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Compressive Strength Development of Seawater-Mixed Concrete Subject to Different Curing Regimes

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The use of seawater as mixing water in reinforced concrete (RC) is currently prohibited by most building codes due to potential corrosion of conventional steel reinforcement. The issue of corrosion can be addressed by using noncorrosive reinforcement, such as glass fiber-reinforced polymer (GFRP). However, the long-term strength development of seawater-mixed concrete in different environments is not clear and needs to be addressed. This study reports the results of an investigation on the effect of different environments (curing regimes) on the compressive strength development of seawater-mixed concrete. Fresh properties of seawater-mixed concrete and concrete mixed with potable water were comparable, except for set times, which were accelerated in seawater-mixed concrete. Concrete cylinders were cast and exposed to subtropical environment (outdoor exposure), tidal zone (wet-dry cycles), moist curing (in a fog room), and seawater at 60°C (140°F) (submerged in a tank). Under these conditions, seawater-mixed concrete showed similar or better performance when compared to reference concrete. Specifically, when exposed to seawater at 60°C (140°F), seawater-mixed concrete shows higher compressive strength development than reference concrete, with values at 24 months being 14% higher. To explain strength development of such mixtures, further detailed testing was done. In this curing regime, the seawater-mixed concrete had 33% higher electrical resistivity than the reference concrete. In addition, the reference concrete showed calcium hydroxide leaching, with 30% difference in calcium hydroxide values between bulk and surface. Reference concrete absorbed more fluid and had a lower dry density, presumably due to greater seawater absorption. Seawater-mixed concrete performed better than reference concrete due to lower leaching because of a reduction in ionic gradients between the pore solution and curing solution. These results suggest that seawater-mixed concrete can potentially show better performance when compared to reference concrete for marine and submerged applications.

Keywords: compressive strength; durability; electrical resistivity; formation factor; seawater; thermogravimetric analysis.

INTRODUCTION

As fresh water is a finite resource, replacing fresh water with seawater in concrete mixing may be potentially advantageous. This is especially true in coastal regions, islands, and desert regions where fresh water may be scarce.[1] In addition, several locations may also face shortages of fresh water after natural disasters, and the use of seawater in reconstruction in such instances is likely to be beneficial. Nevertheless, the use of seawater in reinforced concrete (RC) is generally prohibited due to concerns regarding chloride-induced corrosion of steel reinforcement. However, seawater could potentially be used in unreinforced concrete or in concrete reinforced with non-corrosive rebar. The latter possibility becomes more feasible with advances, cost reductions, and greater usage of non-corrosive reinforcing bars. There are several unreinforced concrete structures along the coasts of Los Angeles and Florida which have used seawater for mixing and curing and have shown no significant long-term degradation at the time of inspection.[2,3] Literature has addressed the strength development of seawater-mixed concrete. Results typically show higher early-age strength in case of seawater-mixed concrete (by approximately 4 to 23%)[4-16]; however, the long-term strength results are inconclusive or contradictory. Some researchers show a slight reduction,[4,16] while others show comparable or higher long-term strength for seawater-mixed concrete.[9,15] Studies on compressive strength of seawater-mixed concrete after 20-year exposure to a simulated tidal pool suggest that the compressive strength of concrete was independent of the type of mixing water.[12] Similar observations have also been reported by others.[17]

Mixing concrete with seawater may also affect the microstructure and hydration products. Early-age gypsum precipitation has been observed; however, at later ages, this was not observed at later ages, and the types and amounts of phases formed after 1 year were not significantly affected by the water type.[8] Work on cement pastes has shown that a certain amount of chlorides could be incorporated in the calcium silicate hydroxide (C-S-H); however, calcium hydroxide and bound water amounts were not affected by the use of seawater as mixing water.[18] The use of seawater slightly increases the density and decreases the porosity and permeability of the concrete.[6,19]

A synergistic effect between supplementary cementitious materials and seawater has been shown in literature where seawater-mixed concrete with 5% metakaolin addition had 52% higher 28-day compressive strength compared to concrete mixed with fresh water and no metakaolin.[20,21] This difference was attributed to the acceleration of the pozzolanic reaction of metakaolin by seawater and a refinement of the pore structure in the seawater-mixed concretes with metakaolin. Seawater was proposed to be an accelerator for fly ash[22] and for ground-granulated blast-furnace slag.[7]

This study is part of a larger funded project that aims for the development of seawater-mixed concrete to be used without reinforcement, or with the use of non-corrosive rebar such

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as glass fiber-reinforced polymer (GFRP). As part of this project, the following topics have been investigated: hydration, pore solution, and porosity of seawater-mixed cement pastes[18]; long-term mechanical behavior of GFRP in seawater-mixed concrete[23]; drying and autogenous shrinkage in seawater-mixed mortars[24]; and hydration and shrinkage in cementitious materials mixed with desalination brines.[25] Long-term durability of the developed concrete mixtures under conditions of sulfate attack and alkali silica reaction is also being investigated. While others have looked at the long-term performance of seawater-mixed concrete, little research has been done on a direct comparison of reference concrete and seawater-mixed concrete in various environments, which is the objective of this study. This study is motivated by the fact that information about later-age strength development of seawater-mixed concretes is contradictory. Ingress and egress of ionic species from the matrix appears to cause reduction in concrete strength under specific conditions and this behavior is explained here using advanced experimental testing. To study this behavior, apart from conventional strength measurements, a set of specimens exposed to one curing condition (immersion in seawater at 60°C) is studied in detail using thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), electrical resistivity, water absorption, and density measurements to fundamentally explain the long-term strength development of seawater-mixed concrete under certain curing regimes.

