**Evaluation Of Sulphates Attack On Concrete**

Olaolu G. Fadugba1 and Bamitale D. Oluyemi-Ayibiowu1, Adesola O. Adetukasi2

1Department of Civil and Environmental Engineering, The Federal University of Technology, Akure Nigeria

2Department of Civil Engineering, Yaba College of Technology, Lagos Nigeria

**Abstract.** This paper evaluates the effect of sulphates ion attack on concrete marine structures and deep foundations. The main variable investigated is the effect of three different industrial salts-sulphates: Sodium Sulphate (Na2SO4), Magnesium Sulphate (MgSO4) and Ammonium Sulphate (NH4)2SO4). Concrete cubes of 100mm by 100mm were cast and immersed into the sulphates solutions of 2.5g/l concentration. The compressive strength and Schmidt Hammer test on the mortar were studied at ages 7, 14, 21 and 28 days respectively, cubes immersed in sodium sulphate environment has an incredibly low compressive strength of 19.1N/mm2 at 28 days as against the normal 215N/mm2 specified by the BS 5328; Part 1; 1991. Surface hardness of the cubes in all the environments increased with age, with the cubes in the sodium sulphate environment having the least surface hardness which shows that Sodium sulphate environment causes severe attack on concrete.

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**1. Introduction**

Durability of concrete in underground structures depends on the chemical properties of the soil and groundwater. Oftentimes, properly designed and constructed concrete infrastructure systems are threatened by deterioration tendencies due to alterations in the internal or host environmental conditions. Consequently, increasing percentages of existing buildings and civil infrastructure have become either structurally deficient or functionally obsolete or both in past one decade as a result of construction defects, aging, material degradation and structural deterioration due to harsh environmental condition (Adewuyi *et al*., 2009, 2010. Adewuyi and Wu, 2011 ).

The future potential for greater marine application of concrete is enormous, with the inevitable growth in demand for the resources of the oceans and the possibility of locating cities, airports, nuclear power plants and various other facilities on offshore floating platforms in order to relieve land masses from urban congestion and pollution. (Dewar, 1985).

The popularity of concrete for marine construction is due to its economy for large structures and also to its generally excellent marine durability. The future applications of concrete in marine environments (coastal, offshore, estuaries) at great depths and in oceans with climatic extremes will stretch the durability of concrete to greater limits and therefore a sound understanding of the durability phenomenon is necessary to face this exciting challenge for the future successfully. However, performance of concrete marine 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 sulphur dioxide 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 lower pipes often lead to the release of sulphate. (Mehta, 1991).

Seawater contains the sodium, magnesium and calcium sulphates in the dissolved form. Therefore, sulphate attack is a common occurrence in marine environments.

The chemical composition of seawater throughout the world is remarkably uniform.

The approximate percentages of various ions due to the salts in seawater are: Chloride, 51.3; Sulphate, 7.2; Sodium, 28.5; Magnesium, 3.6; Calcium, 1.3; Potassium, 1.0. However, the total amount of any ion varies widely. From the standpoint of chemical effects of seawater on marine structures, it is the sulphate content which is problematic.

The range of practical importance of sulphate concentrations are between 150 and 6000 ppm, when attack on unprotected concrete is studied. The fact that, sulphates occur naturally in sea water, ground water and soils (marine environment) have been established. These sulphate ions react with hydrates of Portlant Cement, resulting in deterioration of concrete. The mechanism of sulphate attack on concrete involves two chemical reactions: combination of sulphate ions and hydrated calcium aluminate to form calcium-sulfo-aluminate (ettringite) (3CaO.Al2O3. 3CaSO43H20), and the combination of sulphate ions with calcium ions to form gypsum.

The reaction of sulphate ions with the Ca(OH)2 in the concrete to form gypsum is called acidic type of sulphate attack.

Ca(OH)2 + Na2SO4 => CaSO4 + 2NaOH

Gypsum

Ca(OH)2 + MgSO4 => CaSO4 + Mg(OH)2

Gypsum brucite

The CaSO4 precipitates as CaSO4.2H2O (secondary gypsum). The high concentration of sodium chloride (NaCl) in sea water increases the solubility of gypsum and prevents its rapid crystallization. It also increases the solubility of Ca(OH)2 and Mg(OH)2. The result is leaching of these compounds which make the concrete weak.

