GSJ: Volume 10, Issue 3, March 2022
ISSN 2320-9186

Global Scientific JOURNALS
GSJ: Volume 10, Issue 3, March 2022, Online: ISSN 2320-9186
www.globalscientificjournal.com

Evaluation of Sulphate Resistance of Supplementary Cementitious Material

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ABSTRACT— Degradation of concrete due to sulphate attack is a serious challenge for concrete exposed to sulfate ions. The literature reviewed reflects that a unique mechanism of sulfate attack does not exist and states that sulfate attack can occur in different ways depending upon the exposure conditions and the nature of sulfate ions present in surroundings or inside the concrete mass. The field test of sulfate attack takes 15 to 40 years which is inadequate for research work. This research focuses on the evaluation of sulfate resistance of supplementary cementitious materials. For this purpose, the experimental work was done on basis of partial replacement of sulfate resisting cement with fly ash and bentonite, and American Standard for Testing and Material (ASTM) standard cylinders for strength assessment. 50x50x250 mm3 mortar bars were prepared to assess the expansion of mortar exposed to very sever sulfate environment (50g/L solution of Na2SO4), 50x50x50 mm3 for assessment of microstructures investigation were prepared. For both cylinders and mortars, four type of samples (100% sulfate resistant cement, 30% replacement of sulfate resistant cement with fly ash, 30% replacement of sulfate resistant cement with bentonite, replacement of 15% fly ash and 15% bentonite with sulfate resistant cement), 50% of cylinders were cured in fresh water, while other 50% were cured in 50g/L solution of Na2SO4. The results showed that replacement of fly ash with sulfate resistant cement is very effective from both strength and durability point of view, whereas replacement of bentonite results in a poorer strength and durability. It can be concluded from the research that supplementary cementitious material can mitigate sulfate attack and also reduce the demand of cement production which is a highly exothermic and CO2 emissive process.

Index Terms— Deterioration, durability, expansion, fly ash, sulphate attack, Sodium Sulphate, Curing

1 INTRODUCTION

Sulphate ions exist in groundwater, and sea-water. Decaying organic matter or soil are the main danger to the complete durability of concrete constructions built in such environments. The transmission of these Sulphate ions into the concrete elements and their interaction within the cement matrix leads to cracking and strength-loss of concrete structure [1]. Sulphate attack in general is a complex phenomenon made from a series of chemical reactions and physical interactions. As a consequence of which, cracking, expansion, and spalling of concrete can occur [2]. Sulphate attack can be classified as internal when sulphate ions exist within ingredient of concrete but, when sulphate ions enter the concrete mass from any external source, then the attack is classified as external sulphate attack [3]. On the basis of the phenomenon, sulphate attack can be classified as chemical or physical sulphate attacks. During chemical sulphate attack, delayed ettringite, gypsum or thaumasite can be formed. Formation of delayed ettringite and gypsum manifest in the form of expansion whereas, due to the formation of thaumasite, loss of mass happens [4]. This research paper attempts evaluation of sulphate resistance of partial replacement of fly ash and bentonite with sulphate resisting cement (Type V) as supplementary cementing materials exposed to sever sulphate attack.

2 LITERATURE REVIEW

2.1 Mechanism of Sulphate Attack

Sulfate attack is possibly one of the most injurious forms of deteriorations influencing Portland cement-based constituents. However, in the face of over six decades of investigations, significant ambiguity remains in optimally choosing and proportioning of materials for sulfate resistance, and the present understanding of the real mechanism of deterioration in sulfate environment remains inadequate [5]. According to A. Neville [6], use of the word attack seems inappropriate for the phenomenon of deterioration by sulphate as 'attack' is defined in dictionaries as a damaging stroke by a physical agency, corrosion, eating away, and dissolution, whereas, deterioration due to sulphate can occur in concrete by itself. This is contradictory to the definition of the word 'attack'. Additionally, it is stated that there is a uniquely defined mechanism of sulfate attack, the mechanisms stated in available literature for the phenomenon of sulfate attack show contradictions [6]. The most common types of solutions attacking concrete include sodium, magnesium, calcium, and potassium sulphate [7]. Sulfates in the hardcore or soil are not destructive of the concrete if they remain dry. Water is obligatory to dissolve the sulfates and carry their anions into the concrete [8]. Another great factor which contributes to sulphate attack is the chemistry or chemical composition of sulphate attack among major compounds of cement. The amount C3A and C-S-H2 play a great role in sulphate attack [9]. External sulphate attack happens when sulphate ions from the environment, example from water or from soil, penetrate into concrete pores and within the concrete internal system, whereas internal sulphate attack occurs when the source of sulphate exists within the consequents of concrete such as, sulphate rich aggregate or sulphate contaminated aggregate [10]. When the concrete mass is permeable and exposed to sulfate environment in the presence of water, then external sulphate can occur. However, occurrence of internal sulphate attack needs simultaneous presence of water, late sulphate release, and micro cracking. These conditions are shown in fig. 1. [11]. Sulphate attacks are divided into two types on the basis of nature of reaction, that is, (a) chemical, and (b) physical sulphate attacks.

