

# MECHANISMS OF SULFATE ATTACK IN PLAIN AND BLENDED CEMENTS: A REVIEW

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## ABSTRACT

The recent modifications in the physicochemical characteristics of portland cements and the extensive use of mineral admixtures have introduced significant changes in the chemical and mineralogical composition in the present day cements that need to be addressed by the construction industry. Moreover, the effect of cation associated with the sulfate ions on these changes is inconclusive and highly debated in the concrete literature. In addition, the exposure of many reinforced concrete structures to sulfate-bearing environments has focussed attention on the role of sulfate ions in the corrosion of reinforcing steel.

In view of the above-cited controversies, this paper presents a state-of-the-art review on sulfate attack in plain and blended cements from a civil engineering perspective. In particular, the paper addresses the following subjects: (i) mechanisms of sulfate attack in plain and blended cements; (ii) factors affecting sulfate attack; (iii) modes of deterioration; (iv) the effect of sulfate cation type on the strength and expansion of plain and blended cements; (v) the effect of sulfate ions on weight loss and reinforcement corrosion; and (vi) the role of chloride ions in sulfate attack in plain and blended cements.

## KEYWORDS

**Sulfate attack;** cements; blended cements, mortar; concrete; sodium sulfate; magnesium sulfate; expansion; strength reduction; weight loss.

## INTRODUCTION

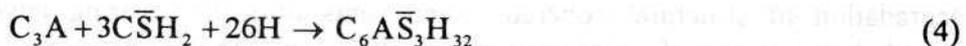
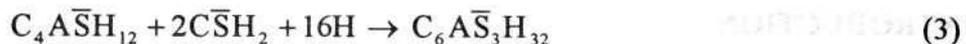
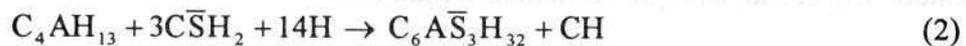
Degradation of structural concrete components in sulfate-bearing environments has recently been concerned with the attack of sulfate ions and their associated cations on the products of hydration of portland cement, particularly the portlandite and calcium silicate hydrate (Mather, 1968; Calleja, 1980; Rasheeduzzafar, 1992; Lawrence, 1990; Cohen and

Bentur, 1988). In fact, the deterioration attributable to sulfate attack probably received attention much earlier compared to all other forms of deterioration such as, for example, corrosion of reinforcing steel or alkali-aggregate reactions (Al-Amoudi, 1995). A literature search indicates that 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 (Al-Amoudi, 1998). 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.

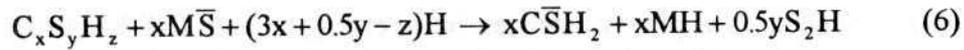
Till today, research related to the effect of sulfate ions on the performance of concrete forms the second subject in the literature of concrete durability. Such a long and continuous research is motivated by the following factors: (i) modifications in the physicochemical characteristic of portland cements during the last four decades; (ii) the significant use of blending materials with portland cement to improve the durability performance of concrete when exposed to harsh environments; and (iii) the existence of some controversial points on the role of some parameters, such a cement content,  $C_3A$ ,  $C_4AF$ , etc., in sulfate attack (Al-Amoudi, 1995). Therefore, there is an urgent need to clarify the mechanisms of sulfate attack to the constructional engineers, particularly those who specify blended cements in their reinforced concrete structures.

## MECHANISMS OF SULFATE ATTACK ON PORTLAND CEMENTS

Research studies on sulfate attack are invariably conducted by exposing cement paste, mortar or concrete specimens to primarily sodium, magnesium and calcium sulfate solutions. Due to the limited solubility of calcium sulfate in water at normal temperatures (approximately 1400 mg/l  $SO_4^{2-}$ ), higher concentrations are, therefore, generally due to the presence of magnesium sulfate or sodium sulfate (Al-Amoudi, 1995). Due to the existence of both or either of these salts in soils, seawater, sewage tanks, etc., there is an exigent need to understand the mechanisms of sulfate attack in order to protect the structural utilities when exposed to these hostile environments. In summary, the mechanisms of attack by sodium sulfate ( $N\bar{S}$ ) and magnesium sulfate ( $M\bar{S}$ ) on hardened cement pastes are generally represented by the following reaction\* (Mather, 1968; Calleja, 1980; Cohen and Bentur, 1988; Al-Amoudi, 1995, 1998; Rasheeduzzafar et al., 1994):



\* C = CaO, N = Na<sub>2</sub>O, M = MgO, S = SiO<sub>2</sub>,  $\bar{S}$  = SO<sub>3</sub>, H = H<sub>2</sub>O



### Mechanisms of $N\bar{S}$ Attack

Sodium sulfate attack is initiated by the reaction of  $N\bar{S}$  with the portlandite (CH) produced by the cement hydration. The sodium hydroxide (NH) produced by this reaction (Eq. 1 above) raises the pH value of the hydrated cement paste to 13.5 (i.e. compared with 12.4 for saturated CH solutions). Such a 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 by Eq. (1) 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. (2) to (4). The term "secondary" is used to differentiate the ettringite produced by  $N\bar{S}$  attack from the "primary" ettringite 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<sup>3</sup> compared to an average of 2.50 g/cm<sup>3</sup> for the other products of hydration), expansion and cracking of concrete are the manifestation of  $Na_2SO_4$  attack. It is worth mentioning that primary ettringite does not produce cracking because the hardened cement paste is still in the plastic state and, therefore, can accommodate any increase in volume.

