- Technical Paper -

IMPROVING CHLORIDE RESISTANCE OF CONCRETE BY PAINTING EMULSIFIED REFINED COOKING OIL

Dongyeop HAN[*1], Cheon-Goo HAN[*2], and Young-Doo Choi[*3]

ABSTRACT

The aim of this study is to evaluate the performance of emulsified refined wasted cooking oil (ERCO) as a surface treatment to prevent chloride penetration. Based on the former research, it was known that when the wasted cooking oil was mixed with concrete it turned to soap and fill the capillary pore of the concrete and prevent carbonation of it. As a solution of drawback of concrete with wasted cooking oil on freeze-thawing damage, painting method was suggested, and using the filling action of soap formed by cooking oil, chloride resistance performance was examined. Using different surface treatment substances, comparative analysis was conducted to control of 100 % OPC and high-volume SCM type concrete mixture with 60 % of blast furnace slag replaced mixture with two-different painting timings. As a result, the concrete mixture incorporating 60 % of blast furnace slag, and one-day painting timing showed favorable performance of preventing chloride penetration. Among the surface treatment substances, ERCO showed the most desired performance of preventing chloride ingression.

Keywords: chloride penetration, ERCO, high-volume SCM concrete, surface treatment, surface treating timing

1. INTRODUCTION

As the most widely-used construction material, concrete has been used to form a various types of structure all around the world. Because of the low tensile and flexural strength of the concrete compared with its high compressive strength, the concrete structure essentially contains steel reinforcement: rebar. Reinforced concrete structure is ideal combination for both concrete and rebar: not only reinforcing against lateral forces but also protecting the corrosion of the rebar [1].

Corrosion of rebar can cause a severe problem for reinforced concrete structure. Corrosion of steel is an oxidizing process of the steel and during this process steel turns from Fe to $Fe(OH)_3$, and the volume is expanded. In ambient conditions, the corrosion of rebar in concrete is hard to occur because of high pH of cement paste, and protective passivity layer. However, as a durability issue, high pH can be lost and the passivity layer can be broken by carbonation, and chloride attack [2]. The chloride, especially, directly attacks the passivity layer and induces corrosion of the rebar with moisture and oxygen. Therefore, the concrete structure which has high possibility influenced by chloride should be considered on preventing corrosion of the rebar by chloride [1,3].

The solutions against the chloride attack should be prepared based on the resources of the chloride: inside or outside of the concrete. The materials consisting concrete can contain chloride: sea sand, sea water, or chemical admixture. To prevent this situation, most standards [1,4] limits the content of chloride [5]. However, in the case of chloride ingression, it needs to be considered preventing method for reaching the chloride to the surface of the rebar. As well as many other durability issues of concrete [6,7], permeability is a key of preventing chloride ingression. Because of the capillary pore of concrete, oxygen or moisture with chloride can be diffused into the concrete microstructure. Therefore, generally, to prevent diffusion of the chloride, the amount of capillary pore should be reduced by decreased water-to-cement ratio or using supplementary cementitious materials for dense microstructure.

According to the former research [8], favorable result of preventing carbonation was achieved by using the wasted cooking oil. Vegetable oil can be turn to free fatty acid under a strong alkali conditions. This chemical reaction is called saponification and can be expressed as follow:

$$R-COO-R'+XOH\rightarrow R-COO-X+R'OH \qquad (1)$$

where, $R-COO-R'$ is fat from oil, but not limited a certain type of oil, and XOH is alkali conditions with vary substances.

This free fatty acid is a soap. Therefore by adding the cooking oil in concrete mixture, the capillary pores can be filled with soap produced and successfully prevent carbonation of concrete. In spite of filling capillary pore provided favorable result against carbonation by preventing diffusion, additional

---

*1 Assistant Professor, Dept. of Architectural Engineering, Gyeongsang Nat’l University, Ph.D., JCI Member
*2 Professor, Dept. of Architectural Engineering, Cheongju University, Ph.D., JCI Member
*3 Vice President, JW Structural Engineering Co., Ltd., Ph.D.

drawback was discovered: free-thawing damage. Because of filling capillary pore of the concrete microstructure, the concrete experiences freeze-thawing damage with lack of air pockets including entrained air. Therefore, as a solution of this drawback, painting method was suggested instead of mixing. Since the painting is only applied on the surface of the concrete, it influences on the surface and few millimeter depth of the concrete, and thus there is no harmful effect on entire concrete structure against freeze-thawing damage. From the previous study (not yet published, but see Figure 1), by painting cooking oil on the surface of the concrete, sufficient results on preventing carbonation were obtained.

