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Performance of Portland Cement and Sulfate Resisting Cement Concretes against Chloride Attack under different curing Methods

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Abstract

This study examines the influence of cement type, water/cement ratio, and curing process on the chloride ion permeability of concrete using ordinary Portland cement (OPC) and sulfate-resistant cement (SRC). Three concrete mixtures containing both types of cement and water/cement ratios of 0.4, 0.5, and 0.6 were investigated with two different curing methods. The cement content was 400 kg/m^3, and the ratio of fines to aggregates was 0.5. In the first curing method, concrete specimens were cured underwater, while in the second method, specimens were cured at 22°C and 80% relative humidity (RH) and sprayed with water twice daily for seven days. The slump, air content, and unit weight were measured as fresh concrete properties. After 28 days of curing, the compression, tension, flexure, pulse velocity, and dynamic modulus of elasticity tests for hardened concrete were carried out. In addition, titration analysis was used to determine the chloride ion permeability of concrete made with water/cement ratio of 0.4. The results reveal that cement type, water/cement ratio, and curing process greatly influence concrete's mechanical characteristics and chloride resistance.

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Keywords: Chloride, Permeability, Concrete, Sulfate resisting cement, Curing method.

1. INTRODUCTION

Numerous variables [1-3] make the research of chloride penetration into concrete as a difficult subject. The presence of chlorides in reinforced concrete can initiate and accelerate steel bar corrosion [4]. The primary chloride ion transport processes in concrete are diffusion, capillary suction, and convection [5]. The chloride ions in concrete may be unbound, bonded, or absorbed by calcium silicate hydrate. Other studies [2, 3, 6, 7] studied the effect of different cement types (slag, sulfate-resistant, and Portland) on the chloride penetration resistance of concrete.

The investigation of chloride penetration into concrete is challenging due to numerous variables [1-3]. Chlorides in reinforced concrete can start and speed up the corrosion of steel bars [4]. Diffusion, capillary suction, and convection are the three main ways chloride ions are transported in concrete [5]. Calcium silicate hydrate can unbind, bond, or absorb chloride ions from concrete. The impact of several cement types (slag, sulfate-resistant, and Portland) on the chloride penetration resistance of concrete was also examined in other research [2, 3, 6, 7].

Ordinary Portland cement (OPC) is the predominant cement used in structures due to its numerous benefits, such as reduced cost, durability, and other qualities. However, aggressive substances like chlorides and sulphates are more susceptible to attack. This is because OPC hydration produces approximately 20% by weight Ca(OH)2, making it extremely vulnerable to negative ions and potentially causing the deterioration of cement-based structures. Researchers looked at how chloride and sulphate infiltration in OPC affected ion diffusivity and compressive strength development [3]. The results demonstrated that chlorides diffused more readily than sulphates. Higher w/c ratios increased the diffusivity of all types of cement. It was discovered that compressive strength increased with curing age, reaching a peak at 28 days. In general, the gain in strength rose as the w/c ratio decreased.

Concrete with various chloride concentrations in the mixing water was tested for sulphate resistance by submerging it in sodium sulfate and magnesium sulfate solutions [3, 8]. OPC and SRC with chloride levels ranging

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from 0 to 4.5% were used to create mortar and concrete cubes. Concretes constructed with sulfate-resistant cement has much higher capillary sorption than other mixtures. The association between chloride permeability and electrical resistivity was confirmed by test results [7, 9-11].

Marine and high-mountain environments are the two most aggressive examples of chloride ions in concrete. In order to increase impermeability, the literature suggests two approaches. The first is using cement with a low percentage of aluminates (sulfate-resistant cement) and the second is using mineral additives (most commonly fly ash and silica fume) [12]. In the circumstances involving aggressive agents, such as mountainous areas, the second approach would be the best choice.

Curing refers to the techniques used to increase the hydration of cement, which Controls the transfer of warmth and moisture from and into the concrete [13-15]. Curing permits continual cement hydration and, consequently, a continuous increase in strength. Insufficient water will prevent hydration, and the resulting concrete may not have the desired strength and impermeability [16]. The near-continuous surface's pore structure may allow corrosive substances to enter and produce a variety of durability issues. In addition, because the concrete cured too rapidly, microscopic fissures known as shrinkage cracks appeared on its surface.