In summary,  $N\bar{S}$  attack is based on the generation of secondary ettringite as per Eqs. (2) to (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 less than 5% to produce  $N\bar{S}$ -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 content of  $C_4AF$  (tetracalcium aluminoferrite). Although this mineral behaves less deleteriously than the  $C_3A$  in terms of  $N\bar{S}$  attack, it contributes to the development of a phase similar to, but less expensive than, ettringite (Lea, 1970). Therefore, to produce  $N\bar{S}$ -resistant cement, ASTM C 150 also limits the total content of  $C_4AF$  plus twice the  $C_3A$  content to 20%. Secondly, the NH produced by Eq. (1) has a stabilizing effect on ettringite thereby making it more expansive and 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  $C_4AF$  (Al-Amoudi et al. 1995a). CH can be reduced by reducing the  $C_3S/C_2S$  ratio or using blended cements (Rasheeduzzafar, 1992).

### Mechanisms of $M\bar{S}$ Attack

Magnesium sulfate ( $M\bar{S}$ ) attack starts by Reaction 5 above. However, unlike NH, the magnesium hydroxide (MH) produced in this reaction 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) (Rasheeduzzafar et al.,

1994). Such a low pH destabilizes both ettringite and C-S-H (Lea, 1970). The consequences of this low pH are (Rasheeduzzafar et al., 1994; Lea, 1970; Al-Amoudi et al., 1995a): (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,  $\overline{M\overline{S}}$  will readily react with C-S-H, as per Eq. (6) above, 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  $\overline{M\overline{S}}$  (as per Reaction 5 above) and, therefore, produces more MH; accordingly (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; (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  $\overline{M\overline{S}}$  stems from the fact that Reactions 6 and 7 go on to completion thereby converting the C-S-H phase to a material (M-S-H) with no binding properties (Rasheeduzzafar et al., 1994). This attack is, therefore, characterized by softening and deterioration of the surficial layers of the hardened cement paste and the profuse formation of gypsum and brucite (Eqs. 5 and 6). However, the brucite content will ultimately decrease due to its conversion to M-S-H (Eq. 7).

## FACTORS AFFECTING SULFATE ATTACK

The above-cited mechanisms indicate that all cements (including the sulfate-resisting one) are vulnerable to  $\overline{N\overline{S}}$  and/or  $\overline{M\overline{S}}$  attack. However, the degree of attack depends on the following factors:

- (i) **Cement Type:** The most important mineralogical phases of cement that affect the intensity of sulfate attack are:  $C_3A$ ,  $C_3S/C_2S$  ratio and  $C_4AF$ .
- (ii) **Sulfate Type and Concentration:** Although the 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 attack, as described previously.
- (iii) **Quality of Concrete:** Since impermeability always reflects the quality and durability of concrete,  $\overline{N\overline{S}}$  attack is inversely related to the concrete quality (i.e. dense concrete tends to resist  $\overline{N\overline{S}}$  attack). In the case of  $\overline{M\overline{S}}$  environments, the conjoint effect of denseness (i.e. permeability) and cement type determines the extent of the attack.
- (iv) **Form of Construction:** The type of structure affects the degree of attack; for example, thin sections will deteriorate much faster than thick ones. Similarly, the attack will be more aggressive if differential exposure is imminent, such as retaining walls or dams, when one side is exposed to sulfates while the other is dry or when wet-dry cycles exist. Such a detrimental attack will often be aided by the physical effect of salt crystallization.

- (v) **Level of Water Table and Its Seasonal Variation:** It is known that sulfate attack takes place only in solution; no attack occurs in dry environments. Therefore, the most susceptible portion of a foundation is the part close to or above the groundwater table. However, observations indicate that deterioration of buildings located in shallow groundwaters (such in eastern Saudi Arabia) often occurs within about one meter above the ground surface (i.e. not at the groundwater table as it is anticipated). This behavior could be attributed to the capillary action which is also aided by atmospheric drying thereby leading to salt crystallization.
- (vi) **Possibility of Replenishment:** Consumption of sulfate ions will reduce their concentration in the exposure medium thereby mitigating the  $\text{SO}_4^{2-}$  attack unless the medium is very large (i.e. sabkha soil) or there is a source of replenishment (i.e. seawater).

## MODES OF SULFATE ATTACK

Although there are two mechanisms of sulfate attack, as has just been described, the modes of deterioration depends also on: (i) the geometry and type of specimen (i.e. whether cement paste, mortar or concrete), and sometimes (ii) the cement type. A review of the literature (Al-Amoudi, 1998) indicates that three modes of deterioration are usually manifested with sulfate attack (Fig. 1). The first mode of deterioration is akin to eating away of the hydrated cement paste and progressively reducing it to a cohesionless granular mass leaving the aggregate exposed and leading to loss of strength. This mode is attributed mainly to the formation of gypsum, and is known as the **acidic type** of  $\text{M}\bar{\text{S}}$  attack (Fig. 1a). The second mode of deterioration, which is normally characterized by expansion and cracking (Fig. 1b), takes place when the reactive hydrated aluminate phases, present in sufficient quantities, are attacked by  $\text{N}\bar{\text{S}}$  ions, thereby forming tricalciumsulfo-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 the presence of high concentrations of portlandite (CH) and sodium hydroxide (NH) in the pore solution. The third mode of sulfate attack is the **onion-peeling type**, which is characterized by scaling or shelling of the surface in successive layers in the form of "onion-skinning" delamination (Figg, 1979). This mode is the least reported in the literature and was observed in the case of paste specimens made with plain and fly ash blended cements exposed to mixed sulfate environments (Fig. 1c) (Al-Amoudi, 1998).

