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Attack on plain and blended cements exposed to aggressive sulfate environments

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Abstract

The recent modifications in the cement manufacturing technology and the extensive use of mineral admixtures have introduced changes in the chemical and mineralogical composition of the present-day cements. These changes may significantly affect the durability of concrete, particularly the sulfate attack. Due to these modifications, the need for understanding the mechanisms of sulfate attack through laboratory and field exposure studies becomes all the more important. This paper reviews the studies conducted at King Fahd University of Petroleum and Minerals (KFUPM) to assess sulfate attack on plain and blended cements exposed to aggressive environments in the laboratory and the field. Based on this review, the mechanisms of sulfate attack are discussed. The effect of cation type associated with the sulfate anions on concrete deterioration due to sulfate attack and the role of chloride ions on sulfate attack in plain and blended cements are also elucidated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Plain and blended cements; Sulfate attack; Chloride-beneficiation; Mechanisms

1. Introduction

Degradation of structural concrete components placed in sulfate-bearing environments has been of concern to the concrete technologists since the early years of the 19th century [1–5]. In fact, concrete deterioration due to sulfate attack received much more attention compared to all other concrete distresses [6]. Vicat, as early as 1818, reported a chemical attack on concrete due to the presence of sulfate ions in seawater, while Candlot established the formation of an expansive hydration product by the interaction of aqueous solutions of calcium aluminates and calcium sulfate in 1890 [7]. Michaelis, in 1892, attributed the disruption of concrete, when attacked by sulfate waters, to the reaction between C_3A in Portland cement and sulfate ions to form ettringite.

Till today, research related to the effect of sulfate ions on the performance of concrete is in progress. Such a long and continuous research is motivated by the following factors:

(i) the modifications in the physico-chemical characteristic of Portland cements during the last four decades;
(ii) the increasing use of blending (i.e., pozzolanic) materials with Portland cement to improve the concrete durability, and
(iii) the controversy on the influence of cement content and cement composition (i.e., C_4AF, and C_3S to C_2S ratio) on sulfate attack [6].

The influence of cement type and concrete mix design on sulfate attack has been the subject of major research at King Fahd University of Petroleum and Minerals (KFUPM) in the later parts of the last century. This interest stems from the fact that the substructural components, in this part of the world, are exposed to hostile sulfate-bearing soils and groundwater. The seawater, soils and groundwater in the Arabian Gulf contain high concentrations of calcium, sodium and magnesium salts of sulfates. The concrete construction in the coastal areas and in the sabkha terrains is continuously exposed to attack by the sulfate ions contributed by calcium, magnesium and sodium salts [8,9]. Since both chloride and sulfate salts are predominantly found in local soils and groundwater, the influence of chloride ions on sulfate attack was also investigated.

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This paper reviews the research conducted at KFUPM on sulfate attack on plain and blended cements exposed to the prevailing service conditions. The mechanisms of sulfate attack are discussed with regard to the effect of cation type associated with the sulfate attack. The effect of chloride ions on sulfate attack in plain and blended cements is also reviewed.

2. Modes of sulfate attack

Deterioration of concrete due to sulfate attack manifests itself in three forms, as illustrated in Fig. 1 [7]. The first mode of deterioration is akin to eating away of the hydrated cement paste and progressively reducing it to cohesionless granular mass leaving the aggregates exposed. This type of deterioration may lead to reduction in the cross-sectional area of the structural component (i.e., loss in weight of concrete) and decrease in strength. This mode of failure is attributed mainly to the formation of gypsum, and is known as the acidic type of sulfate attack (Fig. 1(a)). The second mode of deterioration, which is normally characterized by expansion and cracking (Fig. 1(b)), takes place when the reactive hydrated aluminate phases, present in sufficient quantities, are attacked by sulfate ions, thereby forming tricalcium-sulfo-aluminate hydrate, also called ettringite or Candlot's salt. This expansive type of reaction is ascribable to the formation of a colloidal form of ettringite in high pH media. The third mode of sulfate attack is the onion-peeling type that is characterized by scaling or shelling of the surface in successive layers in the form of delamination [10]. This mode of concrete deterioration due to sulfate attack is the least reported in the literature and was observed in the plain and fly ash-blended cement paste cement specimens exposed to mixed sulfate environments (Fig. 1(c)).

Field studies conducted in the Arabian Gulf [11–14], however, did not reveal many cases of concrete deterioration due principally to sulfate attack. This was due to the usage of Type V cement in almost all the construction that was carried out since the early seventies of the last century [9]. However, softening of the cement matrix and exposure of the aggregates, i.e., the acidic type of

