

Effects of Sulphate in Sea Water on Mechanical Strength of Concrete under Various Environmental Conditions

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Abstract: *This paper investigate the effects of Sulphate compound in sea water on the mechanical strength of concrete through experimentation. Factors affecting action of Sulphate ions on concrete such as porosity, use of pozzolans, salt concentration and environmental cycles were also studied. The paper examined the mechanical properties of solid concrete in exposure to Sulphate as an individual element of sea water under some environmental conditions. The results indicate that compressive and tensile strength loss occurs as the exposure time increase; with extensive strength loss being recorded on completion of the experiment due to the continued physical as well as chemical action of Sulphate ions on concrete.*

Keywords: effect of sea water on concrete, effect of Sulphate on concrete, mechanical properties of concrete, sulphate in sea water

1. Introduction

Concrete is a major building material used in construction. It is composed of water, aggregates and cement; the mix ratios of the three composites of concrete are dependent on the requirements of the structure. Aggregates however form the biggest portion of concrete ranging from 60% to 80% [1]. Concrete is used in construction of buildings, dams, foundations and highways among others. Floating offshore platforms, offshore oil rigs, harbors, floating docks, piers and bridges are some of the coastal and offshore structures constructed using concrete.

Sea water contains a number of conservative (Non-reactive) and Non-Conservative (Biological or Chemical reactive) elements. The major elements are the conservative elements which include Sodium, Chloride, Magnesium, Sulphate, Calcium and Potassium ions represented by chemical symbols Na^+ , Cl^- , Mg^{2+} , SO_4^{2-} , Ca^{2+} and K^+ respectively [2]. On average, the sea water consists of 55% chloride, 31% sodium, 8% Sulphate, 4% magnesium, 1% calcium and 1% potassium ions [1]. Conservative elements do not necessarily affect the chemical composition of cement; however, they can lead to decrease in cement strength. Reactive elements form a small portion of sea water constituents, and they include Carbon (C), Phosphorus (P) and Iron (Fe)[2]. Mechanical strength of concrete is broad; it includes compressive strength, tensile strength among others. Different admixtures have different effects on concrete without taking into consideration compressive strength. Mechanical strength determines the sizes of the pores on the concrete structure; the stronger the mechanical properties, the lesser the size of the pores on the concrete structure.

Hygroscopic salts such as sodium and calcium chlorides within sea waters absorb water from its surroundings increasing the moisture content of concrete; this in turn

reduces the tensile and mechanical strength of the concrete. The sodium Sulphate in sea water can also increase the solid volume in concrete when anhydrous sodium Sulphate (Na_2SO_4) is converted to hydrous Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)[3]; this process leads to fatigue, cohesiveness loss and damage due to salt crystallization[4]. Water flow and the salt content in sea water also leads to concrete deterioration in freezing and thawing cycles [5]. Salts lower the freezing point of water increasing pressure which results in cracking of concrete structures during cold seasons.

Penetration of Sulphate ions into the concrete pores creates a potential for physical and chemical attack. Sea water Sulphate action on concrete occurs through the formation of gypsum and Ettringite, magnesium, thaumasite and sodium Sulphate attack resulting in concrete deterioration and mechanical strength loss. Temperature and humidity fluctuations further increase the effect of Sulphate ions leading to extensive spalling and cracking.

Based on the accrued chemical and the physical effect of the elements of sea water on concrete, this study seeks to investigate and understand how Sulphate of the sea waters affects the mechanical strength of concrete structures.

2. Methodology

Forty concrete cylinder specimens of size 10 x 22 cm were cast as per ASTM 192 standard practices in the making as well as curing concrete specimens were tested in the laboratory. Twenty specimens casted using ordinary Portland cement (OPC), fine aggregates and coarse aggregates mixed in the ratio 1:2:3. The remaining twenty cylinders were casted using ordinary Portland cement with 24% fly ash content (OPC-FA) and aggregates. Crushed stones with diameter ranging between 5 mm as well as 18 mm were put in use as the rough solid concrete while normal river sand was applied as the fine aggregate.

The water cement ratio for all specimens was 0.45, while fine aggregates and coarse aggregates formed 34% and 48% of specimens respectively.

