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Sulfate resistance of high-performance concrete

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Abstract

High-performance concrete mixes containing various proportions of natural pozzolan and silica fume (up to 15% by weight of cement) were prepared and stored in sodium and magnesium sulfate solutions, in Dead Sea and Red Sea waters. The progressive deterioration and the relative sulfate resistance of these mixes were evaluated through visual observations, ultrasonic pulse velocity measurements, and relative strength determinations. The investigation indicated that the concrete mix containing 15% natural pozzolan, and 15% silica fume showed the best protection in sulfates solutions and sea waters. It retained more than 65% of its strength after one year of storage in sulfates solutions and sea waters. The superior resistance of that mix against sulfate attack is attributed to the pore refinement process and further densification of the transition zone occurring due to the conversion of lime forming from the hydration of cement into additional binding material through lime-pozzolan reaction. This investigation recommends the use of silica fume in combination with natural pozzolan for better performance in severe sulfate environments.

Keywords: High-performance concrete; Natural pozzolan; Silica fume; Portland cement mortar

1. Introduction

High-performance concrete is defined as concrete that meets special performance and uniformity requirements that cannot always be achieved routinely by using conventional materials and normal mixing, placing, and curing practices. Thus, a high-performance concrete is a concrete in which certain characteristics are developed for a particular application and environment. For example, concrete that provides substantially improved durability under severe service conditions, extraordinary properties at earlier ages, or substantially enhanced mechanical properties are potential HPCs. These concretes may contain materials such as fly ash, silica fume, ground granulated slags, natural pozzolan, fibers, chemical admixtures, and other materials, individually or in various combinations [1–4].

Engineers are making increasing use of high-performance concrete because of its availability, greater performance, including the highest possible durability, and efficient use of portland cement, which conserves natural resources and energy. From a structural design standpoint, high-performance concrete allows more slender structural elements with greater rigidity (higher modulus of elasticity) for smaller deflection, less creep, and a high MPa/$ ratio. Unfortunately, very few material building codes have provisions for high-performance concrete at present [1].

One of the main causes of deterioration in concrete structures is the corrosion of concrete due to its exposure to harmful chemicals that may be found in nature such as in some ground waters, industrial effluents and sea waters. The most aggressive chemicals that affect the long term durability of concrete structures are the chlorides and sulfates. The chloride dissolved in waters increase the rate of leaching of portlandite and thus increases the porosity of concrete, and leads to loss of stiffness and strength. Calcium, sodium, magnesium, and ammonium sulfates are—in increasing order of hazard—harmful to concrete as they react with hydrated cement paste leading to expansion, cracking, spalling and loss of strength [5].

The rate at which the hardened cement paste is deteriorated due to the exposure to harmful chemicals depends mainly on the concentration of the chemicals in water, the time of exposure and the chemical resistance

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of concrete. Extensive investigations have been carried out on the use of fly ash and silica fume in concrete during the past two decades and have consequently led to their widespread application in the construction industry [6–11]. Many national standards also exist which determine the degree of attack, and this primarily on the basis of the concentration of the aggressive substances. However, the chemical resistance of high-performance concrete using silica fume, fly ash, natural pozzolan, and superplasticizers are issues which have not yet received sufficient attention from the research community [10]. Hence, this investigation was undertaken to study and define a better concrete mix, containing local natural pozzolan and silica fume which can produce the maximum protection of the concrete in sulfate environment. The present work examines the progressive deterioration of concrete mixtures containing various combinations of natural pozzolan and silica fume due to exposure to sulfate solutions and sea waters.

Table 1
Characteristics of cements, natural pozzolan, and silica fume used in this study

Oxide (%)	Natural pozzolan	Silica fume	Cement (Type I)	Pozzolanic cement
SiO_2	40.8	93	20.9	22.3
Al_2O_3	12.8	0.4	5.6	6.0
Fe_2O_3	10.5	1.2	3.1	4.0
CaO	11.8	0.2	62.7	55.8
MgO	9.1	1.2	2.2	4.8
Na_2O	2.3	0.1	0.2	0.4
K_2O	1.1	1.1	0.8	0.8
SO_3	0.1	0.3	2.9	2.7
Loss on ignition (%)	9.30	0.75	1.30	2.48
Specific gravity	2.68	2.10	3.15	3.12
Specific surface (m^2/kg)	600	20,000[a]	300	434

[a] The specific surface of silica fume is measured by the nitrogen adsorption technique.