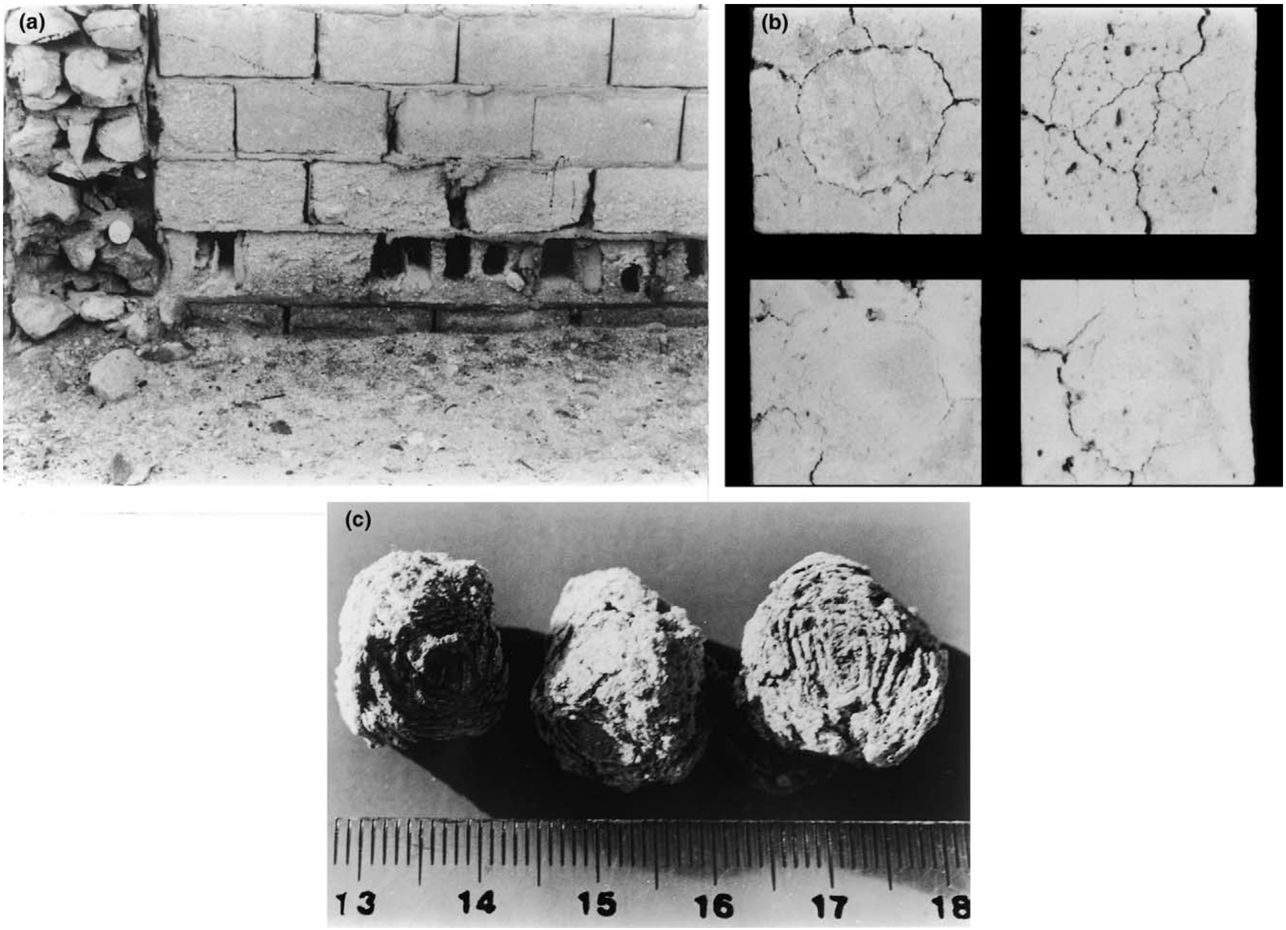

Fig. 1. Modes of sulfate attack: (a) acidic type; (b) expansive type; (c) onion-peeling type.

sulfate attack, was observed in some structures, particularly at the grade level.

Another form of deterioration that is commonly observed in the coastal areas of the Arabian Gulf is attributable to salt scaling. Since the groundwater table is shallow, the foundations of most of the structures in this region are directly exposed to highly concentrated chloride and sulfate salts [8]. The contaminated groundwater seeps through the foundations where proper tanking is not provided, and evaporates at the grade level leaving the salts behind. Further, the groundwater is sucked up due to the wicking action resulting in a high salt concentration at the grade level. At the evaporation face, water will be lost; however, the salts will remain on the concrete surface. Concrete with high permeability characteristics allows higher transport of water through the pores and; therefore, a rapid build-up of salts on the concrete surface takes place. Repeated cycles of salt crystallization caused primarily by the night-day thermal changes and secondly by the variation in the relative humidity produce the destructive power of salt crystallization on the concrete. This type of concrete deterioration is characterized by progressive crumbling, salt blistering or scaling that erodes the surface of concrete leaving the aggregates exposed. The damage is concentrated at the evaporation face where a thin layer of concrete is crumbled or scaled. The eroding process continues as long as the environmental changes of temperature and humidity produce the cycles of salt crystallization.

Salt weathering is also a major problem in the marine environments, particularly in the tidal zones, and in the structures exposed to the water splash, where concrete deterioration is aided by both the deposition of salts and their dissolution due to the cyclic action of wetting and drying. This phenomenon may also be attributed to the materials properties. For example, concretes incorporating pozzolanic materials and low water to binder ratio generate a very fine pore structure that cannot accommodate the build-up of salt crystals [8]. The formation of salt crystals in the fine pore structure of pozzolanic concrete exerts considerable pressure, resulting in greater expansion and deterioration of concrete. Deterioration of the concrete skin, i.e., scaling, is also more prominently evident in blended cement concretes made with silica fume and blast furnace slag, exposed to concentrated salty environments (i.e., sabkha, offshore and marine structures). Scaling of the concrete members exposed to concentrated sulfate environments and to marine environments has been reported by Al-Amoudi et al. [8] and Al-Rabiah et al. [15], respectively. Efficient tanking system for the foundations is, therefore, recommended to avoid concrete deterioration due to salt crystallization.

3. Factors affecting sulfate attack

All cements, including the sulfate-resisting ASTM C 150 Type V, are vulnerable to sulfate attack [3,7]. However, the intensity and rate of attack depend on the following factors:

(i) *Cement type*. The most important mineralogical phases of Portland cements that affect the intensity of sulfate attack in decreasing order of importance are: C_3A, C_3S/C_2S ratio and C_4AF.

(ii) *Sulfate type and concentration*. Although concrete deterioration due to sulfate attack tends to increase with the increase in the concentration of the sulfate solution upto a certain level, the cation associated with SO_4^{2-} has a significant impact on the nature and magnitude of concrete deterioration [7].

(iii) *Quality of concrete*. It is the most important factor influencing the durability of concrete in general and sulfate resistance in particular. Since impermeability always reflects the quality and durability of concrete, sulfate attack, particularly the type of degradation associated with sodium sulfate, is inversely related to the concrete quality, i.e., dense concrete tends to resist sulfate attack more than permeable concrete. In magnesium sulfate environments, however, the cement type dominates the extent of sulfate attack compared to the denseness of concrete, especially at the surficial layers of concrete, as will be elucidated later.

(iv) *Exposure conditions.* It is known that sulfate attack takes place only in solution; therefore, the portion of a foundation most susceptible to sulfate attack is the part within or just above the groundwater table.

