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Durability of Very-High-Strength Concrete with Supplementary Cementitious Materials for Marine Environments

by Tze Yang Darren Lim, Susanto Teng, Sabet Divsholi Bahador, and Odd E. Gjrv

This paper summarizes the findings from a research program to investigate the effects of different amounts of supplementary cementitious materials on improving the concrete mechanical properties and on increasing the resistance to chloride penetration for applications in marine environments. Twelve concrete mixtures with different quantities and compositions of supplementary materials were tested. The durability properties with respect to chloride penetration, such as electrical resistivity and chloride diffusivity, were correlated with each other. A good correlation between them was obtained, as validated by the test results.

The inclusion of supplementary cementitious materials in sufficient amounts, such as ground-granulated blast-furnace slag and silica fume, proved to be highly effective in improving the durability properties of the concrete. In addition, an increase in the fineness of ground-granulated blast-furnace slag would benefit early-age strength development of the concrete. The inclusion of supplementary cementitious materials in sufficient amounts is essential to obtaining a concrete mixture with good mechanical properties and high resistance against chloride ingress.

Keywords: chloride diffusivity; corrosion; durability; electrical resistivity; marine environment; silica fume; ultra-fine slag; very-high-strength concrete.

INTRODUCTION

With the development of concrete technology, achieving concrete strength of 100 MPa (14.5 ksi) or higher no longer poses difficulties. It is common now to have high-rise buildings having columns made of high-strength concrete (HSC) with a compressive strength of 100 MPa (14.5 ksi) or higher. Concrete having a compressive strength of 80 MPa (11.6 ksi) has been used very often for marine structures. When longer service life is expected, especially for marine structures, almost invariably a higher-strength concrete is needed. The HSC typically also contain ground-granulated blast-furnace slag (GGBFS), silica fume, and/or other supplementary materials that can improve durability properties.^{1,2} However, concrete mixtures with GGBFS are known to have slow early-strength development.³⁻⁶ In fact, while the compressive strength depends on a low water-binder ratio (w/b), reducing the amount of mixing water for a given w/b may not always be effective in obtaining a high compressive strength at early age.⁷

The objective of this research is to produce a high-performance concrete with high early strength and good durability properties using readily available constituent materials. In a marine environment, penetration of chloride ions, alkali-silica reaction, sulfate attack, and carbonation are common causes of corrosion. However, the focus of this

paper is producing a concrete with good resistance against chloride penetration. Concrete with good resistance to chloride ingress will delay or prevent corrosion of embedded steel bars and, thus, increases the service life of the marine structure. Of course, such durable concrete will be very suitable for land-based structures as well.

Other than the mechanical properties of the concrete, two types of durability tests were employed to study chloride ingress into concrete: the electrical resistivity test and rapid chloride migration test (RCMT).

The electrical resistivity of concrete represents the ability of concrete to resist the movement of ions into hardened concrete through the pore solution. A higher electrical resistivity would lead to reduction in corrosion rate of the embedded steel bars in concrete.^{3,8,9}

The RCMT is an accelerated, non-steady-state chloride migration test. During the test, the penetration of chloride ions from a sodium chloride solution into concrete would be measured. The measured chloride penetration depth would be used to determine the chloride diffusivity coefficient.¹⁰ The chloride diffusivity coefficient could then be used to interpret the resistance of the concrete against chloride penetration. Furthermore, the chloride diffusivity coefficient can then be used as a primary parameter for analyzing and estimating the service life period of a concrete structure.^{11,12}

RESEARCH SIGNIFICANCE

The purpose of this research was to study the influence of types and amounts of supplementary cementitious materials on the early and ultimate strengths as well as its resistance against chlorides of HSC for applications to marine concrete structures. Various amounts of GGBFS of different fineness along with silica fume were used as cement replacement materials and their effects were evaluated. It is expected that the results will be useful for engineers and/or researchers who need very durable concrete for marine structures.