Several articles [13-15, 17, 18] analyzed the efficacy of various curing techniques and investigated the effect of climate on the strength and permeability of concrete. Conventional water curing is the most efficient approach compared to membrane curing, self-curing, wrapped curing, and dry air curing [13]. Moreover, the curing of concrete is influenced primarily by temperature and time. The curing temperatures had little effect on the concrete's water permeability, but they dramatically affected the chloride permeability and compressive strength [17]. Curing greatly affects how cement hydrates [19], which greatly affects the qualities of hardened concrete, especially how long it will last.

In this study, the chloride ion permeability of concrete made using SRC and OPC is examined in connection to the impacts of cement type, water/cement ratio, and curing method. Three concrete mixtures were studied using both types of cement and water/cement ratios of 0.4, 0.5, and 0.6 with two different curing methods. The properties of fresh and hardened concrete were investigated. In addition, the chloride ion permeability of concrete mixtures with a water/cement ratio of 0.4 was determined using titration analysis.

2. EXPERIMENTAL WORK

The experimental tests of this research work were carried out to investigate the intensive mechanical properties and chloride ion permeability of concrete made with OPC and SRC due to changes in the water/cement ratio and curing method. Commercial Japanese OPC and SRC were used to produce concrete specimens used in the experimental research work. OPC was used to produce the concrete control mixtures for comparison. As provided by the manufacturer, the main properties, and chemical compositions of both OPC and SRC are listed in Tables 1 and 2, respectively. The used cement complies with the Japanese Standard Industrial Specifications (JIS).

High-range water-reducing admixture (HRWR), termed superplasticizer, was added to all concrete mixtures to enhance the concrete workability. It was added as 1.4% of the cement content by weight. The specific gravity, water absorption, and fineness modulus of used sand are, 2.55, 1.62% and 2.00, respectively. In contrast, the specific gravity, nominal maximum size, and fineness modulus of used coarse aggregate (crushed basalt) in the mixtures are 2.61, 15 mm and 6.18, respectively. Three concrete mixtures with 0.4, 0.5, and 0.6 water/cement ratios (w/c) were prepared for each cement type. The fines to aggregate ratio and cement content were constant at 0.5 and 400 kg/m^3, respectively. The mix proportions for concrete mixtures are listed in Table 3.

TABLE 1: MAIN PROPERTIES OF OPC AND SRC

Property		OPC	SRC
Unit weight (g/cm^3)		3.16	3.22
Fineness	Surface area (cm^2/g)	3310	3210
Setting time	Initial (h-min)	2-20	3-10
	Final (h-min)	3-30	4-40
Compressive strength (kg/cm^2)	3 days	291	219
	7 days	440	314
	28 days	613	508
Heat of hydration (J/g)	7 days	330	276
	28 days	375	322

TABLE 2: OPC AND SRC CHEMICAL COMPOSITION

Chemical compound (%)	OPC	SRC
Loss on ignition (LOI)	1.96	0.90
Magnesium oxide (MgO)	1.49	0.80
Sulfur trioxide (SO_3)	2.06	2.00
Chloride ion (Cl^-)	0.008	0.002
Sodium oxide (Na_2O)	0.58	0.55
Tricalcium silicate (C_3S)	52	54
Dicalcium silicate (C_2S)	22	23
Tricalcium aluminate (C_3A)	9	3
Tetracalcium alumina (C_4AF)	9	14

The mixing technique was employed for all concrete combinations: The coarse aggregate, sand, and cement were mixed (dry) for 1.5 minutes. Water and superplasticizer were added and mixing was continued for 1.5 minutes. After mixing, the concrete was removed from the mixer, and fresh properties, including slump, air content, and unit weight were determined. The specimen moulds were then filled with concrete and compacted. After 24 hours, the concrete specimens were removed from the moulds. Two types of curing were used. The first curing type consisted of submerging the specimens in water until the testing date (curing A). In the second curing, called "curing B", specimens were put in a room with 80% relative humidity and a temperature of 22 ºC for seven days and spraying with water twice a day.