RESEARCH SIGNIFICANCE

Although researchers generally agree that mixing concrete with seawater results in higher early-age strengths, information about later-age strength is contradictory. In addition, a detailed comparison of the performance of reference concrete and seawater-mixed concrete in various environments has not been performed. It is hypothesized that the use of different curing regimes could in part explain why differences in performance between reference concrete and seawater-mixed concrete are observed in literature. In addition, this study is novel as it shows why different later-age strength development in reference concrete and seawater-mixed concrete may be expected and identifies environmental regimes in which it may be advantageous to use seawater-mixed concrete by presenting data on long-term compressive strength and leaching characteristics. The latter is done by using advanced testing techniques such as TGA, EDX, and electrical resistivity which have not been extensively used for seawater-mixed concrete. Understanding of long-term strength behavior is required for the widespread usage of seawater-mixed concrete.

EXPERIMENTAL INVESTIGATION

Materials

A Type II cement (which is a commonly used cement type in the United States) meeting the requirements of ASTM C150/C150M-18[26] and a Type F fly ash conforming to ASTM C618-19[27] were used in this study. Their oxide compositions and the phase composition of the cement are listed in Table 1. Tap water and seawater from Biscayne Bay, FL were used as mixing water, with chemical composition (determined by inductively coupled plasma atomic emission spectroscopy [ICP-AES]) as shown in Table 2. Further details are presented elsewhere.[1,23] Miami oolite with a nominal maximum size of 25 mm (1 in.) was used as the coarse aggregate and silica sand with a nominal maximum size as 4.75 mm (3/16 in.) was used as the fine aggregate.

Table 1—Composition of cement and fly ash

Composition	Mass, %	
	Type II cement	Fly ash
SiO_2	20.50	46.80
Al_2O_3	4.90	19.30
Fe_2O_3	3.90	18.99
CaO	64.40	5.50
MgO	0.90	0.90
SO_3	2.60	2.23
$Na_2O_{eq.}$	0.25	0.88
Loss on ignition	2.10	3.10
Bogue phase calculation*		
C_3S	60	—
C_2S	14	—
C_3A	7	—
C_4AF	12	—

*According to cement chemistry notation, C is CaO, S is SiO_2, A is Al_2O_3, and F is Fe_2O_3.

Table 2—Chemical compositions of tap water and seawater used in concrete mixtures

Ions	Concentration, ppm	
	Tap water	Seawater
Calcium	90	389
Chloride	44	18,759
Iron	—	0.5
Potassium	6	329
Magnesium	6	1323
Sodium	26	9585
Sulfate	8	2489
Nitrate	1	0.1

Concrete mixtures

Two different concrete mixtures with water-cementitious materials ratio (*w*/*cm*) of 0.40 were cast: Mix A is the reference concrete (made with potable water), and Mix B is the seawater-mixed concrete. The mixture proportions of Mix B are identical to those of Mix A, but fresh water is substituted with seawater from Biscayne Bay, FL. Table 3 shows the mixture proportions. Concrete was mixed using a drum mixer. Aggregate moisture content was measured, and the amount of mixing water was adjusted accordingly. Aggregates were added into the mixer with approximately one-third of the mixing water and mixed for 3 minutes, after which the cementitious materials and the remaining water were added and mixed for 3 more minutes. Mixing

Table 3—Mixture proportions

Material	Units	Mix A	Mix B
Portland cement I-II (MH)	kg/m^3 (lb/yd^3)	332 (559)	332 (559)
Fly ash	kg/m^3 (lb/yd^3)	83 (140)	83 (140)
Tap water	kg/m^3 (lb/yd^3)	168 (283)	—
Seawater	kg/m^3 (lb/yd^3)	—	168 (283)
Coarse aggregate	kg/m^3 (lb/yd^3)	1038 (1750)	1038 (1750)
Fine aggregate	kg/m^3 (lb/yd^3)	612 (1032)	612 (1032)
Set-retarding admixture	mL/m^3 (gal./yd^3)	—	830 (0.2)
Air-entraining admixture	mL/m^3 (gal./yd^3)	310 (0.1)	310 (0.1)

was paused for 2 minutes while the sides of the mixing drum were scraped. Chemical admixtures were added as applicable, and the mixture was mixed for a final duration of 3 minutes. Slump, density, and air content of the fresh concrete were measured in accordance with ASTM C143/C143M-15a,[28] ASTM C138/C138M-17a,[29] and ASTM C231/C231M-17a,[30] respectively. The time of setting on the corresponding cement pastes was also measured by Vicat needle per ASTM C191-18.[31] The paste samples were mixed using mechanical mixer per ASTM C305-14.[32] Mixing water was placed in the mixing bowl to which cement was added and left to absorb water for 30 seconds. Then, the mixture was mixed at slow speed (140 ± 5 rpm) for 30 seconds. The mixer was paused for 15 seconds to scrape the sides of the bowl, after which the mixture was mixed for 60 seconds at medium speed (285 ± 10 rpm).

