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# SULFATE ATTACK ON PLAIN AND BLENDED CEMENTS IN SEA WATER

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## ABSTRACT

*As part of a comprehensive program to study the effect of the conjoint presence of chlorides and sulfates on the sulfate resistance of hydrated cements, this study was conducted to investigate the sulfate attack of two plain cements (Type I and Type V) and three blended cements made with fly ash, silica fume and blast furnace slag in marine environments. The performance of these cements was evaluated by exposing the specimens to a fresh sea water for a period of two years and measuring the strength development, reduction in compressive strength, and expansion of the mortar specimens, visual inspection, weight change of the concrete specimens; and mineralogical analysis using x-ray diffraction technique of cement paste specimens. The results of these tests indicated that the sulfate attack was somewhat hindered on plain and blended cements despite the high sulfate concentration in the sea water medium which is classified as "aggressive" and the relatively long exposure period.*

**Keywords:** *Sea water, plain cements, blended cements, sulfate attack, chloride-sulfate media, performance.*

## الملخص

تمثل هذه الورقة جزء من دراسة موسعة تتعلق ببحث تأثير أيونات الكبريتات والكلوريدات على مقاومة أنواع الإسمنت للتدهور بالكبريتات. وتوضح هذه الورقة تأثير الكبريتات الموجودة في مياه البحر على الإسمنت العادي (نوع واحد ونوع خمسة) وثلاثة أنواع من الإسمنت المخلوط بالرماد المتطاير وغبار السيليكا وخبث الفرن العالي. وتم تقييم أداء هذه الأنواع من الأسمنت بعد تعريضها لماء البحر لفترة تزيد عن سنتين وقياس تطور قوة الضغط (بإنضاجها بالماء) ونقص القوة (بعد تدهورها في ماء البحر) وتمدد العينات الملاطية , وملاحظة التدهور نظرياً, وتغير وزن العينات الخرسانية والتحليل المعدني باستخدام تقنية أشعة إكس. وتدل نتائج هذه الاختبارات على عينات الإسمنت العادي والمخلوط أن التدهور بالكبريتات في مياه البحر لم يكن شديداً (حسب التوقعات) رغم تركيز أيونات الكبريتات العالي وطول مدة الدراسة.

## 1. INTRODUCTION

Durability of concrete in marine environment has been the subject of major concern and research since the invention of cement as a binding material [Al-Amoudi, 2002a]. Due to the extensive spread of seas all over the world, as compared with the continental land available for human beings, marine structures and offshore oil facilities will grow and will continue to be made of concrete [Mehta, 1980] because concrete is not only the most economical structural material for construction of such structures, but also the most durable. The performance of concrete structures in sea water is of great importance because the durability of these structures is the most complicated system to investigate; where concrete deterioration is caused by a maze of interwoven mechanisms (i.e. chemical, physical and mechanical factors) [Al-Amoudi, 1992]. The situation will be worse if premature microcracking by any means does exist.

Research on durability of reinforced concrete in seawater is mostly concerned with two deteriorating actions; chloride-induced corrosion of reinforcing steel and sulfate attack on concrete [see the list of references]. The need for continued research on these aspects stems from the fact that there have been considerable changes in the physico-chemical characteristics of Portland cement in the past century, particularly in terms of $C_3A$ and $C_3S$ phases. Further, the usage of supplementary cementing materials, such as fly ash, silica fume and blast furnace slag, in Portland cement has significantly increased, particularly in the aggressive exposures of the Arabian Gulf. As part of a comprehensive research program initiated at KFUPM in the early 1990s to study the durability of plain and blended cements in high sulfate-chloride media [Al-Amoudi, 1992], this paper summarizes the investigation conducted to assess the sulfate attack on plain and blended cements exposed to marine environments.