Tests (destructive and non-destructive) were conducted to assess the qualities of each mixture's hardened concrete at 28 days. Compression, tension, and flexure tests were carried out as destructive one. For the determination of pulse velocity and dynamic modulus of elasticity were executed as non-destructive tests. On 100 x 200 mm cylinders, non-destructive examinations were conducted, followed by a compression test. The chloride ion permeability of the two concrete mixtures with a w/c of 0.4 was also determined using a Potentiometric Titration apparatus.

TABLE 3: MIX PROPORTIONS OF CONCRETE MIXTURES

Cement type		OPC	SRC
Cement content		400 kg/m^3	
Sand/aggregate ratio		0.5	
Admixture		5.6 litre/m^3	
W/C= 0.4	Water	160 litre/m^3	
	Sand	877 kg/m^3	881 kg/m^3
	Gravel	898 kg/m^3	902 kg/m^3
W/C= 0.5	Water	200 litre/m^3	
	Sand	826 kg/m^3	830 kg/m^3
	Gravel	845 kg/m^3	849 kg/m^3
W/C= 0.6	Water	240 litre/m^3	
	Sand	775 kg/m^3	779 kg/m^3
	Gravel	793 kg/m^3	797 kg/m^3

In addition, a flexure test was conducted on prismatic specimens of 100×100 mm cross-section and 400 mm length after 28 days. After this test, damaged beam sections were immersed in a 5% chloride salt solution for five months. After 1, 3, and 5 months of immersion, the concentration of total and soluble chloride ions and the diffusion coefficient were measured. Chloride is extracted from concrete samples using titration analysis to determine the total chloride level. In contrast, the free (soluble) chloride is assessed by submerging the specimen in hot water. The total and soluble sodium chloride content of concrete was determined as a percentage of the concrete's total weight using Potentiometric Titration at depths of $0 \sim 10$, $10 \sim 20$, and $20 \sim 30$ mm from the surface of the specimens. The titration method determined the powdered samples' soluble and total chloride concentrations. Reference [20] gives additional information regarding the adopted specimen preparation, experimental process, and testing.

3. RESULTS DISCUSSION

3.1. Fresh Concrete Properties

Table 4 and Figs. 1 and 2 illustrate the measured properties of fresh concrete. A slump test was conducted for concrete mixtures with w/c of 0.4, whereas concrete flow was assessed for mixtures with w/c ratios of 0.5 and 0.6. Table 4 indicates that the slump and flow values of SRC concrete are greater than those of OPC concrete at all w/c ratios. As the w/c ratio increases, the concrete's air content and unit weight drop for both types of cement. Fig. 1 represents that all OPC concrete mixtures include more air content than SRC concrete mixtures. Fig. 2 shows that the unit weight values of SRC concrete mixtures are greater than those of similar mixtures prepared with OPC because the unit weight of OPC is less than that of SRC.

TABLE 4: FRESH CONCRETE PROPERTIES

W/C ratio	Concrete Property	Cement type	
		OPC	SRC
0.4	Slump (cm)	19.2	20.2
	Air content (%)	1.8	1.5
	Unit weight (t/m^3)	2.384	2.388
0.5	Slump (cm)	—	—
	Flow (cm)	69.4	71.3
	Air content (%)	1.2	0.8
	Unit weight (t/m^3)	2.361	2.369
0.6	Slump (cm)	—	—
	Flow (cm)	71.9	73.7
	Air content (%)	0.9	0.7
	Unit weight (t/m^3)	2.342	2.352