3. Specimens Preparation and Preliminary Tests

Cement, sand and fly ash used in the experiment were mixed until they were thoroughly blended before the addition of coarse aggregates for approximately 15 minutes. Crushed stones were then added and mixed till uniform distribution was established. Water was added, and a further machine mixing done for approximately 25 minutes till homogeneity and consistency in the concrete paste was established. Preparation of specimens was conducted in a moist room as per ASTM C511 standards on moist cabinets, mixing rooms, water storage tanks as well as rooms were put in use in hydraulic cement testing as well as concrete. The temperature in moist rooms and missing H₂O was maintained on 20°C while relative humidity was kept 95%. The internal vibration at 110 Hz and external vibration at 70 Hz were performed on the concrete paste to enable air bubbles in the paste to move to the surface.

The concrete paste was then casted in cylindrical molds for 24 hours. All specimens were subjected to standard wet curing by submersion in fresh water and 28-day moist curing at 20°C and 95% after de-molding.

After curing concrete specimens were subjected to preliminary compressive strength, pore volume, pore volume distribution and tensile strength tests. The compressive strength in the concrete specimens made of OPC only was 38.6 megapascals (5600 Psi) while specimens containing 24% fly ash in the cement mixture OPC-FA had compressive strengths of 37.8 megapascals (5500 Psi). Tensile strength was measured as per the ASTM C78 which is the standard test used for flexural force on concrete structures. The tensile strength in OPC specimens was 1.54 megapascals while that of the OPC-FA specimens was 1.53 megapascals.

The initial mass of the specimens was also measured; all specimens were air dried at 20°C and relative humidity of 95% before measurement of the initial mass.

Pore distribution and volume were also measured as per ASTM D4404 standard regulations for testing determination of pore distribution as well as pore volume. Testing the pore parameters was examined using Mercury Intrusion Porosimetry (MIP) as well as the distribution being determined by a Micrometric Auto Pore IV porosimeter with a pressure of 0 to 60000 psi. The test samples were obtained from the surface of the specimens and immersed in isopropanol solvent which is used in preventing hydration. Samples were taken and then dried till optimal minimum mass achievement. Samples taken were then tested at 24 oC and 0.48 N/m mercury surface tension.

4. Exposure conditions and experimentation procedure

Twenty specimens were exposed to 3.5% and 7% concentrated Sodium Sulphate solutions under constant environmental conditions while the remaining twenty specimens were exposed to 3.5% concentrated solutions under cyclic changes in the environment. The first twenty specimens (OPC and OPC-FA) were immersed in differently concentrated liquids also exposure to controlled temperatures of 20°C as well as 95% comparative humidity.

Freeze and thaw conditions; twenty OPC specimens and twenty OPC-FA specimens were immersed in 3.5% concentrated Sodium Sulphate solution and exposed to twenty-eight of 24-hour freeze and thaw cycles. A freezing chamber was used to freeze the specimens at -20°C for 16 hours the specimens were then the air warmed to 24°C before being immersed in 24°C solutions for 8 hours. The specimens were then air cooled to -20°C to complete one cycle. Specimens' testing was conducted after 7, 14, 21 and 28 days.

Wet and dry conditions; the remaining twenty specimens were immersed in salt solutions at 5°C for 14 hours then air dried at 23°C for 10 hours and 55% relative humidity to complete one 24-hour cycle. The specimens were subjected to twenty-eight days cycles at with testing being conducted intervals of seven cycles and at the end of the experiment.

The concentration of the solution in all three conditions was monitored after every seven cycles; with the solution being replaced in circumstances where there was a decline.

5. Tests and analysis procedures

Compressive strength, mass loss, tensile strength, porosity and micro structural damage tests were done at 7, 14, 21 and 28 days. Concrete micro structural damage in the cylinder specimens were investigated using energy dispersive X-ray spectrometer analysis (SEM - EDS) and a scanning electron microscope. Samples from the concrete beams were dried for 24 hours at 90°C then coated with an ultra-thin layer of steel before testing. A Schottky field emission SEM with 200 µm resolution at 5 kV as shown in figure 1 below was used in the SEM EDS analysis.

X-ray diffraction examination was also done on samples from specimens to identify the crystallization phases of the pore solution in the concrete. In order to be filtered through the 200 µm sieve, samples were crushed and dried in a desiccator. An x-ray diffractometer at 40 kV radiation and Jade 7 diffraction software were used to analyze the crystal content of the specimens' samples.

