

## FACTORS INFLUENCING THE SULPHATE RESISTANCE OF CEMENT CONCRETE AND MORTAR

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### ABSTRACT

Cement concrete continues to be the pre-eminent construction materials for use in any type of civil engineering structure. Performance of these structures in terms of their strength and stability has withstood the test of time but the life span of the structures has become a matter of concern. This is on account of the environment becoming chemically ever more aggressive. The atmosphere is found increasingly laden with higher percentages of Sulfur Dioxide, Carbon Dioxide and Chlorides. Oxides of Sulfur are injurious to concrete while Chlorides are harmful to the reinforcing steel. As a consequence of these, the life-span of the reinforced concrete structures have got compromised significantly from its original estimated life of about ninety years. The role of Sulphate ions in causing deterioration of concrete has been investigated intensively. Based on the literature available, the present paper discusses this aspect with particular attention to the use of blended cement in recent times with the influences of the parameters related to the Sulphate resistance of cement concrete and mortar.

**Keywords:** cement concrete, cement mortar, marine environment, sulphate resistance

### 1. INTRODUCTION

Cement concrete is the most widely used building material due to its satisfying performance in strength requirements. But when one deals with the durability aspects of concrete, the chemical attack, which results in volume change, cracking of concrete and the consequent deterioration of concrete, becomes an important part of discussion. The reaction of Sulphate ions ( $\text{SO}_4^{--}$ ) with hydrated cement products is a volume increasing reaction and denoted as Sulphate attack on concrete. Most soil contains some Sulphates in the form of Calcium, Magnesium, Sodium, and Potassium. Ammonium sulphate is frequently present in agricultural soil and water. Decay of organic matter in the marshes, shallow lakes, mining pit and sewer pipes often lead to the formation of  $\text{H}_2\text{S}$ .

Water used in the concrete cooling towers is also a source of Sulphate attack, because of the gradual built up of Sulphate from evaporation of the water. Seawater contains the

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Sodium, Magnesium, and Calcium sulphate in the dissolved form. So, Sulphate attack is the common occurrence in concrete environments. Solid Sulphate does not attack the concrete severely but when chemicals are in solution, they find the entry into porous concrete and react with the hydrated cement products. The range of practical importance of the Sulphate concentrations are between 150 and 6000 ppm, when attack on unprotected concrete is studied.

Vicat was the first to report a chemical attack attributed to the presence of Sulphate in seawater as early as 1818, after which a lot of work was carried out in this area. Due to the modern change in cement industry and its composition, more research is needed on Sulphate attack. The objective of this paper is to understand the Sulphate attack mechanism and study the effects of various parameters associated with the Sulphate attack.

## 2. MODES OF CONCRETE DETERIORATION

Three modes of concrete deterioration are usually associated with Sulphate attack on concrete as shown in Figure 1. The first mode of deterioration is due to eating away of the hydrated cement paste and leaving cohesion less granular mass. This mode of deterioration is known as acidic type and attributed mainly to the formation of Gypsum. The second mode of deterioration is due to the reaction of Sulphate to hydrated Aluminates phase, forming Tricalcium Sulpho Aluminate Hydrate, also called Ettringite. This mode is expansion type and attributed mainly to the formation of Ettringite in the presence of high concentration of Calcium Hydroxide (Portlandite). The third type of deterioration is the onion-peeling type, which is characterized by scaling of concrete surface in successive layers.