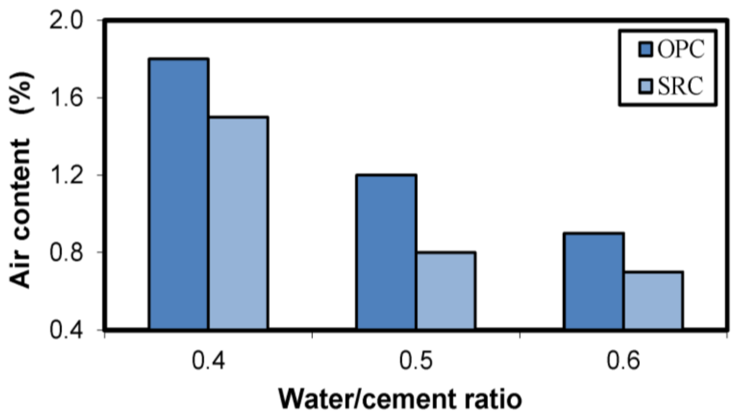

Fig. 1: Measured Air content.

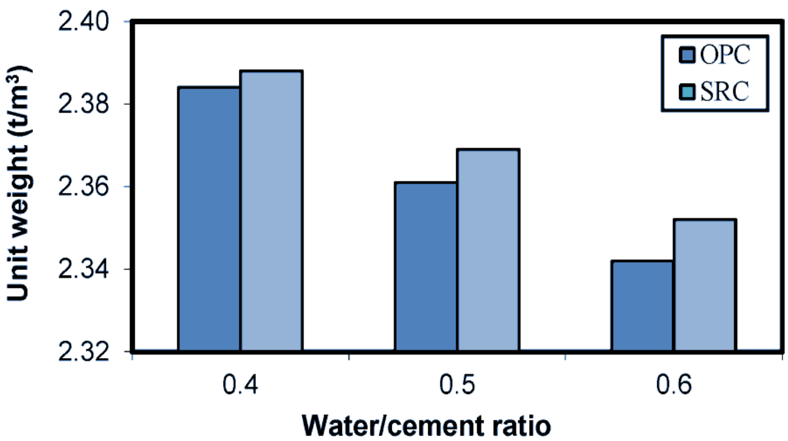

Fig. 2: Unit weight of studied concrete mixtures.

3.2. Properties of hardened concrete

As stated previously, compression, tension, flexure, pulse velocity, and dynamic elastic modulus tests were carried out on concrete samples at age of 28 days. The results are depicted in Figs. 3 to 7. In general, the compressive strength values of concrete mixtures made with SRC are greater than those of concrete mixtures made with OPC for all tested w/c ratios and curing procedures. This is true for both types of cement and all adopted w/c ratios, except the OPC mix with w/c of 0.6, which exhibits a slightly better compressive strength than SRC with curing A.

In addition, it is possible to make workable concrete with good mechanical qualities using OPC or SRC with a w/c ratio of 0.4 and an appropriate amount of superplasticizer. The tested tensile and flexural strengths of concrete mixtures are depicted in Figs. 4 and 5. The results indicate that the tensile strength values of SRC concrete are greater than those of OPC concrete cured in either of the two curing types. While the flexural strength values of SRC concrete are lower than those of OPC concrete with the two curing types. SRC concrete has a higher compressive strength. Further, the results of tensile strength and flexural concrete of curing A show more values than those of curing B.

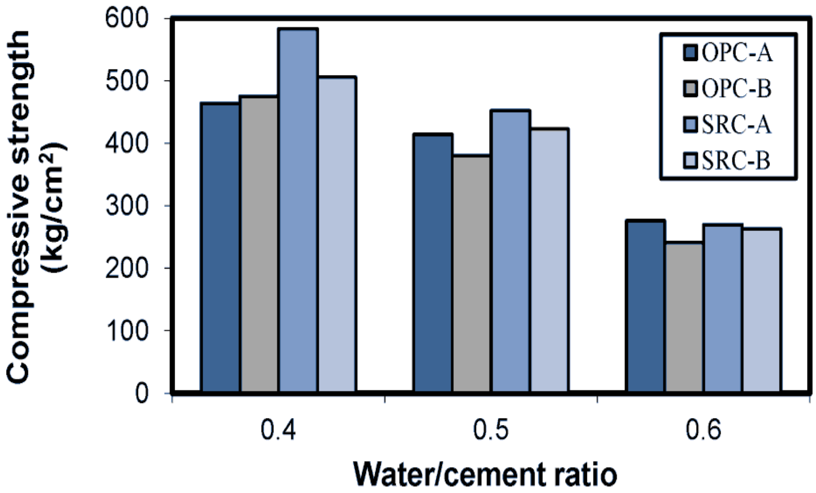

Fig. 3: Compressive strength of studied concrete mixtures.

