity by 7 to 15%. For the ERCO mix ratio of 2%, the fluidity of mixes OPC, FA30 and BS60 degraded by approximately 20 to 28% compared to the plain mix. This loss of fluidity can be explained by the larger viscosity of ERCO than water and the water dispersion action inside concrete.

Fig. 4 presents the variation of the air content with respect to the mix ratio of ERCO. For the ERCO mix ratio of 0%, all the mixes satisfied the target air content of 4.5 ±1.5 % but the air content reduced by minimum 50% to maximum 80% with larger mix ratios of ERCO. The larger reduction of the air content with larger mix ratios of ERCO can be attributed to the adsorption by the air-entraining agent according to the use of the organic substances of the lipid component.

4.2 Characteristics of compressive strength

Fig. 5 plots the variation of the compressive strength with the age per type of binder and mix ratio of ERCO. Until 56 days, OPC exhibited the highest strength compared to the other mixes regardless of the mix ratio of ERCO.

Besides, all the mixes with ERCO mix ratios of 1% and 2% developed smaller compressive strength than the mixes without ERCO. This loss of the strength can be explained by the fact that the fat component of ERCO degrades the hydration of cement and reduces the shrinkage.

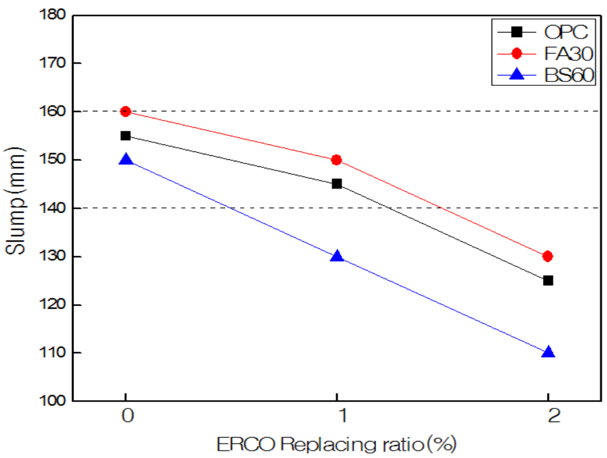

Fig. 3 Slump according to the mix ratio of ERCO

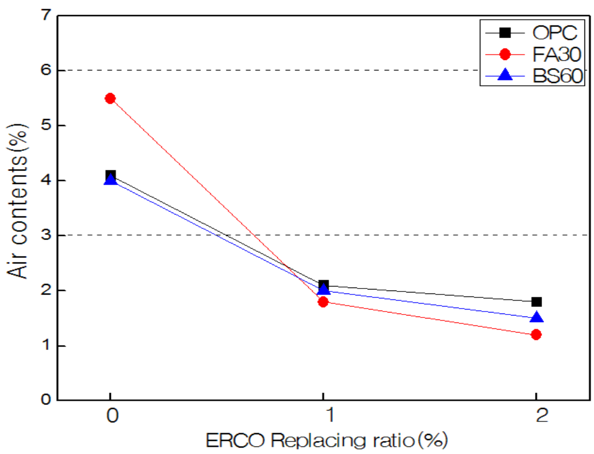

Fig. 4. Air content according to the mix ratio of ERCO

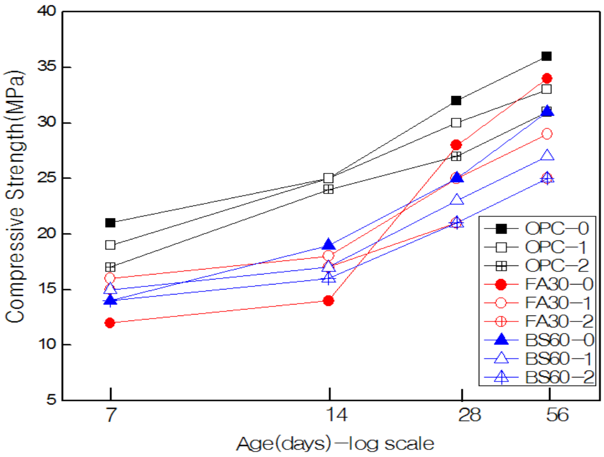

Fig. 5 Variation of compressive strength with age (MPa)