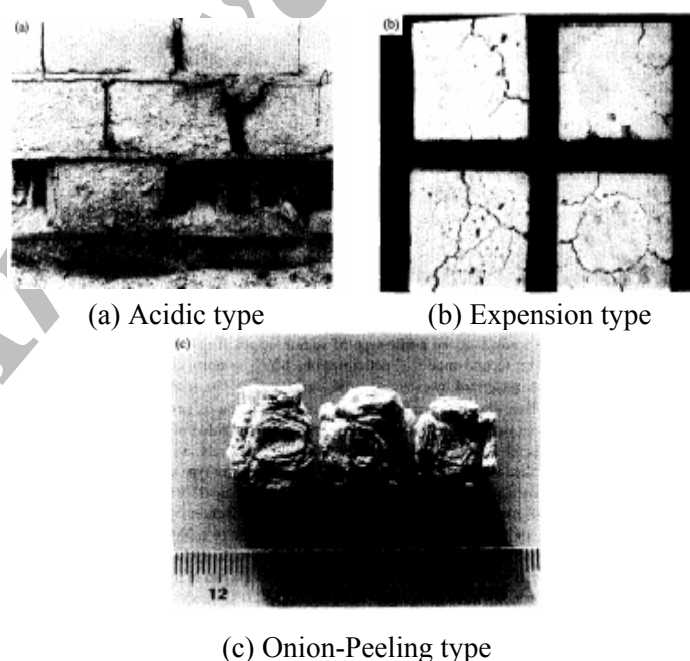
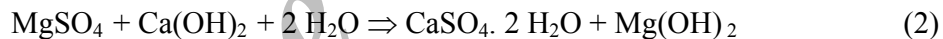


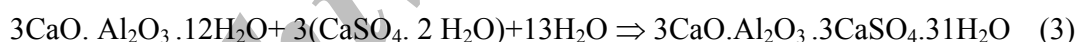
Figure 1. Modes of failure under Sulphate attack [1]

### 3. MECHANISM OF SULPHATE ATTACK

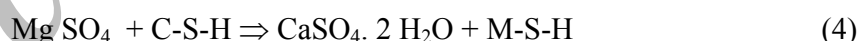
Calcium Hydroxide and Alumina-bearing phase of hydrated cement are more vulnerable to attack by Sulphate ions. Ettringite and Gypsum are the primary products of the chemical reaction between a Sulphate bearing solution and cement hydration products. Failure by expansion of concrete in the presence of Sulphate is due to the formation of Ettringite. The attack of Sodium Sulphate on concrete is due to two principal reactions: the reaction of Sodium Sulphate  $[\text{Na}_2\text{SO}_4]$  or Magnesium Sulphate  $[\text{MgSO}_4]$  and Calcium Hydroxide  $[\text{Ca}(\text{OH})_2]$  to form Gypsum (Equations 1 and 2) and the reaction of the formed Gypsum with Calcium Aluminate Hydrates to form Ettringite (Equation 3). In addition to above, the Magnesium Sulphate reacts with all cement compounds, including Calcium Silicate Hydrates  $[\text{C-S-H}]$  and subsequently forming Gypsum and Ettringite (Equation 4). The Magnesium Hydroxide reacts with silica gel to form Magnesium Silicate Hydrate  $[\text{M-S-H}]$ , being a soft material and affects the strength and durability of concrete. The form of Ettringite developed in the cement paste is depending on phase of Calcium Aluminate Hydrates, which reacts with Sulphate. In the fresh concrete, the Gypsum, which is blended to prevent flash set, reacts with Calcium Aluminate Hydrates to form primary Ettringite  $[\text{C}_3\text{A}_3\text{H}_{32}]$ . This primary Ettringite is converted to Monosulphate  $[\text{C}_3\text{A}_3\text{H}_{32}]$  with time [2]. The chemical reactions associated with Sulphate attack are as follows [3]:



(Gypsum)



(Ettringite)



### 4. FACTORS AFFECTING SULPHATE RESISTANCE

The deterioration of concrete due to sulphate attack is considered a complex problem and it depends on many parameters related to materials and exposure conditions, as given below.

1. Parameters related to material properties: Cement types and its content in mix, Mineral admixture types and its content in mix, Water/binder ratio of mix, Degree of hydration, Curing conditions etc.
2. Parameters related to hydrated concrete properties: Pore structure, Permeability, Diffusivity, Mechanical properties etc.
3. Parameters related to exposure conditions: Types of ions associated with Sulphate, Concentration of Sulphate, Time of exposure, Temperature of exposure etc.