Physical inspection of specimens was also conducted and concrete deterioration rated based on a proposed rating. Statistical analysis of the compressive strength data collected, a dynamic modulus of elasticity and correlation analysis between various variables affecting concrete in salt solutions were conducted.

Percentage mass loss during the test time intervals was measured as per equation (19) below:

Mass loss at a time $t = (M_t - M_{t-1})/M_{t-1} * 100$ t is taken as a test period interval, M_t as the mass of the concrete beam at a time t while M_{t-1} as the mass of specimens of the previous test time period ($t-1$)

6. Results and Discussion

Compressive strength and tensile strength data analysis indicates a correlation between exposure of the specimens to solution action in freeze - thaw and wet – dry conditions and loss in concrete strength. Compressive and tensile strength loss was exhibited in all specimens; the effect however was significantly higher with the specimens in exposure to freezing-thawing cycles due to combined physical and the chemical effects of Sulphate ions in the solution. Figures 2 and 3 below shows the comparative effects of the exposure environment:

Table 1: Comparative analysis of the effect of Sulphates on compressive strength under different exposure environments using OPC specimens

OPC			
No Cycles	Freez & Thaw	Wet – Dry	No Exposure
0	38.6	38.6	38.6
7	31.266	32.424	33.582
14	24.95078	28.04676	29.88798
21	21.9284091	24.9616164	27.3176137
28	18.8145750	22.8036846	24.6785569

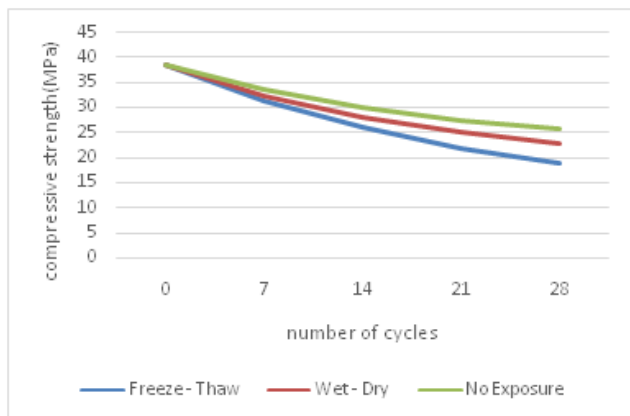


Figure 2: Comparative analysis of the effect of Sulphates on compressive strength under different exposure environments using OPC specimens

Table 2: Comparative analysis of the effect of Sulphates on tensile strength under different exposure environments using OPC specimens

OPC			
Cycles	Freeze - Thaw	Wet - Dry	No Exposure
0	1.43	1.43	1.43
7	1.33577575	1.37212293	1.404286873
14	1.17242896	1.237938685	1.29428179
21	1.042044423	1.1496452	1.215321491
28	0.936110971	1.07988395	1.163806224

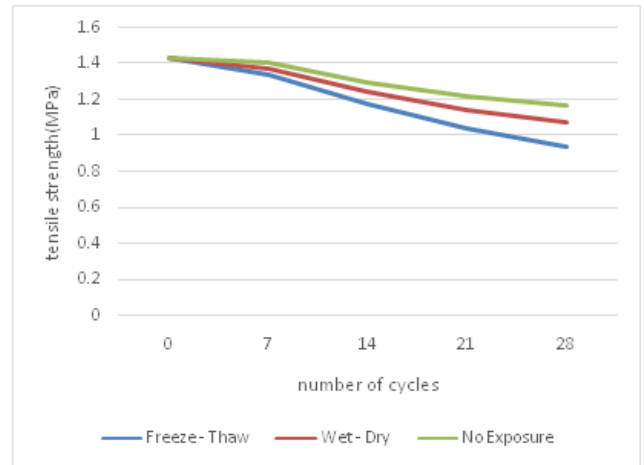


Figure 3: Comparative analysis of the effect of Sulphates on tensile strength under different exposure environments using OPC specimens.