When the deterioration of concrete is the result of physical weathering and crystallization, the sulphate attack is classified as physical sulphate attack whereas, if the deterioration is due the chemical reaction with a combination of physical interaction, then this type of attack is named as chemical sulphate attack. Due to chemical sulphate attack, delayed ettringite formation, gypsum formation or thaumasite formation can occur [12].

Ettringite is the product of chemical reaction between mono-sulfate hydrate with sulfate in the presence of calcium hydroxide and water as stated by the following chemical reactions [13].

$$\mathbf{C3A.CS.H18 + 2CH + 2S + 12H \rightarrow C3A.3CS.H32} \quad (1)$$

$$\mathbf{C3A.CS.H18 + 2CH + 3S + 11H \rightarrow C3A.3CS.H32} \quad (2)$$

Formation of ettringite causes concrete to expand and crack. When mono sulfate converts to ettringite, it does not produce expansion in the mass of concrete. Instead, it produces a loss in volume. However, the precipitation of ettringite at the expense of mono sulfate is expected to double the solid volume of concrete mass, for example, from 312 mole/ml to 714 mole/ml [14]. Gypsum (CaSO4-2H2O) is another form of chemical sulphate attack which can form as a result of topo chemical reaction or a reaction between components in solution which cause the formation of gypsum as expansion of concrete leads to cracking and spalling of concrete [15].

$$Ca\,(OH)2 + Na2SO4 + 2H2O \rightarrow CaSO4 - 2H2O + 2NaOH \quad (3)$$

Thaumasite sulfate attack (TSA) contrasts with conventional sulfate attack during thaumasite sulfate attack, an external origin of sulfate joins with calcium silicate hydrate. Thaumasite resembles a white incohesive mush, and has no bending capacity. Thaumasite is the result of the chemical reaction between C-S-H calcium sulfate, calcium carbonate, and water as shown in [16].

$$C\!-\!S\!-\!H + CaCO3 + CaSO4 + xH2O$$
$$\rightarrow CaSiO3.CaSO4.CaCO3.15H2O\ (\text{thaumasite}) \quad (4)$$

2.2 Degrees of Severity of Sulphate Environment

The intensity of sulphate attack does not depend only on the concentration of sulphate ions in an environment, but also depends on the level of water table and its seasonal fluctuations. The flow of ground water and soil porosity, the form of construction, and the quality of concrete. According to ACI Building Code 318-83, degrees of severity of sulphate environment can be divided into four groups as shown in Table 1. This classification is carried out on the basis of concentration of sulphate ions [15].

TABLE 1.

DEGREES OF SEVERITY OF SULPHATE ENVIRONMENT

S. No.	Intensity of Attack	Concentration of Sulphate Ions in Soil	Concentration of Sulphate Ions in Water(ppm)	ACI Recommendations for Cement Type and W/c Ratio
1	Negligibl e	Less than 0.1%	Less than 150	No restriction on cement type and W/C ratio
2	Moderate	0.1% to 0.2%	150 to 1500	ASTM Type-II cement should be used and W/C should be kept less than 0.5
3	Sever	2%	1500 to 10,000	ASTM Type-V should be used with keeping W/C less than 0.45
4	Very sever	over 2%	Over 10,000	ASTM Type-V plus a plus a pozzolanic admixture should be used with keeping W/C ratio less than 0.45

GSJ: Volume 10, Issue 3, March 2022
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3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Cement: ASTM Type-IV cement (High sulphate resistant cement) was used during the study and by [14] the fineness of cement used was confirmed.

3.1.2 Aggregates: The fine and coarse aggregate used in the study was obtained from local quarries. Tests were conducted on the aggregate specimen to collect the material properties data for mixture design of concrete [16 - 18]. The results obtained are given in Table 2.

TABLE 2.