2. Experimental investigation

An experimental program was designed to produce a high-performance concrete mix for the best protection in sulfate environment by adding several combinations of a local natural pozzolan and silica fume. The materials used and the experimental procedures are described in the following sections.

2.1. Materials

Locally available ordinary portland cement (ASTM Type I) and portland pozzolana cement complying with Jordanian specification JSS 219 were used. The natural pozzolan was a blend of certain volcanic tuffs from Tal Rimah region of north eastern Jordan and the same material used in the production of portland pozzolana cement. The Silica fume was in powder form with an average of 93% silicon dioxide. The chemical composition and some physical characteristics of these materials are given in Table 1. The superplasticizer used was a naphthalene formaldehyde sulfonated superplasticizer with 41% solids content and a specific gravity of 1.21. The superplasticizer was incorporated in all mixes and the content was adjusted slightly for some mixes to maintain the same workability. The coarse and medium-size aggregates were crushed limestone with maximum size of 10 and 5 mm, respectively. Natural silica sand with a fineness modulus of 2.66 was used for making mortar and concrete mixes.

2.2. Mix proportions

The objective was to produce high-performance and workable concretes containing local natural pozzolan and silica fume. The laboratory program conducted in this investigation focused on five basic mixes in which silica fume and natural pozzolan contents were varied between 0 and 15% (by weight of cement). For comparison purposes, one of these mixes (Mix 2) was designed using commercially produced portland pozzolana cement which contains approximately 15% natural pozzolan as an interground with cement clinker. The details of these mixes are given in Table 2. All the concrete mixes were prepared with superplasticizer at a dosage of approximately 2 l per 100 Kg of the total cementitious materials. The concretes made were of similar workability and water to cementitious materials ratio. They consisted of approximately 400 Kg/m^3 of portland cement (Type I) with the addition of 0, 20, 40, and 60 Kg/m^3 of silica fume and natural pozzolan (0%, 5%, 10%, 15% by weight of cement).

2.3. Mixing and casting

The concrete mixes were prepared using a tilting drum mixer of 0.15 cubic meter capacity. The interior of the drum was initially washed with water to prevent absorption. The coarse and medium aggregate fractions were mixed first, followed by the cement, part of the sand, and the water containing the required amount of superplasticizer. The final mixing stage involved the addition of the natural pozzolan and silica fume, and the remaining sand. One-forth of the superplasticizer was always retained to be added during the last 3 min of the mixing period. The concrete prepared was poured in steel molds which were oiled and placed on the vibration table, and vibrated at low speed. After each mold was properly filled the vibration speed was increased to ensure good compaction.

Table 2
Concrete mix quantities (kg/m^3)

Mix designation	W/(C + SF + NP)	CA (10 mm)	CA (5 mm)	S	C	NP	SF	SP (L)	W
1	0.35	995.0	115.0	740.0	400.0	–	–	10	140
2[a]	0.35	992.0	112.0	740.0	400.0	–	–	10	140
3	0.35	955.0	106.1	707.4	400.0	20	20	10	154
4	0.35	913.1	101.5	676.6	400.0	40	40	10	168
5	0.35	871.6	96.8	645.6	400.0	60	60	10	182

CA: coarse aggregate, S: sand, C: cement, NP: natural pozzolan, SF: silica fume, SP: superplasticizer, W: water.
[a] Mix 2 only contains commercially produced portland pozzolana cement; Mixes 1,3,4,5 contain ordinary portland cement.

Table 3
Compressive strength of concrete mixes

Mix designation	28-day strength	Compressive strengths at 360 days (MPa)				
		Na_2SO_4	$MgSO_4$	Red Sea	Dead Sea	Tap water
1	54.8	37.2 (0.56)	28.4 (0.43)	44.5 (0.67)	25.5 (0.38)	66.5 (100)
2	67.1	65 (0.85)	35.4 (0.46)	72.8 (0.95)	42 (0.55)	76.5 (100)
3	71.9	60 (0.70)	41.5 (0.48)	75 (0.88)	48.5 (0.57)	85.7 (100)
4	79.5	76 (0.77)	49.8 (0.51)	73 (0.74)	58.5 (0.60)	98.2 (100)
5	71.8	71 (0.93)	49.8 (0.65)	57.5 (0.75)	50.2 (0.66)	76.5 (100)

2.4. Curing and testing

After casting, the specimens were covered with wet burlap and stored in the laboratory at 23 °C and 65% relative humidity for 24 h and then demoulded and placed under water. Each specimen was labeled as to the date of casting, mix used and serial number. The specimens were then taken out of water a day before testing and dried in air. Some of the specimens were used for compressive strength determination, and the rest were kept in sulfate solutions and sea waters for sulfate resistance evaluation.