4.3 Characteristics of carbonation

4.3.1 Effect of ERCO on the carbonation of concrete

Fig. 6 presents the progress of the carbonation depth with the age per type of binder and mix ratio of ERCO. The carbonation depth is shown to increase with the age. The carbonation appears to be larger with larger replacement ratios by the admixtures. For the ERCO mix ratios of 1% and 2%, the measured carbonation depth reduced more significantly with time than the mixes without ERCO. The reduction of carbonation depth can be explained by the mitigation of the carbonation through the prevention of the penetration of CO_2 owing to the filling of the capillary pores inside the hardened concrete by the soap fine particles resulting from the accelerated generation of fatty acid calcium salts by the hydrolysis of the fatty acids of ERCO in calcium hydroxide $Ca(OH)_2$ according to the absorption of ERCO in concrete.

On the other hand, FA30 and BS60 with ERCO mix ratio of 1% showed that the carbonation could be prevented to a level quasi-identical to the mix OPC without ERCO despite of their large replacement ratio by the admixtures.

4.3.2 Porosity by mercury intrusion penetration

Fig. 7 shows the accumulative pore distribution measured at 28 days in the high volume admixture concretes with 1% of ERCO and without ERCO. It can be observed that, regardless the pore size, the pore volume inside concrete decreases as ERCO dosages increase. This is because, after emulsifying, the waste cooking oil distributes homogeneously inside the concrete and the products generated by its saponification reaction fill the pores. As ERCO belongs to fatty acid ($RCOOCH_2$), the chemical reactivity is activated with high OH^- in the concrete, and the so-generated products fill the pores in the concrete. The chemical reaction can be expressed as follows,