The data collected also indicates a correlation between the concentration of the solution and the losses in compressive and tensile strength in the specimens. Specimens exposed to a highly concentrated solution exhibited significantly higher strength loss rates. Figures 4 and 5 below shows, the study findings on the effect of Sulphate concentration on strength loss:

Table 3: Effect of Sulphate ion concentration on compressive strength of the concrete

Cycles	3.5% Concentration	7% Concentration
0	38.6	38.6
7	34.1119496	28.79179867
14	31.98698609	21.61296676
21	29.57196864	17.52350167
28	27.76807855	14.64456558

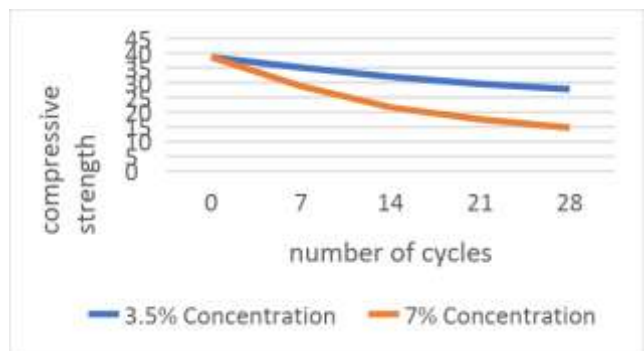


Figure 4: Sulphate ion concentration effects of compressive strength on concrete

Table 4: Effects of sodium Sulphate concentration on tensile strength of concrete

OPC		
Number of Cycles	3.5% Concentration	7% Concentration
0	1.548076291	1.548076291
7	1.44877877	1.260867364
14	1.357258503	1.0315287
21	1.284687244	0.890668047
28	1.229315412	0.785515558

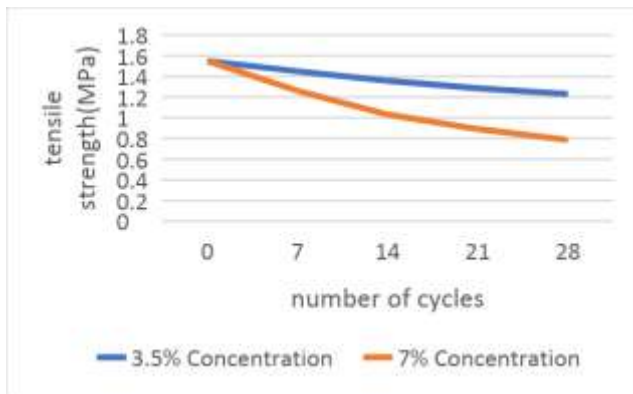


Figure 5: Effects of sodium Sulphate concentration on tensile strength of concrete.

Correlation analysis of the compressive strength tests also indicated a relationship between the rate of strength loss, and the porosity of the concrete specimens. OPC specimens with relatively larger pores exhibited significantly higher compressive and tensile strength losses as compared to OPC – FA specimens with 24% fly ash content. Figure 6 below shows, the relationship between concrete air content and compressive strength loss:

Table 5: Pozzolan effect on porosity and its impact on Sulphate action and compressive strength of concrete

Cyc les	F. Th. (OPC)	Wet - Dry (OPC)	Freeze - Thaw (OPC - FA)	Wet - Dry (OPC - FA)
0	38.6	38.6	37.8	37.8
7	31.266	32.424	36.721917	36.768816
14	24.950	28.046	31.231763	32.75160399
21	21.928	24.961	26.867783	29.9913821
28	18.814	22.803	23.407212	28.12361327

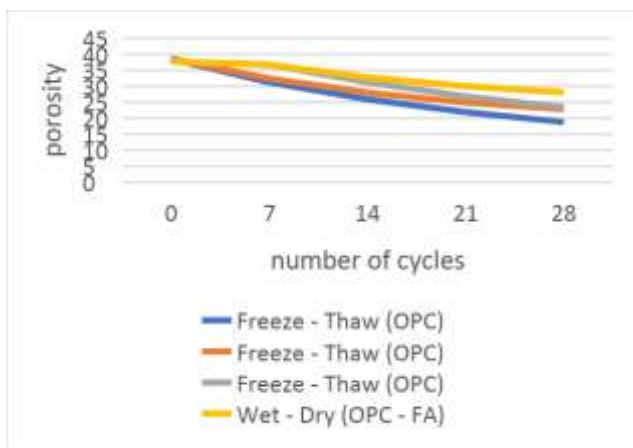


Figure 6: Pozzolan effect on porosity and its impact on Sulphate action and compressive strength of concrete

Extensive deterioration was observed in the specimens immersed in Sulphate solutions under freeze - thaw and wet - dry conditions. More deterioration and surface scaling were observed in concrete cylinders in exposure to freezing and thawing conditions as compared with wet as well as dry cycles. Comparatively lower scaling and deterioration was observed in specimens that were not bare to freezing and thawing or wetting and drying conditions. Figures 7, 8 and 9 below shows, the OPC specimens at 28 days.