## SULFATE ATTACK ON BLENDED CEMENTS

In the context of this paper, blended cements are those portland cements to which mineralogical (i.e. pozzolanic) admixtures are added either as a replacement of the parent cement or as an addition to it (Mehta, 1987). Pozzolanic admixtures include a variety of natural materials (i.e. natural pozzolans such as volcanic ashes, diatomaceous earths, etc.) (Type N as per ASTM C 618) or byproducts of the manufacturing of certain minerals or the combustion of coal (i.e. blast furnace slag, fly ash, silica fume, etc.). When these materials are added to cements, they produce the following main advantages: (i) reduce the heat of hydration; (ii) reduce significantly the permeability of concrete; (iii) inhibit the

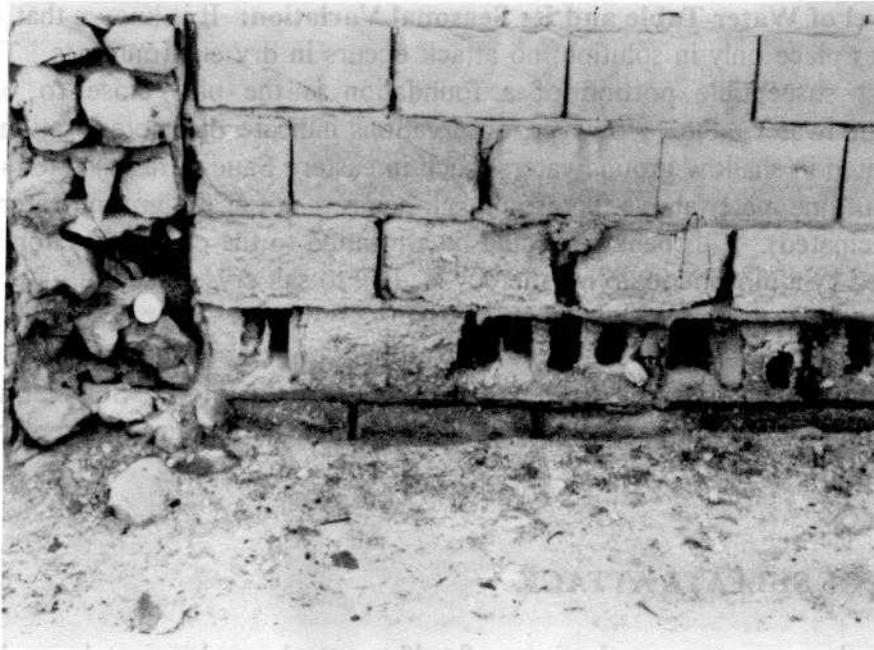


Fig. 1. Modes of sulfate attack: 1a: Acidic type

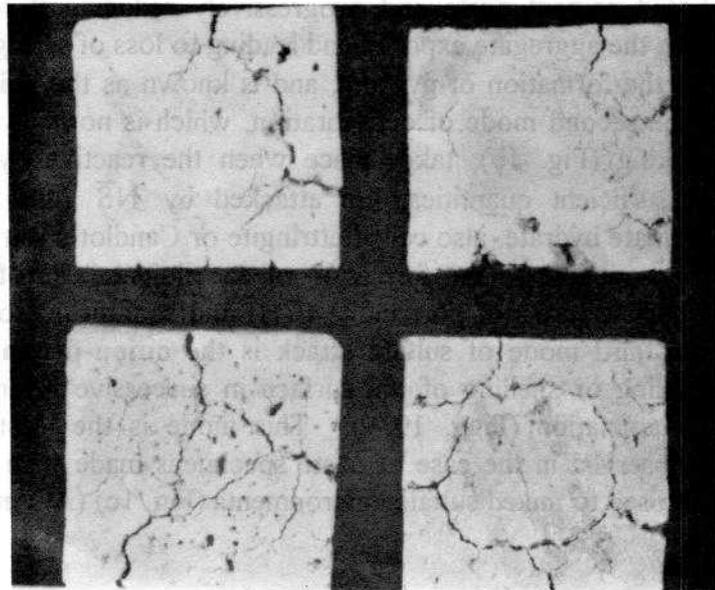


Fig. 1. (continued): 1b: Expansive type

alkali-silica reactivity; (iv) often enhance the sulfate resistance; and (v) often increase the ultimate strength. The negative consequences of incorporating these materials with cement are: (i) the early strength is often reduced; (ii) the “water” curing period should be extended; and (iii) sometimes (i.e. such as in the Arabian Gulf) the cost of these materials is higher than that of cement.