## 2. EXPERIMENTAL PROGRAM

ASTM C 150 Type I and Type V Portland cements with 8.5% and 3.5% $C_3A$ content, respectively, were used in preparing plain cement paste, mortar and concrete specimens. ASTM C 618 Class F fly ash (FA), silica fume (SF) and blast-furnace slag (BFS) were used at 20, 10 and 60% replacements by weight of Type I cement, respectively, to prepare FA, SF and BFS blended cements. Table 1 depicts the chemical analysis of the plain and blended cements used in this investigation. An effective water to binder (w/b) ratio of 0.50 was kept invariant in all the paste, mortar and concrete specimens. In the mortar specimens, the sand to binder ratio was maintained at 2.75, while a binder content of 350 $kg/m^3$ and a coarse-to-fine aggregate ratio of 2.0 by weight were kept constant in all the concrete mixtures. The aggregates were 19-mm maximum size crushed limestone and dune sand from eastern Saudi Arabia.

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After casting, all the specimens were covered with wet burlap in the moulds for 24 hours and, thereafter, cured in potable water for a further period of 14 days. They were then air-dried in the laboratory (23 ± 2°C) for one day before being placed in the seawater. The seawater was obtained from the Arabian Gulf (KFUPM beach) and was changed every month.

Cement paste specimens were used to study the effect of seawater on the chemical attack of sulfate ions on the hydration products using X-ray diffraction (XRD) technique after 24 months of exposure to seawater.

Mortar specimens were used to determine the strength development in water and strength reduction and expansion due to exposure to sea water. The strength tests were conducted on 25-mm cube specimens according to ASTM C 39, while the expansion measurements were conducted on two 25×25×285 mm prismatic specimens as per ASTM C 441. Concrete cylinders, 76 mm in diameter and 152 mm high, were used to study the effect of sea water on the weight loss of concrete. See Al-Amoudi [1995] for further details on these tests.

Table 1: Chemical Composition of Cements and Blending Materials.

| Constituent (% by weight) | Fly Ash | BFS* | Silica Fume | Type V Cement | Type I Cement |
|---|---|---|---|---|---|
| Silicon dioxide | 52.3 | 27.7 | 92.5 | 22.0 | 20.5 |
| Aluminum oxide | 25.2 | 12.8 | 0.4 | 4.1 | 5.6 |
| Ferric oxide | 4.6 | 1.2 | 0.4 | 4.2 | 3.8 |
| Calcium oxide | 10.0 | 44.0 | 0.5 | 64.1 | 64.4 |
| Magnesium oxide | 2.2 | 8.8 | 0.9 | 2.2 | 2.1 |
| Sulfur trioxide | 0.6 | 3.1 | 0.5 | 2.0 | 2.1 |
| Loss of ignition | 0.4 | 0.9 | 2.6 | 0.8 | 0.7 |
| Potassium oxide | — | — | — | 0.3 | 0.3 |
| Sodium oxide | — | — | — | 0.2 | 0.2 |
| $C_3S$ | | | | 54.6 | 56.7 |
| $C_2S$ | | | | 21.9 | 16.1 |
| $C_3A$ | | | | 3.5 | 8.5 |
| $C_4AF$ | | | | 12.9 | 11.6 |

*Blast furnace slag

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## 3. RESULTS

The compressive strength development in all the plain and blended cement mortar specimens placed in water is depicted in Figures 1 and 2, respectively. All the cements exhibited somewhat similar strength after 14 days of curing, except the blast furnace slag (BFS) cement. After 180 days of curing, the maximum compressive strength was observed in the silica fume and fly ash cements. The strength development in BFS cement specimens, however, was the lowest at all curing periods due to the high quantity of BFS (60%) in this cement.

The reduction in strength in plain and blended cement mortar specimens exposed to sea water is plotted in Figures 3 and 4, respectively. The strength reduction was less than 20% in all types of cements after one year of exposure. After two years of exposure, the reduction in strength was in the range of 22 to 26% in all the cements except in the BFS cement which was 13%. The lowest reduction in strength in BFS cement may be attributed to their initially low strength, as was stated earlier.