Upon the idea of preventing diffusion of ions by filling the capillary pore, it is considered that preventing carbonation and chloride ingression are same idea, thus, in this research, as an application of the painting-type of wasted cooking oil, the performance of preventing chloride ingression was evaluated. As an advanced method of improving durability of concrete, especially for chloride ingression, this research is expected to contribute on providing the fundamental idea for a sustainable concrete structure under the chloride conditions.

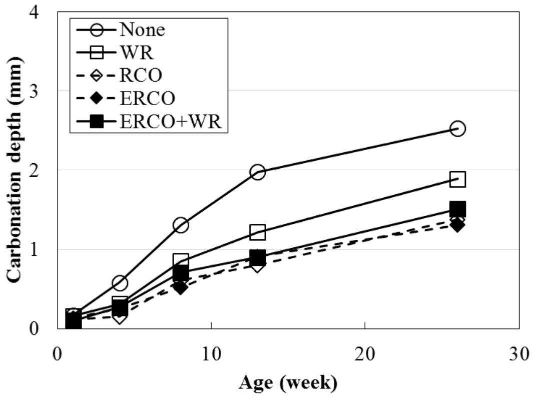


Figure 1. Representative data of preventing carbonation of concrete by surface applicable substances (including cooking oil)

2. EXPERIMENT

2.1 Experimental Plan

In this research, to evaluate the chloride resistance performance of the painting-type waste cooking oil, different painting substances including water repellent (hereafter, WR) and refined waste cooking oil (hereafter, RCO), emulsified refined waste cooking oil (hereafter, ERCO), and combined substance of ERCO and WR and their influence depending on two different painting timings were tested with control with 100 % concrete and high-volume SCM type concrete of blast furnace slag 60 % replaced concrete. Table 1 summarized the experiment plan for this research. As shown in the table, the concrete mixtures were designed to satisfy the target slump and air content of 180 ±10 mm and 4.5 ±1.5 %, respectively. As a tests to evaluate the basic performances of the concrete, slump, slump flow, air content, and unit weight were measured for fresh state properties, and compressive strength was measured at ages of 3, 7, 28, and 91 days. For direct assessment of the influence of painting substances and timings, chloride penetration depth test was conducted at ages of 1, 4, 8, and 13 weeks (7, 28, 56, and 91 days).

Table 1. Experimental plan

Mixture*			
w/b		0.45	
S/a		0.475	
Target slump		180 ±10 mm	
Target air content		4.5 ±1.5 %	
Binder		Control	
		BS60	
Surface treatm-ent	Painting substance	○ None ○ WR ○ RCO	○ ERCO ○ ERCO + WR
	Painting timing	○ Applying after one-day drying ○ Applying after 28 days	
Tests			
Fresh state		○ Slump ○ Slump flow ○ Air content ○ Unit weight	
Hardened state		○ Compressive strength (@ 3, 7, 28, and 91 D) ○ Chloride penetration depth (@ 1, 4, 8, and 13 W)	

*w/b: water-to-binder ratio
S/a: sand-to-aggregate ratio
WR: water repellent
RCO: refined wasted cooking oil
ERCO: emulsified refined wasted cooking oil

Table 2. Properties of blast furnace slag

Physical properties			
Specific gravity	Fineness (cm^2/g)	Loss on ignition (%)	Moisture content (%)
2.90	4254	1.91	0.23

Chemical composition				
MgO (%)	SO_3 (%)	Cl (%)	SiO_2 (%)	CaO (%)
5.26	1.95	0.002	34.20	42.50