2.4.1. Compressive strength determination

The compressive strength of the concrete mixes was measured on 10-cm cubes that were cast and cured in steel molds, and tested using Avery Denison compression machine of 2000 kN capacity at a rate of 150 kN/min following ASTM C 39 standards [12]. The compressive strengths were determined after 28 days, and one year of water curing. The strength results listed in Table 3 are the average of three specimens.

2.4.2. Resistance to sulfate attack

To evaluate the resistance of the proposed mixes to sulfates and aggressive chemicals, 10-cm cubic specimens were prepared following the guide lines of ASTM C 39. After 28-day moist curing, the specimens were submerged in 20% magnesium sulfate solution, 20% sodium sulfate solution, sea waters and Tap water. Sulfates concentrations were kept relatively high to accelerate deterioration and also to compensate for small variations in concentration during the test.

3. Results and discussion

The progressive deterioration of the specimens submerged in sulfate solutions, sea and tap waters was monitored periodically by observing the visual changes in the cubes such as cracking, abrasions and spallings. Relative strength determination with respect to strengths of control specimens stored in tap water were conducted at final stages of the test. Since the strength tests meant the termination of the experiment, they were delayed as much as possible in this investigation. The compressive strength of the cubes was determined after one year of submersion in sulfates solutions and sea waters. The results are presented in Table 3. For comparison, relative strengths as fractions of control specimen values stored in tap water were also calculated and indicated inside parantheses beside the strength figures. Ultrasonic pulse velocity (UPV) measurements were also taken at the beginning of the test and periodically afterwords for all mixes.

4. Exposure to sulfates

Sulfates react with various phases of hydrated cement paste leading to expansion, cracking, and spalling. The sulfate attack is generally attributed to the formation of expansive ettringite and gypsum, which are known to precipitate by through-solution mechanism [5]. Investigations by Mehta, however, suggested that the sulfate attack is partially due to the cement paste losing its stiffness when exposed to sulfate rich environment [5].

As seen from Table 3 and Fig. 1, after one year of storage in sulfate solutions (Na_2SO_4, and $MgSO_4$), the

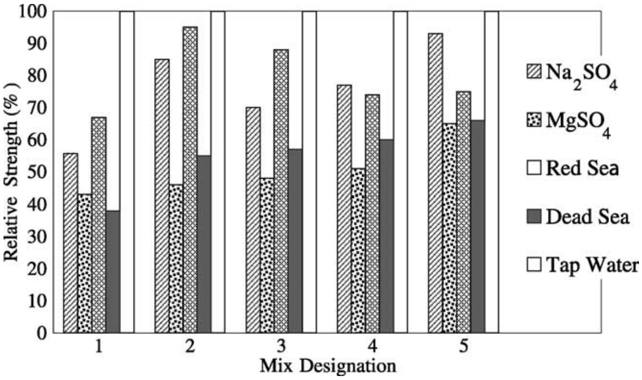

Fig. 1. Relative strength of concrete mixes stored in sulfate soutions and sea waters with respect to concrete mix stored in tap water.

mix containing ordinary portland cement only (Mix 1) showed a sharp reduction in compressive strength compared to those stored in tap water. The periodic visual observation indicate that signs of deterioration due to sulfate attack occurred near the corners of the cubes submerged in the previous solutions as shown in Figs. 2 and 3. The corners were the first to spall off because near the corners the intrusion will be from the two adjacent faces of the cube.

Fig. 2. Relative behavior of concrete mixes stored in Na_2SO_4 solution.

Fig. 3. Relative behavior of concrete mixes stored in $MgSO_4$ solution.