The expansion data are presented in Figures 5 and 6 for plain and blended cement mortar specimens, respectively. After 540 days of exposure to sea water, the expansion in plain cements was more than that in all the blended cements. The better performance of blended cements could be ascribed to the dilution of the reactive cement phases (i.e., mainly $C_3A$ and $C_3S$) in the parent cement due to its replacement by the pozzolanic materials [Al-Amoudi, 2002b]. The maximum expansion of 0.08% was noted in Type I cement after 18 months, followed by Type V cement, which had an expansion of 0.070%. The marginal improvement of Type V cement might be ascribed to its relatively lower $C_3A$. Among blended cements, BFS cement exhibited distinctly the lowest expansion of 0.056%. After 540 days, the expansion was 0.067% in both FA and SF cements.

The data on weight change for the concrete specimens made with plain and blended cements are plotted in Figures 7 and 8, respectively. Surprisingly, an increase, rather than a decrease, in the weight was noted in all the concrete specimens, even after 24 months of exposure to the sea water. Visual inspection of these specimens did not reveal any type of “distinct” deterioration below or above the sea water level, as was observed in other aggressive exposures [Al-Amoudi, 1998; Al-Amoudi et al., 1994]. Only salt deposition was noted on the specimens in a way exactly similar to what has been observed on the specimens placed in sabkha (i.e., high sulfate-chloride) brines [Al-Amoudi, 1995]. The salt precipitation increased in proportion to the increase in weight. In fact, salt precipitation was noted even on the portions of the specimens above the sea water level though to a lesser extent.

The X-ray diffractograms (XRDs) for plain and blended cements exposed to the seawater for a period of 24 months are depicted in Figure 9, where C = calcite, CCA = calcium chloro-aluminate, G = gypsum, B = brucite and PSA = primary sulfo-aluminate hydrate. A comparison of these diffractograms with those in water [see Rasheeduzzafar et al., 1994] indicates that the portlandite peaks noted in the specimens cured in water were either totally eliminated or significantly reduced. Most of the peaks noted in Figure 5 are very small; either the remnants of portlandite (at 17.9° and 34.5° 2θ), or gypsum (at 11.7°, 20.7° and 28.9° 2θ),

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or the calcium chloro-aluminate, known as Freidel's salt (at 11.2°, 22.8° and 30.9° 2θ), or the magnesium hydroxide (at 32.4°, 26.2° and 18.5° 2θ) [Al-Amoudi, 1992]. These peaks are small and cannot be easily identified, as was noted previously in the case of the specimens exposed to a high sulfate-chloride environment [Al-Amoudi et al., 1994]. However, the formation of calcite due to carbonation of cement was noted in both the specimens cured in water or exposed to seawater.

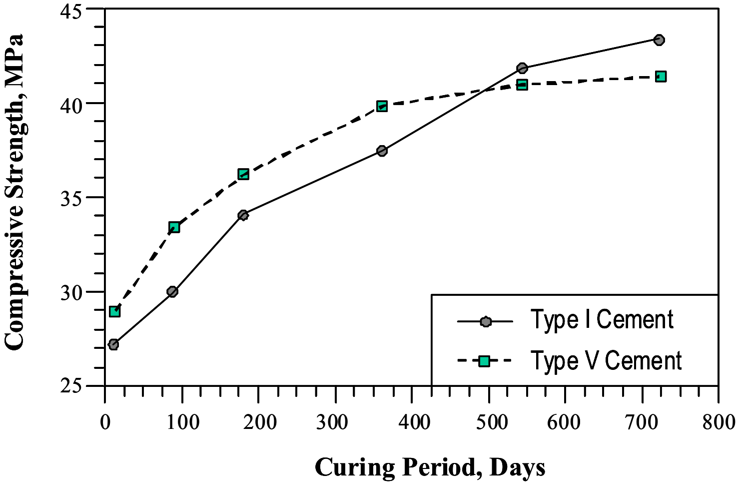

Figure 1: Strength Development of Plain Cements.