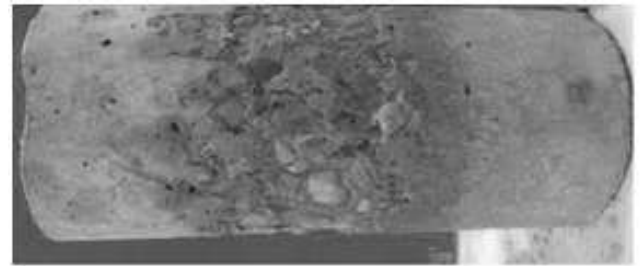


Figure 7: Concrete cylinder Specimen 28th day after immersion 3.5%, concentrated Sulphate solutions with no exposure to freeze - thaw or wet - dry cycles

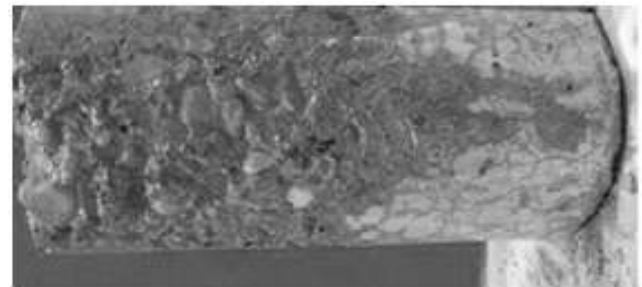


Figure 8: Specimens 28th day after immersion in 3.5% concentrated Sulphate solution under exposure to wet and dry condition.

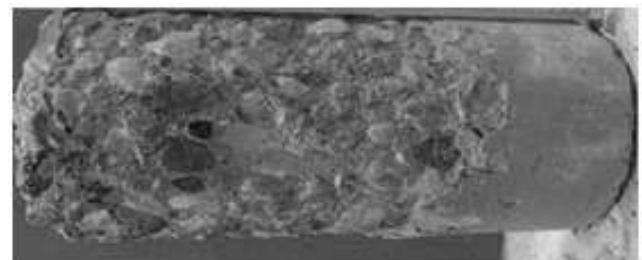


Figure 9: Specimens after 28 days of dipping in 3.5% concentrated Sulphate solution under freeze and thaw conditions.

Actions of sea water Sulphates on concrete aided using cyclic environmental changes leads to humidity and temperature changes in the concrete micro structure and hence observation of slightly higher deterioration in specimens under exposure to freezing-thawing as well as wet-dry conditions.

Comparatively higher deterioration and surface scaling was also observed in specimens exposed to a highly concentrated solution. Figure 10 and 11 below shows, the effect of increased concentration on concrete cylinders:



Figure 10: Specimens after 14 days of immersion in 3.5% concentrated sodium Sulphate solution.

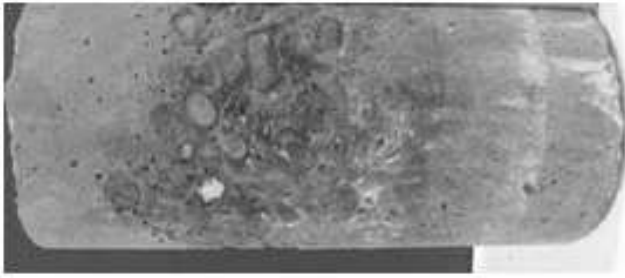


Figure 11: Specimens after 14 days of dipping in 7% concentrated sodium Sulphate solution

Sulphate attack on the specimens due to the Sulphate ions in the solution was also observed to increase with an increase in the porosity of the specimens. Comparatively higher deterioration was observed in OPC specimens with relatively larger pores compared to OPC – FA specimens [50]. Figures 12 and 13 shows, effect of increased porosity on Sulphate action in specimens exposed to wet and dry conditions after 28 days:

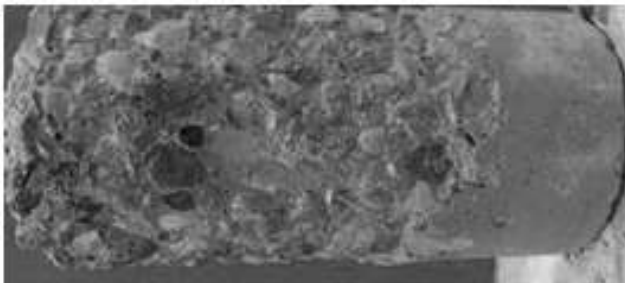


Figure 12: OPC specimens after 28 days of dipping in 3.5% concentrated solution.