2.2 Materials and sample preparation

Concrete was mixed with general products commercially available from Korean market. Ordinary Portland cement used was Korean product similar to the properties of type I cement of ASTM C150 [9]. According to the cement manufacturer’s provided information, specific gravity was 3.15, and fineness was 3390 cm^2/g. For setting times, initial and final setting time of the cement were 230, and 345 minutes, respectively. For high-volume SCM concrete, blast furnace slag used was obtained from Korean steel

Table 3. Physical properties of water repellent

Phase	Appearance	Main component	pH	Dry time
Liquid	Ivory white emulsion	Silicone	5	45 min.

Table 4. Physical properties of RCO and ERCO

Substance	Phase	Density (g/cm^3)	Color	Viscosity (cP)
RCO	Liquid	0.98	Brown	52
ERCO	Liquid	0.98	Brown	25

Table 5. Types of fatty acid of RCO and ERCO

Substance	Fatty acid (%)			
	Saturated	Multi-unsaturated	Omega-3	Simple unsaturated
RCO	15	54	8	23
ERCO	10	61	5	24

Table 6. Mix design

ID	w/b	Unit water (kg/m^3)	S/a	SP/B (%)	AE/B (%)
Control	0.45	185	0.475	0.5	0.006
BS60				0.4	0.009

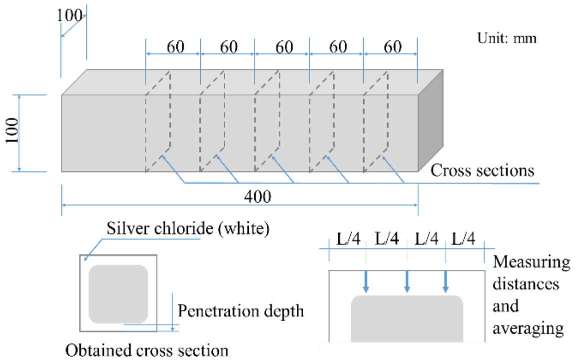


Figure 3. Schematic idea of measuring chloride penetration depth (after submerging chloride bath)

making plant and its brief properties were summarized in Table 2. For aggregate, fine aggregate was mixed aggregate of natural river sand to crushed sand of 6 : 4, and coarse aggregate was crushed granite aggregate. As a chemical admixtures, superplasticizer and air entrainer were used and both are generally used products. The superplasticizer used was liquid phased polycarboxylate-based one and its pH was 6.5. The air entrainer used was anion typed liquid admixture. The painting substances prepared were WR, RCO, and ERCO. The RCO and ERCO were produced and provided a Korean company and difference between two substances were emulsifying for better mixing performance to water. The WR was commercially available product for construction purpose. The brief properties of water repelling admixture, and RCO and ERCO are briefly summarized in Table 3, and 4, respectively. Specially, the types of acid for RCO and ERCO are analyzed and shown in Table 5.

The concrete mixtures of control (100 % of OPC), and high-volume type concrete (60 % of blast furnace slag) were designed as shown in Table 6. The concrete mixing was conducted using twin shaft mixer for 50 liters capacity. For mixing protocol, cementitious binders with aggregate was mixed with 20 rpm for 30 seconds followed by introducing water and mixed with 30 rpm for 60 seconds. As a final mixing step, superplasticizer was added and mixed with 40 rpm for 90 seconds and the mixed concrete was discharged.

Concrete specimens were molded right after the mixing and demolded one day later. After demolding, each specimens were prepared depending on different painting method: 1) painting after one-day drying 2) painting in 28 days of wet curing and additional one-day drying. After the painting, all specimens were submerged in chloride bath until tested ages (see Figure 2).