Curing regimes and compressive strength

Concrete cylinders with dimensions of 100 x 200 mm (4 x 8 in.) were cast per ASTM C39/C39M-18[33] using reference concrete (Mix A) and seawater-mixed concrete (Mix B). These samples were moist cured in a fog room (100% relative humidity and temperature of 23 ± 1°C [73.4 ± 1.8°F]) for 28 days. Early-age compressive strength was tested at 3, 7, and 28 days of moist curing (testing was performed as described in the following section using three repeat specimens). The effect of different curing regimes was then examined by monitoring the compressive strength after exposing the concrete cylinders to four different environments: subtropical environment, tidal zone, moist curing, and seawater at 60°C (140°F). While the study of tensile and flexural strength is also potentially interesting, these tests are out of the scope of this work, especially as the relationships between compressive strength and tensile (or flexural strength) should not change very significantly with the use of seawater. A short analysis of tensile strength data is presented elsewhere.[1] The curing regimes were selected considering possible environments that seawater-mixed concretes could be exposed to in real life. These environments are shown in Fig. 1 and are described as follows.

Subtropical environment—Specimens were placed outdoors in Coral Gables, FL, with an average temperature range of 15 to 33°C (59 to 91.4°F) and monthly average precipitation of 131 mm (5.16 in.).[34]

Tidal zone—The tidal zone used in this study is located at Biscayne Bay, FL with average water temperature range of 23 to 30°C (73.4 to 86°F)[34] and salinity range of 1.7 to 3.1%.[35] The specimens were placed such that they experienced wetting-and-drying cycles during and high and low tides, respectively.

Moist curing—Moist curing was done in a fog room with 100% relative humidity and a temperature of 23 ± 1°C (73.4 ± 1.8°F). This was considered to be the control environment.

Seawater at 60°C—Samples were immersed in seawater at 60°C (140°F) in a tank filled with the same seawater that was used for mixing (Table 2). A constant temperature was maintained using an immersion heater. Seawater was slowly circulated in and out of the tank to provide a constant exposure to seawater of fixed chemical composition. This is not an exposure that specimens are conventionally exposed to in real life; however, it was chosen as it causes the most degradation in GFRP mechanical properties and can be used for long-term GFRP performance prediction.[23] This exposure can be considered as an accelerated curing regime due to the elevated temperature increasing the rate of hydration[36] and the rate of potential chemical degradation.[23,37]

Concrete exposed to seawater at 60°C (140°F) is expected to show some reduction in strength due to leaching effects. To quantify the leaching and its effects on the strength development, further testing (detailed in the following sections) was performed on specimens immersed in seawater at 60°C (140°F) for 24 months. Other reasons that additional testing was performed for this curing regime are: a) seawater-mixed concrete shows significantly better performance than reference concrete in this curing regime (as discussed later in the text); and b) GFRP showed significant degradation of selected mechanical properties in this curing regime.[23] The testing regime that is carried out is quite extensive and it is therefore performed for only one curing condition; however, based on the findings here, performing such testing for other curing conditions can be advantageous, especially if smaller-scale specimens, such as cement paste or mortar are used. Such work is ongoing in the lab.

Concrete compressive strength was tested after 6, 12, 18, and 24 months. Three concrete specimens for each mixture were extracted from the different environments, surface dried, and brought to the laboratory. Sulfur capping was applied on all the samples which were left at ambient temperature inside the lab for 8 to 12 hours before testing. Compressive strength testing was carried out using a mechanical testing device and at a stress rate of 0.25 ± 0.05 MPa/s (35 ± 7 psi/s).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on concrete samples exposed to seawater at 60°C (140°F) after 24 months. Concrete samples were extracted from seawater, surface dried using a towel, and then broken into pieces. Pieces were collected from near the surface and the bulk of these specimens. These pieces were gently crushed with mortar and pestle separating out the coarse and fine aggregate. The samples were then sieved through a 75 μm (ASTM No. 200) sieve to ensure that only cement paste was used for the TGA testing (although some sand could still be present

Fig. 1—Different curing regimes: (a) subtropical environment; (b) tidal zone; (c) moist curing; and (d) immersed in seawater at 60°C (140°F).

in the paste). To obtain a representative value, five samples from each location, surface and bulk, were tested for both mixtures. The TGA was performed in an inert nitrogen atmosphere by increasing the temperature at the rate of 10°C/minute (18°F/minute) from 23 to 1000°C (73.4 to 1832°F). The tangential method was used to quantify the amount of calcium hydroxide present in the sample.[38]

Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) was used to investigate potential ingress and egress of various ions from and into the concrete after being cured in seawater at 60°C (140°F) for 24 months. Representative samples were taken from near the surface and the bulk of concrete cylinders (in the same manner as was done for TGA testing) and impregnated in hot acrylic resin at a temperature of 120°C (248°F) and pressure of 50 mbar (0.73 psi). After the acrylic resin hardened, samples were polished using SiC grit at different levels (that is, 180, 300, 600, and 1200) using grinding and polishing equipment. The specimens were then fine polished using a wet-polishing agent and 3 μm and 1 μm polycrystalline diamond paste. Prior to imaging, specimens were placed in a vacuum oven at 50°C (122°F) for 24 hours to remove any moisture introduced during polishing and then gold-coated prior to imaging. EDX was performed on randomly chosen near-surface or bulk specimens from the concretes. Analysis was performed on at least 10 different spots on the sample. While the exact parameters used for testing varied, typical settings were: accelerating voltage = 20 kV, working distance = 10 mm (0.39 in.), spot size = 65, magnification = 1500×, and dead time = 20 to 30%.