EXPERIMENTAL INVESTIGATION

Materials

The physical and chemical properties of the cementitious materials used to produce the very-high-strength concrete in

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Table 1—Physical properties and chemical compositions of ordinary portland cement (OPC), GGBFS, ultra-fine slag (UFGGBFS), and silica fume (SF)

	OPC	GGBFS	UFGGBFS	SF
Physical properties				
Blaine surface area, m ² /kg	360	410	870	—
BET surface area, m ² /kg	1466	2100	4968	20340
Particle mean diameter, μm	15.96	9.20	4.09	<0.1
Density, kg/m ³	3150	2720	2720	2200
Oxide compositions, %				
SiO ₂	21.5	36	31.2	93
Al ₂ O ₃	5.5	9	9	2
Fe ₂ O ₃	4.5	1	1	1
CaO	63	44	35.1	1
SO ₃	2.5	1	0.1	0.3
MgO	2	8	11.8	1

Notes: 1 m²/kg = 4.88 ft²/lb; 1 μm = 3.94 × 10⁻⁵ in.; 1 kg/m³ = 0.06 lb/ft³.

Table 2—Calculated cement compound compositions using Bogue's equations

Major compounds of cement	%
C ₃ S	42.5
C ₂ S	29.8
C ₃ A	7.0
C ₄ AF	13.7

Table 3—Mixture proportions of concrete

Mixture	SCM* content, %	water/(cement + SCM*)	Total cementitious materials	Water	Cement	GGBFS	UFGGBS	SF	Fine aggregate	Coarse aggregate
			kg/m ³							
25CM	0	0.25	590	148	590	0	0	0	841	841
25UG30	30	0.25	585	146	409	0	175	0	833	833
25UG30G15	45	0.25	582	145	320	87	175	0	829	829
25SF10 [†]	10	0.25	585	146	527	0	0	59	834	834
25UG30SF10 [‡]	40	0.25	580	145	348	0	174	58	826	826
25UG45	45	0.25	582	145	320	0	262	0	829	829
25G45	45	0.25	582	145	320	262	0	0	829	829
25UG60	60	0.25	579	145	232	0	347	0	825	825
28CM [§]	0	0.28	523	146	523	0	0	0	876	876
28UG30	30	0.28	518	145	363	0	155	0	868	868
35CM	0	0.35	448	157	448	0	0	0	896	896
35UG30	30	0.35	445	156	312	0	133	0	890	890

*SCM: supplementary cementitious materials.

[†]This mixture was included in another paper by the authors, labeled as Mixture C.²

[‡]This mixture was included in another paper by the authors, labeled as Mixture D.²

[§]This mixture was included in another paper by the authors, labeled as Mixture A.²

^{||}This mixture was included in another paper by the authors, labeled as Mixture B.²

Note: 1 kg/m³ = 0.06 lb/ft³.

this study are presented in Tables 1 and 2. Two types of slag with different fineness were used to evaluate the effect of particle size on the properties of concrete. The Brunauer-Emmett-Teller (BET) surface area of the normal blast-furnace slag and ultra-fine blast-furnace slag was 2100 and 4968 m²/kg (10,248 and 24,243 ft²/lb), respectively. The BET surface area of the silica fume was 20,340 m²/kg (99,259 ft²/lb). The type of cement used was ASTM C150 Type I portland cement (BET surface area was 1466 m²/kg [7155 ft²/lb]). All the supplementary cementitious materials were finer than the cement particles. Crushed granite with a maximum size of 20 mm (0.8 in.) was used as the coarse aggregate and normal sand (maximum size of 2 mm [0.08 in.]) was used as the fine aggregate. A polycarboxylate-based high-range water-reducing agent was added into the mixtures to increase the workability of the concrete mixtures.

Mixture proportions

The detailed mixture proportions of the 12 mixtures are given in Table 3. A w/b of 0.25 was maintained for eight mixtures, 0.28 for two mixtures, and 0.35 for the last two mixtures. The mixtures are labelled according to their w/b and the percentages of various cementitious materials used.

Casting and curing

Two types of specimens were cast for each mixture to conduct the various tests: 100 x 200 mm (4 x 8 in.) cylinders and 100 x 100 mm (4 x 4 in.) cubes.

The specimens were cast in a controlled laboratory environment according to BS EN 12390-2: 2009.¹³ The concrete molds were vibrated using shake tables and were covered

immediately with a plastic sheet to prevent any moisture loss. The specimens were removed from the molds on the next day and then placed in water (77°F [25°C]) continuously until the designated test dates.