2.3 Tests Methods

All tests conducted in this research were followed ASTM or Korean standard (KS). For fresh state concrete properties, slump, slump flow, air content, and unit weight were measured by following ASTM C143 [10], C1611 [11], C231 [12], and C138 [13] standards. For hardened concrete property, compressive strength was measured by following ASTM C39 [14]. For chloride resistance performance of the concrete, KS F 2737 method was followed. Concrete specimens were prepared with 100 mm of height, 100 mm of depth, and 400 mm of length. The prepared concrete specimens were submerged in the chloride solution of 20 ±2 ℃ of temperature, and 4.0 ±0.5 % of chloride concentration. The specimens were tested at 1, 4, 8, and 13 weeks. The chloride penetration depth was measured with the pre-designated cross sections (every 60 mm). The specimens were sliced into six pieces and the chloride penetration depth was measured after spraying the 0.1 M of silver nitrate ($AgNO_3$) solution. Because of the reaction between chloride and silver, the chloride penetrated

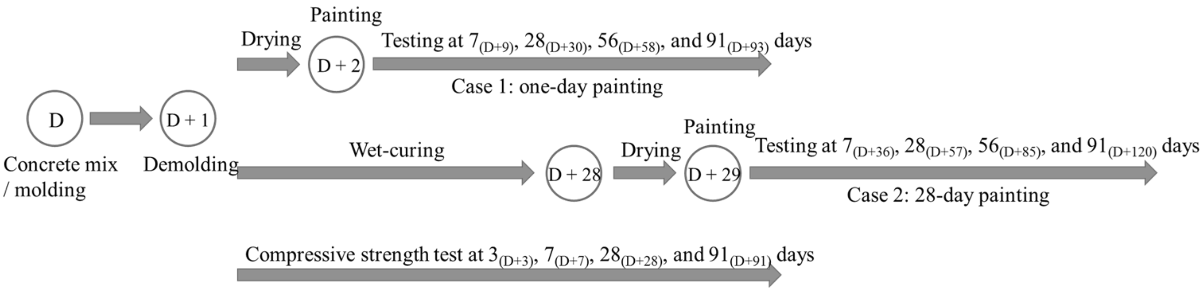


Figure 2. Schematic idea of tests scheduling

location was turned to white, so the distances from surface to the end of white area were measured at 3 locations per one edge out of two edges of the single cross section and averaged (see Figure 3). The measurement was read to 1 mm. Therefore, total thirty six readings (six slices, two edges, and three spots) were averaged for single age’s value.

3. RESULTS AND DISCUSSION

3.1 Evaluating basic properties of concrete

For basic properties of concrete, fresh state properties are shown in Table 7. As shown in the table, slump and slump flow values were satisfied the target slump and slump flow range. Also for air content and unit weight of the concrete mixtures, air content results satisfied the target air content range. Table 8 summarized the results of the compressive strength at designated ages: 3, 7, 28, and 91 day. In the case of the high-volume SCM type mixture (BS60), because of the replaced blast furnace slag, the compressive strength values were relatively lower than the compressive strength of the control mixture until approximately 28 days, while after 28 days, BS60 mixture showed higher compressive strength than the control mixture. As well-known theory on incorporating SCMs in concrete, it is considered that the high-volume SCM type concrete mixture would have denser and less permeable microstructure than the control mixture after approximately 28 days of age. Therefore, based on this result, it is expected that in the case of high-volume SCM type mixture, earlier surface treatment is needed rather than control mixture because of it slow hydration and microstructural formation.

Table 7. Summary of fresh state properties of concrete

Mixture	Slump (mm)	Slump flow (mm)	Air content (%)	Unit weight (kg/m^3)
Control	175	260	5	2 325
BS60	190	275	4.7	2 284

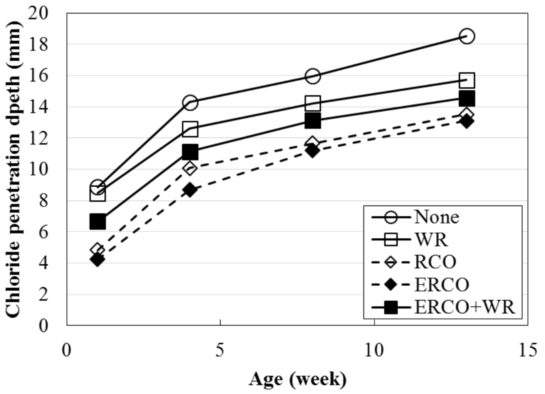
Table 8. Summary of compressive strength values of concrete depending on the ages