4. Effect of cement type on sulfate attack

The type of cement significantly affects all types of sulfate attack on concrete. Among the hydration products, calcium hydroxide and alumina-bearing phases are more vulnerable to attack by sulfate ions. On hydration, Portland cements with more than 5% tricalcium aluminate (C_3A) will contain most of the above alumina in the form of monosulfate hydrate, $C_3A \cdot C\overline{S} \cdot H_{18}$ or $C_3A \cdot C\overline{S} \cdot H_{12}$ [16]. If the C_3A content of cement is more than 8%, the hydration products will also contain the hydrogarnet, $C_3A \cdot CH \cdot H_{18}$ or $C_3A \cdot CH \cdot H_{12}$. In the presence of calcium hydroxide, when the cement paste comes into contact with sulfate ions, both of the alumina-containing hydrates are converted to ettringite ($C_3A \cdot 3C\overline{S} \cdot H_{32}$), as shown stochastically below in the following two equations:

$$C_4A\overline{S}H_{12} + 2C\overline{S}H_2 + 16H \rightarrow C_6A\overline{S}_3H_{32} \qquad (1)$$

$$C_4AH_{13} + 3C\overline{S}H_2 + 14H \rightarrow C_6A\overline{S}_3H_{32} + CH \qquad (2)$$

The formation of ettringite generates excessive expansion in concrete. However, the mechanisms by which ettringite formation causes expansion is still a subject of controversy. Exertion of pressure by forming ettringite crystals, and swelling due to adsorption of water in an alkaline environment by poorly crystalline ettringite, are two of the several hypotheses that are supported by most researchers [17].

Therefore, realizing the role of C_3A on sulfate attack, cements of low C_3A are recommended in situations where the substructural components are exposed to sulfate environments. However, cements with low C_3A generally have a higher C_3S/C_2S ratio. An increase in the C_3S content of cement, therefore, generates a significantly higher quantity of calcium hydroxide. The produced calcium hydroxide may directly combine with the sulfate ions leading to the formation of gypsum, as will be elucidated later. The deterioration of hardened Portland cement by gypsum formation goes through a process leading to reduction of stiffness and strength and, to a lesser degree by, expansion and cracking, and eventual transformation of the material into a mushy or non-cohesive mass.

The earliest studies conducted in the Arabian Gulf to evaluate the effect of cement type and content on sulfate attack were reported by Rasheeduzzafar et al. [18]. The results of that study indicated that replacement of cement with 20% fly ash improved the durability of concrete. The effect of fly ash addition on the sulfate resistance of concrete was more predominant for high C_3A cements. Increasing the cement content without decreasing the water to binder ratio did not provide any benefit, vis-à-vis sulfate resistance.

Rasheeduzzafar et al. [19] investigated the influence of cement composition on the sulfate resistance of concrete made with cements of varying C_3A contents. Their results indicated that in addition to the C_3A content, the C_3S to C_2S ratio has a significant influence on sulfate resistance. They cited an example where comparisons were drawn between the sulfate deterioration for Type I cements with C_3A contents of 11.9% and 9.3%. It was reported that the C_3S to C_2S ratio for the cement having the higher C_3A was 7.88 whereas it was 2.57 for the lower C_3A cement. After 150 days of accelerated sulfate exposure, Type I cement with the higher C_3A content was found to have a level of deterioration that was 2.5 times higher than that of the Type I Portland cement with the lower C_3A content. Moreover, significant retrogression of strength was observed on immersion in the sulfate solution even in a Type V (C_3A: 1.88%) cement that had a C_3S to C_2S ratio of 5.28. These findings indicate that the C_3S to C_2S ratio does play a significant role, in addition to the C_3A content, in the sulfate attack of plain cements. On the other hand, when 20% silica fume was blended with a Type I cement having a 14% C_3A content, this blended cement performed 1.4 times better than a plain Type V cement having 1.88% C_3A [19].

Recent investigations at KFUPM [20] have indicated that the type of cement significantly affects the resistance of concrete to sodium sulfate media. Significant deterioration was noted in a moderate Type I ($C_3A = 8.5\%$) cement compared to a Type V ($C_3A = 3.5\%$) cement and blended cements. While minor deterioration was noted in Type V cement exposed to sulfate concentrations of 2.5% and 4%, significant deterioration was noted in Type I cement exposed to sulfate concentrations of as low as 1%. Blending the high C_3A cement with fly ash (20%) or silica fume (8%) significantly improved the sulfate resistance of these blended cements.

Blended cements are now increasingly used to improve concrete durability. When pozzolans are added to cement, they react with the calcium hydroxide, in the presence of moisture, to produce secondary calcium silicate hydrate (C–S–H). This pozzolanic reaction has the following beneficial impacts on sulfate attack:

(i) the consumption of portlandite reduces the formation of gypsum;

(ii) the replacement of part of the cement by a pozzolanic material entails a reduction in the C_3A content (i.e., dilution effect), hence, all the aluminate-bearing phases will accordingly be reduced;

(iii) even if it is formed, ettringite becomes expansive only at high pH values ($pH > 12$); since blended cements consume a significant proportion of the portlandite produced by the cement hydration and reduce the pH, the ettringite becomes less expansive [16];

(iv) the formation of secondary C–S–H produces a film or a coating on the alumina-rich and other reactive phases thereby hindering the formation of secondary ettringite; and lastly

(v) the formation of secondary C–S–H also results in the densification of the hardened cement paste since it is deposited in the pores thereby making blended cements impermeable and, therefore, the sulfate ions cannot easily penetrate through the concrete matrix, as in the case of plain Portland cements.