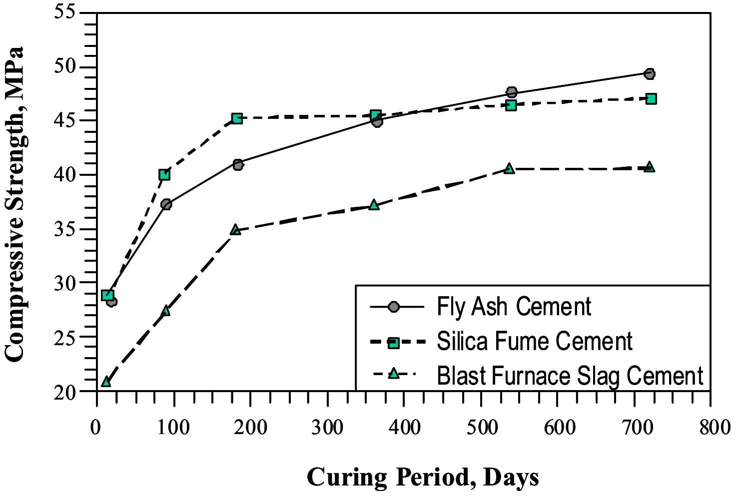

Figure 2: Strength Development of Blended Cements.

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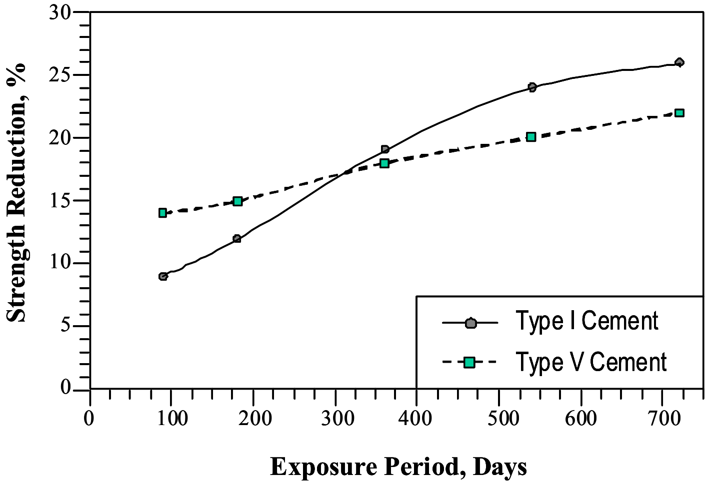

Figure 3: Reduction in Compressive Strength of Plain Cements.

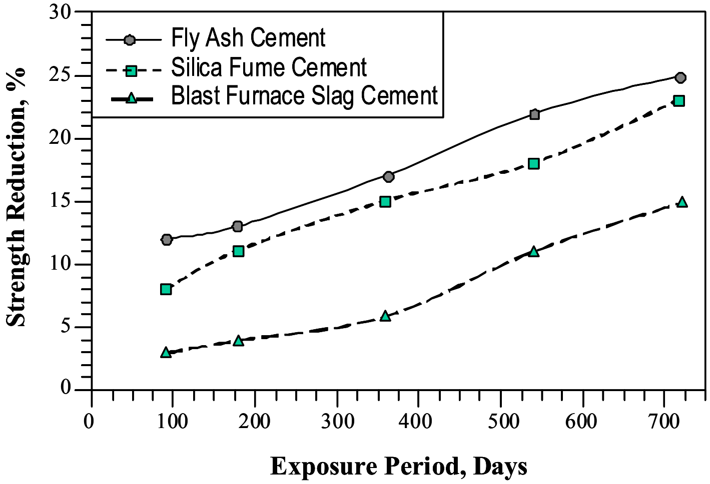

Figure 4: Reduction in Compressive Strength of Blended Cements.