Mixture	Compressive strength (MPa)			
	3 day	7 day	28 day	91 day
Control	16.8	24.5	27.1	31.5
BS60	9.5	16.5	27.3	34.7

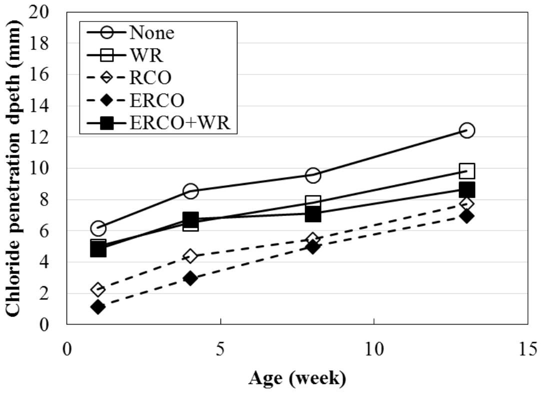
3.2 General performance of chloride resistance

The influence of different mixtures and surface treatment substances with different timings on chloride penetration depth of different concrete mixtures is measured and shown in Figure 4. For all cases, as time passes, the chloride penetration depth was increased. Generally, depending on the mixtures, control mixture showed more chloride penetration depth than high-volume SCM type mixture (BS60) regardless the painting timings. It is considered that the microstructure of the concrete incorporating high-volume SCM is denser and thus less permeable against chloride ion.

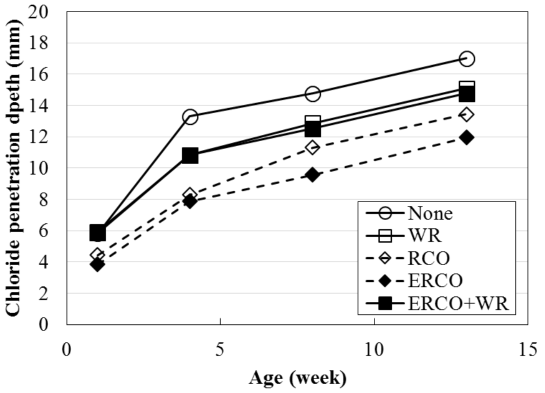
Additionally, comparing the concrete specimens



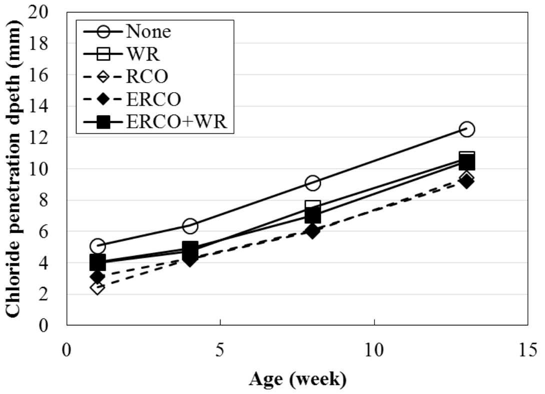
(a) Control_1 day apply



(b) BS60_1 day apply



(c) Control_28 day apply



(d) BS60_28 day apply

Figure 4. Influence of surface treatment substances on chloride penetration depth depending on ages

without surface treatments, 28-day applied cases showed better resistance performance than one-day applied cases. It can be explained that the concrete specimen for 28-day application had longer curing period than the concrete specimen for one-day application, and thus denser microstructure was formed with more hydration. Because of this denser microstructure of the base concrete, the chloride resistance performance with various substances showed better results. Depending on the surface treatment substances, any of painting substances showed the valid chloride preventing performance. Among the painting substances, generally, ERCO showed the highest performance of preventing chloride penetration followed by RCO, and WR. Interestingly, although ERCO showed the best performance of preventing chloride, when it was mixed with WR, the chloride preventing performance showed worse than RCO. Comparing ERCO and RCO, because of low viscosity of ERCO and emulsification, it can be stated that ERCO can be penetrated through the capillary pore of concrete rather than RCO, and thus it can be stated that ERCO works better than RCO. Regarding the WR, although WR can repel the water from the surface of the concrete, it is not enough to prevent penetration of chloride ion rather than filling the capillary pore by RCO or ERCO.