Rasheeduzzafar et al. [21] investigated the sulfate resistance of plain and blended cements when exposed to combined magnesium and sodium sulfate environments. After two years of exposure, deterioration was noted in all the cements. However, the deterioration was more pronounced in blast furnace slag and silica fume cements. Deterioration in these cements significantly exceeded that observed in the plain and fly ash cements. X-ray diffraction and scanning electron microscopic analyses indicated massive gypsum formation in blended cements, which was attributed to the conversion of calcium silicate hydrate to non-cementitious, non-crystalline, fibrous M–S–H due to the reaction of magnesium and sulfate ions with the C–S–H. According to the authors [21], in the absence of calcium hydroxide, which is consumed by the pozzolanic reaction, magnesium and sulfate ions react directly with the C–S–H leading to the formation of M–S–H. They attributed the aggravated deterioration of silica fume and blast furnace slag cements to the absence of the protective brucite layer (i.e., magnesium hydroxide).

The performance of blended cements in sodium sulfate environments was, however, observed to be better than that of plain cements as will be elucidated in a subsequent section.

5. Role of water to cement ratio

It is well known that dense, low water to cement (w/c) ratio concrete is recommended for any construction from durability perspective. This is because all the deterioration phenomena are directly related to the permeability of concrete which is inversely proportional to the water to cement ratio [22].

The effect of low w/c ratio on the strength of mortar specimens exposed to $N\overline{S}$ and $M\overline{S}$ solutions is shown in Table 1. It can be easily observed that lowering the w/c ratio tends to improve the performance in the $N\overline{S}$ exposure whereby the strength reduction was reduced from 39% to 26% when the w/c ratio was reduced from 0.50 to 0.35. The mitigation of sulfate attack may be ascribed to the reduction of the pore size thereby decreasing the diffusion of sulfate ions into concrete [2–7]. Hence, the formation of ettringite (Eqs. (1) and (2) above) will be mitigated.

In the case of $M\overline{S}$ solutions, the data in Table 1 indicate that reducing the w/c ratio tends to aggravate the sulfate attack. For example, the strength reduction in Type I cement mortar specimens increased from 62% to 81% when the w/c ratio was decreased from 0.50 to 0.35. Similar behavior was noted in the concrete specimens made with plain (i.e., Type I and Type V) cements and blended (i.e., silica fume and blast furnace slag) cements [6]. The data in Table 2 indicate that the weight loss in Type I and Type V cement concrete specimens exposed to a mixed-sulfate (i.e., $N\overline{S} - M\overline{S}$; $SO_4^{2-} = 2.1\%$) solution for 44 months increased from 0.86% and 0.93% to 8.88% and 4.72%, respectively. Similarly, for blended cements, the weight loss of the concrete specimens increased from 8.99%, 14.8% and 37.4% to 11.6%, 15.5% and 44.0% for SF + Type I, SF + Type V and BFS cements, respectively, when the water to binder ratio decreased from 0.50 to 0.35 [6].

The above results vividly confirm the fact that $M\overline{S}$ exposures are more deleterious on the physical properties of low water to binder (w/b) ratio plain and blended cement mortar and concrete specimens. Ben-Yair [23] reported more expansion of the low w/c ratio cements after eight years of exposure to mixed sulfate–chloride media. He attributed this behavior to the salt crystallization in the very fine pore structure of the low w/c ratio specimens, which could not be accommodated therein thereby producing higher expansion and deterioration than in the specimens prepared with high w/c ratio, whose coarse pore structure could accommodate the power of salt crystallization [8,23]. Al-Amoudi et al. [24] attributed the inferior performance of low w/b ratio, dense microstructure of these specimens to their limited pore space for the expansive reaction products to occupy (i.e., primarily gypsum and M–S–H and, to a lesser degree, ettringite). Similar results indicating the poor performance of dense hydrated cements in $M\overline{S}$ environments have been reported in the literature [25–27]. Our experience with $M\overline{S}$ exposures indicates that the deterioration is only surficial; i.e., the bulk of the specimens maintain their initial, dense microstructure [7]. For example, the data in Table 2 reveal that the silica

Table 1
Strength reduction and expansion in plain and blended cements exposed to $N\overline{S}$ and $M\overline{S}$ environments [24]

Mix no.	Cement type and blending material	Strength reduction (%)			Expansion (%)	
		$N\overline{S}$	$M\overline{S}$	Difference	$N\overline{S}$	$M\overline{S}$
1	Type I	39	62	23	0.104	0.046[a]
2	Type V	34	53	19	0.113	0.031
3	Type I + FA (20%)	22	65	43	0.111	0.056[a]
4	Type I + SF (10%)	9	72	63	0.082	0.096
5	Type I + SF (20%)	−1	89	90	0.061	0.090[a]
6	Type I + BFS (70%)	18	75	57	0.099	0.067[a]
7	Type I ($w/c = 0.35$)	26	81	55	0.095	0.088
8	Type V + FA (20%)	17	66	49	0.089	0.086
9	Type V + SF (10%)	7	71	64	0.073	0.082

[a] Expansion measurements taken earlier than 360 days.

Table 2
Performance of concrete mixtures after 44 months of exposure to the mixed-sulfate environment [6]

Mix number	Cement type	Blending material (replacement)	*w/c*[b]	Concrete weight loss (%)	Corrosion potential, SCE (mV)	Polarization resistance (kΩ cm^2)
1	I	–	0.50	0.86	395.1	56.7
2	V	–	0.50	0.93	337.7	76.6
3	I	Fly ash (20%)	0.50	23.1	681.1	24.1
4	I	Silica fume (10%)	0.50	8.99	252.1[c]	844
5	I	BFS[a] (60%)	0.50	37.4	696.2	12.8
6	II	–	0.50	3.13	577.9	70.7
7	I	–	0.35	8.88	259.4	696
8	V	Fly ash (20%)	0.50	11.6	670.7	8.92
9	V	Silica fume (10%)	0.50	14.8	652.2	30.5
10	V	–	0.35	4.72	188.5[c]	386
11	I	BFS[a] (60%)	0.35	44.0	669.4	6.81
12	I	Fly ash (20%)	0.35	18.5	713.0	27.4
13	V	Fly ash (20%)	0.35	11.0	668.8	44.2
14	I	Silica fume (10%)	0.35	11.6	503.3	162
15	V	Silica fume (10%)	0.35	15.5	350.8	327

[a] Blast-furnace slag.
[b] Water-to-cementitious materials ratio.
[c] Passive corrosion state.

fume blended cements (i.e., Mix Nos. 4, 14 and 15) and the low *w/c* ratio mixtures of plain cements (i.e., Mix Nos. 7 and 10) preserved the passivity of the embedded reinforcing steel (i.e., the polarization resistance was more than the threshold resistance of 87 kΩ cm^2) despite their advanced stage of deterioration, as evidenced by the high values of weight loss of concrete which were much more than the threshold value of 5%. On the contrary, the reinforcing steel in the high *w/c* ratio concrete specimens (i.e., Mix Nos. 1, 2 and 6) were corrosively active though the weight loss in these concrete specimens was not high (i.e., the concrete weight loss of these mixes was less than the threshold value). Therefore, these findings confirm the fact that $M\overline{S}$ attack is surficial and progresses with time in the core matrix of concrete.