ITEMS OF INVESTIGATION

Compressive strength

The specimens were tested on Days 3, 7, 28, 56, and 90 for the compressive strengths according to BS EN 12390-3: 2009.¹⁴ The 100 x 100 mm (4 x 4 in.) cubes were tested for all the mixtures while the 100 x 200 mm (4 x 8 in.) cylindrical specimens were also provided for mixtures 25CM, 25UG30, 25UG30G15, 25UG45, 25G45, and 25UG60. The surfaces of the cylinder specimens were ground before testing according to ASTM C39.¹⁵ The average result of three tests was taken as the compressive strength of each mixture.

Modulus of elasticity

Three cylinder specimens were tested on Day 28 according to ASTM C469¹⁶ to determine the moduli of elasticity of the mixtures. The average result of three tests was taken as the modulus of elasticity for each mixture.

Rapid chloride migration test (RCMT)

Three specimens of 100 mm diameter and 50 mm height (4 x 2 in.) were cut from the cylinder specimens and tested on Days 3, 28, 56, and 90 to determine chloride diffusivity coefficient. The tests were conducted according to Nord-Test NT BUILD 492.¹⁰ An illustration of the test setup is presented in Fig. 1. An external electrical potential was applied across the specimen to force the chloride ions from the sodium chloride solution into the concrete specimen during the duration of the test. After the test, the specimen was split into two to measure the average penetration depth of chloride ions into the concrete. The chloride diffusivity coefficient was calculated using the chloride penetration depth. The chloride diffusivity coefficient can then give an indication of the durability property of the concrete with respect to chloride penetration.

Four-electrode electrical resistivity test¹⁷

The electrical resistivity of the hardened concrete was measured from Day 3 to 90 with Werner's four-electrode measuring equipment. A low-frequency alternating electric current was applied by the two outer electrodes to pass through the concrete. The drop in voltage between the two inner electrodes was measured. The electrical resistivity of the concrete was calculated and displayed by the equipment. The electrical conductivity, reciprocal of electrical resistivity, had been shown to be well correlated with the results obtained from RCMT.¹⁸ This relationship is shown to be independent of age. The electrical resistivity measurements were taken on the surface of the cylinder specimens. The average reading of three measurements was determined as the electrical resistivity of the concrete.

Fig. 1—Test setup for RCMT based on NordTest NT Build 492: (a) plastic tube; (b) 0.3M sodium hydroxide; (c) anodic stainless steel plate; (d) concrete specimen; (e) cathodic stainless steel plate; (f) 10% NaCl; and (g) plastic container.

EXPERIMENTAL RESULTS

Compressive strength and modulus of elasticity

The cube compressive strength of the control mixture 35CM reached 55.67 MPa (8.07 ksi) on Day 3. At Day 28, the strength increased to 76.24 MPa (11.05 ksi). The compressive strength of the concrete is directly affected by the w/b of the concrete. With a w/b of 0.28, the Day 3 and Day 28 strengths were 62.52 and 84.48 MPa (9.06 and 11.96 ksi), respectively. The strength of Mixture 25CM (the lowest w/b —0.25) was the highest among the three plain concrete mixtures, reaching 95 and 108 MPa (13.7 and 15.6 ksi) at Days 3 and 28, respectively. The long-term strength of Mixture 25CM at Day 90 was also the highest among the three plain concrete mixtures. The cylindrical compressive strength of Mixture 25CM on Days 3, 28, 56, and 90 were 82, 91, 94, and 98 MPa (11.9, 13.2, 13.6, and 14.2 ksi), respectively.

The compressive strength development for the 12 mixtures is presented in Fig. 2. Generally, the compressive strengths of all mixtures with supplementary cementitious materials were higher than that of the control mixtures with similar w/b after Day 28. The effects of ultra-fine slag seems to be more significant in mixtures with lower w/b , as observed by Teng et al.¹ The specimens from Mixture UG30SF10 achieved the highest cube compressive strength of 135 MPa (19.6 ksi) on Day 28 among all the mixtures. The strength of this mixture on Day 90 was 138 MPa (20.0 ksi). Further analysis on the results are discussed in later sections.

The moduli of elasticity of all the mixtures are presented in Table 4. The moduli of elasticity for the three plain concrete mixtures were in the range of 30 to 39 GPa (4350 to 5656 ksi). The moduli of elasticity for the blended mixtures were higher than that of the plain concrete mixtures, in the range of 40 to 45 GPa (5801 to 6525 ksi), except for Mixture 25SF10. The modulus of elasticity for mixture 25SF10 was 34.8 GPa (5047 ksi), lower than that of the control mixture, 25CM (38.8 GPa [5626 ksi]).