The effects of some parameters on Sulphate attack are discussed in next parts.

#### 4.1 Type of cement

The Sulphate attack depends on availability of  $\text{Ca}(\text{OH})_2$  and  $\text{C}_3\text{A}$  in hydrated concrete, hence chemical composition of binder have a important role in Sulphate resistance. Cement that has low  $\text{C}_3\text{A}$  has good Sulphate resistance. Sulphate Resisting Portland Cement (SRPC) is good under Sulphate attack due to its less content of  $\text{C}_3\text{A}$ . The higher content of cement in concrete increases its Sulphate resistance (Figure 2) [4]. Modern cement is made for rapid development of strength resulting an increase in Tri-Calcium Silicate [ $\text{C}_3\text{S}$ ] content in the cement. This increase in the  $\text{C}_3\text{S}$  results in an increased Calcium Hydroxide content in the hardened cement, thereby enhancing the susceptibility to Sulphate attack. Rasheeduzzafar et. al. [5] reported that, in addition to the  $\text{C}_3\text{A}$  content, the  $\text{C}_3\text{S}/\text{C}_2\text{S}$  ratio of cement has a significant effect on the Sulphate resistance of cement mixes (Figure 3).

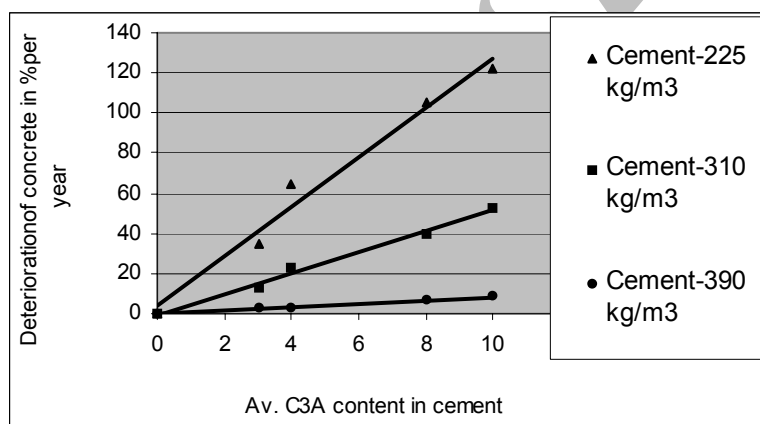


Figure 2. Effect of cement type and its content in concrete [4]

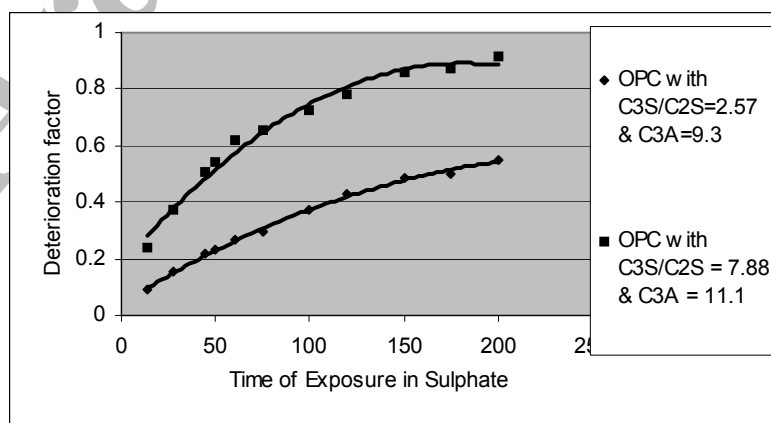


Figure 3. Effect of chemical composition of cement [5]

Blending of mineral admixtures like Ground Granulated Blast Furnace Slag (GGBFS), Fly Ash (FA), Silica Fume (SF) etc in cement increases resistance of concrete to Sulphate attack. The superior performance of blended cement over plain cement concrete is attributed to the pozzolanic reaction that consumes the Calcium Hydroxide and to the dilution of Calcium Aluminate Hydrates phase due to a reduction in the quantity of plain cement in total binder. Hekal et. al. [6] reported that the hardened cement paste containing 40% GGBFS shows a significant improvement in Sulphate resistance.