$$C_3H_5(OCOR)_3 + 3Ca(OH)_2 \rightarrow C_3H_5(OH)_3 + 3RCOOCa. \qquad (1)$$

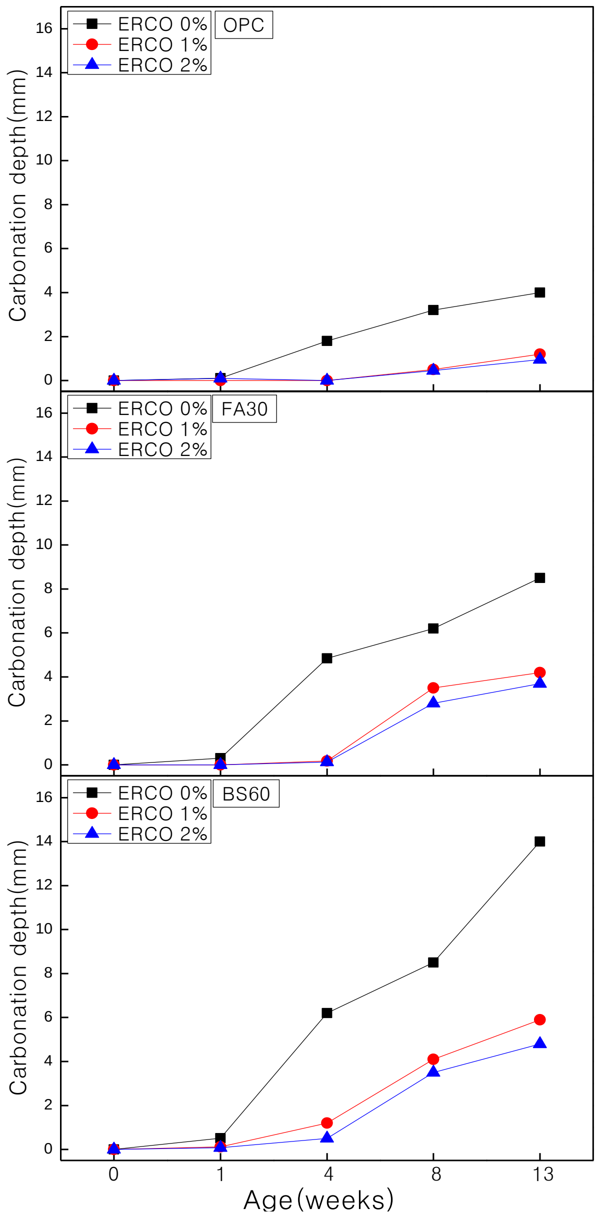

Fig. 6 Progress of carbonation depth with age

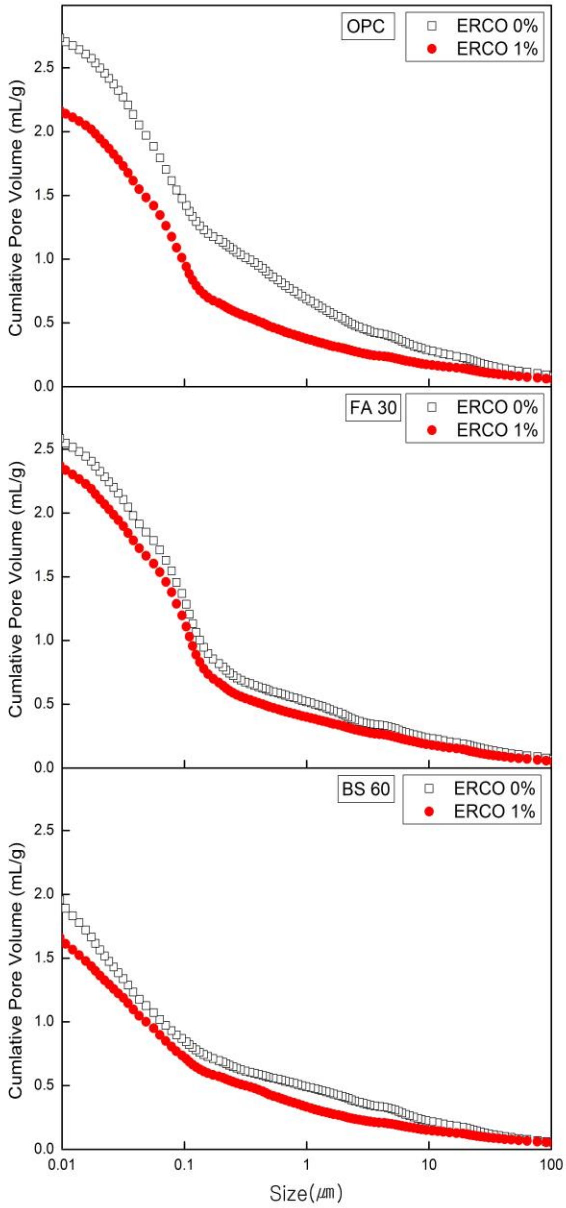

Fig. 7 Pore distributions with ERCO dosages

5. CONCLUSIONS

This study intended to investigate experimentally the effect of ERCO on the physical properties and carbonation reduction of high volume admixture concrete incorporating 30% of fly ash and 60% of blast furnace slag. The following conclusions can be drawn.

1) The slump and air content tended to decrease with larger amount of ERCO. This loss of fluidity could be explained by the large viscosity of ERCO, the adsorption of the AE agent and the water dispersion action.

2) The compressive strength of the concrete with ERCO appeared to be slightly

lower than that of OPC concrete. This loss of the strength due to ERCO could be explained by the fact that the fat component of ERCO degraded the hydration of cement.

3) The use of ERCO provided remarkable carbonation mitigation effect compared to the OPC mix. This could be attributed to the mitigation of carbonation by the filling of the capillary pores inside concrete by ERCO. Moreover, the mixes using FA30 and BS60 with ERCO mix ratio of 1 % showed nearly identical carbonation to that of the mix using only OPC.

Consequently, the use of ERCO resulted in slight losses of the slump, air content and compressive strength but appeared to provide outstanding carbonation mitigation effect compared to the plain mix and was verified to be very effective in improving the durability of concretes with large contents in admixture substitutes.

ACKNOWLEDGEMENT

This study (NRF-2012R1A1A4A01018971) was supported by Ministry of Education, Science and Technology.

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