Electrical resistivity and formation factor

Electrical resistivity and formation factor (a parameter that describes the microstructure and transport properties of the concrete)[39-42] of the concrete cylinders made with reference concrete and seawater-mixed concrete were measured after immersion in seawater at 60°C (140°F) for 24 months. Concrete cylinders were removed from the storage chamber and wiped with a cloth to achieve surface-dry conditions. Two stainless steel plate electrodes with a diameter of 102 mm (4 in.) were used with two pieces of sponge saturated with seawater between specimen and plate electrodes to ensure an electrical connection. The resistivity of the concrete cylinders was measured using a bulk resistivity meter with a frequency of 1 kHz at 23 ± 1°C (73.4 ± 1.8°F).[41] Although resistivity measurements are a good indicator of the concrete quality, to have a better understanding of the porosity and the pore connectivity, the chemistry of the pore solution should also be considered. To this end, the formation factor was determined through normalization of the bulk electrical resistivity by the pore solution resistivity. Because the storage solution (seawater) was being circulated and replaced regularly and the specimens were immersed for a long period of time at high temperature (60°C [140°F] for 24 months), it was assumed that the concentration of the pore solution in the concrete was the same as the storage solution (seawater).[39] In addition, it was assumed that the

Table 4—Fresh properties and setting time

Mixture	Slump, mm (in.)	Density, kg/m^3 (lb/ft^3)	Air content, %	Setting time, min	
				Initial	Final
Mix A	100 (4)	2350 (146.7)	1.3	255	435
Mix B	95 (3.75)	2359 (147.3)	1.0	195	375

specimens are fully saturated after exposure to these storage conditions. Formation factor (F) of the concrete specimens cast with reference concrete and seawater-mixed concrete was calculated from Eq. (1)[41]

$$F = \rho_{SAT}/\rho_{ps\text{-}SAT} \tag{1}$$

where ρ_{SAT} is the electrical resistivity of the concrete specimen (Ω-m); and $\rho_{ps\text{-}SAT}$ is the electrical resistivity of the pore solution (Ω-m). The value of $\rho_{ps}\text{-}_{SAT}$ is the same as the resistivity of the seawater which was estimated from OH^-, K^+, and Na^+ concentrations using methods from literature.[43]

Water absorption and dry density

Water absorption of the concrete cylinders made with reference concrete and seawater-mixed concrete was measured after immersion in seawater at 60°C (140°F) for 24 months. It was assumed that the specimens are fully saturated after 24-month immersion. Three specimens from each mixture were removed from the storage chamber and wiped with a cloth to achieve saturated surface-dry conditions, and then dried in the oven at 105°C (221°F) for 48 hours. Water absorption was calculated from Eq. (2)

$$\text{Water absorption}\,(\%) = \frac{\text{Saturated weight} - \text{Oven-dry weight}}{\text{Oven-dry weight}} \times 100 \tag{2}$$

The oven-dry weight was also used to calculate the dry density of these samples. The water absorption and dry densities (measured based on ASTM C642-13[44]) are used as indicators of ingress of seawater and leaching of material into seawater, respectively.

TGA, EDX, electrical resistivity, and water absorption were carried out only on concrete cylinders immersed in seawater at 60°C (140°F) to explain the long-term compressive strength behavior in this regime because all other environments generally showed a difference of less than 10% in the strengths between the two mixtures.

EXPERIMENTAL RESULTS AND DISCUSSION

Fresh properties

Fresh properties of the concrete and setting times of the cement pastes are shown in Table 4. Slump, density, and air content of reference concrete and seawater-mixed concrete are similar. The same trend has been reported by other researchers.[6,10] Setting times were affected by the use of seawater. Cement paste mixed with seawater showed an earlier setting by approximately 60 minutes, which was also qualitatively observed during casting concrete specimens. This is due to the acceleration of the cement hydration by the chlorides in seawater.[6-8] When accelerated setting is not desirable, set times may be controlled by using set retarding admixtures.[11]

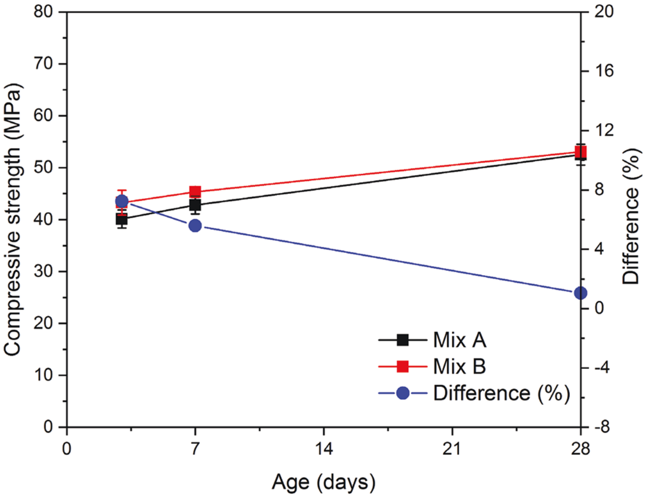

Fig. 2—Early-age compressive strength and percentage difference. (Note: 1 MPa = 145 psi.)