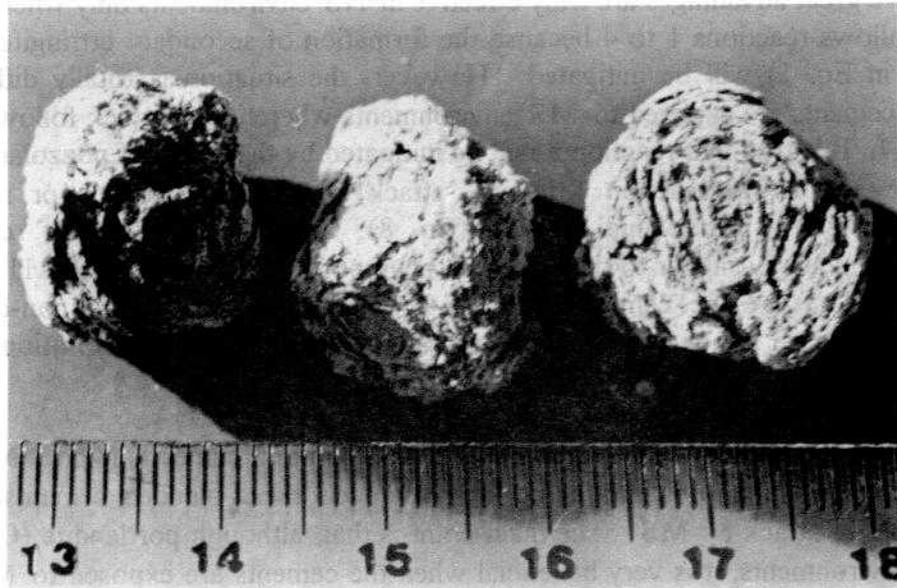
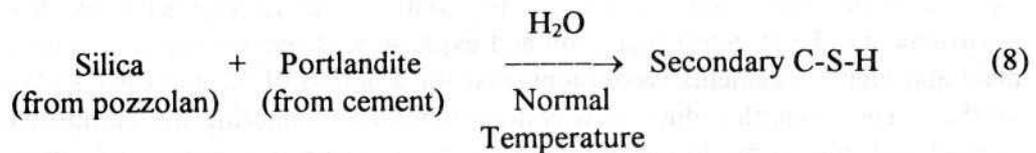


Fig. 1. (continued): 1c: Onion-peeling type

The interaction of pozzolanic materials with the products of hydration of portland cements is known as the **pozzolanic reaction** which can be simplified by the following equation:



The “secondary” calcium-silicate hydrate so formed is similar in essence to the “primary” C-S-H produced by the hydration of portland cement itself although the former is less dense (Al-Amoudi et al., 1995a). This pozzolanic reaction has the following beneficial impacts on sulfate attack: (i) the consumption of portlandite in Eq. (8) reduces the formation of gypsum in reactions described by Eqs. (1) and (5). Therefore, both  $\overline{\text{N}}\overline{\text{S}}$  and  $\overline{\text{M}}\overline{\text{S}}$  attacks are alleviated; (ii) the replacement of part of the cement by a pozzolanic material entails a reduction in the  $\text{C}_3\text{A}$  content (i.e. **dilution effect**). Hence, all the aluminate-bearing phases will accordingly be reduced. Therefore, the formation of secondary ettringite [as per reactions delineated by Eqs. (2) to (4)] will be mitigated; (iii) even if it is formed, ettringite becomes expansive only at high pH values ( $\text{pH} > 12$ ). Since blended cements consume a significant proportion of the portlandite produced by cement hydration and reduce the pH, the ettringite becomes less expansive; (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, sulfate ions cannot easily penetrate through the concrete matrix (as in the case of plain portland cements).

The above great advantages are truly effective in  $\overline{N\overline{S}}$  environments only where the sulfate attack follows reactions 1 to 4 because the formation of secondary ettringite (as well as gypsum in Eq. 1) will be mitigated. However, the situation is totally different when blended cements are exposed to  $\overline{M\overline{S}}$  environments whereby the attack follows Reactions 5, 6 and 7. It is true that reaction 5 will be mitigated by the usage of pozzolanic materials (in a way similar to reaction 1 in  $\overline{N\overline{S}}$  attack) due to the absence or reduction of portlandite by the pozzolanic reaction (Eq. 8). However, instead of reacting with portlandite in a way similar to the attack on plain portland cements,  $\overline{M\overline{S}}$  will directly and energetically attack the cementitious C-S-H and convert it to the non-cementitious M-S-H. Such an attack is very instrumental to the enhanced deterioration of blended cements.

In summary, the above mechanisms indicate that blended cements are more resistant to  $\overline{N\overline{S}}$  attack than plain portland cements. However, these blended cements are readily susceptible to attack by  $\overline{M\overline{S}}$ . The main point is that, although portlandite (CH) is "bad" in  $\overline{N\overline{S}}$  environments, it is very beneficial when the cements are exposed to  $\overline{M\overline{S}}$  because **CH constitutes the first line of defense against  $\overline{M\overline{S}}$  attack and, therefore, it serves to protect C-S-H.** However, in the long term, all cements, whether blended or plain, may suffer equally from  $\overline{M\overline{S}}$  attack. Therefore, protection of the substructures exposed to  $\overline{M\overline{S}}$  environments should be more augmented.

## MECHANICAL PROPERTIES OF MORTAR SPECIMENS

To assess the mode and degree of degradation due to exposure to  $\overline{N\overline{S}}$  and  $\overline{M\overline{S}}$  environments, the strength reduction and expansion of mortar specimens made with nine plain and blended cements were monitored for a period of 12 months (Al-Amoudi et al., 1995a). The strength reduction was determined by comparing the compressive strength of small (25 mm) cubes in the sulfate environments with the strength of similar specimens cured in water. The expansion measurements were conducted on prismatic (25×25×285 mm) mortar specimens. The water to binder or cementitious materials ratio (w/b), type of cement and content of blending materials of the nine mixes is shown in Table 1 while the sand to binder ratio was maintained at 2.75. The sulfate ( $\text{SO}_4^{2-}$ ) concentration was maintained at 2.1%.