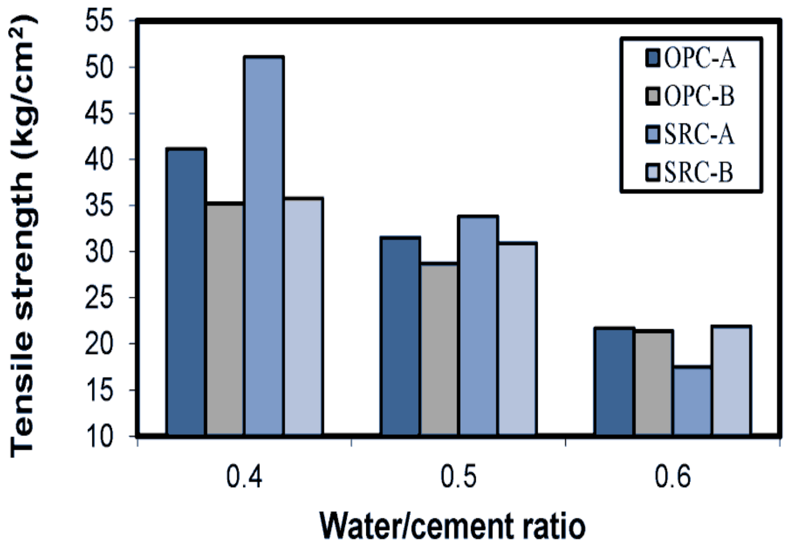

Fig. 4: Tensile strength of studied concrete mixtures.

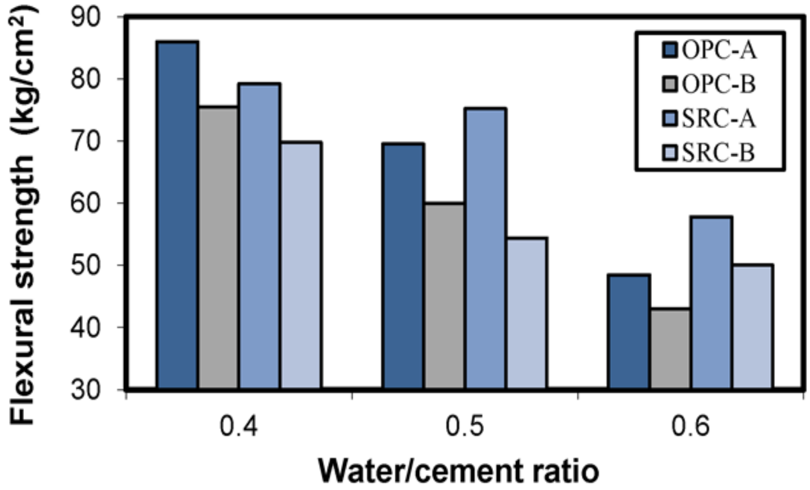

Fig. 5: Flexural strength of studied concrete mixtures.