The mixes containing various combinations of natural pozzolan and silica fume (Mix 3, 4, and 5), exhibited good resistance to sulfates. Even though, the relative strength of these mixes were reduced significantly as shown in Table 3, still they remained within the strength range of high-performance concretes reported in the literature [13]. The periodic observation indicate that all the cubes of the pozzolanic mixes performed well in sulfate solutions. None of the cubes have shown significant deterioration or spalling even at the corners as shown in Figs. 2 and 3. The mix containing a commercially produced portland pozzolana cement (Mix 2) showed better sulfate resistance compared to ordinary portland cement (Mix 1). Among all the mixes investigated, Mix 5, that contains 15% natural pozzolan and 15% silica fume showed the best performance in sulfate environment.

The results presented in Table 3. clearly show that magnesium sulfates has a more damaging effect than sodium sulfates; this is consistent with the data available in the literature [14], because $MgSO_4$ leads to the decomposition of the hydrated calcium silicates as well as of $Ca(OH)_2$ and of hydrated C_3A; hydrated magnesium silicate is eventually formed and it has no binding properties [15].

The superior resistance of the mixtures containing pozzolanic products against sulfate attack is attributed to the pore refinement process occurring due to the conversion of lime forming from the hydration of cement into additional binding material through lime-pozzolan reaction. In addition to the pozzolanic reaction, the filler action due to the finer particle size of silica fume (0.1–0.2 μm) further densifies the pore structure to enhance the resistance to sulfate attack [16]. Furthermore these pozzolanic materials play an important role in improving the aggregate-paste bond through the densification of the transition zone and formation of more calcium silicate hydrates [9].

5. Exposure to sea waters

The Dead Sea water was obtained from the north-eastern shores of the Dead Sea whereas the Red Sea water was obtained from the shores near Aqaba. The waters were taken from areas away from possible pollution with organic or foreign matter. The average compositions of the sea waters are shown in Table 4, [15]. Among the sea waters Dead Sea water has unusual composition as seen from Table 4, with a total salinity around 27%, about half of it being magnesium chloride followed by sodium and calcium chlorides. The Red Sea water has a composition similar to that of Mediterranean with slightly more total salinity reaching to about 4.1%, [15].

Table 4
Composition of sea waters

	Principal ions (g/l)								
	Na	K	Mg	Ca	Cl	Br	SO_4	HCO_3	pH
Dead Sea	33.5	6.3	34.5	13	180.0	4.1	0.9	0.25	6.3
Red Sea	12.2	0.44	1.88	0.51	22.7	0.07	3.16	0.15	8.2

Considering the relative strength results listed in Table 3 and Fig. 1, it is observed that after one year of storage in Dead Sea water, the mix containing ordinary portland cement only (Mix 1) lost more than 60% of its compressive strength compared to those stored in tap water. The visual observations over the specimens stored in Dead Sea water revealed severe signs of deterioration of Mix 1 as shown in Figs. 4 and 5. The corners were completely destroyed, and the cubes lost more than 50% of their weight.

The mixes containing various combinations of natural pozzolan and silica fume (Mix 2, 3, 4, and 5), exhibited good performance and retained somehow appreciable proportions of their strength when submerged in Dead Sea water for one year. The visual observations over the specimens did not reveal any cracking as shown in Fig. 4. Among all the mixes investigated, Mix 5, showed the best performance in Dead Sea water, followed by Mix 4, 3 and 2. The relatively superior behavior of the mixes containing natural pozzolan and silica fume could be explained in a way similar to that discussed previously in case of sulfate solutions.

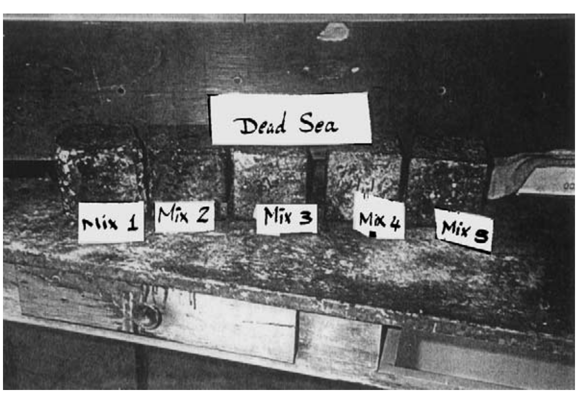

Fig. 4. Relative behavior of concrete mixes stored in Dead Sea water.