The second type of attack mainly results from the chemical reaction between the tricalcium aluminate (C3A) present in Portland cement and sulphate ions supplied by the aggressive environment. By this reaction, ettringite is formed. The chemical reaction can be represented as:

MgSO4­ + [Ca(OH)2 + 3CaO.Al2O3.CaSO4.18H2O] => Mg(OH)2 + 3Ca).Al2O3.3CaSO4.32H2O

(ettringite)

Na2SO4 + [Ca(OH)2 + 3Ca).Al2O3.CaSO4.18H2)] => 2NaOH + 3CaO.Al2O3.3CaSO4.32H2O

(ettringite)

The reaction products, i.e. gypsum and ettringite have greater volume than the compounds they replace. The increase in volume due to gypsum has been reported to be more than double the original volume and that due to expansion causes cracking of the matrix, which leads to the loss in strength and disruption. Marine sulphate attack leaves the concrete soft and brittle. The leaching of compounds and softening of concrete due to sulphate attack are further aggregated by the presence of chlorides in seawater. Sulphate attack in the submerged zone of marine concrete structures is slower than the higher zones where alternate wetting and drying accelerate the deterioration process.

Sulphate concentrations normally form the basis of a first approximation in assigning degree of severity of attack expected.

* “Negligible” attack up to 190ppm sulphate in ground water or up to 0.10% sulphate in soil.
* “Mild but positive” where the corresponding values are 150-1000ppm and 0.10-0.20%.
* “Considerable” attack at 1000-2000ppm and 0.20-0.50%.
* “Severe” over 2000ppm and over 0.5%.

A classification of soil and groundwater conditions is given in Table 1.

**Table 1: Summary of BS 8110 Classification of Sulphate Soil Conditions**

|  |
| --- |
| **Concentration of sulphates expressed as SO­4** |
|  | **In Soil** |  | **In groundwater** |
| **Class** | **Total SO4** | **SO4 in 2:1****Water: Soil Extract** |  |
|  | (%) | g/L | g/L |
| 1 | <0.2 | <1.0 | <0.3 |
| 2 | 0.2 – 0.5 | 1.0 – 1.9 | 0.3 – 1. 2 |
| 3 | 0.5 – 1.0 | 1.9 – 3.1 | 1.2 – 2.5 |
| 4 | 1.0 – 2.0 | 3.1 – 5.6 | 2.5 – 5.0 |
| 5 | >2 | >5.6 | >5.0 |

**2.0 Material And Method**

*Sand*: The sand collected from Owena River was used as fine aggregate, the sand sample was clean, sharp and free from clay and organic matter and well graded in accordance with BS 881, 1983.

*Crushed Stones*: Coarse aggregate used was crushed stones with 20mm maximum size supplied from Quarry in Akure, Nigeria and it conformed to BS 881, 1983.

*Water:* Tap water was used for the mixing and it was properly examined to ensure that it was clean, free from contaminants either dissolved or in suspension and good for drinking as specified in BS 3148, 1983.

*Ordinary Portland cement* produced by West African Portland Cement Company was used in the experimental investigation.

The chemical composition of Ordinary Portland Cement is given in Table 2.

**Table 2: Composition of Ordinary Portland Cement**

|  |  |
| --- | --- |
| Oxide Composition (%) | Compound Composition |
| CaO | SiO2 | Al2O3 | Fe2O3 | C3S | C2S | C3A | C4AF |
| 63 | 20.6 | 6.3 | 3.6 | 40 | 30 | 11 | 11 |

The industrial salts-sodium sulphates (Na2SO4), magnesium sulphate (MgSO4) and ammonium sulphate (NH4)2SO4) were procured from Akure, South Western Nigeria.

The solutions of the salts were prepared in the laboratory, with each, having a concentration of 2.5g/l (2500ppm) to simulate as closely as possible site conditions for offshore structures and sulphate-bearing agricultural soils and groundwater. Class 3 groundwater condition 2.5g/L (2500ppm) was selected for this study (See Table 1).