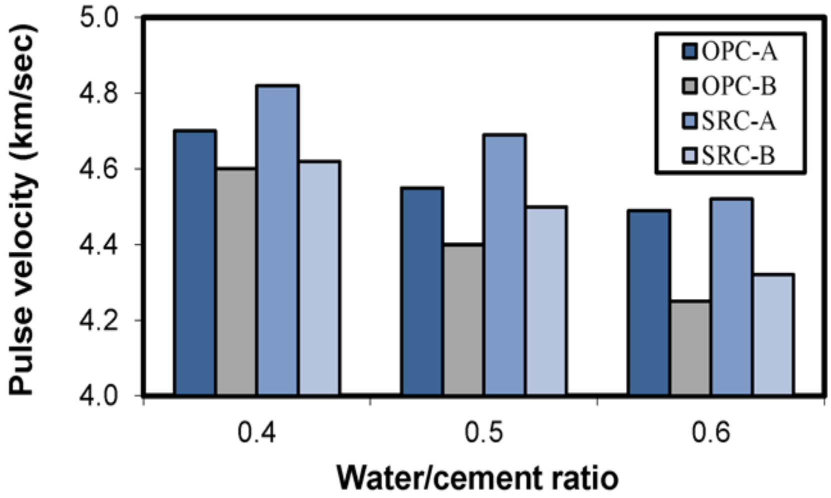

Fig. 6: Measured Pulse velocity.

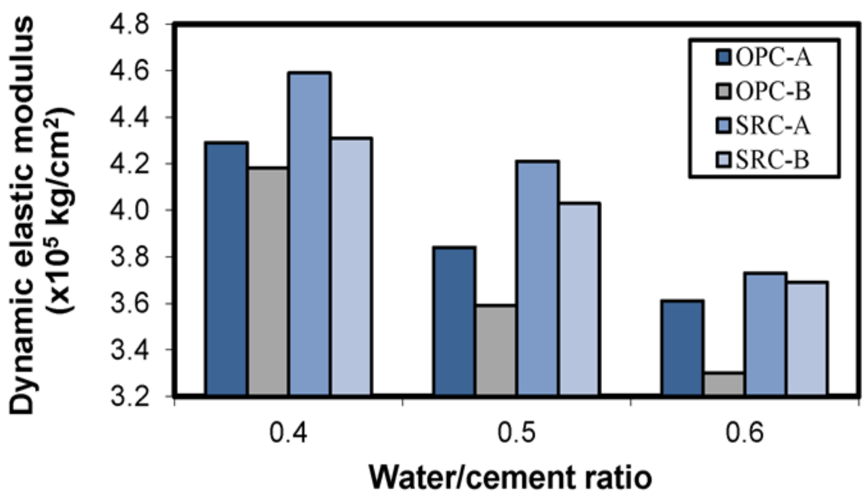

Fig. 7: Dynamic Young's modulus of studied concrete mixtures.

3.3. Chloride ion permeability

The presence of chloride in concrete significantly contributes to its degradation [21]. The chlorides in concrete can be separated into two categories: chlorides that seep into concrete from the outside after construction and chlorides that were already present at the time of mixing. It is believed that later chlorides move into concrete and concentrate due to causes such as the addition of additional chlorides, wetting, drying, neutralization, and temperature changes. It has been suggested that the movement of chloride ions in concrete can be viewed as a diffusion process in which ions travel according to their concentration gradient [22]. Concrete may include chloride ions in various states [23]. water-soluble in solution and firmly bound by tricalcium aluminate hydrates, but only weakly by calcium silicate hydrates.

Concrete's sodium chloride content, both total and soluble, has been measured as a percentage of its weight using potentiometric titration. Table 5 displays the contents of total and soluble chloride ions after 1, 3, and 5 months, given as a percentage of the total weight of concrete. The findings show that total and soluble chloride concentrations dramatically dropped as the concrete zones under the study's depth increased. The findings also show that concrete samples' initial 10 millimeters have limited resistance to chloride penetration, emphasizing the importance of concrete covering the reinforcement. Figs. 8 and 9 show that when the curing procedure altered, the influence of cement type on chloride penetration tended to become more evident. Additionally, the SRC mixture's third zones (20~30 mm) have lower chloride levels than the OPC concrete's A and B curing.