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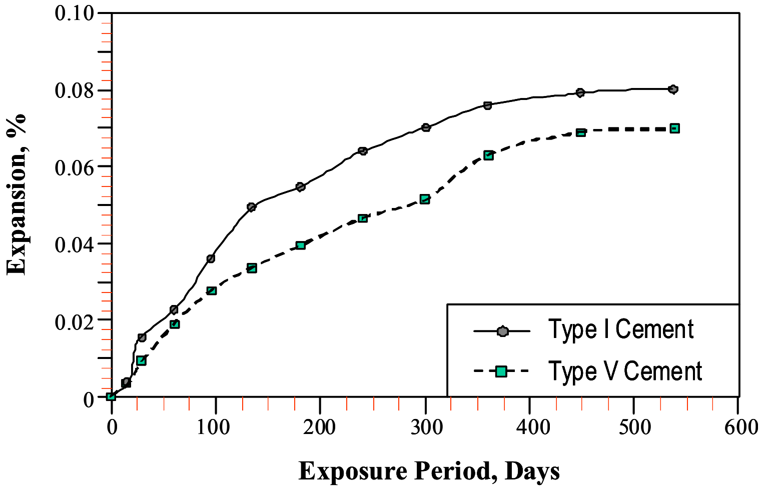

Figure 5: Expansion of Mortar Specimens Made with Plain Cements.

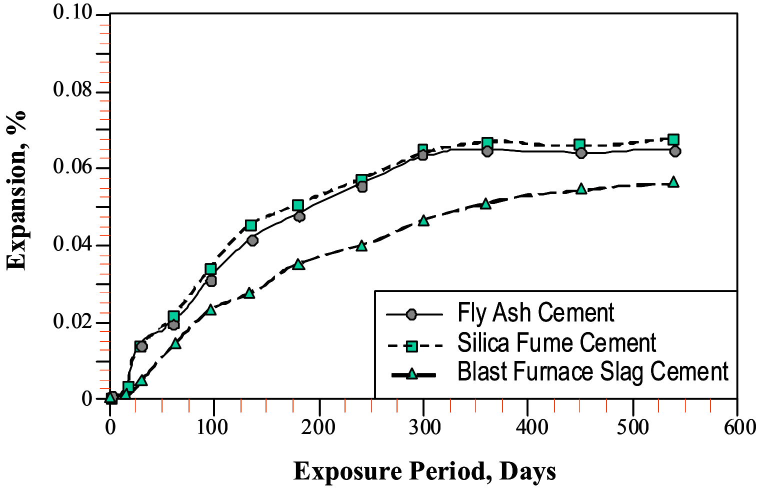

Figure 6: Expansion of Mortar Specimens Made with Blended Cements.

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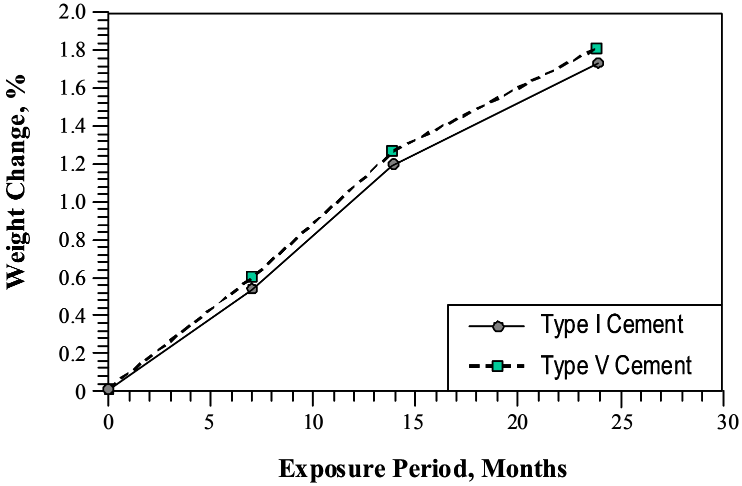

Figure 7: Change in Weight of Concrete Specimens Made with Plain Cements.