6. Effect of cation type on sulfate attack

Sulfate attack on concrete is primarily attributed to sodium, magnesium and calcium sulfate salts. Due to the limited solubility of calcium sulfate in water at normal temperatures (i.e., approximately 1400 mg/l SO_4^{2-}), sulfate attack is normally ascribable to the presence of magnesium sulfate or sodium sulfate [6]. Laboratory studies [6,24] were conducted by the author and his colleagues to evaluate the effect of cation type associated with the sulfate ions on sulfate attack. The effect of sulfate ions on plain and blended cements in magnesium–sodium sulfate environments was evaluated by conducting visual inspection and measuring the reduction in strength and expansion. In one of these studies, nine different mortar mixtures were exposed to both sodium sulfate and magnesium sulfate solutions [24]. The various types of plain and blended cements used in this investigation are shown in Table 1, while the sand to binder ratio and water to binder ratio were maintained invariant at 2.75 and 0.5, respectively. The sulfate concentration in the exposure solutions was preserved at 2.1%.

In this study, the data on strength reduction, summarized in Table 1, indicate that all blended cements exhibited superior performance in the sodium sulfate environment as compared with plain cements. Among the blended cements, silica fume cement displayed distinctly the best performance. However, the strength reduction was very high in all the cements exposed to magnesium sulfate solution. Further, the reduction in strength in the blended cements was more than that in the plain cements. These results indicate that blended cements, particularly those prepared with silica fume and blast furnace slag, are very deleteriously affected by magnesium sulfate, primarily due to the reduced calcium hydroxide (CH) content.

The data in Table 1 also indicate higher expansion in the specimens exposed to sodium sulfate environment compared to those exposed to the magnesium sulfate solution. Blended cements, particularly those prepared with silica fume, exhibited the best performance in the sodium sulfate environment as compared with plain cements. Further, the lower expansion noted in the specimens exposed to magnesium sulfate, as compared to that noted in the sodium sulfate, indicates that the reaction products in the specimens exposed to the former solution do not produce excessive expansive products.

6.1. Mechanisms of $N\bar{S}$ attack

Sodium sulfate ($N\bar{S}$) attack is initiated by the reaction of $N\bar{S}$ with the portlandite (CH) produced by the hydration of cement. It is followed by the reaction of gypsum with monosulfate and the other alumina-bearing phases to form secondary ettringite, as shown in the following reactions:

$$\mathrm{CH} + \mathrm{N\bar{S}} + 2\mathrm{H} \rightarrow \mathrm{C\bar{S}H_2} + \mathrm{NH} \tag{3}$$

$$\mathrm{C_3A} + 3\mathrm{C\bar{S}H_2} + 26\mathrm{H} \rightarrow \mathrm{C_6A\bar{S}_3H_{32}} \tag{4}$$

The sodium hydroxide (NH) produced in Eq. (3) raises the pH of the hydrated cement paste to about 13.5. Such pH rise has a stabilizing effect on the C–S–H and ettringite ($C_6A\bar{S}_3H_{32}$). The gypsum ($C\bar{S}H_2$), produced in Eq. (3), will react with some of the hydration products, namely calcium aluminate hydrate (C_4AH_{13}), monosulfate ($C_4A\bar{S}H_{12}$) and/or unhydrated (i.e., surplus) tricalcium aluminate (C_3A), to produce "secondary" ettringite, as summarized in Eqs. (1), (2) and (4). The term "secondary" is used to denote the ettringite produced by $N\bar{S}$ attack and to differentiate it from the "primary" ettringite that is formed during the setting of Portland cements when the concrete is in the plastic stage. Since ettringite is expansive in nature (i.e., it has a low density of 1.73 g/cm^3 compared to an average of 2.50 g/cm^3 for the other products of hydration), expansion and cracking of concrete are the manifestation of Na_2SO_4 attack.

In summary, $N\bar{S}$ attack is based on the generation of secondary ettringite as per Eqs. (1), (2), and (4). The reactants in these equations are truly aluminate based (i.e., monosulfate, hydrated aluminate and/or unhydrous C_3A). Thus, it is rational to specify a C_3A content of less than 5% to produce sulfate-resistant cements. If the C_3A content is between 5% and 8%, the $N\bar{S}$ attack is possible. If the C_3A is more than 8%, the attack will be probable. There are two more factors that influence this type of attack; the first being the C_4AF (i.e., tetracalcium alumino-ferrite) content in cement. Although this mineral behaves less deleteriously than the C_3A in terms of $N\bar{S}$ attack [28], it contributes to the development of a phase similar to, but less expansive than, ettringite. Therefore, to produce $N\bar{S}$-resistant cement, ASTM C 150 also limits the sum of C_4AF plus twice the C_3A content to 20%. Secondly, the gypsum produced in Eq. (3) has more volume than that of the reactants, and the NH produced in Eq. (3) has a stabilizing and expansive effects on ettringite thereby making it more detrimental. Accordingly, if a $N\bar{S}$-resistant cement is to be produced, the portlandite content should be reduced in addition to the ASTM C 150 limitations on C_3A and C_4AF [22]. CH can be reduced by decreasing the C_3S/C_2S ratio or using blended cements [3].