Early-age compressive strength

Figure 2 shows the compressive strength evolution in the first 28 days. The figure also shows the percentage difference between the reference concrete and seawater-mixed concrete (calculated as [Mix B – Mix A]/Mix A, expressed as a percentage). In this figure and in similar figures in the paper, the error bars on each side represent one standard deviation of the average. Seawater-mixed concrete showed higher compressive strength after 3 and 7 days by 7.5% and 6%, respectively. This is due to the accelerating effect of chloride on the early-age hydration.[7,8] This difference decreases with time, as both mixtures show comparable performance after 28 days (at this age, seawater-mixed concrete shows 1% higher strength). The same trend was observed by other researchers.[2,5-16]

Later-age compressive strength

Subtropical environment—Figure 3 shows the compressive strength development and the percentage difference of the reference concrete and seawater-mixed concrete cylinders exposed to the subtropical environment of Coral Gables, FL. The strength of the seawater-mixed concrete increases continuously whereas the strength of the reference concrete increases until 12 months and then subsequently slightly reduces. In general, the strength development of the concrete mixtures is comparable; however, at 24 months exposure to ambient temperature, the seawater-mixed concrete shows a 7% higher compressive strength than the reference concrete. This is likely explained by the accelerating effect of

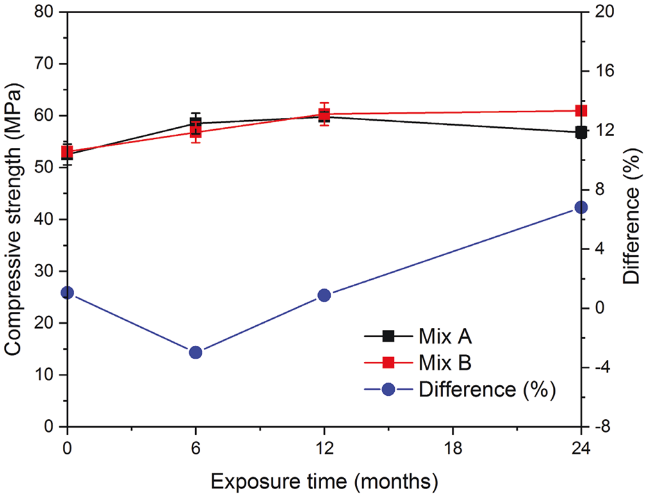

Fig. 3—Compressive strength and percentage difference in subtropical environment for 24 months. (Note: 1 MPa = 145 psi.)

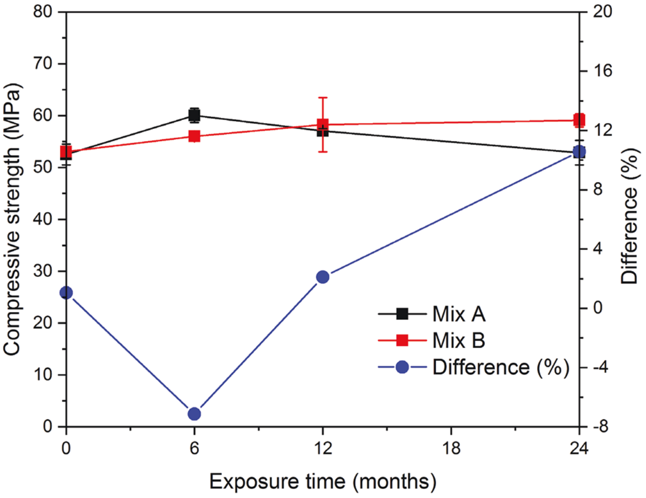

Fig. 4—Compressive strength and percentage difference in tidal zone for 24 months. (Note: 1 MPa = 145 psi.)

seawater on the fly ash reaction.[22] It is possible that in these conditions, seawater-mixed concrete has a greater degree of pozzolanic reaction of the fly ash, leading to greater strength at later ages. These results are in agreement with literature. Authors who tested concrete cylinders after 28 months air curing at 20°C (68°F)[4] and fly ash-blended paste specimens for 12 months at 20°C (68°F)[22] both showed similar or slightly higher strength development in seawater-mixed concrete.