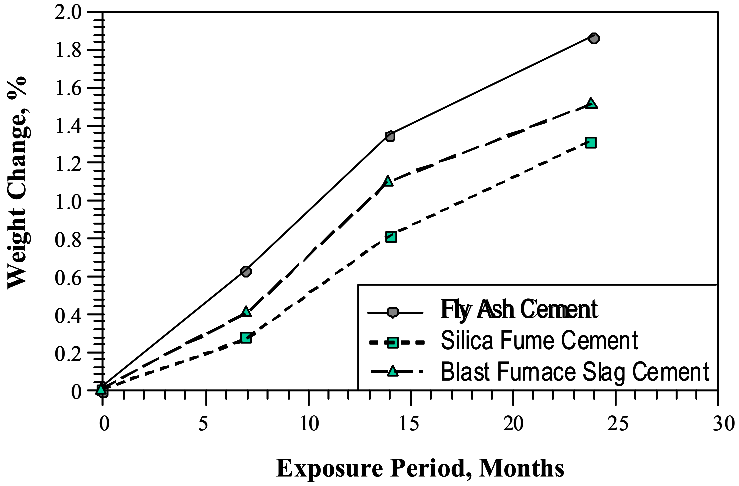

Figure 8: Change in Weight of Concrete Specimens Made with Blended Cements.