Chloride diffusivity coefficient

The chloride diffusivity coefficients of the 12 mixtures are presented in Table 5. The chloride diffusivity coefficient obtained by the three plain concrete mixtures (25CM, 28CM, and 35CM) on Day 28 were 3.91, 7.91, and 10.61 $\text{m}^2/\text{s} \times 10^{-12}$ (42.09, 85.14, and 114.20 $\text{ft}^2/\text{s} \times 10^{-12}$).

(a)

(b)

Fig. 2—(a) Cube compressive strengths of all the mixtures; and (b) cylinder compressive strengths of six mixtures.

The reduced amount of water used in the concrete mixtures increased the compressive strength and reduced the porosity in the hardened concrete.¹ The reduced porosity resulted in lower chloride diffusivity coefficient. As shown in Table 5, the chloride diffusivity coefficients for the blended mixtures were significantly smaller than the control mixtures, with the exception of Mixture 25G45 on Day 28. The diffusivity coefficient reduced as the age of the concrete increased. The trend of increased development of microstructure resulting in reduced chloride diffusivity coefficient was evident in all the mixtures. On Day 90, the chloride diffusivity coefficient recorded for Mixtures 25CM, 28CM, and 35CM were 1.71, 3.80 and $9.47 \text{ m}^2/\text{s} \times 10^{-12}$ (18.40, 40.90, 101.93 $\text{ft}^2/\text{s} \times 10^{-12}$),

Table 4—Compressive strength and moduli of elasticity of the different mixtures

Mixture	Compressive strength at Day 28, MPa (ksi)	Modulus of elasticity at Day 28, GPa (ksi)
25CM	107.80 (15.64)	38.8 (5627)
25UG30	111.93 (16.23)	41.9 (6077)
25UG30G15	112.23 (16.28)	44.4 (6439)
25SF10	120.60 (17.49)	34.8 (5047)
25UG30SF10	135.43 (19.64)	40.1 (5816)
25UG45	118.07 (17.12)	43.4 (6294)
25G45	109.87 (15.94)	40.6 (5888)
25UG60	112.53 (16.32)	40.4 (5859)
28CM	91.63 (13.29)	34.1 (4945)
28UG30	109.80 (15.93)	40.1 (5816)
35CM	76.24 (11.06)	30.6 (4438)
35UG30	82.48 (11.96)	33.8 (4902)

respectively. The chloride diffusivity coefficients for most of the blended mixtures at Day 90 were below the value of $1 \text{ m}^2/\text{s} \times 10^{-12}$ ($10.76 \text{ ft}^2/\text{s} \times 10^{-12}$). The resistance of the concrete against chloride penetration can be classified based on the chloride diffusivity coefficient as shown in Table 6.¹¹ The classification of resistance against chloride penetration for the 12 mixtures is also presented in Fig. 3. Most of the mixtures reached the classification of “Extremely high” resistance against chloride penetration even on Day 7, except for Mixtures 35CM, 28CM, 25CM, 35UG30, and 25G45. Mixture 25G45 reached the classification of “Extremely high” resistance against chloride penetration on Day 28, whereas mixture 25CM did not reach that classification until Day 56. Mixtures 35UG30 and 28CM reached the classification of “Very high” resistance on Day 90. The highest classification of resistance reached by mixture 35CM was “High.” It shows that concrete structures made from a mixture with plain concrete may have high strength by reducing the w/b . However, chloride penetration into that concrete might be possible at early ages of the concrete. It will not be beneficial to the long-term durability of the structure. Therefore, it is not advisable to use a concrete material without any supplementary cementitious materials when long-term durability is required.