**3. Results And Discussion**

**3.1 Identification Of Fine And Coarse Aggregate**

The properties of sand and crushed stones used for the study are summarized in Table 3 while Figures 1 and 2 show their particle size distribution for sand and crushed stones respectively. The sand was poorly graded and classified in zone 1 in accordance with BS882 2002 classification for aggregates. The fineness modulus of sand and crushed stones are 3.65 and 3.36 respectively, while their specific gravities are 2.63 and 2.76 which is in good agreement with the recommendation of BS 1377 1990 for clean quartz and flint sands. Also Shirley 1975 reported that normal-density aggregates generally have specific gravities between 2.5 and 3.0. The bulk density of the sand and crushed stoneare 1700and 2750 kg/m3 respectivelyand it conforms to BS882 2002 recommendation for aggregates from natural sources for concrete.

Table 3: Properties of Cement, Sand and Crushed Stone

|  |  |  |  |
| --- | --- | --- | --- |
| Property | Cement | Sand | Crushed stone |
| Natural Moisture Content (%) |  | 21.15 | 0.50 |
| Water Absorption (%) |  | 1.5 | 0.25 |
| Fineness Modulus |  | 3.65 | 3.36 |
| Specific Gravity | 3.15 | 2.63 | 2.76 |
| Density (kg/m3) |  | 1700 | 2750 |
| Aggregate Crushing Value (ACV) (%) |  |  | 30.7 |
| Aggregate Impact Value (AIV) (%) |  |  | 20.9 |

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**Figure 1**. Particle size Distribution Curve for Sand

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**Figure 2**. Particle size Distribution Curve for Crushed Stone

**3. 2 Compressive Strength**

Results of the compressive strength test on concrete produced for the all salts and unpolluted samples are presented in Table 4 and Figure 3. The strength developments with age in reference to the control and test samples in the three sulphate environment, at day 7, all samples in various sulphates environment and the control compressive strength varies from 11N/mm2, 11.1n/mm2, 11.2N/mm2 and 11.4N/mm2 for ammonium sulphate, Magnesium sulphate, control and sodium sulphate respectively.

At 28days, Ammonium surface has a compressive strength of 19.7N/mm2 follow by Magnesium sulphate with compressive strength of 19.3N/mm2 and Sodium sulphate has the lowest compressive strength of 19.1N/mm2 while control has the highest compressive strength of 20.5 N/mm2. The results of the compressive strength shows that concrete in sodium sulphate has attack the concrete than other sulphate environment and this is in agreement with (Scherer, 2004, Thaulow and Sahu, 2004, and Skalny *et al.*, 2002), that concrete damage is a result of an increase in the salt volume. For instance, sodium sulphate can increase by 314% in volume when anhydrous sodium sulphate (Na2SO4, thenardite) transforms to the hydrous form(Na2SO4.10H2O, mirabilite) When it occurs, this process leads to fatigue and loss of cohesiveness of the cement paste within a concrete matrix (Skalny *et al.*, 2002).

Figure 3: Compressive Strength Relationship for all the Sulphate Salts and Control.

Table 4 Result of Compressive Strength (N/mm2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Days | Sodium Sulphate (Na2So4) | MagnesiumSulphate (MgSO4) | AmmoniumSulphate (NH4)2SO4 | Control (Unpolluted Water) |
| 7 | 11.41 | 11.08 | 11.08 | 11.6 |
| 14 | 12.1 | 13 | 13.9 | 14.81 |
| 21 | 17 | 16.9 | 17.2 | 18.15 |
| 28 | 19.1 | 19.3 | 19.7 | 20.5 |

**3.3 Surface Hardness**

Table 5 presents the surface hardness of cubes immersed in different salts and the control for the period of curing. The Surface hardness of the test cubes increased significantly with age for all the samples in different sulphate environment, although, cubes immersed in sodium sulphate has the least surface hardness and the control exhibited highest surface strength with age. (Figure 4)

Table 5 Surface Hardness of the Cubes

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Days | Sodium Sulphate (Na2So4) | Magnesium Sulphate (MgSO4) | Ammonium Sulphate (NH4)2 | Control (Water) |
| 7 | 6.40 | 9.00 | 10.10 | 11.10 |
| 14 | 9.60 | 10.80 | 12.50 | 14.0 |
| 21 | 10.6 | 11.0 | 14.7 | 16.0 |
| 28 | 12.0 | 12.70 | 15.20 | 17.0 |

Figure 4: Surface Hardness Relationship for all the Sulphate Salts and Control Cubes

**5. Conclusions**

The compressive strength and the surface hardness tests show that sodium sulphate environment is more severe than magnesium and ammonium sulphate environment.

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