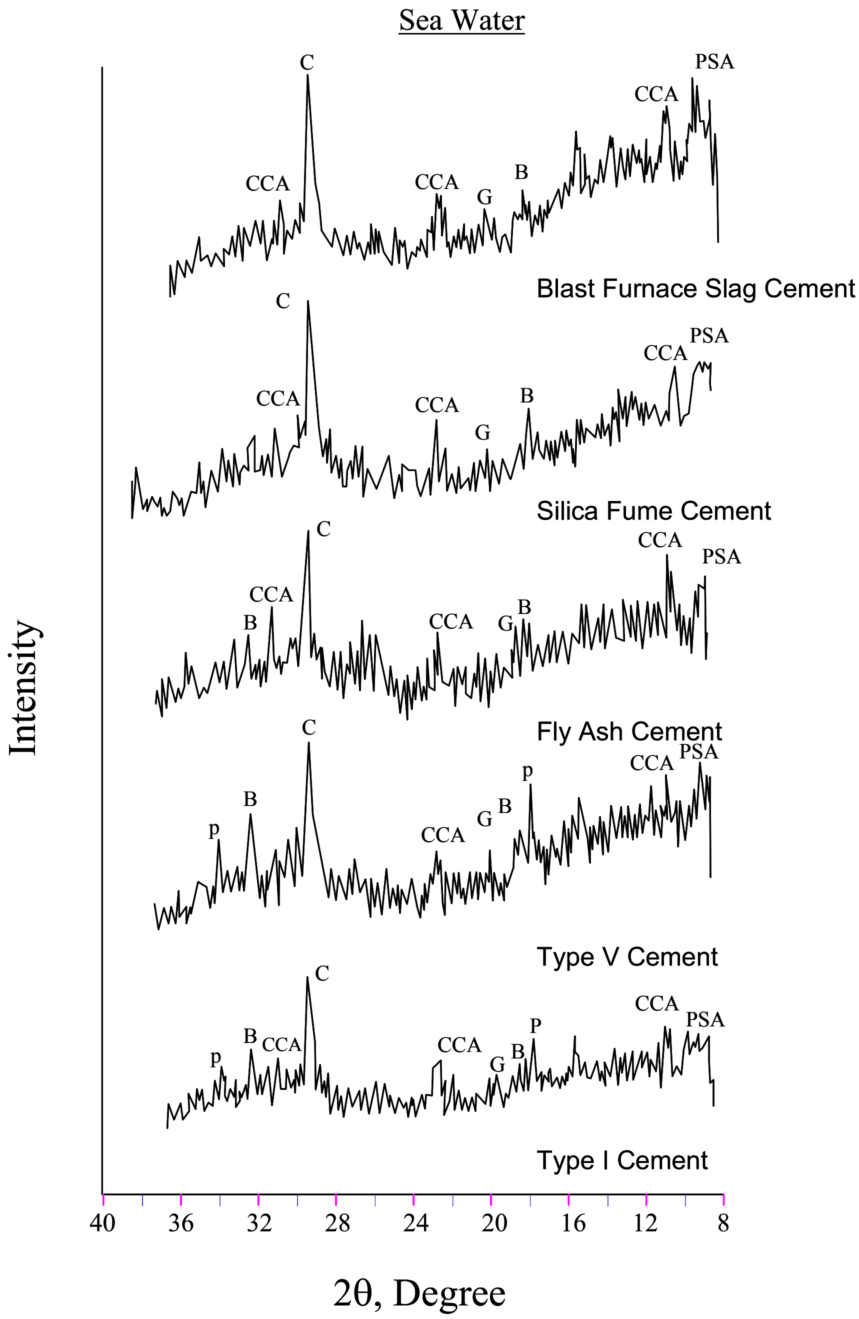

Figure 9: XRD Micrographs of Plain and Blended Cements Exposed to Seawater for 24 Months.

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## 4. Discussion of Results

The data reported in this paper indicates that the maximum strength reduction noted in this investigation was about 25% in Type I and FA cements after two years of exposure to the marine media. Such a reduction can be considered as "small" for the following reasons: (i) the duration of the exposure was relatively long (24 months); (ii) the specimen size was designed to be small (25 mm cubes) so as to accelerate the deterioration phenomena by the sulfate ions in the sea water; and (iii) the sea water had a sulfate ($SO_4^{2-}$) concentration of 5, 120 ppm [Al-Amoudi, 2002b], which is considered as severe, according to the Canadian Standard CAN3-A23.1-M77 [Mindess and Young, 1981] and ACI 318 [American Con., 1995]. The strength reduction in all the mortars was less than 30% that is generally considered as the threshold value for failure due to sulfate attack on small specimens similar to those utilized in this investigation [Al-Amoudi and Maslehuddin, 1996].

The expansion data also supports the results of strength reduction whereby the expansion of both plain and blended cements was vividly low. The expansion of all cements during the 18-month exposure to sea water did not exceed the 0.1% that is generally specified as the failure criterion for expansion [Al-Amoudi, 2002b].

The relatively mild attack of sea water on all the cements used in this investigation is further supported by the weight change data generated by exposing the concrete specimens to sea water. As stated earlier, an increase in the weight of these specimens, rather than weight loss, was noted thereby confirming the absence of noticeable concrete deterioration after two years of maritime exposure. The increase in weight may be ascribed to salt penetration and precipitation that was visually noted on all the concrete specimens, both below and above the sea water level, as was discussed previously. Similar observation was noted when fifteen different concrete mixtures with different cement types and blending materials prepared at different w/b ratios were exposed to a high chloride-sulfate "sabkha" solution [Al-Amoudi, 1995].

Literature review indicates that there are two forms of concrete deterioration that are ascribed to sulfate attack [Al-Amoudi, 1998]. The first mode of deterioration is akin to eating away of the hydrated cement paste and its progressive reduction to a cohesionless granular mass leaving the aggregate exposed and leading to loss of strength and reduction in weight. This mode is attributed mainly to the formation of gypsum and the non-cementitious magnesium silicate hydrate, and is known as the **acidic type** of sulfate attack. The second mode of deterioration, which is normally characterized by expansion and cracking, takes place when the reactive hydrated aluminate phases, present in sufficient quantities, are attacked by sulfate ions, thereby forming tricalciumsulfo-aluminate hydrate, also called ettringite or Candlot's salt. This **expansive type** of sulfate attack is ascribable to the formation of a colloidal form of ettringite in the presence of high concentrations of $Ca(OH)_2$ in the pore solution [Mehta, 1973].