Electrical resistivity

The electrical resistivity measurements from six mixtures are presented in Fig. 4. Measurements were not recorded for the other mixtures. The value of electrical resistivity of the concrete increased with the age of the concrete due to continued hydration of cementitious materials. Smith et al³ also observed the trend that the electrical resistivity values increases as the concrete increases in strength. According to Fig. 4, all the mixtures reached the classification of low corrosion rate by Day 20.¹⁸ The electrical conductivity, reciprocal of electrical resistivity, was plotted against the chloride diffusivity coefficient in Fig. 5 to show the consistency of the test results. A correlation factor of 0.97 was obtained and was similar to other studies conducted for lower-strength concrete.^{18,19}

Table 5—Chloride diffusivity coefficient of concrete, $\text{m}^2/\text{s} \times 10^{-12}$ ($\text{ft}^2/\text{s} \times 10^{-12}$)

Mixture	Day				
	3	7	28	56	90
25CM	—	5.48 (58.99)	3.91 (42.09)	2.36 (25.40)	1.71 (18.40)
25UG30	—	1.60 (17.22)	1.45 (15.60)	1.01 (10.87)	0.92 (9.90)
25UG30G15	—	1.47 (15.82)	1.25 (13.45)	0.42 (4.52)	0.36 (3.88)
25SF10	1.85 (19.91)	—	0.16 (1.72)	0.12 (1.29)	0.04 (0.43)
25UG30SF10	1.71 (18.41)	—	0.11 (1.18)	0.07 (0.75)	0.01 (0.11)
25UG45	—	1.11 (11.95)	0.65 (7.00)	0.52 (5.60)	0.42 (4.52)
25G45	—	5.03 (54.14)	2.35 (25.30)	2.03 (21.85)	1.05 (11.30)
25UG60	—	1.95 (20.99)	0.60 (6.46)	0.47 (5.06)	0.37 (3.40)
28CM	10.18 (109.58)	—	7.91 (85.14)	6.01 (64.69)	3.80 (40.90)
28UG30	2.63 (28.30)	—	0.95 (10.23)	0.71 (7.64)	0.50 (5.38)
35CM	15.64 (168.35)	—	10.61 (114.20)	9.88 (106.35)	9.47 (101.93)
35UG30	8.35 (89.88)	—	7.92 (85.25)	6.39 (68.78)	4.33 (46.60)

Table 6—Classification of chloride diffusivity coefficients of concrete mixtures¹¹

Chloride diffusivity, $D_{28} \times 10^{-12} \text{ m}^2/\text{s}$ ($\times 10^{-12} \text{ ft}^2/\text{s}$)	Classification of resistance to chloride penetration
> 15 (161.4)	Low
10 to 15 (107.6 to 161.4)	Moderate
5 to 10 (53.8 to 107.6)	High
2.5 to 5 (26.8 to 53.8)	Very high
< 2.5 (26.8)	Extremely high

Fig. 3—Chloride diffusivity coefficients of various mixtures.

DISCUSSION OF RESULTS

Effects of ground-granulated blast-furnace slag

The compressive strength test results of Mixture 25CM will classify it as a very-high-strength concrete mixture. The

Fig. 4—Classification of the various mixtures based on electrical resistivity values.

high compressive strength was achieved with the inclusion of a relatively high amount of cementitious material (portland cement only) and low w/b . However, its durability properties would not classify the mixture as a high-performance concrete with good durability properties. The pores within the microstructure that were not filled by the product of hydration may allow a relatively high rate of chloride ion penetration into the concrete, resulting in a relatively rapid corrosion rate of embedded steel reinforcement. Mixture 25G45 is a mixture with a 45% cement replacement by normal slag. The inclusion of normal slag affects early strength development of the concrete, as observed by others as well.⁴⁻⁶ Apart from the results at Day 3, the compressive strengths of both mixtures (25CM and 25G45) were similar on various test days. The 90-day compressive strengths obtained by Mixtures 25CM

Fig. 5—Correlation of the electrical conductivity values and chloride diffusivity coefficients.

and 25G45 were very close—98 and 102 MPa (14.2 and 14.8 ksi), respectively. This shows that the inclusion of normal slag may delay the early strength development, but it will not affect the long-term strength of the concrete mixture.