#### *4.2 Water/Binder ratio*

Water to binder ratio is the main factor that control strength development of concrete. Concrete with lower water/binder ratio is mostly denser and having higher strength. So any one can assumes that the concrete with low water/binder ratio have better Sulphate resistance, but it is not true. Al-Amaudi et al. [7] studied this effect and find that the reduction in the water/binder ratio enhanced the strength reduction and expansion of mortar specimen when exposed to the Sulphate solution. Same conclusion of aggravated deterioration of dense mix is also reported by Kalousek et. al. [8]. The possible reasons for such behavior could be (i) Sulphate attack is not physical in nature hence independent from permeability of mix, (ii) expansive product formed due the reaction between cement and Sulphate salt are not well accommodated in the finer pore structure of low water/binder ratio mix. Thus dense concrete mixtures aggravated the deterioration process attributed to Sulphate attack.

#### *4.3 Curing condition*

Curing condition of concrete influence its hydration process. For full hydration of binder and strength development in the concrete the continuous, longer and moist curing is required. Initial curing condition affects the Sulphate resistance of concrete or mortar. Mangat and Khatib [9], and Osborne [10] reported a beneficial effect of short initial air curing, as opposed to continuous moist curing, on long-term Sulphate resistance of plain and blended concrete. The possible reasons for such behavior could be (i) initial dry curing reduces the Calcium Hydroxide concentration in surface zone and (ii) initial dry curing do little carbonation in surface zone and reduce the availability of Calcium Hydroxide for Sulphate attack.

#### *4.4 Type of Sulphate*

Deterioration rate of concrete under sulphate attack also depends on the type of Sulphate. Al-Amaudi et al. [7] presented the results of Sodium, Magnesium, and mixed Sulphate solution attack on mortar and concrete specimen. The authors used plain Type I, Type V, Fly ash, Silica fume and Ground Granulated Blast furnace Slag blended cement in specimens. The mortar specimen consisted of 25 mm size cubes used for strength reduction measurement and prism of size 285x25x25 mm used for expansion measurement. The concrete cylinders of size 75 mm dia. and 150 mm height were used for weight loss measurements. Results of strength reduction and expansion of mortar specimen under Sodium and Magnesium Sulphate exposure for 12 months are given in Table1 and shown in Figure 4. The strength reduction was almost similar in both environment up to about 100

days of exposure and thereafter the reduction is more in Magnesium Sulphate for all types of specimens. The expansion data indicates that the Sodium Sulphate environment leads to introduce more expansion on all mortar specimens. Results show the superior performance of blended cement in Sodium Sulphate solution.