6.2. Mechanisms of $M\bar{S}$ attack

The sequential reactions of magnesium sulfate ($M\bar{S}$) with the cement hydration products are shown below:

$$\mathrm{CH} + \mathrm{M\bar{S}} + 2\mathrm{H} \rightarrow \mathrm{C\bar{S}H_2} + \mathrm{MH} \tag{5}$$

$$\begin{aligned} &\mathrm{C}_x\mathrm{S}_y\mathrm{H}_z + x\mathrm{M\bar{S}} + (3x + 0.5y - z)\mathrm{H} \\ &\quad \rightarrow x\mathrm{C\bar{S}H_2} + x\mathrm{MH} + 0.5y\mathrm{S_2H} \end{aligned} \tag{6}$$

$$4\mathrm{MH} + \mathrm{SH}_n \rightarrow \mathrm{M_4SH_{8.5}} + (n - 4.5)\mathrm{H} \tag{7}$$

Magnesium sulfate attack starts by reaction (5) above. However, unlike NH, the magnesium hydroxide (MH) produced in Eq. (5) is insoluble (i.e., its solubility is 0.01 g/l compared to 1.37 g/l for CH) and its saturated solution has a pH value of 10.5 (compared to a pH of 12.4 and 13.5 for CH and NH, respectively) [21]. Such a low pH destabilizes both ettringite and C–S–H [28]. The consequences of this low pH are [21,24,28]:

(i) secondary ettringite will not form;

(ii) since the magnesium and calcium ions associate well with each other due to their equal valence and similar radii, $M\bar{S}$ will readily react with C–S–H, as per Eq. (6), thereby producing gypsum, brucite (MH) and silica gel (S_2H). This gel is less cementitious than the original cementing C–S–H gel;

(iii) C–S–H tends to liberate lime to raise the pH and to establish its own equilibrium (i.e., this process is known as decalcification of C–S–H). The liberated lime, instead of re-establishing the pH, reacts further with $M\bar{S}$ (as per Eq. (5)) and, therefore, produces more $C\bar{S}H_2$ and MH;

(iv) the concentration of gypsum and brucite in the paste matrix will increase while the C–S–H progressively loses its lime and becomes less cementitious; and finally

(v) with the increase in brucite, a further deleterious action of MH is ascribable to its reaction with the hydrosilicates (S_2H), as shown in Eq. (7), thereby producing magnesium silicate hydrate (M–S–H), which is non-cementitious.

Therefore, the damaging attribute of $M\bar{S}$ stems from the fact that reactions (6) and (7) go on to completion thereby converting the C–S–H phase to M–S–H with no binding properties [21]. This attack is, therefore, characterized by softening and deterioration of the surfacial layers of the hardened cement paste and the profuse formation of gypsum and brucite, as elaborated in Eqs. (5) and (6). However, the brucite content will ultimately decrease due to its conversion to M–S–H, as detailed in Eq. (7).

7. Effect of chloride ions on sulfate attack

In the marine environments and arid saline soils and groundwater, chloride and sulfate salts do exist concomitantly. The conjoint presence of these two salts may cause deterioration of concrete due to reinforcement corrosion and sulfate attack. Hjorth [29] reported that sulfate ions react preferentially with C_3A to form two compounds of calcium sulfoaluminate hydrates, namely trisulfo-aluminate hydrate ($C_3A \cdot 3CaSO_4 \cdot$ aqueous) and monosulfo-aluminate hydrate ($C_3A \cdot CaSO_4 \cdot$ aqueous). The preferential reaction of sulfates with the C_3A phase has also been reported by Holden et al. [30] and Rasheeduzzafar et al. [31,32].

Al-Amoudi et al. [33] investigated the role of chloride ions on sulfate attack in OPC and blended cements. Paste and mortar specimens, prepared with Type I and Type V cements, as well as with Type I cement blended with fly ash, silica fume and blast furnace slag, were exposed to four sulfate and/or chloride environments for a period of two years. Their results indicated that sulfate deterioration in plain cements was mitigated by the presence of chloride ions, whereas in blended cements, particularly those prepared with silica fume and blast furnace slag, the beneficial effect of chloride was only marginal. The compressive strength results (i.e., sulfate deterioration factor; SDF) of the various types of cements in two of those sulfate–chloride exposures are shown in Table 3 [33]. After 360 days of exposure, the beneficial effect of chloride was noted to be maximum in the fly ash cement, where the sulfate deterioration factor was reduced from 77% in the pure sulfate solution to 20% in the mixed sulfate–chloride solution, indicating a beneficial effect of 57%. After 720 days of exposure, the maximum beneficial effect of chloride was observed in Type V cement; the reduction in the SDF value being 45% compared with 39% in the fly ash cement, 30% in Type I cement, 11% in the BFS cement and 9% in the silica fume cement.

Based on these experimental results and also using X-ray diffraction and scanning electron microscopy analyses, the authors [33] attributed the exacerbated sulfate deterioration in silica fume and blast furnace slag cements when exposed to both the sulfate and sulfate–chloride environments, to the magnesium-oriented type of sulfate attack that was more operative in blended cements due to the absence of calcium hydroxide. In contrast to the gypsum and ettringite-oriented sulfate attacks, this type of attack was not inhibited in the presence of chloride ions.

Due to the effect of the magnesium ions on concrete deterioration in blended cements, the authors recommended the usage of additional protective measures, such as the application of a water-resistant, epoxy-based coating to the exterior surface of the structure [33,34], to protect the reinforced concrete structural utilities in these exposures. The beneficial effect of chloride ions in mitigating the expansion due to sulfate attack is also illustrated by the data in Table 4 [34]. The data therein vividly indicate that the chloride beneficiation was manifested by the strength reduction and expansion which were both mitigated by the concomitant presence of chloride ions in the sulfate medium. The ameliorative effect of chloride ions on sulfate attack is also visually illustrated in Fig. 2.