### Strength Reduction

The strength reduction data in Table 1 indicates that all blended cements exhibited superior performance in  $\overline{N\overline{S}}$  environment as compared with plain cements. Among the blended cements, silica fume (SF) cement displayed distinctly the best performance whereby the reduction in strength ranged from -1% to 9% (for 20 and 10% SF additions, respectively). The negative strength reduction proves the very dense microstructure of the 20% SF cement whereby the strength of the specimens exposed to  $\overline{N\overline{S}}$  solution was higher than that of the specimens exposed to water due to the densifying effect of the reaction products in the existing dense microstructure. Further, comparing the performance of Mix No. 4 and 9 (both of them have 10% SF) indicated that SF cements do not significantly depend on the type of parent cement (i.e. whether Type I or Type V).

Table 1. Strength reduction and expansion in plain and blended cements exposed to  $\overline{N\overline{S}}$  and  $\overline{M\overline{S}}$  environments (Al-Amoudi et al., 1995a)

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

\*Expansion measurements taken earlier than 360 days.

Blast furnace slag (BFS) cement (Mix No. 6) showed the second best performance while fly ash (FA) cement exhibited an intermediate performance between blended and plain cements. In fact, the performance of FA cement (Mix No. 3 and 8) was equivalent to the cement made with low w/b ratio (Mix No. 7).

On the contrary to  $\overline{N\overline{S}}$ , the strength reduction was observed to be very high in all the cements exposed to  $\overline{M\overline{S}}$  solution. However, all blended cements exhibited greater reduction in strength than plain cements. To quantify the difference in performance between the two exposures, the difference in strength reduction in  $\overline{M\overline{S}}$  exposure in comparison to  $\overline{N\overline{S}}$  exposure was included in Table 1. SF-blended cements displayed uniquely extreme difference in performance in the two exposures (i.e. from the best in  $\overline{N\overline{S}}$  to the worst in  $\overline{M\overline{S}}$ ) followed by BFS, low w/b ratio, and FA cements. These results prove that blended cements, particularly those made with SF and BFS, are very deleteriously affected by  $\overline{M\overline{S}}$ , primarily due to their low content of portlandite (Cohen and Bentur, 1988; Al-Amoudi, 1995, 1998; Rasheeduzzafar et al., 1994), as was explained.

The low performance of the specimens made with low w/b ratio was probably attributed to their dense microstructures thereby providing limited space for the expansive reaction products to occupy, as documented in the literature (Al-Amoudi, 1995; Al-Amoudi et al., 1995a). A question would be raised as to why not the same reduction in strength occurred when these low w/b ratio specimens were exposed to  $\overline{N\overline{S}}$  solution? The reason may be ascribable to the fact that  $\overline{N\overline{S}}$  attack predominantly proceeds via penetration of the sulfate ions into the interconnected porosity and the strength reduction takes place mainly when the reaction products are distributed into the whole specimens and partly by the leaching of soluble reaction products (Israel et al., 1997). Accordingly, such a process is hindered in the low w/b ratio cement due to its dense microstructure and is, therefore, responsible for its better resistance in  $\overline{N\overline{S}}$  environment. In  $\overline{M\overline{S}}$  exposure, however, the extensive gypsum precipitation (Eqs. 5 and 6) and massive M-S-H

formation (Eq. 7) mostly occurred on the surfaces of the specimens thereby leading to loss of material and strength; this loss tends to keep up with the penetrating front of  $\overline{M\bar{S}}$  (Israel et al., 1997). Such an attack is accentuated in dense matrices such as those of low w/b ratio cements. It is worth mentioning that owing to the surficial effect of  $\overline{M\bar{S}}$  on blended cements as well as to its poor penetration, degradation in the specimens' cores is restricted to the region close to the surface. On the contrary, the penetration of  $\overline{N\bar{S}}$  causes changes within the core of the specimens. These conclusions are vividly supported by the expansion data.

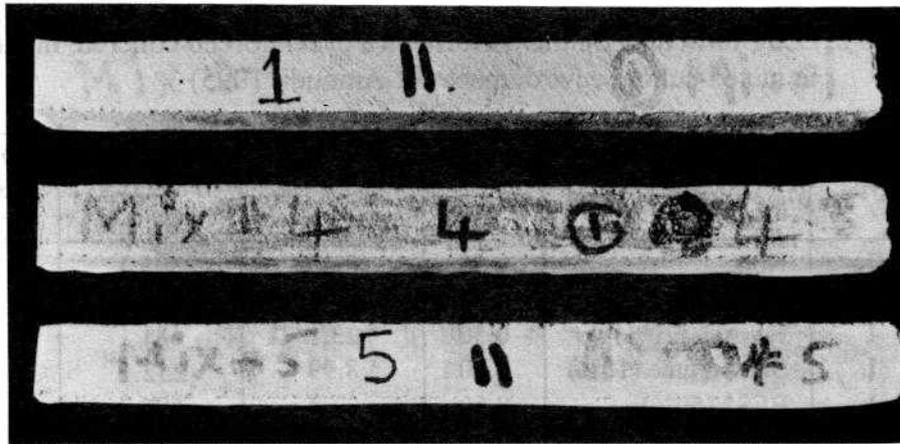
### Expansion

The expansion data in Table 1 clearly indicates that, except for SF cements which exhibited significant deterioration, all plain and blended cements exposed to  $\overline{N\bar{S}}$  solution displayed higher expansion than those in  $\overline{M\bar{S}}$ . Furthermore, blended cements, particularly those made with SF, exhibited the best performance in  $\overline{N\bar{S}}$  as compared with plain cements. Therefore, the trend of the expansion results is almost exactly similar to the strength reduction of the specimens exposed to  $\overline{N\bar{S}}$ . The reasons for such distinct behavior in the performance of blended cements were clarified previously. Surprisingly, the lower values of expansion of the specimens exposed to  $\overline{M\bar{S}}$  environment do not *commensurate* with the data on strength reduction. Further, the lower expansion of the specimens exposed to  $\overline{M\bar{S}}$ , as compared with  $\overline{N\bar{S}}$ , indicates that the deteriorating mechanisms herein do not produce expansive products, particularly in the interior portions (i.e. cores) of the specimens. Consequently, the degradation of mortar specimens is proven to be *superficial* and *does not extend to the core of the specimens*. This conclusion is also evidenced by the fact that some of the stainless steel studs on the sides of the expansion specimens were loosened by the extensive deterioration (Fig. 2) leading to termination of the test measurements before the 360 days (Al-Amoudi et al., 1995a).