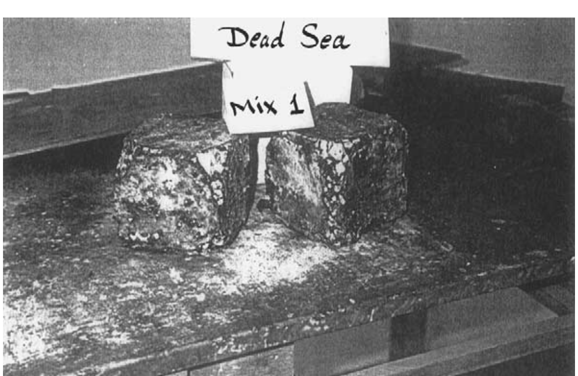

Fig. 5. Deterioration of Mix 1 in Dead Sea water.

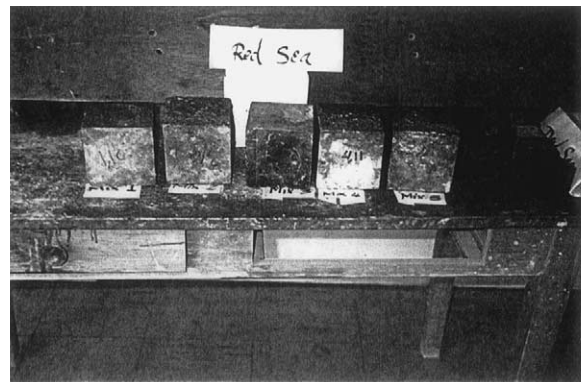

Fig. 6. Relative behavior of concrete mixes stored in Red Sea water.

All the mixes behaved in a similar manner inside the Red Sea and did not show any significant deterioration during the test period of one year as shown in Fig. 6. Mix 2 (commercially produced portland pozzolana cement that contains 15% natural pozzolan interground with the cement during manufacturing) showed the best performance in Red Sea water. It lost about 5% of its strength at the end of the test period. Some other researchers [15] have reported a weekened sulfate attack from the Red Sea water due to increased solubility of ettringite and gypsum.

6. Assessment of concrete deterioration using ultrasonic pulse velocity tests

UPV tests are commonly used in attempting to define the extent and magnitude of deterioration resulting from fire, mechanical or chemical attack. In this investigation UPV measurements were taken monthly for all mixes stored in sulfate solutions, tap and sea waters. Unfortunately some of these measurements did not correlate well with the condition of the test. Some reduction in UPV values was noticed only after the specimens were considerably deteriorated. Therefore, this method may not be reliable for comparative studies. However most of the UPV measurements taken in this investigation were rather consistent with the strength results obtained previously and agreed with the values given in the literature for high strength concrete [14]. After one year of storage in sulfate solutions, and sea waters, all the mixes showed a significant decrease (about 30%) in UPV values compared to those stored in tap water as seen from Figs. 7–11. Within the range of UPV values obtained in

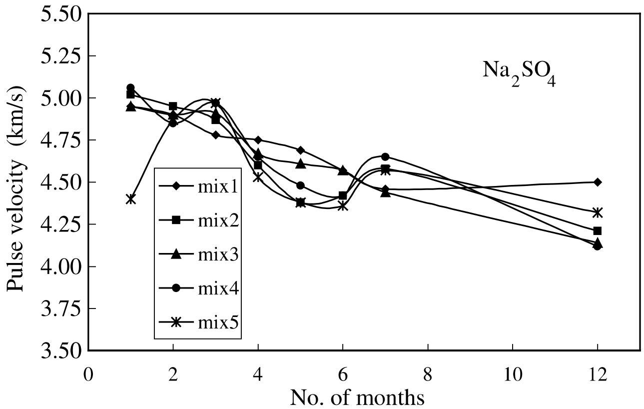

Fig. 7. UPV for mixes stored in Na_2SO_4 soution.