Tidal zone—Figure 4 shows the compressive strength development and the percentage difference of the reference concrete and seawater-mixed concrete cylinders exposed to the tidal zone. The strength of the seawater-mixed concrete increases continuously whereas the strength of the reference concrete increases until 6 months and subsequently decreases. At 24 months exposure to the tidal zone, the seawater-mixed concrete shows a 12% higher compressive strength than the reference concrete. One reason for the better performance of seawater-mixed concrete could be the greater degree of pozzolanic reaction of the fly ash, leading to greater strength at later ages.[22] Another possible reason is lower leaching in the seawater-mixed concrete compared to reference concrete when exposed to the tidal zone. The difference between the pore solution ionic concentration of the reference concrete and the surrounding seawater could lead to the leaching of alkalis and calcium hydroxide from the sample, which can cause an increase in the porosity and reduce the strength.[41] The pore solution ionic concentrations in the seawater-mixed concrete are more similar to the surrounding seawater (as an example, sodium and chloride concentrations in pore solutions extracted from a paste mixture similar to Mix A at 28 days are 0.1 M and 0.0 M; corresponding values for a mixture similar to Mix B are 0.7 and 0.5 M, while values for seawater are 0.5 and 0.6 M). Therefore, leaching in the seawater-mixed concrete is likely reduced.[18] Results from literature for tidal zone exposure are contradictory. Mohammed et al.[12] showed similar or higher compressive strength for the concrete cast using cement and fly ash blends mixed with seawater compared to reference concrete exposed to simulated tidal zone for 15 years. Otsuki et al.[17] also reported approximately 5% higher compressive strength for the concrete specimens mixed with seawater without any supplementary cementitious materials exposed to tidal zone for 20 years. On the other hand, higher compressive strength by 5 to 10% for concrete specimens mixed with fresh water without any supplementary cementitious materials was reported after exposure to alternate wetting-and-drying cycles in simulated tidal zone for 18 months.[11] This contradiction could be possibly due to variability in the used materials or differences in mixture designs. Nevertheless, when one considers the effect of leaching, it is intuitive that seawater-mixed concrete shows a better compressive strength development.

Moist curing—Figure 5 shows the compressive strength development and percentage difference of the reference concrete and seawater-mixed concrete cylinders exposed to moist curing. Both concretes show an increase in strength until 6 months and then a subsequent decrease. The strength development of the concrete mixtures is comparable, however, at 24 months exposure to moist curing, the seawater-mixed concrete shows a 4% lower compressive strength than the reference concrete. The same ideas regarding leaching are also applicable in this context. In a moist curing condition, the surface of the concrete samples is covered with water. There is a larger difference in ionic strengths between water and the seawater-mixed concrete when compared to reference concrete (as an example, ionic strengths of pore solutions extracted from paste mixtures similar to Mix A and Mix B at 28 days are approximately 0.3 M and 1.0 M, respectively).[18] This may result in leaching of calcium hydroxide and alkalis from the seawater-mixed concrete, which may alter the porosity and microstructure[45,46] and result in a reduction of the strength. These results are in agreement with literature, which shows reductions between 5 and 20% in compressive strength of seawater-mixed concrete, compared to reference concrete, increasing with the curing duration (which varied between 6 and 28 months).[4,6,47] The aforementioned results are for concrete made without supplementary cementitious materials and they show a greater reduction in

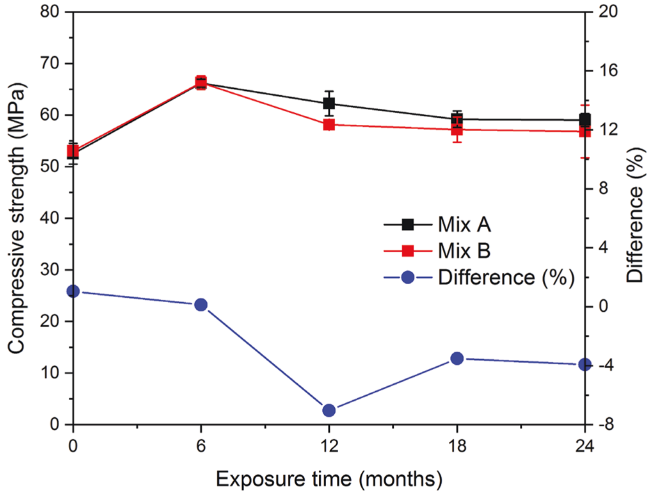

Fig. 5—Compressive strength and percentage difference in moist curing for 24 months. (Note: 1 MPa = 145 psi.)

seawater-mixed concrete strength (compared to reference concrete) that the one observed here. This is possibly due to the enhanced pozzolanic reaction of fly ash somewhat mitigating the strength reduction due to leaching[24] or a reduction in the extent of calcium hydroxide leaching in the presence of fly ash.[48]

Seawater at 60°C (140°F)—Figure 6 shows the compressive strength development and percentage difference of the reference concrete and seawater-mixed concrete cylinders exposed to seawater at 60°C (140°F). Both concretes show an increase in strength until 6 months and then a subsequent decrease. In general, seawater-mixed concrete shows higher compressive strength development and values at 24 months are 14% higher than reference concrete.

The leaching mechanism explained for the tidal zone also likely applies to this scenario. The higher temperature and the submersion may cause a greater extent of leaching, which explains the greater difference in strength between reference concrete and seawater-mixed concrete (as compared to the tidal zone). Figure 7 shows a layer of leached material covered the surface of a concrete cylinder cast with reference concrete and immersed in seawater at 60°C (140°F) for 24 months. Strength loss due to leaching has been suggested by other researchers for reference concrete exposed to seawater at room temperature.[22] Jensen and Pratt[22] immersed cement and fly ash pastes mixed with seawater and distilled water in seawater at 8°C (46°F) for 12 months and observed that seawater-mixed specimens showed higher compressive strength due to the leaching of calcium hydroxide in pastes mixed with distilled water when cured in seawater. The same trend was noted by others[49] when mortar specimens with 20% fly ash replacement were immersed in seawater for 5 months. On the other hand, other studies[16] reported 20% lower compressive strengths for the concrete specimens mixed with seawater compared to specimens mixed with fresh water after curing in seawater for 3 months. Islam et al.[47] showed 1 to 7% reduction after 3 months curing in seawater when seawater was used as the mixing water. Concrete samples mixed with seawater and supplementary cementitious materials show better performance than samples without supplementary cementitious materials, showing the synergistic effect of seawater and supplementary cementitious materials.[12,17]