The beneficial role of chloride ions in inhibiting concrete damage due to sulfate attack has also been reported recently by Dehwah [35]. In his study, the deterioration was not noted in plain and blended cement concrete specimens exposed to sodium chloride plus sodium sulfate solutions even when the SO_4^{2-} concentration was as high as 4%. However, in the case of magnesium sulfate solutions, deterioration, in the form of surface damage, was noted in the plain and fly ash cement concrete specimens when the SO_4^{2-} concentration was 2.5% and above. In the silica fume and blast furnace slag cement concrete specimens exposed to the magnesium sulfate solutions, deterioration was noted when the SO_4^{2-} concentration was as low as 1%.

The author [35] has observed a dense C–S–H microstructure in the scanning electron micrographs for the plain and silica fume cement concrete specimens exposed to the sodium chloride plus sodium sulfate solution. However, a heterogeneous microstructure of the C–S–H was noted in the specimens exposed to the magnesium sulfate solutions.

8. Effect of internal sulfate ions

As was discussed earlier, deterioration of concrete due to sulfate attack is initiated mainly due to the con-

Table 3
Beneficial effect of chloride ions on sulfate attack in plain and blended cements [33]

Cement type	SDF in 2.1% SO_4^{2-} after		SDF in 2.1% SO_4^{2-} + 15.7% Cl after		Beneficial effect of chloride (%)	
	360 days	720 days	360 days	720 days	360 days	720 days
Type I	65	85	25	55	40	30
Type V	55	75	26	30	29	45
Fly ash	77	85	20	46	57	39
Silica fume	74	90	44	81	30	9
BFS	67	95	58	84	9	11

Table 4
Summary of strength reduction and expansion test results in sulfate and sulfate–chloride environments [34]

Mix no.	Cement type	Blending material	w/b[a]	Strength reduction (%)		Expansion (%)	
				Sulfate solution	Sulfate–chloride solution	Sulfate solution	Sulfate–chloride solution
1	I	None	0.50	42	16	0.106	0.045
2	V	None	0.50	48	17	0.093	0.046
3	I	20% Fly ash	0.50	47	9	0.099	0.039
4	I	10% Silica fume	0.50	53	41	0.094	0.036
5	I	None	0.35	48	14	0.114	0.040
6	V	None	0.35	54	26	0.096	0.046
7	V	20% Fly ash	0.50	55	16	0.088	0.025
8	V	10% Silica fume	0.50	49	40	0.093	0.033
9	I	70% BFS	0.50	55	45	0.113	0.059

[a] Water-to-binder ratio.

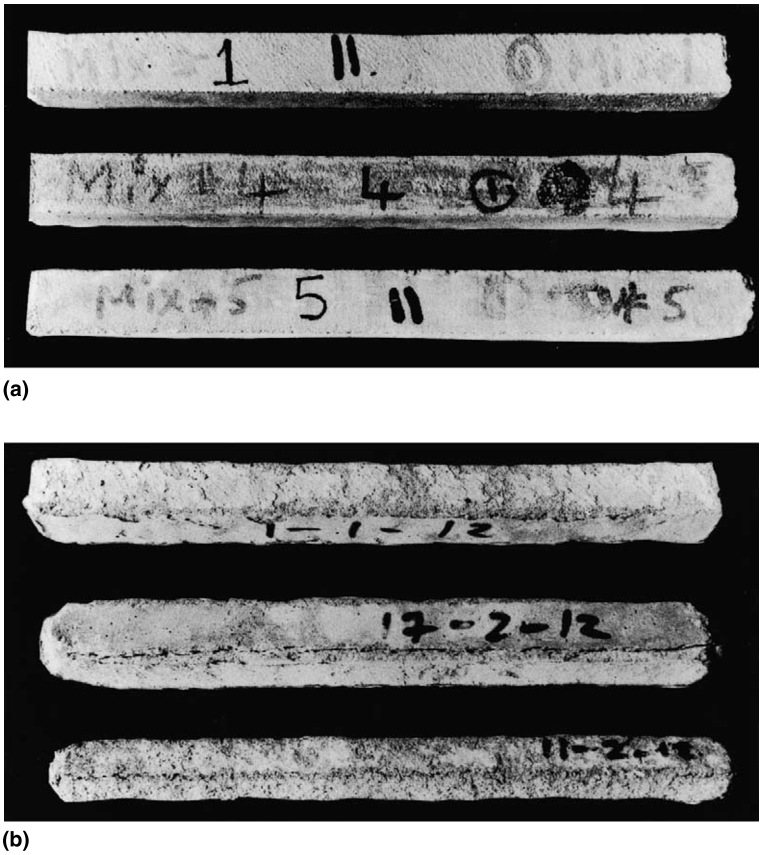

Fig. 2. Visual documentation of the specimens exposed to sulfate solutions: (a) in $N\overline{S}$ solution; (b) in $M\overline{S}$ solution.

tribution of sulfate ions by the exposure conditions. However, the sulfate ions are sometimes contributed to the concrete mix from internal sources, such as the aggregates, mixing and curing water, and admixtures. The role of these ions, due to delayed ettringite formation, has been a subject of considerable debate and discussion among concrete technologists [36]. It is hypothesized that the sulfate ions that have been bound with the cement hydration products are released back into the pore solution at a later point of time thereby enhancing the chances of formation of secondary ettringite. Such a phenomenon has been noted in steam-cured, precast elements, such as railway sleepers.

Maslehuddin et al. [37] reported an increase in the sulfate concentration in the pore solution of specimens contaminated with sodium chloride plus sodium sulfate in comparison with those contaminated with only sodium sulfate, as summarized in Table 5. The data in

Table 5
Sulfate concentration in the pore solution of uncontaminated and contaminated cement mortar specimens [37]

Cement type	Sulfate concentration (mM/l)			
	No contamination	Cl	SO_4^{2-}	$Cl + SO_4^{2-}$
Type V	7.9	16.9	86.5	140.1
Type I	5.5	20.7	115.8	210.5

Table 5 indicate that the sulfate binding of cements was decreased due to the conjoint presence of chloride and sulfate ions.

