

Performance of Anthill Soil Replaced Concrete in Sulfate Solutions

John Kamau, Ash Ahmed, Paul Hirst and Joseph Kangwa

Abstract—Durability of concrete is defined as its ability to resist any form of deterioration, allowing it to retain its original form and quality after it has been exposed to the environment of its intended use. Sulfate attack causes concrete to lose its compressive strength through the decomposition of the products of hydration of cement. Pozzolanic reactions from Supplementary Cementitious Materials (SCMs) help in resisting the sodium sulfate (Na_2SO_4) attack. This work investigated the potential use of Anthill Soil (AHS) to improve the performance of concrete in sulfate aggressive environments. An AHS replacement of 30% (per cent) by the weight of cement was used to make concrete test bars and cubes. The 0% replacement also referred to as the control was used as the point of reference from which all performances were measured. The specimens were immersed in 5% Na_2SO_4 , 5% magnesium sulfate (MgSO_4), and 5% mixed solution of Na_2SO_4 and MgSO_4 . Elongation measurements were taken over a period of 9 months, whereas compressive strength tests, which were used to work out the Strength Deterioration Factors (SDFs) and visual observations for surface deterioration were carried out at 9 months. From the results, AHS specimens that were immersed in the Na_2SO_4 , MgSO_4 and mixed Na_2SO_4 and MgSO_4 solutions performed poorly in elongation compared with the control specimens, but had lower SDFs in the Na_2SO_4 and mixed solutions of Na_2SO_4 and MgSO_4 . The surface deterioration of AHS specimens in the MgSO_4 solution was worse than that of the control specimens but was similar to that of the control in the mixed sulfate solution of Na_2SO_4 and MgSO_4 . The SDF results highlight the potential of using AHS with an advantage in Na_2SO_4 and mixed Na_2SO_4 and MgSO_4 environments.

Index Terms—Anthill Soil; Sulfate Attack; Sulfate Resistance; Sulfate Aggressive Environments.

I. INTRODUCTION

Durability of concrete is defined as its ability to resist any form of deterioration, allowing it to retain its original form and quality after exposure to the environment of its intended use [1].

Deterioration can be from external chemical attack, or internal chemical reactions from the constituents of concrete [1]. Sulfate attack is a durability concern that causes concrete to lose its compressive strength, with severity

depending on the type of sulfate [2].

Sulfate attack brings about the decomposition of the products of hydration of cement, resulting in the formation of new compounds, which may be leached out if soluble or disruptive if insoluble [1].

The products of hydration that are susceptible to sulfate attack are calcium hydroxide [$\text{Ca}(\text{OH})_2$] and Calcium Silicate Hydrates (C-S-H) [3], [4].

All commonly available water-soluble sulfates are deleterious to concrete, but the most severe effects are observed when the attack is associated with magnesium cations [2].

Higher sulfate concentrations in water are due to magnesium sulfate (MgSO_4), which is highly soluble in water at room temperature (20°C) when compared to sodium sulfate (Na_2SO_4) [2].

$\text{Ca}(\text{OH})_2$ in Na_2SO_4 environments reacts with sulfates to form calcium sulfate [$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$], also known as gypsum, and/or with unhydrated tri-calcium aluminate, also known as alite (C_3A) and alumina-bearing hydration products to form expansive ettringite [5]. A precipitation of gypsum and ettringite can generate stresses within the concrete, which if greater than the tensile strength of the concrete may result in strength loss, expansion, spalling and severe degradation [2]. As a result, Na_2SO_4 attack is manifested and evaluated through expansion [2].

MgSO_4 attack, on the other hand is determined by the outwards diffusion of hydroxide ions to form brucite and inwards diffusion of sulfate ions to form gypsum [6]. This combined layer of gypsum and brucite retards the harmful effects of MgSO_4 attack in the early ages, but it later peels off at latter ages due to the formation of expansive ettringite and gypsum, which causes cracking on the surface of the brucite layer [2]. As a result, the decomposition of C-S-H gel to the non-cementitious Magnesium Silicate Hydrate (M-S-H) gel permits the easy diffusion of sulfate ions into the hardened cement matrix [4]. This alteration of C-S-H to M-S-H is probably the major process and final stage of MgSO_4 attack, and it brings about the reduction in strength of concrete [2]. As a result, MgSO_4 attack is manifested and evaluated through the loss of strength of concrete [2].

Following the attack of magnesium ions on C-S-H, a poor performance of Supplementary Cementitious Materials (SCMs) concrete in MgSO_4 environments has been reported [2], [7].

Alongside the presence of $\text{Ca}(\text{OH})_2$, low sulfate resistance is also characterised by high contents of Sulfate (SO_4), iron oxide (Fe_2O_3) and C_3A , and low levels of silicon dioxide (SiO_2) [3]. A high molar ratio of sulfite (SO_3) to aluminium oxide (Al_2O_3) increases the risk of the formation of monosulfate that otherwise results in expansive ettringite

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and gypsum on exposure to sulfate attack [2].

Pozzolanic reactions from SCMs such as Pulverised Fuel Ash (PFA), Ground Granulated Blast Furnace Slag (GGBS), Silica Fume (SF), Rice Husk Ash (RHA) and Corncob Ash (CCA) help in resisting the Na_2SO_4 attack as they refine pores, dilute C_3A and due to their low ratio of calcium to silica, remove $\text{Ca}(\text{OH})_2$ by converting it into the cementitious C-S-H gel, thereby reducing permeability and the quantities of gypsum formed [2, 3].