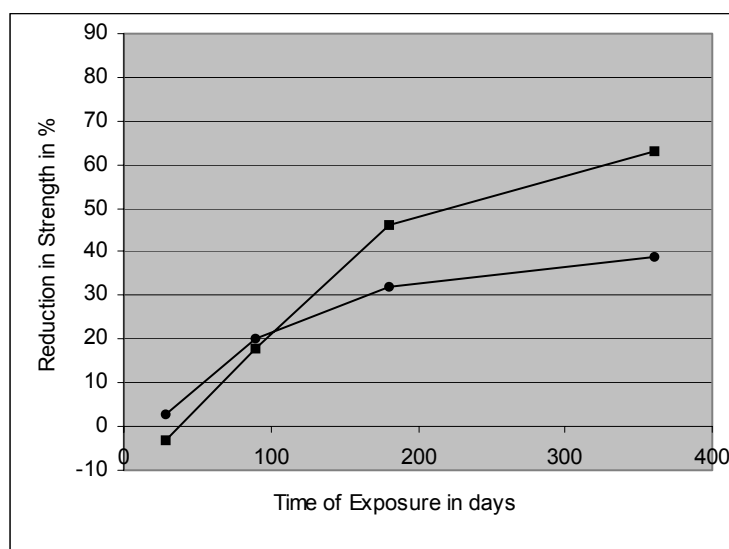
In mixed Sulphate environment, the modes of Sulphate attack is predominantly controlled by Magnesium Sulphate due to the generation of Magnesium Hydroxide (Brucite). Magnesium Hydroxide being insoluble (its solubility is 0.01 g/lit. compared to 1.37 g/lit. for Calcium Hydroxide) and its saturated solution having a pH of about 10.5 that causes the destabilization of both Ettringite and Calcium Silicate Hydrate. Therefore, the formation of Ettringite is significantly hindered in such environment and deterioration of concrete is attributed mainly to the formation of Gypsum.

#### 4.5 Sulphate concentration

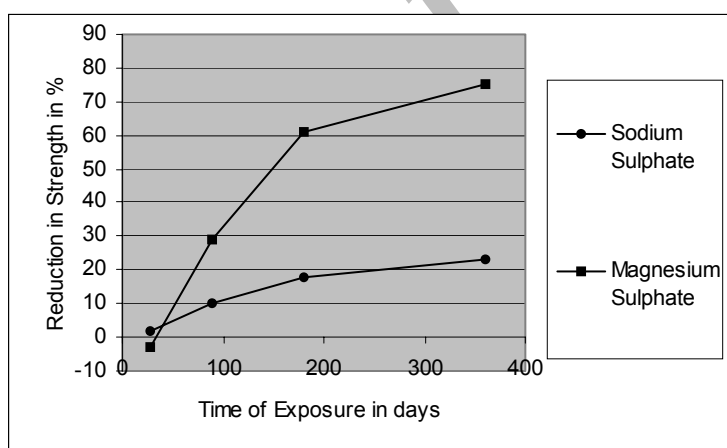
Deterioration of concrete in Sulphate attack depends on concentration of Sulphate in exposure solution. Higher concentration of Sulphate leads to quick deterioration. Al-Dulaijan et. al. [11] studied the performance of plain and blended cement mortar cubes of 50 mm size, exposed to Sodium Sulphate solution of varying concentration (1.0, 1.5, 2.0, 2.5 and 4.0%) for up to 24 months. The degree of deterioration was evaluated by strength reduction and by visual inspection. Results of the study indicate that the rate of deterioration increased with increase in Sulphate concentration for both plain and blended cement. The sample prepared by fly ash blended cement shows less deterioration in comparison to the others for all concentration and all time of exposure. Reduction in strength of mortar cubes after 24 months exposure is shown in Figure 5. Higher strength reduction was noted in Type I cement mortar specimen while the strength reduction in other cement mortars was not significantly different from each other.

Table 1. Effect of Sodium and Magnesium Sulphate on mortar [7]

Cement Type	Strength Reduction in %		Expansion in %	
	In Sodium Sulphate	In Magnesium Sulphate	In Sodium Sulphate	In Magnesium Sulphate
OPC	39	62	0.104	0.046
SRPC	34	53	0.113	0.031
OPC+20% FA	22	65	0.111	0.056
OPC+10% SF	9	72	0.082	0.096
OPC +70% GGBFS	18	75	0.099	0.067



(a) OPC mortar



(b) GGBFS blended mortar

Figure 4. Effect of sulphate type of on strength reduction [7]