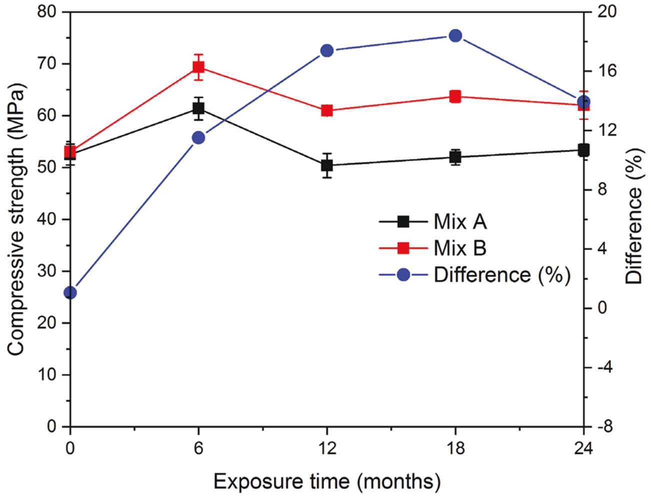

Fig. 6—Compressive strength and percentage difference in seawater at 60°C (140°F) for 24 months. (Note: 1 MPa = 145 psi.)

Fig. 7—Layer of leached material covering surface of concrete cylinder cast with reference concrete (Mix A) after immersion in seawater at 60°C (140°F) for 24 months.

Comparison of compressive strength development in different curing regimes—Reference concrete performed well when cured in the moist room or outside the lab. However, the lowest compressive strengths for reference concrete were recorded at 24 months of curing in tidal zone and when cured in seawater at 60°C. As postulated earlier, the differences between the pore solution ionic concentration of the reference concrete and surrounding seawater could lead to the leaching of alkalis and calcium hydroxide from the sample which can cause an increase in the porosity and negatively affect the strength. On the other hand, seawater-mixed concrete cured in seawater at 60°C (140°F) had the highest compressive strength at 24 months compared to other curing regimes and the lowest compressive strength was in moist curing conditions. The leaching mechanism due to the large difference in ionic strengths between pore solution and curing environment can also explain the relatively inferior performance of the seawater-mixed concrete in the moist room. Analysis of variance (ANOVA) shows no significant difference between the compressive strength of reference and seawater-mixed concrete at 24 months considering all curing regimes.

Thermogravimetric analysis (TGA)

Table 5 shows the calcium hydroxide content near the surface and in the bulk of the reference concrete and seawater-mixed concrete specimens after exposure to seawater at 60°C (140°F) for 24 months. The amounts of calcium hydroxide near the surface and in the bulk of the concrete specimens cast with seawater-mixed concrete are 4.87 g/100 g (0.17 oz/3.52 oz) paste and 4.61 g/100 g (0.16 oz/3.52 oz) paste, respectively. However, lower amounts of calcium hydroxide, 2.92 g/100 g (0.10 oz/3.52 oz) paste and 4.23 g/100 g (0.15 oz/3.52 oz) paste were measured for the reference concrete near the surface and in the bulk, respectively. Significantly lower calcium hydroxide content near the surface of the reference concrete confirms the hypothesis that the ionic concentration gradient between the pore solution and surrounding environment causes the leaching, which negatively affects the compressive strengths. As the unaltered calcium hydroxide contents are unknown, the extent of leaching is not possible to determine accurately, however, the large difference (30%) in values between the surface and the bulk for the reference concrete suggests that the calcium hydroxide leaching is significant. Others[22] reported similar calcium hydroxide leaching in paste specimens mixed with distilled water and cured in seawater at 8°C (46°F) for 365 days and suggested that it was responsible for strength loss in these specimens.

Energy-dispersive X-ray spectroscopy (EDX)

EDX was used to find patterns in the chemical compositions of the bulk and areas near the surface of the reference concrete and seawater-mixed concrete specimens after exposure to seawater at 60°C (140°F) for 24 months. Similar chloride contents were observed in the bulk and near the surface of both concrete mixtures (1.72 to 1.87%). The lack of a significant gradient between the chloride contents in the bulk and surface, and the similar values between the two concrete specimens suggests that the chloride has fully diffused into the reference concrete specimens due to ionic gradients between the initial pore solution and seawater and the high exposure temperature (60°C [140°F]).