Dehwah [35] evaluated the effect of sulfate concentration and the associated cation type on the pore solution chemistry. The sulfate concentration in the pore solution of both plain and blended cements contaminated with sodium sulfate increased with the quantity of sulfate. However, no increase in the sulfate concentration was noted in the specimens contaminated with magnesium sulfate. He attributed the increase in the sulfate concentration in the specimens contaminated with sodium sulfate to the increase in the alkalinity of the pore solution. According to Dehwah [35], it is possible that the monosulfate is not stable at high pH. This hypothesis is aptly supported by the sulfate complexation noticed in the cements contaminated with magnesium sulfate.

9. Field studies

The performance of plain and blended cements, vis-à-vis sulfate attack, has been evaluated by the author and his colleagues in the field [8]. After 14 days of water curing, plain and blended cement mortar specimens were buried in a sabkha soil in eastern Saudi Arabia. This type of soil is very saline (i.e., $SO_4^{2-} = 0.55\%$ and $Cl^- = 15.7\%$) and the groundwater table is close to the ground surface [38]. The compressive strength of these specimens was determined after 3, 6, 12 and 18 months and the results were compared with the initial (i.e., 14-day water-cured) strength, as shown in Figs. 3 and 4 [8].

As shown in Fig. 3, the compressive strength of the mortar specimens made with Type I and Type V cements continued to be higher than the 14-day value, even after an exposure period of 540 days in the sabkha medium. The data in Fig. 4 indicate that the fly ash cement displayed similar behavior to plain cements. In the case of silica fume cement, the strength increased up to about 210 days. Thereafter, there was some reduction in strength. After 540 days of burial, the strength of silica fume blended cement specimens was less than the initial 14-day strength. The specimens made with blast furnace slag cement exhibited an intermediate behavior between the fly ash and silica fume cement specimens.

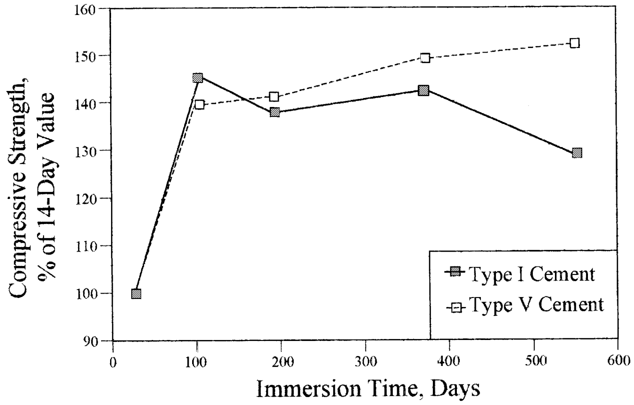

Fig. 3. Compressive strength development in plain cements immersed in sabkha soil.

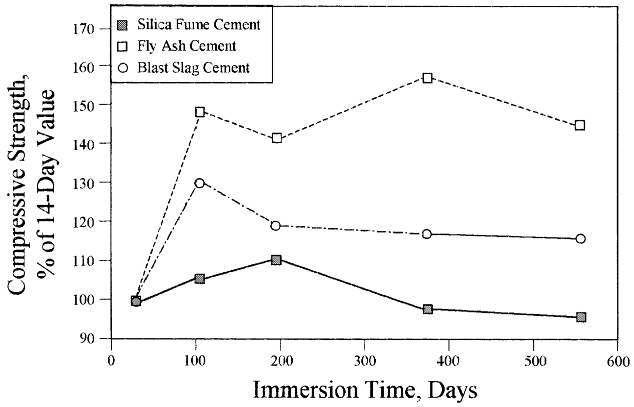

Fig. 4. Compressive strength development in blended cements immersed in sabkha soil.

The reduction in the compressive strength of the silica fume blended cement specimens, as compared with the other cements, was ascribed to their fine pore structure. As was discussed previously, the formation of salt crystals in the fine pores induces considerable pressure that tends to degrade the surfacial layers of the dense microstructure of SF cement thereby reducing its compressive strength with extended exposure to salty environments [8].

10. Conclusions

This paper presents a review of the studies conducted at KFUPM on sulfate attack. Such studies were initiated to evaluate the effect of sulfate type and concentration on plain and blended cements. Blended cements, particularly those prepared with silica fume (SF) and blast furnace slag (BFS), were observed to be highly resistant to $N\bar{S}$ attack due to an interplay of several factors; the most important being the reduction in the portlandite (CH) produced by cement hydration and the densification of the microstructure of the hardened cement paste matrix. These factors mitigate the production of expansive ettringite. The $N\overline{S}$ attack was manifested by expansion and strength reduction. Low *w/b* ratio cements moderately alleviate $N\overline{S}$ attack by mitigating the diffusion of SO_4^{2-} ions into the matrix of the specimens.

Upon exposure to $M\overline{S}$, blended cements, particularly those prepared with SF and BFS, displayed inferior performance in terms of strength reduction and weight loss of concrete as compared with plain cements. The inferior performance of blended cements is ascribable to the consumption of portlandite by the pozzolanic reaction thereby causing a shift in the reaction mechanisms. Such a shift exacerbates the sulfate attack on C–S–H leading to softening, loss of surfacial concrete material and excessive reduction in strength. Ultimately, $M\overline{S}$ attack transforms the cementitious C–S–H into fibrous, non-crystalline M–S–H that possesses no cementing properties. Accordingly, the $M\overline{S}$ attack was manifested by weight loss of material and strength reduction. Low *w/b* ratio cements displayed inferior performance as compared with normal *w/b* ratio cements due to the finer pore structure of the former cements.

The concomitant presence of chlorides with the sulfate ions tends to mitigate $N\overline{S}$ attack due to the enhanced solubility of gypsum and ettringite thereby inhibiting their expansive characteristics. In $M\overline{S}$ exposures, the chlorides alleviate the gypsum attack in a way similar to that in $N\overline{S}$ environments. However, the chloride ions do not significantly affect the attack of $M\overline{S}$ on C–S–H. As a consequence, $M\overline{S}$ attack on blended cements exposed to sulfate–chloride environments progresses unhindered by chlorides, thereby converting the cementitious C–S–H to the non-cementitious M–S–H.

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