#### 4.6 Presence of Chloride with Sulphate

The Chloride ions are inadvertently associated with Sulphate in the attack of ground water or marine environment on concrete. Chloride reacts with the hydrates of cement and form Freidel's salt that does not have any harmful effects on concrete, but when chloride content in concrete reaches more than the threshold value, the protective alkaline layer of steel reinforcement is broken and in the presence of oxygen and humidity, steel reinforcement gets corroded. Presence of Chloride in Sulphate solution effects the deterioration of concrete under Sulphate attack. Al-Amoudi et al. [12] studied this effect on plain and blended cement

mortar specimen, by exposing specimens to 2.1%  $\text{SO}_4^{--}$  solution and 2.1%  $\text{SO}_4^{--}$ +15.7%  $\text{Cl}^-$  solution for 365 days. Deterioration was measured on the basis of strength reduction and expansion of specimens. Results shows that the deterioration was relatively more intense in the specimen exposed to pure Sulphate solution in compared with those exposed to Sulphate-Chloride solution. The results for ordinary portland cement mortar are shown in Figure 6. Similar behavior is observed for blended cement mortars also.

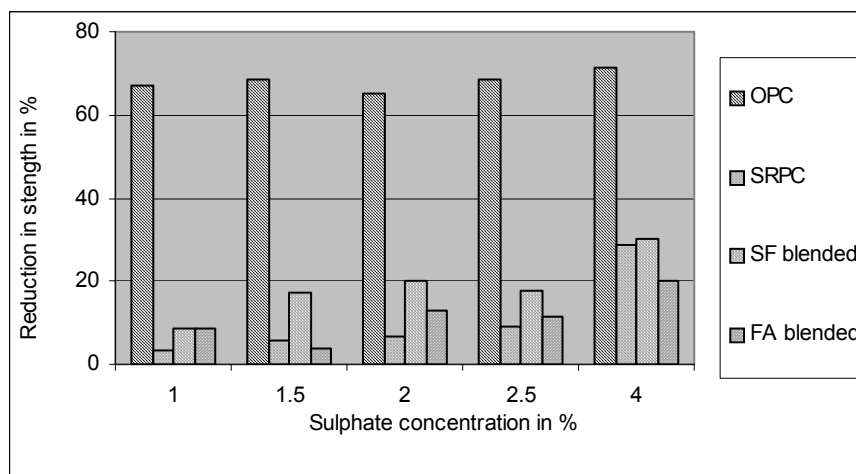


Figure 5. Effect of sulphate concentration on strength [11]

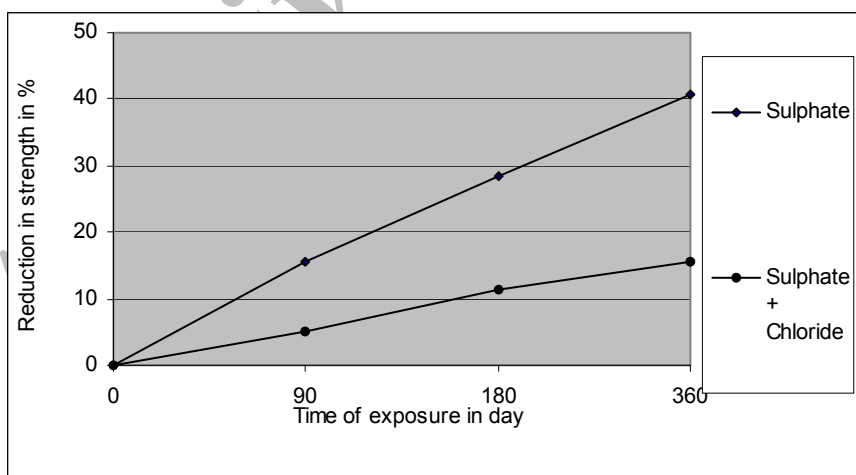


Figure 6. Effect of chloride presence in sulphate solution [7]