Figure 13: OPC - FA specimens after 28 days of dipping in 3.5% concentrated sodium Sulphate solution.

SEM and X-ray diffraction analysis indicate thenardite (anhydrous sodium Sulphate), gypsum (hydrous calcium Sulphate) and Ettringite (hydrous calcium aluminium Sulphate) growth within the concrete micro structure as shown, in figures 14, 15 and 16 below:

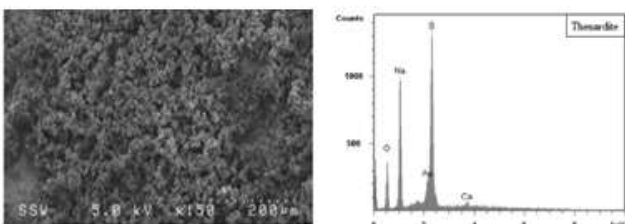


Figure 14: X-Ray Diffraction analysis.

Figure 14 X-Ray Diffraction analysis, as well as Scanning Electron Microscope showing the formation of

orthorhombic thenardite crystals in the concrete microstructure of specimens immersed in the sodium Sulphate solution

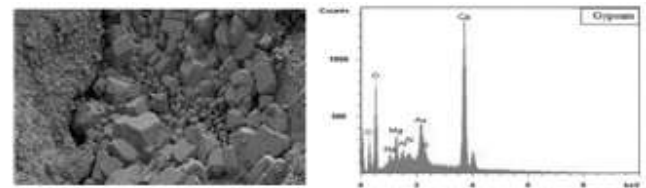


Figure 15: X-Ray Diffraction analysis.

Figure 15 X-Ray Diffraction analysis, and Scanning Electron Microscope showing gypsum formation in concrete microstructure of the specimens dipped in Sodium Sulphate liquid.

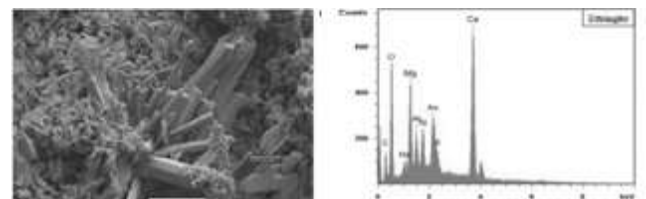


Figure 16: X-Ray Diffraction analysis.

Figure 16 X-Ray Diffraction analysis and Scanning Electron Microscope displaying hexagonal Ettringite crystals formation in concrete microstructure of specimens dipped in Sodium Sulphate liquid.

7. Conclusion

Investigations were done using twenty types of cement mixes. They were exposed to different solution concentration and different environmental changes by use of cyclic wet and dry conditions and cyclic freeze and thaw conditions.

The conclusions drawn from the experimental results:

- Sulphate ions affect the integrity and durability of concrete structures; deterioration due to the physical and chemical action of the ions is exhibited through compressive and tensile strength losses, mass loss, scaling and spalling of the concrete specimens.
- Cyclic environmental changes accelerate the effect of Sulphates on concrete structures with specimens immersed in Sulphate solutions under freeze and thaw conditions exhibiting comparatively higher levels of deterioration as compared to other exposure conditions due to volumetric expansion pressure caused by freezing water.
- Compressive and tensile strength loss occurs as the exposure time increase; with extensive strength loss being recorded on completion of the experiment due to the continued physical as well as chemical action of Sulphate ions on concrete
- Concrete deterioration increases with increased concentration of the Sulphate solution due to an increased number of free ions that induce physical and chemical attack the concrete

- Physical and chemical action of Sulphate ions depends on the volume and distribution of pores within the concrete microstructure. Increases in porosity and pore parameters such as distribution, volume and connectivity results in increased damage due to increased capillary action, evaporation and accumulation of Sulphate ions.
- Reactions between Sulphate ions and concrete components resulted in the growth of Ettringite, Gypsum and Thenardite crystals with the concrete microstructure; exerting pressure which in turn results to cracking and breakage of the structure.

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