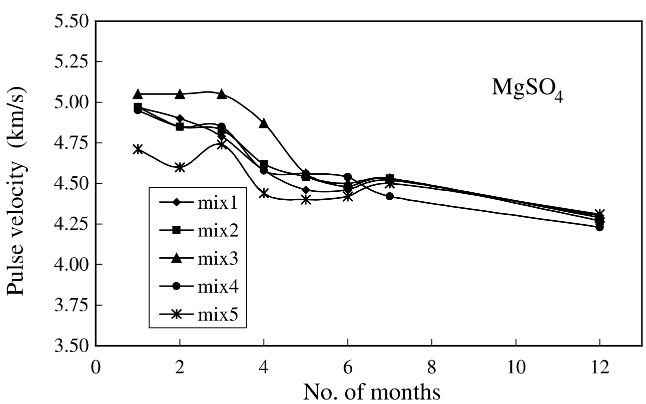

Fig. 8. UPV for mixes stored in $MgSO_4$ solution.

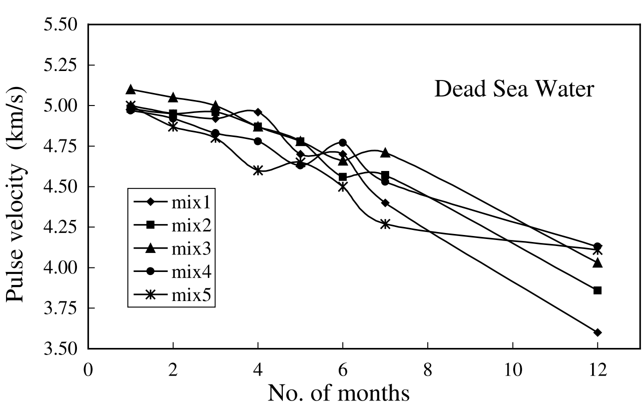

Fig. 9. UPV for mixes stored in Dead Sea water.

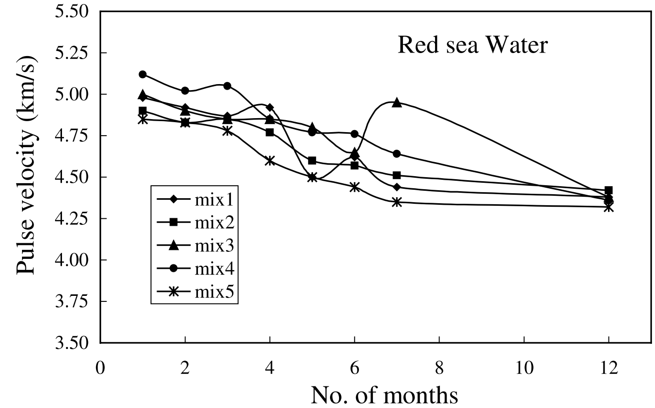

Fig. 10. UPV for mixes stored in Red Sea water.

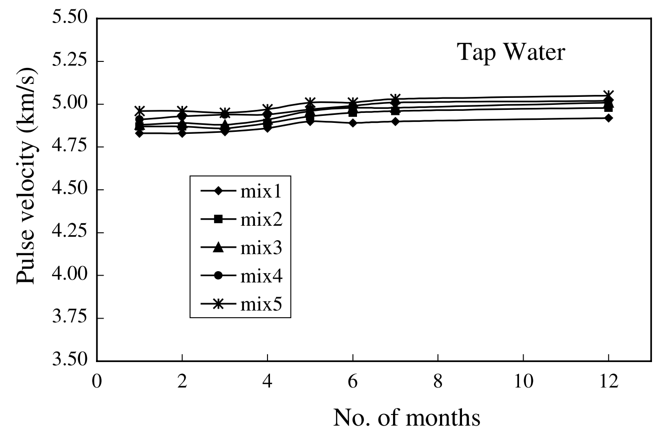

Fig. 11. UPV for concrete mixes stored in Tap water.

this investigation (3.75–5.25 km/s) it is difficult to draw comparisons from the figures shown.

7. Conclusions

Based on the results of this study it can be concluded that:

1. After one year immersion in sulfates solutions and sea waters, the concrete mix containing a combination of 15% silica fume, and 15% natural pozzolan (by weight of cement) showed a maximum protection against sulfate attack compared to those investigated in the present study.
2. High-performance concretes that contain various combinations of silica fume and natural pozzolan, can provide good balance between strength and durability, and can be recommended for use in concrete industry.
3. The present research showed that the high strength concrete mix made using ordinary portland cement

only did not perform satisfactorily in sulfate solutions and sea waters.

4. The sulfate resistance of the concretes stored in Dead Sea water deserves further investigation, due to the unique composition of its water.

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