If a threshold value for expansion is taken as 0.10%, as normally reported (Al-Amoudi et al., 1995a), then the expansion data in Table 1 clearly indicates that none of the plain and blended cements exposed to  $\overline{M\bar{S}}$  environment reached failure, even after 360 days of exposure. Furthermore, in  $\overline{N\bar{S}}$  solution, only plain Type I and Type V cements as well as FA cement (with Type I) passed the threshold expansion value of 0.1% after 12 months. This group of cements is followed by BFS cement, low w/b ratio cement and FA cement (with Type V). The lowest expansion readings were attained by the SF cements. This classification of cements agrees very well with the strength reduction data in  $\overline{N\bar{S}}$ , which clearly indicates the superiority of blended cements; specifically the SF ones followed by BFS cement, in resisting  $\overline{N\bar{S}}$  attack.

### DURABILITY OF REINFORCED CONCRETE SPECIMENS

In order to assess the effect of sulfate attack on plain and blended cements, fifteen reinforced concrete mixtures were exposed to a mixed sulfate solution (Al-Amoudi, 1995). Details of the plain and blended cements, w/b ratio, etc., are presented in Table 2. The concentration of test solution was kept as 2.1% ( $\text{SO}_4^{2-}$ ); similar to the concentration of the sulfate solutions used to generate the data in Table 1. In this investigation, the



2a:  $\overline{N\overline{S}}$  solution



2b:  $\overline{M\overline{S}}$  solution

Fig. 2. Visual documentation of the specimens exposed to sulfate solutions

weight loss of concrete and the degree of corrosion of reinforcing steel were assessed after a long exposure period of 44 months. The threshold values of weight loss, corrosion potential and polarization resistance are 5%,  $-270$  mV and  $87$   $k\Omega\text{cm}^2$ , respectively (Al-Amoudi, 1995).

A review of the test results in Table 2 indicates that all the concrete specimens made with blended cements have already passed the failure criterion of 5% weight loss. On the contrary, plain cement concretes made with a w/b ratio of 0.50 exhibited minor weight losses of less than 5%. Therefore, all plain cements (Type I, Type II and Type V) performed very well in this exposure environment despite the fact that their  $C_3A$  content varied from 3.5% to 8.5%. However, when the w/b ratio of these plain cement concrete specimens decreased from 0.50 to 0.35, the weight loss accordingly increased (i.e. compare Mix No. 1 and 2 with 7 and 10). Similarly, when the w/b ratio of all blended cement concrete specimens decreased, the weight loss of concrete increased (i.e. compare

Table 2. Long-term data on the performance of reinforced concrete mixtures in mixed-sulfate environment (Al-Amoudi, 1995)

Mix No.	Cement Type	Blending Material (Replacement)	w/b**	Concrete Weight Loss (%)	Corrosion Potential, SCE (-mV)	Polarization Resistance ( $k\Omega cm^2$ )
1	I	None	0.50	0.86	395.1	56.7
2	V	None	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 <sup>+</sup>	844 <sup>+</sup>
5	I	BFS* (60%)	0.50	37.4	696.2	12.8
6	II	None	0.50	3.13	577.9	70.7
7	I	None	0.35	8.88	259.4 <sup>+</sup>	696 <sup>+</sup>
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	None	0.35	4.72	188.5 <sup>+</sup>	386 <sup>+</sup>
11	I	BFS* (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 <sup>+</sup>
15	V	Silica Fume (10%)	0.35	15.5	350.8	327 <sup>+</sup>