TABLE 5: CHLORIDE CONTENTS OF TESTED CONCRETES ($w/c = 0.4$)

Cement Type	Curing type	depth (mm)	1-month		3-month		5-month	
			Total %	Soluble %	Total %	Soluble %	Total %	Soluble %
OPC	A	0~10	0.26700	0.06933	0.29315	0.18574	0.32375	0.19236
		10~20	0.01791	0.00893	0.01937	0.01096	0.02225	0.01224
		20~30	0.00965	0.00801	0.00988	0.00964	0.01173	0.01013
	B	0~10	0.34524	0.08563	0.41305	0.19468	0.36321	0.22395
		10~20	0.02217	0.01197	0.02328	0.01234	0.02851	0.01557
		20~30	0.01310	0.00912	0.01471	0.00981	0.01589	0.01093
SRC	A	0~10	0.19019	0.08981	0.14317	0.05436	0.19053	0.09005
		10~20	0.00687	0.00426	0.01095	0.00789	0.04181	0.01716
		20~30	0.00444	0.00406	0.00667	0.00639	0.00732	0.00689
	B	0~10	0.31164	0.15495	0.36681	0.16283	0.54109	0.25273
		10~20	0.00961	0.00627	0.01571	0.00798	0.13414	0.05815
		20~30	0.00440	0.00423	0.00696	0.00648	0.01060	0.00671

TABLE 6: CHLORIDE SUPPLY CONCENTRATION OF TESTED CONCRETE (C_0)

Cement Type	1-month		3-month		5-month	
	A	B	A	B	A	B
OPC	0.45	0.55	0.50	0.80	0.50	0.60
SRC	0.34	0.55	0.25	0.70	0.35	0.90

TABLE 7: COEFFICIENT OF DIFFUSION OF TESTED CONCRETE (X 10^{-7} CM^2/SEC)

Cement Type	1-month		3-month		5-month	
	A	B	A	B	A	B
OPC	1.56	1.62	0.465	0.483	0.348	0.361
SRC	1.15	1.21	0.560	0.412	0.361	0.386

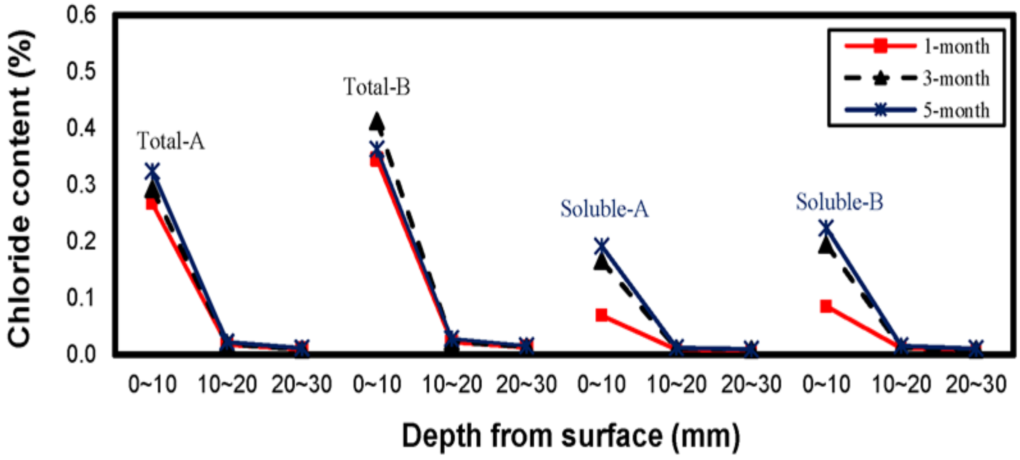

Fig. 8: Total and soluble chloride contents of OPC mix.