Increase in Sulphate resistance of the cement in presence of Chlorides is attributed to (i) increased solubility of Calcium Aluminate Hydrate phase leading to Calcium Sulpho Aluminate crystallization i.e. Ettringite formed in a non expensive form, (ii) a decrease in



lime concentration in the pure solution leading conversion of the insoluble highly basic Aluminate Hydrate phase to soluble low basic compounds, forming Ettringite of liquid phase in the non expensive forms, (iii) a transformation of Aluminate Hydrate phase into Chloro Aluminate phase, thereby reducing the quantity of Ettringite formed (iv) the rate of diffusion of Chloride ions being much higher than that of the Sulphate ions, allows the Chloride to react with  $C_3A$  to form Calcium Chloro Aluminate Hydrate, as a result the quantity of  $C_3A$  available for Sulphate ions to react and form Ettringite is reduced.

#### 4.7 Temperature at exposure

Physical conditions of Sulphate solution related to its temperature and submersed level of specimens also influence deterioration of mixes. Hekal et al. [6] studied this effect by observing Sulphate exposure at room temperature, at 60° C temperature, and at 60° C temperature with drying-immersion cycle. The increase in temperature of Sulphate solution accelerated the Sulphate attack on all types of specimens of mortars. The drying-immersion cyclic process at 60° C accelerated the Sulphate attack very much and it can be considered as an accelerated method to evaluate Sulphate resistance. Change in compressive strength of ordinary Portland cement mortar cubes with time at different exposure conditions are shown in Figure 7. The curve shows that the reduction in strength is more at higher temperature. Hence Sulphate attack is more aggressive in summer or in hot climatic areas.

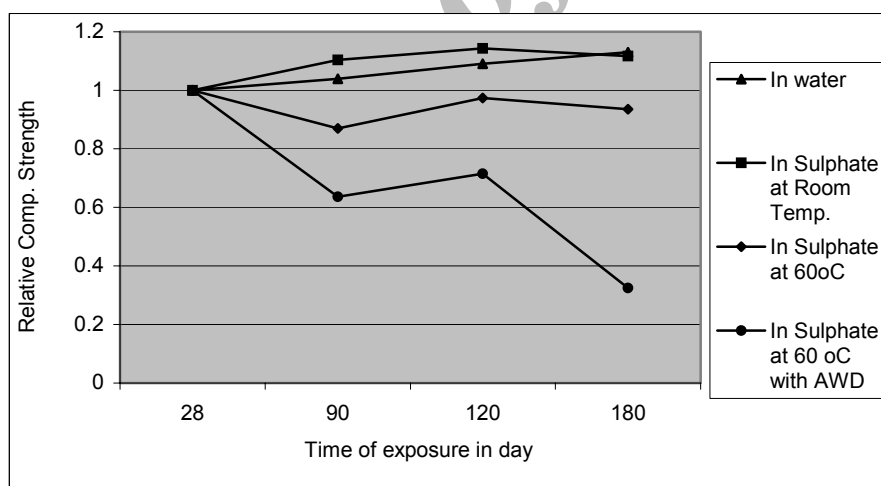


Figure 7. Effect of physical condition of exposure [6]

## 5. CONCLUSIONS

Based on the present study, the following conclusions, with respect to Sulphate resistance of cement concrete and mortar, are drawn.

1. The blended cements, particularly those made with Silica Fume and Ground Granulated Blast Furnace Slag, are better in Sodium Sulphate environment.
2. The blended cement mixes show more deterioration in Magnesium Sulphate exposure

in compared to plain cement mixes.

3. The Magnesium Sulphate environment is more severe than Sodium Sulphate environment.
4. The performance of low water/binder ratio mixes is inferior in Sulphate resistance.
5. The little initial air curing of mixes is beneficial for Sulphate resistance.
6. The deterioration of cement mixes increases with increase in the concentration of Sulphate.
7. The presence of Chloride ions with Sulphate ions reduces the rate of Sulphate attack on cement mixes.
8. The deterioration rate of mixes due to Sulphate attack is higher at high temperature with alternate wetting and drying cycles.

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