\*Blast furnace slag

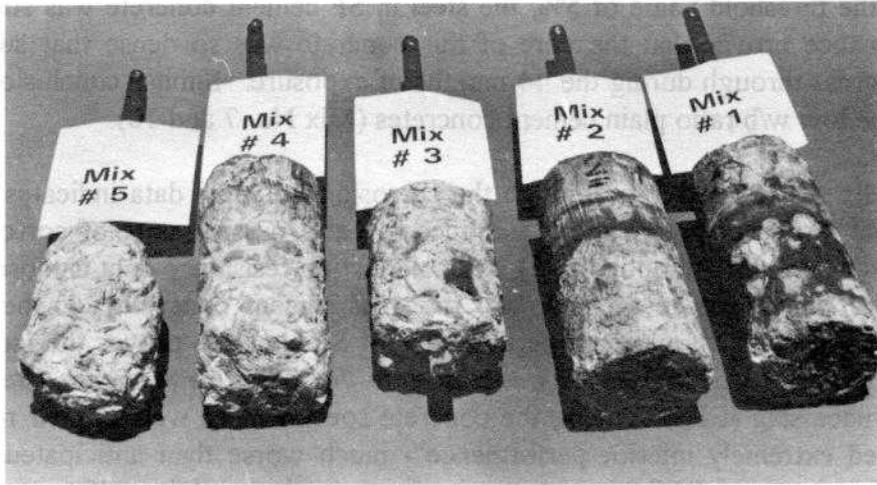
<sup>+</sup>Passive corrosion state

\*\*Water-to-binder ratio

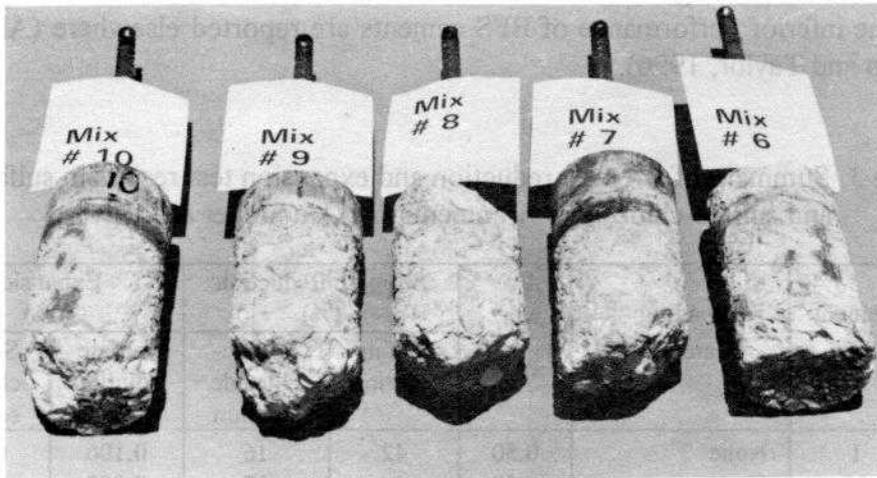
Mix No. 3, 4, 5, 8 and 9 with 12, 14, 11, 13 and 15, respectively). Therefore, it can be concluded that there is a detrimental effect associated with the reduction in w/b ratio of all plain and blended cement concretes. This finding is in parallel agreement with the results of strength reduction of plain and blended cement mortar specimens in the  $M\bar{S}$  environment presented previously. It is worth mentioning that the mode of deterioration in mixed-sulfate exposures is predominantly controlled by  $M\bar{S}$  due to the generation of MH in Eq. 5 above (Al-Amoudi, 1998; Rasheeduzzafar et al., 1994). Such an attack is typically manifested by softening of the surficial layers and a reduction in strength and loss of weight (i.e. acidic mode of attack). Visual documentation of the various reinforced concrete mixtures graphically confirms this conclusion, as shown in Fig. 3.

Regarding the corrosion resistance of steel in the various concrete mixtures in Table 2, the data therein indicates that most of the steels in plain and blended concrete specimens were in an active state of corrosion because the corrosion potentials were numerically more negative than  $-270$  mV with respect to saturated calomel electrode and the polarization resistance was less than  $87 k\Omega cm^2$ . Even those mixtures which exhibited negligible deterioration (i.e. Mix No. 1 and 2) could not protect the passivity of steel. This may be ascribable to the ability of sulfate ions to diffuse through their matrix and reach the reinforcing bars. In the case of blended cement concretes, the corrosion was certainly attributable to the significant weight loss (i.e. more than 10%) whereby their concrete cover was tremendously diminished by  $M\bar{S}$  attack.

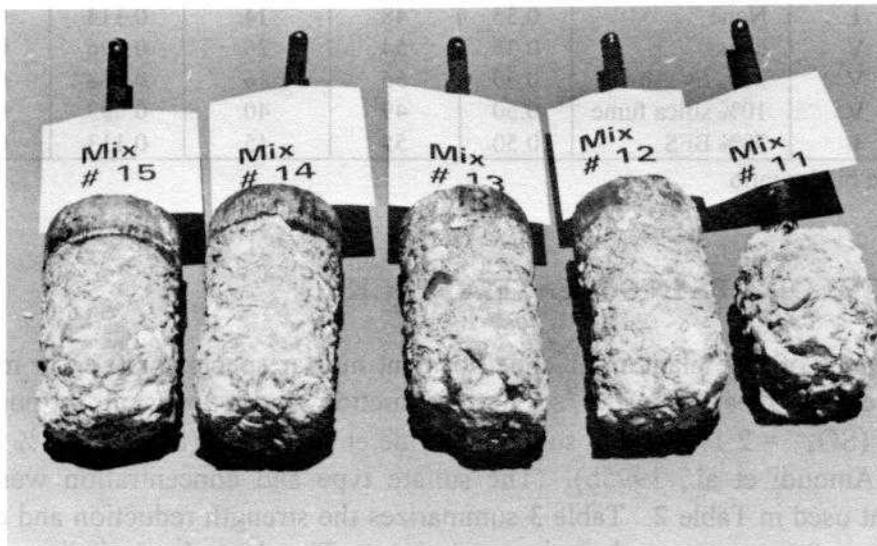
For the passive reinforcing steels, the SF cement concrete specimens (Mix No. 4) displayed distinguished performance. Despite its high weight loss (9%), which was much



3a: Mixes # 1 to 5



3b: Mixes # 6 to 10



3c: Mixes # 11 to 15

Fig. 3. Visual documentation of the various reinforced concrete mixtures

higher than the threshold value of 5%, the steel in SF cement concrete was still passive. This performance proves that the core of this concrete was so dense that sulfate ions could not ingress through during the 44 months of exposure. Similar conclusions can be said about the low w/b ratio plain cement concretes (Mix No. 7 and 10).