Electrical resistivity and formation factor

Table 6 shows electrical resistivity and formation factor values of the reference concrete and seawater-mixed concrete specimens after exposure to seawater at 60°C (140°F) for 24 months. The electrical resistivity of seawater-mixed concrete, 540.2 Ω-m (21268 Ω-in.), was 33% higher than the electrical resistivity of the reference concrete, 406 Ω-m (15984 Ω-in.). These results are in agreement with the compressive strength results (16% greater compressive strength for seawater-mixed concrete) and confirm that the seawater-mixed concrete performs better when immersed in seawater at 60°C. These results are broadly similar to values in literature which suggests electrical resistivity values of 300 to 1000 Ω-m (11,811 to 39,370 Ω-in.) for concrete mixtures with 25% or more fly ash at ages of 10 years or greater.[50] An exact comparison is not possible as data does not exist for seawater-mixed concretes or for concretes immersed in seawater at 60°C (140°F). The formation factor of these concretes can be determined through normalization of the bulk electrical resistivity by pore solution resistivity. Due to the sufficiently long storage time and the use of circulating seawater during the storage, it is assumed that there is a complete ingress of the seawater into the concrete, or, in other words, that the pore solution in both concretes is the seawater. A method from literature[43] was used to calculate the resistivity of seawater based on its composition, which is 0.222 Ω-m (8.74 Ω-in.). Formation factor can then be calculated for both concrete mixtures. Formation factor of seawater-mixed concrete (2422) was 33% higher than that of the reference concrete (1829). In a related study, the electrical resistivity of pore solutions extracted from paste mixtures similar to Mix A and B at 91 days was determined to be 0.147 Ω-m (5.79 Ω-in.) and 0.08 Ω-m (3.15 Ω-in.), respectively.[18] If an incomplete extent of solution ingress is assumed, then the pore solution resistivity values of Mix A and Mix B would be between 0.147 to 0.222 Ω-m (5.79 to 8.74 Ω-in.) and 0.08 to 0.222 Ω-m (3.15 to 8.74 Ω-in.), respectively, which suggests that the difference in the formation factors would be even greater than 33%.

Table 5—Calcium hydroxide content near surface and in bulk of concrete specimens exposed to seawater at 60°C (140°F) for 24 months

Mixture	Calcium hydroxide content, g/100 g paste (oz./3.52 oz. paste)	
	Near surface	Bulk
Mix A	2.92 (0.10)	4.23 (0.15)
Mix B	4.87 (0.17)	4.61 (0.16)

Water absorption and dry density

Table 7 shows water absorption and dry density values of the reference concrete and seawater-mixed concrete after 24 months immersion in seawater at 60°C. In that time period, reference concrete absorbed 3.5% water (seawater), which is larger than the corresponding value for seawater-mixed concrete (2.8%). This shows a greater extent of seawater ingress in the reference concrete than the seawater-mixed concrete. The dry density of the seawater-mixed concrete (2350 kg/m^3 [146.7 lb/ft^3]) is greater than reference concrete (2312 kg/m^3 [144.3 lb/ft^3]). When compared to the fresh density (Table 4), reference concrete showed a 38 kg/m^3 (2.36 lb/ft^3) reduction; however, seawater-mixed concrete showed a 9 kg/m^3 (0.56 lb/ft^3) reduction, showing that the leaching of material from the seawater-mixed concrete

Table 6—Resistivity measurements and formation factor

Mixture	Resistivity, Ω-m (Ω-in.)	Standard deviation, Ω-m (Ω-in.)	Formation factor
Mix A	406.0 (15,984)	57.1 (2248)	1829
Mix B	540.2 (21,268)	142.4 (5606)	2433

Table 7—Water absorption and dry density

Mixture	Water absorption, %	Dry density, kg/m^3 (lb/ft^3)
Mix A	3.46	2312 (144.3)
Mix B	2.79	2350 (146.7)

is significantly reduced. These observations confirm the hypothesis that ionic concentration gradients between the pore solution and surrounding environment cause leaching and negatively affect the compressive strengths in reference concrete exposed to seawater.

The leaching phenomena and the potential synergy between seawater and fly ash strongly suggest that the long-term performance of seawater-mixed concrete would be better than reference concrete in seawater-submerged applications or marine environment. These results provide a clear motivation for the use of seawater in construction applications for unreinforced members or using GFRP. Further testing, including demonstrating long-term durability under conditions of sulfate attack and alkali silica reaction is underway.

CONCLUSIONS

This study focused on a detailed comparison of the strength development of reference concrete and seawater-mixed concrete exposed to different curing regimes and explained the differences in strength in these curing regimes. The following conclusions are drawn from this study:

1. Comparable performance in terms of compressive strength was observed between reference concrete and seawater-mixed concrete when exposed to subtropical environment (outdoor exposure), tidal zone (wet-dry cycles), and moist curing (in a fog room); however, seawater-mixed concrete showed 14% higher compressive strength at 24 months when exposed to seawater at 60°C (140°F).
2. Strength differences between reference concrete and seawater-mixed concrete may be explained by fluid ingress and egress of calcium hydroxide and alkalis, depending on concrete mixture design and external environment.
3. A synergistic effect between seawater and fly ash seems to exist, which in part may explain the better performance of seawater-mixed concrete when exposed to seawater at 60°C.
4. Thermogravimetric analysis results confirmed that calcium hydroxide leached from the surface of the reference concrete specimens after exposure to seawater at 60°C (140°F) after 24 months as differences in the amounts of calcium hydroxide in bulk and surface were approximately 30%.
5. Electrical resistivity and formation factor were about 33% higher for seawater-mixed concrete compared to reference concrete after exposure to seawater at 60°C (140°F) after 24 months.
6. Higher water absorption and a greater reduction in the density of reference concrete compared to seawater-mixed concrete were observed after exposure to seawater at 60°C (140°F) after 24 months.

These results suggest that seawater-mixed concrete can potentially show better performance when compared to reference concrete for marine and submerged applications. This is mainly due to the lower ionic gradients between the pore solution of the seawater-mixed concrete and surrounding marine environment, and consequently lower leaching.

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