3.3 Efficiency of painting substances

In this chapter, based on the penetration depth data obtained from 3.2 chapter, the influence of different factors including mixtures and painting timings on chloride penetration resistance with painting substances are analyzed. Using the chloride penetration depth at 13 weeks of age, the chloride penetration depths of each mixture are converted when the penetration depth of non-surface treated concrete is assumed 100. Additionally, these values were re-calculated from "penetration depth" to "penetration resistance" by follows:

$$100 - D_C = R_C \tag{2}$$

where, D_C is chloride penetration depth converted based on the assumption of the chloride penetration depth of non-surface treated concrete is 100, and R_C is chloride resistance.

Figure 5 shows the comparative analysis of the influence of the high-volume SCM on chloride resistance. As shown in the figure, the high-volume SCM mixture showed worse performance on chloride resistance for all surface treatment substances. Comparing the chloride penetration depth results, it can be state that although the concrete incorporating high-volume SCM can prevent chloride ingression [15], the efficiency of painting substances are worse than the concrete with 100 % OPC. It is considered that because of the denser microstructure and smaller capillary pores formed by SCM, it is hard to fill the pores with viscous substances of ERCO and RCO. Therefore, the high-volume SCM type concrete mixture produces low permeable microstructure and this low permeable microstructure decrease the efficiency of surface applicable substances.

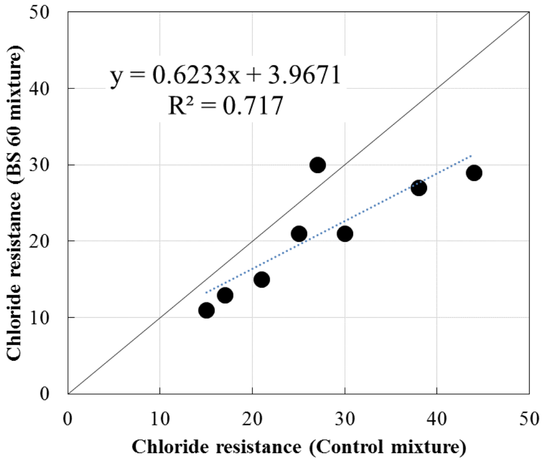


Figure 5. Comparative analysis regarding the efficiency of painting substances depending on mixture type (OPC vs. BS60) regardless the painting timing

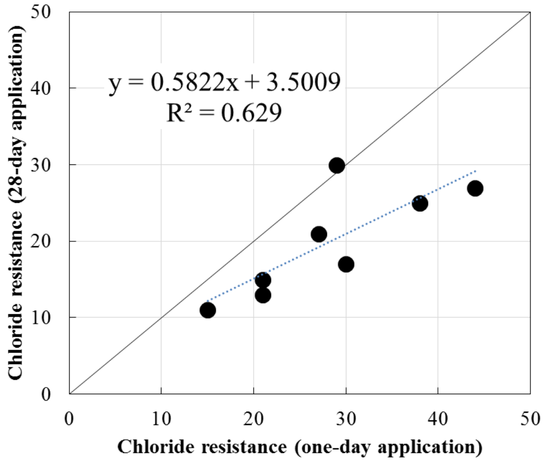


Figure 6. Comparative analysis regarding the efficiency of painting substances depending on painting timings (1 day vs. 28 days) regardless the mixture types

Additionally, as shown in Figure 6, the painting timing influences on the chloride penetration resistance of the concrete. Because of later painting timing, the concrete specimens painted after the 28 days have denser microstructure. In spite of this advantage of hydration period on microstrucutre, regardless the mixture type, it was shown that the painting timing of the surface treatment substances should be earlier for better performance of chloride resistance. From this result, it can be state that when apply the surface treating substances, to achieve more efficient capillary filling action of ERCO or RCO, earlier painting timing is better than the later timing of painting, although a longer curing period can provide well developed microstructure with dense hydration products. However, considering the actual concrete structure conditions, applying early age is better way of improving chloride resistance performance because the concrete microstructure becomes denser with time after the surface treatment.