Regarding Mix No. 14 and 15, although the corrosion potential data indicates an active corrosion, the results of polarization resistance reveal a passive state of corrosion. As discussed elsewhere (Al-Amoudi, 1995), the polarization resistance data is more accurate and, therefore, the rebars in the low w/b ratio SF cement concretes can be assumed passive. Once again, such excellent performance of SF concrete proves the fact that *the core of this material was dense and intact despite the extensive surficial deterioration*. For blast furnace slag (BFS) cement, the concrete specimens as well as their reinforcing steel exhibited extremely inferior performance - much worse than anticipated. Similar inferior performance of BFS cement specimens was observed in sulfate and sulfate-chloride exposures (Table 3), as is discussed in the subsequent part. The reasons could be partly attributed to its high MgO and SO<sub>3</sub> contents (8.8% and 3.1%, respectively). Details on the inferior performance of BFS cements are reported elsewhere (Al-Amoudi, 1995; Gollop and Taylor, 1996).

Table 3. Summary of strength reduction and expansion test results in sulfate and sulfate-chloride environments (Al-Amoudi et al., 1995b)

Mix No.	Cement Type	Blending Material	w/b*	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

\*Water-to-binder ratio

## ROLE OF CHLORIDES IN SULFATE ATTACK

The performance of nine plain and blended cement mortar specimens (i.e. 50 mm cubes) was evaluated by measuring the strength reduction and expansion in pure sulfate environment (SO<sub>4</sub><sup>2-</sup> = 2.1%) and in sulfate-chloride environment (SO<sub>4</sub><sup>2-</sup> = 2.1% and Cl<sup>-</sup> = 15.7%) (Al-Amoudi et al., 1995b). The sulfate type and concentration were exactly similar to that used in Table 2. Table 3 summarizes the strength reduction and expansion after one year of exposure to these two solutions. The data clearly indicates that the concomitant presence of chlorides with the sulfate ions mitigated the strength reduction. However, the extenuation of sulfate attack by chloride addition was more pronounced in plain cements (Mix No. 1, 2, 5 and 6) as well as in fly ash cements (Mix No. 3 and 7). In

contrast, the chloride-triggered mitigation was marginal in blended cements made with silica fume and blast furnace slag. Based on microstructural analyses using X-ray diffraction and scanning electron microscopy, Al-Amoudi et al. (1995b) have shown that the significant mitigation of sulfate attack (i.e. termed chloride beneficiation) on plain cements was ascribable to the inhibition effect of chlorides on the expansive gypsum- and ettringite-oriented types of sulfate attack, which are predominantly operative in plain cements (Reactions 1 to 4 above). Such inhibition is also manifested by the low values of expansion of all cements in the sulfate-chloride exposure (see Table 3). Contrarily, the beneficial effect of chlorides was marginal on blended cements because of the inability of chlorides to inhibit the Mg-oriented type of sulfate attack (Eqs. 6 and 7) which is predominantly operative in blended cements (Al-Amoudi et al., 1995b).

Despite their inferior performance in sulfate-chloride exposures, blended cements made with SF and BFS have shown extremely superior resistance to corrosion of reinforcing steel, much more than all the other plain concrete mixtures (Al-Amoudi et al., 1994b). As it is well known, corrosion of reinforcing steel is the predominant mode of deterioration in chloride-sulfate exposures (i.e. sabkha soils, coastal and offshore structures, etc.). Therefore, it is rational to specify SF-blended cement in such aggressive exposures to retard or inhibit the corrosion of reinforcing steel. However, to mitigate  $\overline{MS}$  attack on the concrete material, additional protective measures are warranted (such as the application of a water-resistant epoxy-based coating to the exterior surfaces that are in direct contact with  $\overline{MS}$  solutions).

## CONCLUSIONS

This paper presented a review on the effect of sulfate attack on plain and blended cements. Blended cements, particularly those made with silica fume, were observed to be highly resistant to  $\overline{NS}$  attack due to an interplay of several factors; the most important factor being the reduction in the portlandite produced by cement hydration and the densification of the microstructure of hardened cement paste. These factors mitigate the production of expansive ettringite and gypsum. Low w/b ratio cements moderately alleviate  $\overline{NS}$  attack by mitigating the penetration of  $SO_4^{2-}$  ions into the matrix of the specimens.

Upon exposure to  $\overline{MS}$ , blended cements, particularly those made 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 causing a shift in the reaction mechanisms. Such a shift exacerbates the attack on C-S-H leading to softening, loss of concrete material and excessive reduction in strength. Ultimately,  $\overline{MS}$  attack transforms the cementitious C-S-H to a fibrous, non-crystalline M-S-H that possesses no cementing properties.

Despite the excessive deterioration of SF cement concrete specimens in  $\overline{MS}$  exposures, they succeeded in protecting the reinforcing steel more than all the other plain and blended cements. This superior performance indicates that the  $\overline{MS}$  attack was only surficial and the core of SF cement specimens remained dense and impermeable. Similar

excellent performance of SF cement concrete has been observed in sulfate-chloride exposures. Therefore, this cement has been recommended to be used in these aggressive environments. However, if the concentration of Mg ions is high, additional protection (i.e. usage of epoxy-based coating) should be incorporated.

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

### ACKNOWLEDGEMENT

This work was initiated by late Professor Rasheeduzzafar who contributed significantly to the elucidation of mechanisms of sulfate attack in sulfate-chloride environments. His guidance during the author's graduate studies at King Fahd University of Petroleum and Minerals (KFUPM) has been greatly appreciated. The support of the Department of Civil Engineering at KFUPM is also appreciated. Prof. M.H. Baluch is acknowledged for reviewing the manuscript.

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