PROPERTIES OF COARSE AND FINE AGGREGATES

Sample	Density(g/cm3)	Max Size	Fineness Modulus	Specific Gravity	Apparent (SG)	Absorption%
Coarse aggregate	1.47	1 inch	7.9	2.78	2.8	0.2
Fine aggregate	1.55	0.375 inch	2.0	2.65	2.71	0.8

3.1.3 Fly ash: Fly ash class- C was obtained from Sika Chemicals, Pakistan. The material properties as supplied by manufacturer are given in Table 3.

TABLE 3.

PROPERTIES OF FLY ASH

Form	Powdered particles
Color/ Appearance	Grey
Specific Gravity	2.60
Chloride content	Nil
Packing	25 kg/ bag
Replacement	15, 30 percent by weight with cement
SiO2 + Al2O3+Fe2O3	0+1%+2.5%
Moisture Content	0.4%
Loss on Ignition	0.75%

3.1.4 Bentonite: The bentonite used in this research was Ca- class. It was heated to 3500C^{o} and then blended to powder; further properties of Bentonite used in this research have been stated in TABLE 4.

TABLE 4

PROPERTIES OF BENTONITE

Form	Powdered particles
Color/ Appearance	Late
Specific Gravity	2.7
Chloride content	Nil
Packing	45 kg/ bag
Replacement	15, 30 percent by weight with cement

4 METHODS

Mix designs were prepared according to ACI design method by using the data given in the tables-2, 3, and 4. The target strength was 4000 psi, the final proportions obtained were: 1: 1.4: 2.6: 0.42. Using these ratios, four types of samples were prepared. These groups were SRC (100% sulphate resistant cement), FSRC (30% sulphate resistant cement replaced with fly ash), BSRC (30% sulphate resistant cement replaced with bentonite), and Fly ash plus bentonite plus sulphate resisting cement (FBSRC), that is, (30% sulphate resistant cement was replaced with 15% fly ash and 15% bentonite). Half of these samples were cured in fresh water and half in 10% solution of Na2SO4, these cylinders were tested on 7th, 14th, 28th, and 56th day for Ultraviolet Pulse Velocity (UPV) and in Universal Testing Machine (UTM) for compressive strength. Then the results were analyzed and compared to each other. In the second part of research, 50x50x25 mm3 mortar bars were prepared with a ratio of 1:3 from SRC, SRC+30% Fly ash, SRC+30% Bentonite, SRC+15%Fly ash+15% Bentonite, and Ordinary Portland Cement (OPC), the strain in the bars was checked every four days for 68 days and the results were compared. In the third part, 50x50x50mm3 of mortar with a ratio of 1:3 made for SRC, SRC+30%Fly ash, SRC+30% Bentonite, SRC+15%Fly ash + 15% Bentonite. These samples were cured in 10% solution of Na2SO4. After completion of the curing period, pellet type samples were taken for Scanning Electron55 Microscopy (SEM) analysis as shown in fig. 1. Also, fig.2 represents the preparation, curing and testing process of the cylinders prepared from various combinations of materials with the ratios discussed above.

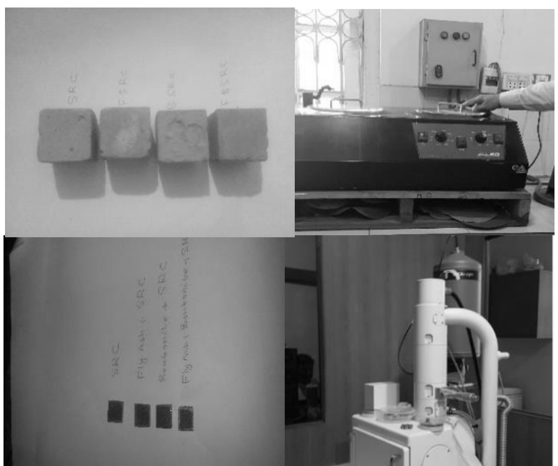

Fig. 1. Preparation of samples for SEM analysis from the cubes of various types of Mortars cured in 10% Sodium sulphate Solution.

Fig.2. Preparation of 10% Sodium Sulphate Solution, Casting of Cylinders, Curing of Cylinders, and Crushing of Cylinders for Compression strength test.

5 RESULTS AND DISCUSSION

The results are discussion for all the mechanical and physical tests in the following sections.