As shown from the results in Table 5, there was a significant difference in the chloride diffusivity coefficient of Mixture 25G45 compared to Mixture 25CM after Day 28. The reduction in chloride diffusivity coefficients of between the two mixtures at Day 90 was 38% (1.71 and $1.05 \text{ m}^2/\text{s} \times 10^{-12}$). Comparing the chloride diffusivity coefficients of mixtures with the same w/b (35CM and 35UG30, 28CM, and 28UG30), the blended mixtures will also show lower diffusivity coefficients regardless of the w/b .¹ The pozzolanic reactions due to the addition of slag results in the formation of secondary calcium silicate hydrate (C-S-H). The additional C-S-H can fill up the pore space in the concrete, resulting in reduced pore volume and pore connections.^{6,20-22} The physical densification of microstructure and, thus, reduction in porosity, reduces the capacity of concrete to physically absorb and react with chloride ions.¹ A lower diffusivity coefficient represents better microstructure development and low pore connectivity in the microstructure. The partial replacement of cement with supplementary cementitious materials results in less-permeable concrete against chloride ingress starting from very early age. Thomas et al.²³ reported chloride penetration depths in concretes containing slag after being exposed to marine environment for 25 years. The results showed that the inclusion of slag increased the resistance against chloride penetration significantly for concrete with a w/b of 0.4.²³ With greater resistance against chloride ingress, the slag-blended mixtures would be a more durable reinforced concrete material compared to plain concrete mixtures.²

A similar explanation can be used to explain the increase in the electrical resistivity measurements between the

blended mixtures and the plain concrete mixtures. The reduction of pore solution due to the filling up of pore space by secondary C-S-H will improve the electrical resistivity of the concrete.²⁴ The electrical resistivity measurements of Mixture 25G45 showed consistently higher readings than those of Mixture 25CM at different ages. These results again show that the inclusion of slag improved the durability properties of concrete with regards to chloride ingress.

Effect of fineness of ground-granulated blast-furnace slag

The effect of the fineness of blast-furnace slag can be observed from the results of mixtures 25UG45 (containing ultra-fine slag) and 25G45 (containing normal slag). Both the mixtures had 45% replacement of cement content with slag. However, the fineness of slag used in the two mixtures was different. The increased fineness of slag in Mixture 25UG45 meant that the total surface area of the ultra-fine slag was increased. The increased total surface area of ultra-fine slag represents more surface area for reactions to take place. The rate of reaction would be increased, thus improving the early-age properties of the hardened concrete. The inclusion of slag with increased fineness would also reduce the average pore radius in the microstructure.²⁵ As shown in Fig. 2, it is clear that the compressive strength of Mixture 25UG45 was higher than that of Mixture 25G45 at any test date. The increased rate of hydration in Mixture 25UG45 allowed a higher early cylinder compressive strength of 85 MPa (12.3 ksi) at Day 3 compared to 72 MPa (10.4 ksi) for Mixture 25G45. The strength results from these two mixtures showed that the increase in fineness can increase the rate of hydration and, hence, the early-age strength. The 90-day strength of the ultra-fine slag-blended mixture was also higher than that of the normal slag-blended mixture. Swamy²⁶ and Tomisawa and Fujii,²⁵ similarly reported observations that increasing the fineness of slag increased the long-term compressive strength of the concrete.

The three mixtures of 25G45, 25UG30G15, and 25UG45 have the same amount of cement replacement. The percentages of ultra-fine slag and normal slag in these mixtures were different. The early strength of Mixture 25UG30G15 (91 MPa [13.2 ksi]) was slightly higher than that of Mixture 25UG45 (85 MPa [12.3 ksi]). However, the 90-day strengths for these two mixtures were close. The different effects between the ultra-fine slag and normal slag can be shown in the durability properties of the two mixtures.

The chloride diffusivity coefficients of Mixtures 25G45, 25UG30G15, and 25UG45 were 5.03 , 1.47 , and $1.11 \text{ m}^2/\text{s} \times 10^{-12}$ (54.14 , 15.82 , and $11.95 \text{ ft}^2/\text{s} \times 10^{-12}$) at Day 7, respectively. There is a 78% reduction between the highest and lowest diffusivity coefficients (25G45 and 25UG45). The electrical resistivity results for the three mixtures were 18, 31, and 42 k-ohm.cm (7.1, 12.2, and 16.5 k-ohm.in.), respectively. Among the three mixtures, 25UG45 has the highest amount of ultra-fine slag. The chloride diffusivity coefficient at Day 7 for Mixture 25UG45 was the lowest among the three mixtures, and its electrical resistivity was the highest. This again shows the effect of increased fineness in improving the microstructure of the concrete at early age. The finer mineral

admixture fills up more spaces between the interfaces of aggregates and cement paste due to better particle packing. This filler effect confirms previous observations that it can densify the interfacial transition zone (ITZ) and improve the homogeneity of the concrete.²⁷ The densification of ITZ would result in low connectivity and permeability of the pore system. Swamy²⁶ showed that increasing the fineness of the slag would increase the resistance against water penetration. Increased resistance against water penetration essentially leads to reduced risk of chloride penetration.