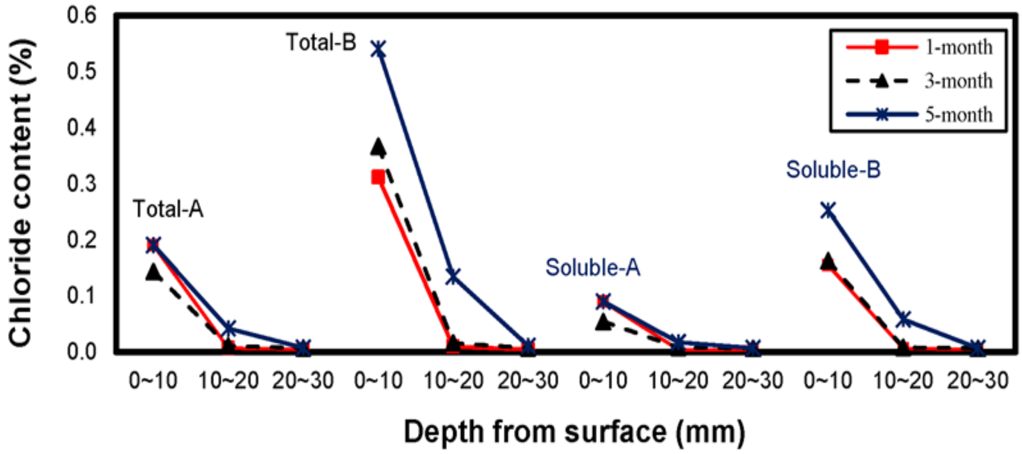

Fig. 9: Total and soluble chloride contents of SRC mix.

The corrosion threshold limit for the concentration of soluble chloride ions in normal-weight reinforced concrete is around 0.03% by weight of concrete, according to Marusin [24]. According to Table 4, all samples tested after 5 months at a depth of 20~30 mm in concrete had soluble chloride concentrations below the corrosion threshold levels. Because the SRC mixture has less soluble chloride, concrete made with it might only need a shorter cover depth to protect reinforcing steel. Additionally, concrete curing A has lower total and soluble chloride contents than concrete curing B.

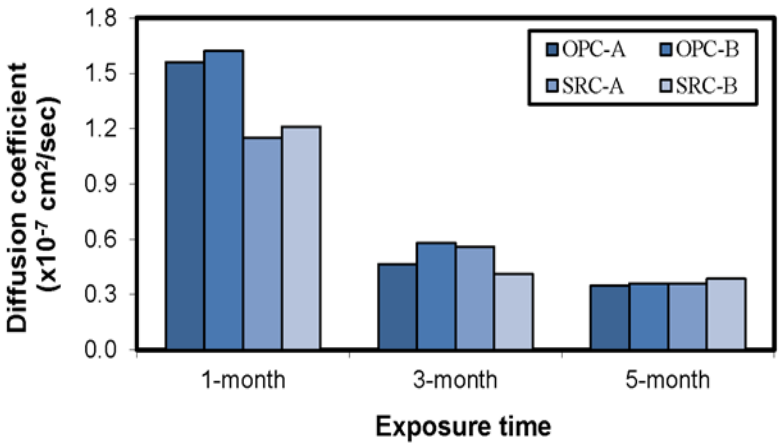

Fig. 10: Chloride diffusion coefficient of the studied concretes.

Table 6 contains the chloride supply concentration results for tested concrete. It is observed that the chloride supply concentration values fluctuate as a result of both changes in cement type and curing technique. In addition, the chloride supply concentration of concrete cured with method A is smaller than that of concrete cured with method B. The SRC mixture has a lower chloride supply concentration for curing A than the OPC mixture. Fig. 10 and Table 7 provide the results of the chloride ion diffusion coefficient across the concrete samples. It is obvious from Fig. 10 that diffusion coefficient values vary due to changes in cement type and curing technique. It is fascinating to note that the diffusion coefficient values of various mixtures vary slightly. According to Nagaro and Naito [25], the arbitrary limits of diffusion coefficient lie between 10-7 and 10-8 cm2/sec, and the findings obtained after 5 months of exposure for all mixes fell within these limits.

4. CONCLUSIONS

1. At the age of 28 days, the measured properties of hardened concrete cured with method A are higher than those concrete cured with method B.
2. Due to the integration of sulfate-resistant cement (SRC) into concrete, the chloride ion permeability is significantly reduced. Zone 20~30 mm findings for all examined samples are below the steel corrosion threshold.
3. The chloride concentration and diffusion coefficients of sulfate-resistant cement (SRC) concrete are lower than those of ordinary Portland cement (OPC) concrete.
4. As the curing method varied, the influence of cement type on chloride penetration tended to become more pronounced. In addition, curing A yields concrete with lower soluble and total chloride concentrations and diffusion coefficients than curing B.

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