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Visual inspection of the specimens exposed to sea water did not reveal any of the above two forms of deterioration during the two year exposure period. Previous studies in the 1950s and 1970s had reported excessive expansion and extensive deterioration in concrete structures exposed to sea water [Mehta and Haynes, 1975; Kalousek and Benton, 1970; Figg, 1979]. The reason for the increased proneness of old cements to expansion and spalling by sea water is probably ascribable to the high $C_3A$ content of "old" Type I cements that were manufactured before 1950s. When the $C_3A$ content is more than 11%, the susceptibility of concrete to expansion and cracking is significantly increased [Gjorv, 1971]. On the contrary, the present-day Type I cements often have a maximum $C_3A$ content of about 9% [Al-Amoudi, 2002a]. Accordingly, the expansion of Type I portland cement when exposed to sulfate media is much mitigated. The expansion characteristics are further reduced by the conjoint presence of chlorides with the sulfate salts in sea water [Figg, 1979; Harrison, 1990]. Even if ettringite or gypsum is formed, the expansive stresses will be much reduced due to the concomitant presence of chloride ions [Lea, 1970; Al-Amoudi et al., 1994].

Considering the long-term (i.e., more than 15 years) performance of concrete, some researchers [Mehta and Haynes, 1975] reported that all Portland cements, including Type V cements with $C_3A$ of up to 3%, will be significantly affected by sea water. The reason may be attributed to the first "acidic" type of sulfate attack, which is ascribable to the portlandite produced by the hydration of $C_3S$ and $C_2S$ phases. In fact, the portlandite content is proportional to the $C_3S$ to $C_2S$ ratio of the cement and this ratio is responsible for the early strength development of the cement. Since the manufacturers of modern cements do care a lot about the high early strength only, they deliberately make the $C_3S/C_2S$ ratio extremely high thereby increasing the portlandite content. Therefore, these cements will readily deteriorate after long exposure periods. The principal form of deterioration will be the gypsum “acidic” type, whereby the portlandite produced by the hydration of calcium silicate phases will react with the sulfate ions of sea water to produce gypsum according to the following reaction:

$$Ca(OH)_2 + SO_4^{2-} \xrightarrow{2H_2O} CaSO_4 \cdot 2H_2O + 2OH^-$$

To mitigate the inferior role of portlandite, it is recommended to use pozzolanic (i.e., mineral) admixtures to consume this portlandite as shown in the following “pozzolanic” reaction:

$$3Ca(OH)_2 + 2SiO_2 \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$

In addition to consuming the portlandite, the pozzolanic reaction produces secondary C-S-H, which reduces the permeability of concrete thereby improving the sulfate resistance of blended cements. Therefore, the long-term performance of blended cements, particularly

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those incorporating silica fume, is expected to be much better than plain portland cements exposed to marine environments, especially when the concrete mixture is to be prepared at low water to binder ratio, similar to what is being used in the offshore structures [Hoff, 1991; Mehta, 1991].

## 5. CONCLUSIONS

Cement paste, mortar and concrete specimens prepared using Type I and Type V cements and Type I cement blended with fly ash (20%), silica fume (10%) and blast furnace slag (60%) were exposed to sea water for a period of 720 days. The performance of these cements was evaluated through visual inspection, measuring the reduction in compressive strength, expansion and weight change. X-ray diffraction of the cement paste specimens was used to study the mineralogical changes upon exposure to the maritime environment. Based on the data developed in this investigation, the following conclusions can be drawn:

The reduction in compressive strength and expansion data indicated better performance by blended cements, particularly the BFS cement. The performance of Type V cement was marginally better than that of Type I cement.

An increase, rather than a decrease, in weight was noted in all the concrete specimens. The lowest increase in weight of about 1.50% was noted in SF and BFS after two years of exposure. The weight change was 1.85% in plain and FA cements.

No signs of deterioration were observed on plain and blended cements, even though the sulfate concentration in the sea water was high. The weight loss, expansion and reduction in compressive strength were less than the threshold values reported in the literature, even after two years of exposure.

Considering the long-term durability performance of concrete in marine and offshore structures, SF or BFS cement can be used at a low water to binder ratio. To further enhance the resistance against deterioration by sulfate ions and/or salt crystallization, additional protective measures, such as the application of a water-resistant epoxy-based coating, may be considered.

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