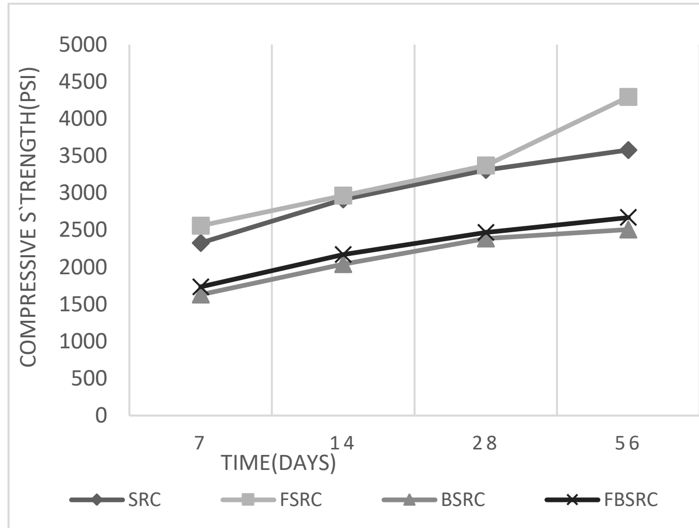

Fig. 3. Average Compressive Strength Growth of Cylinders Cured in Fresh Water

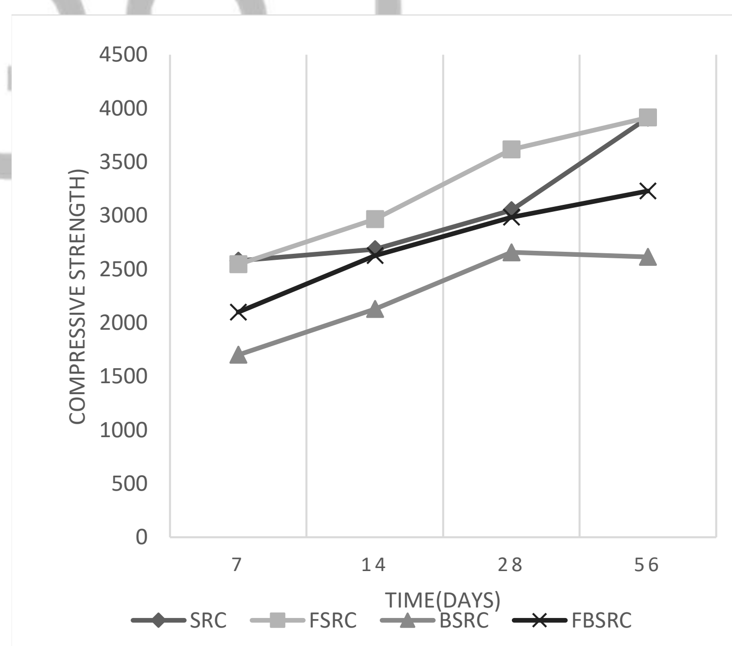

Fig. 4. Average Compressive Strength Growth of Cylinders Cured in 10% Solution of Sodium Sulphate

A comparison of fig. 3 and fig.4 shows that there is decline of compressive strength for the samples cured in brackish water for those sample except for the samples of SRC and FSRC, which has good resistance to sulfate attack.

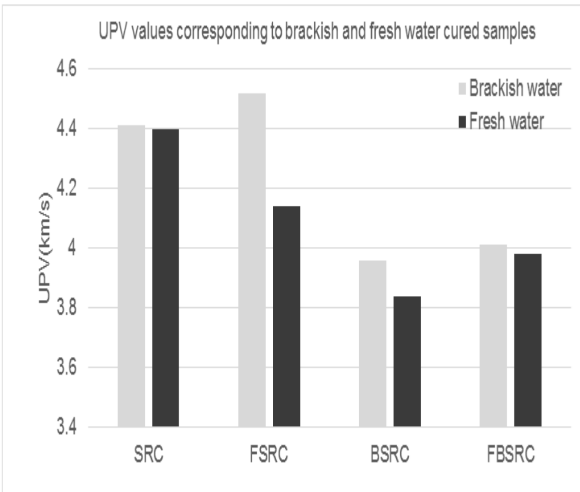

Fig. 5. Comparison of UPV Values for Samples Cured in Brackish Water Versus Samples Cured in Fresh Water.

It is evident from the graph given in fig. 5 that, SRC maintain same quality for both cases of curing whereas, FSRC shows better quality for brackish water as compared to fresh water. The SRC and FSRC samples can be classified excellent but, Bentonite plus Sulphate resisting cement BSRC) and FBSRC are classified as having good quality.