4. CONCLUSIONS

In this research, to improve the chloride penetration resistance of concrete, the performance of surface applied cooking oil was evaluated. Because of the capillary pore filling action of ERCO, when it mixed, it showed outstanding durability against permeable factors, while it has a drawback on freeze-thawing damage. Hence, as an alternative method of mixing ERCO in mixture, ERCO and other painting substances were applied on the surface of the concrete, according to a series of tests, the conclusion was obtained as follow:

1) The capillary filling action caused by ERCO or RCO is still available in the case of surface application, and thus has sufficient performance on preventing outer factors' ingressions.
2) Among the three surface treatment substances of WR, RCO, ERCO, ERCO shows the highest performance on preventing chloride ingression. Furthermore, when the combined substance of ERCO and WR is applied on the surface of the concrete, the chloride prevent performance is less than when ERCO is applied solely.
3) For chloride resistance of concrete mixtures, the concrete mixture incorporating high-volume SCM helps better performance than 100 % of cement based concrete mixture.
4) For efficiency of surface application method, dense microstructure of based concrete is unfavorable conditions. Hence, to achieve high efficiency of surface treatment method, applying earlier and on concrete with 100 % cement is suggested.
5) Considering the durability improvement against any types of outer factors, keeping dense microstructure with high-volume SCMs is suggestable. Additionally, capillary pore filling by ERCO or RCO can be a desirable method of improving durability of concrete.

ACKNOWLEDGEMENT

This work was financially supported by a grant from a SEON Architecture & Engineering Group Research Project.

REFERENCES

[1] Neville, A., "Properties of Concrete", Pearson Education Limited, Harlow, UK, 2012.

[2] Al-Amoudi, O., and Maslehuddin, M., "Carbonation and corrosion of rebars in salt contaminated OPC/PFA concretes", Cement and Concrete Research, 21, 1991, pp.38–50.

[3] Ann, K., and Song, H., "Chloride threshold level for corrosion of steel in concrete", Corrossion Science, 49, 2007, pp. 4113–4133.

[4] ASTM International, "ASTM C1528, Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Reinforcing Steel in Concrete", ASTM International, West Conshohocken, PA, 2012.

[5] Angst, U., and Elsener, B., "Critical chloride content in reinforced concrete—a review", Cement and Concrete Research, 39, 2009, pp. 1122–1138.

[6] Hilsdorf, H., and Kropp, J., "Performance criteria for concrete durability", Taylor & Francis, London, 2004.

[7] Basheer, L., Kropp, J., and Cleland, D., "Assessment of the durability of concrete from its permeation properties: a review", Construction and Building Materials, 15, 2001, pp. 93–103.

[8] Han, M., Han, D., and Woo, D., "High-Volume SCMs Using Emulsified Refined Cooking Oil (ERCO) for Improving Concrete Durability", Contemperary Engineering Sciences, 7, 2014, pp. 1071–1078.

[9] ASTM International, "ASTM C150, Standard Specification for Portland Cement", ASTM International, West Conshohocken, PA, 2012.

[10] ASTM International, "ASTM C143, Standard Test Method for Slump of Hydraulic-Cement Concrete", ASTM International, West Conshohocken, PA, 2012.

[11] ASTM International, "ASTM C1611, Standard Test Method for Slump Flow of Self-Consolidating Concrete", ASTM International, West Conshohocken, PA, 2010.

[12] ASTM International, "ASTM C231, Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method", ASTM International, West Conshohocken, PA, 2010.

[13] ASTM International, "ASTM C138, Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete", ASTM International, West Conshohocken, PA, 2013.

[14] ASTM International, "ASTM C39, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens", ASTM International, West Conshohocken, PA, 2012.

[15] Papadakis, V., "Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress", Cement and Concrete Research, 30, 200, pp. 291–299.