Effect of silica fume

The cube compressive strength of Mixture 25SF10 (83 MPa [12.0 ksi]) was slightly lower than that of Mixture 25CM (95 MPa [13.7 ksi]) at Day 3. The results between the two mixtures were similar at Day 7. Beyond Day 7, the compressive strength of Mixture 25SF10 was always higher. This observation was similar to those in other studies where the mixtures with silica fume recorded lower strength at the early ages, but higher long-term strength.^{7,28} The addition of the 10% silica fume was reported to be able to have a 30% reduction of the porosity in the hardened concrete and almost 70% reduction in the average pore diameter.²⁹ The reduction in porosity can be indirectly reflected in lower chloride diffusivity coefficient from the rapid chloride migration test (RCMT). The chloride diffusivity coefficient of Mixture 25SF10 at Day 3 was already significantly lower than the diffusivity coefficient of the plain concrete mixture, 25CM, at Day 7. At Day 28, the chloride diffusivity coefficient of Mixture 25SF10 was $0.16 \text{ m}^2/\text{s} \times 10^{-12}$ ($1.72 \text{ ft}^2/\text{s} \times 10^{-12}$). This value was 96% lower than the chloride diffusivity coefficient of Mixture 25CM.

Compared to Mixture 25SF10, Mixture 25UG30SF10 had an addition of 30% cement replacement by ultra-fine slag. The cube compressive strength of Mixture 25UG30SF10 was high at Day 3, achieving 110 MPa (16.0 ksi), compared to 83 MPa (12.0 ksi) for 25SF10. From this observation, it seems that the 30% ultra-fine slag in Mixture 25UG30SF10 was able to improve the strength at an early age. The effect of silica fume would appear only after Day 7, as shown in the results from Mixture 25SF10. There seems to be no significant difference in the durability results between the two mixtures containing 10% silica fume. The chloride diffusivity coefficient of Mixture 25UG30SF10 was lower than that of Mixture 25SF10 across all ages, but the difference was not significant. The difference between the diffusivity coefficients from the two mixtures (25UG30SF10 and 25SF10) on Day 28 was only $0.05 \text{ m}^2/\text{s} \times 10^{-12}$ ($0.54 \text{ ft}^2/\text{s} \times 10^{-12}$). The electrical resistivity measurement of both Mixtures 25SF10 and 25UG30SF10 were significantly higher than Mixture 25CM, as shown in Fig. 4. However, similar to the chloride diffusivity coefficient, the difference in electrical resistivity measurements between Mixtures 25SF10 and 25UG30SF10 was not significant. This suggests that the influence of 10% silica fume alone was significant enough for the development of good microstructure and, thus, durability properties. Thus, the further 30% cement replacement by ultra-fine slag does not bring further significant improvement.

Fig. 6—Comparison of mixtures with different cement replacement: (a) cylinder compressive strength results; and (b) electrical resistivity. (Note: 25CM = 0%; 25UG30 = 30%; 25UG45 = 45%; and 25UG60 = 60%.)

Effect of cement replacement percentage

The percentage of cement replacement by ultra-fine slag in Mixtures 25UG30, 25UG45, and 25UG60 was 30%, 45%, and 60%, respectively. The results of these three mixtures and the control mixture are presented in Fig. 6. The early strength of Mixture 25UG30 was the highest among the three mixtures, whereas the strength of Mixture 25UG60 was the lowest. This could be due to the high amount of ultra-fine slag added into the mixture. It seems that the low rate of hydration from the high amount of ultra-fine slag content in the mixture overshadowed the early strength contribution of the ultra-fine slag. The strengths of Mixtures 25UG45 and

25UG60 were higher than that of mixture 25UG30 as the age of the concrete increased. The 90-day strengths of Mixtures 25UG45 and 25UG60 (109 and 105 MPa [15.8 and 15.2 ksi], respectively) were close, even though there was more cement replacement by ultra-fine slag in Mixture 25UG60.