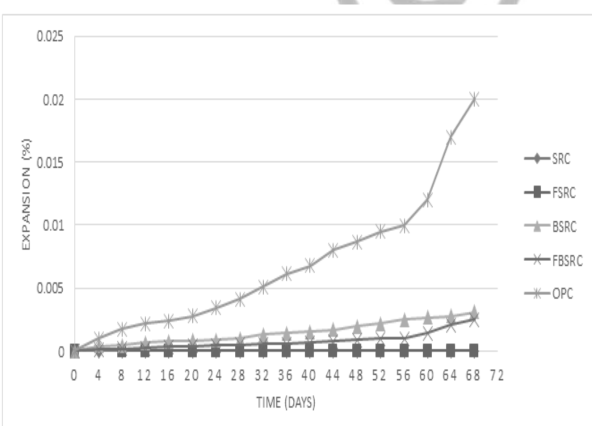

Fig. 6. Expansion of Mortar Bars Exposed to Sever Sulphate Attack

Fig. 6. shows expansion of mortar bars cured in water contain 10% sodium sulfate for 68 days and the strain was measured at a time interval of four days. The horizontal axis shows time in days, the vertical axis shows strain, the five types of mortar bars are given the legends with the help of colors. The mortar bars made with SRC and (SRC+30%FA) does not show any elongation throughout the period, whereas the samples made with (SRC+15%FA+15%B) show slight elongation to a maximum of 0.025%. The sample made with (SRC +30%B) shows slightly more elongation) to a maximum of 0.0031%. The fifth sample made with ordinary Portland cement shows excessive elongation and proves that sever sulfate attack can damage the samples of OPC very rapidly and proves its poor durability to the exposure of sulfate containing environment. A look at the graph shows that FA has a vital role in offering durability against sulfate attack.

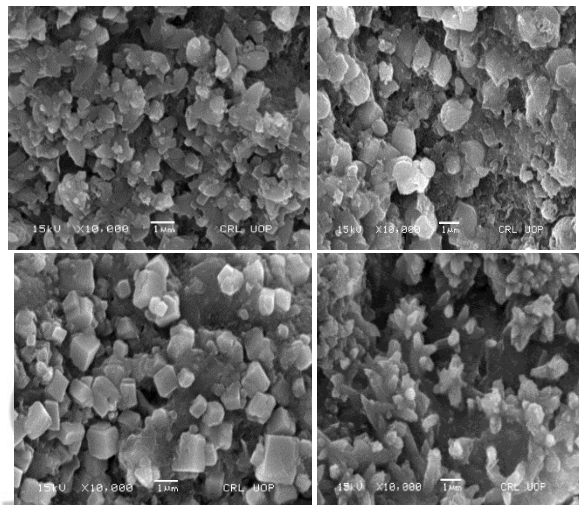

Fig. 7. SEM results for all four types of mortars, top left is SRC, top right FSRC, bottom left is BSRC, and bottom right shows FBSRC

From the visual analysis of images made by Scanning Electron Microscopy (SEM) with a magnification factor of 10,000, it can be concluded from top right of fig.7. that FSRC has compacted microstructure with proper bond between particles of sand, fly ash, and cement, whereas BSRC has porous micro structure and poorer bond between bentonite sand and, cement particles as shown in bottom right of fig. 7. In addition, bottom left of fig. 7. and top right of fig.7. show that SRC and FBSRC samples respectively, the FBSRC show better microstructure and bond than BSRC samples.

CONCLUSION

As a product of this research work, it is concluded that fly ash has a vital role in resisting sulphate attack and providing higher strength as compared to sulphate resistant cement, the dense and compacted micro structure of fly ash SEM revealed that partial replacement of fly ash results in a concrete of low permeability which does not allow harmful agents to penetrate into the concrete. This can indirectly reduce sulphate attack. The greater the permeability of concrete elements, lower the probabilities of entrance of injurious agents into the concrete elements and an overall growth in the service life of the structure is guaranteed. However, further research is needed to measure the optimized value of fly ash amount in order to arrest the maximum effects of fly ash on sulphate attack. It can also be concluded that fly ash shows the same trend of strength for both conditions of exposure. Moreover, replacement of bentonite is not satisfactory to achieve the target strength as well as to resist sulphate attack because, due to addition of bentonite, inadequate bond is developed between constituents of concrete and in addition bentonite by itself is expansive. The compressive strength values acquired are fairly lower than those of the ordinary concrete specimens. Consequently, it is recommended to conduct a study on optimization of bentonite measure in order to obtain the target strength for a given exposure state.

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