The specimens from Mixture 25UG60 had higher electrical resistivity and lower chloride diffusivity coefficient than Mixture 25UG45 at Day 28. However, the difference between those results were not significant. Leng et al.³⁰ indicated that chloride diffusion into the concrete was reduced as the amount of slag replacement was increased. However, the reduction of chloride diffusion was recorded when the slag replacement level was increased from 40 to 50%.²⁸ Considering the limited improvement in the results when the replacement amount was increased to 60%, it seems that the cement replacement percentage of 45% represented the ideal amount of cement replacement. This amount of cement replacement would allow maximum contribution from the ultra-fine slag on the mechanical and durability properties of the concrete. Tomisawa and Fujii.²⁵ observed that mixtures with replacement percentages higher than 70% by normal slag obtained lower compressive strength than the mixtures with lower normal slag content. Megat Johari et al.²⁹ similarly reported reduced compressive strengths in concrete mixtures with increasing amounts of normal slag replacement. A mixture with slag may have a more compact pore structure due to the formation of finer hydration products. However, when excessive slag was added into a mixture, the unreacted slag could form a weak link in the microstructure, resulting in reduced compressive strength.^{25,31} Regardless of the type and fineness of slag used in concrete mixtures, the compressive strength of the mixtures is reduced when the amount of slag in the mixture is too high.

CONCLUSIONS

The purpose of this research was to study the influence of types and amounts of supplementary cementitious materials on the early and ultimate strengths as well as durability properties of high-strength concrete for applications to marine concrete structures. Based on the study, the following conclusions can be made:

1. A good correlation exists between the electrical conductivity (reciprocal of electrical resistivity) and the chloride diffusivity coefficient of a concrete mixture. The two parameters are good indications of the development of concrete microstructure. Therefore, any of these two test methods can give an indication of the durability properties of very-high-strength concrete material.

2. The electrical resistivity of concrete increases as the concrete age increases. For a plain concrete mixture with a w/b of 0.25 (25CM), the electrical resistivity increases by 45, 24, and 8% between the ages of 7, 28, 56, and 90 days. The chloride diffusivity coefficient is reduced as the age and strength of the concrete mixtures increased. Between the ages of 7, 28, 56, and 90 days, the diffusivity coefficient reduces by 29, 40, and 28%, respectively. These two trends signified the improvement of the microstructure and the reduction in porosity of the mixtures.

3. The reduction of water in a concrete mixture will increase the compressive strength of the concrete, but it might not reduce the porosity significantly. In a mixture with a low w/b of 0.25, the inclusion of ground-granulated blast-furnace slag (GGBFS) may not improve the mechanical properties significantly. However, the contribution of the GGBFS to the durability properties of the concrete mixture is significant. This contribution was shown by the higher electrical resistivity and lower chloride diffusivity coefficients. A slag replacement of 45% will increase the durability (in terms of diffusivity coefficient) by 40%.

4. Increasing the fineness of the GGBFS increases the surface area available for hydrating reactions to take place. The increased rate of hydration can improve early-age concrete properties. In addition to the improvement in early-age properties, the long-term mechanical and durability properties of the mixtures with ultra-fine slag were also better. There is a 78% reduction in the chloride diffusivity coefficients at Day 7 between the two mixtures with 45% slag replacement (25G45 and 25UG45). At 90 days, the difference between the diffusivity coefficients is 60%.

5. The contribution from a small replacement of 10% silica fume has greater advantage to the long-term properties of the hardened concrete than a 30% cement replacement by ultra-fine GGBFS. The reduction in diffusivity coefficient on Day 28 with the inclusion of 30% ultra-fine GGBFS was only $0.05 \text{ m}^2/\text{s} \times 10^{-12}$ ($0.54 \text{ ft}^2/\text{s} \times 10^{-12}$) compared to Mixture 25SF10.

6. The ideal replacement level of cement by GGBFS to achieve the best results seems to be 45% based on the discussed results. Increasing the amount of cement replacement beyond 45% may not have further significant improvements in the concrete properties.

7. The inclusion of GGBFS and silica fume have similar effects in concretes with a w/b as low as 0.25, and it is essential in producing concrete material for durable marine structures, with very high early-age strength and long-term resistance against chloride ingress.

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