Anthills, shown in Fig. 1 are made up of soil grains that are coated with sticky rapidly hardening secretions from the recta and mouths of ants, and are very cohesive [8]. Their suitability to be used as a SCM was investigated by “unpublished” [9]. Table I shows the chemical composition of AHS that was obtained by [9] from an X-ray diffraction. ASTM C618 [10] and [11] require that natural pozzolans should contain a combined sum of silicon dioxide (SiO_2), Aluminium oxide (Al_2O_3), and Iron oxide (Fe_2O_3) of at least 70% of the total mass and a LOI of between 5% and 10%. From the results, AHS contained the required chemical composition to allow them to be characterised with natural pozzolans.



Fig. 1. Anthill soil in Tsavo National Park West (picture by authors)

Table II and Fig. 2 show the compressive strengths obtained by [9] from AHS-replaced specimens. From these results, AHS achieved compressive strengths that are among those listed by [12] as being durable and suitable for structural applications.

According to [13], the durability of concrete is directly proportional to its compressive strength, and from the findings of [9] it may be deduced that Anthill Soil (AHS) could pose a high durability after longer periods of curing, as it has been reported that the early strength of pozzolanic concrete is lower, but is higher at latter ages due to the consumption of $\text{Ca}(\text{OH})_2$ by the pozzolanic reaction to form further C-S-H, which is strength giving [2]. Pozzolanic concretes have therefore been reported to achieve strengths that are either close to or above those of 100% cement concretes [2].

TABLE I. PERCENTAGE CHEMICAL COMPOSITION OF AHS USED

Chemical	Percentage Composition
Silicon dioxide (SiO_2)	51.9
Aluminium oxide (Al_2O_3)	23.4
Iron oxide (Fe_2O_3)	7.0
Calcium oxide (CaO)	1.6

Magnesium oxide (MgO)	2.4
Sodium oxide (Na_2O)	0.4
Potassium oxide (K_2O)	1.9
Loss on ignition (LOI)	9.3
Sulphur trioxide (SO_3)	0.1

TABLE II. COMPRESSIVE STRENGTH OF AHS SPECIMENS (N/MM²) BY KAMAU, ET AL. [9]

Curing age (days)	Compressive strength at percentage replacement (N/mm ²)							
	0%	5%	7.50%	10%	15%	20%	25%	30%
7	56.2	40.4	40.3	38.1	33.2	32.6	27.1	22.3
28	61.6	50.8	53.4	46	43.4	38.7	34.6	28.8
56	67.6	53.4	50.6	47.9	48.1	44.8	39.2	31.8
91	71.3	59.3	63.1	55.6	54.1	49.1	44.4	37.8

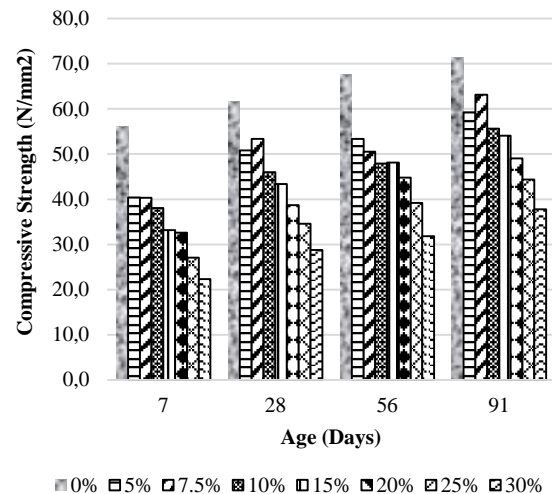


Fig. 2. Compressive strengths of AHS specimens (N/mm²) by [9]

Table III and Fig. 3 show the densities obtained by [9]. From these findings, the densities of AHS-replaced specimens remained below those of 100% cement specimens throughout all replacements and decreased with further replacement and curing age. This behaviour in density is a characteristic of SCMs due to their lower particle specific gravity and also the consumption of $\text{Ca}(\text{OH})_2$ with curing to form the less dense Calcium Silicate Hydrate (C-S-H) [2], [14].

TABLE III. DENSITIES OF AHS-REPLACED SPECIMENS OVER 91 DAYS OF CURING (KG/M³) [9]

Age (days)	Densities of AHS specimens at percentage replacements (kg/m ³)							
	0%	5%	7.5%	10%	15%	20%	25%	30%
7	2350	2330	2329	2326	2325	2278	2274	2266
28	2350	2320	2327	2325	2323	2271	2265	2259
56	2356	2320	2326	2323	2316	2258	2247	2238
91	2366	2318	2314	2312	2307	2250	2243	2202

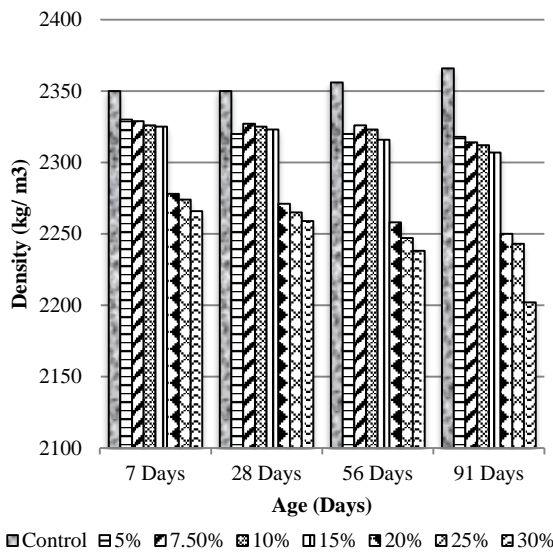


Fig. 3. Densities of AHS-replaced specimens against curing age (kg/m³) [9]

II. RESEARCH SIGNIFICANCE

There is generally a shortage of portable tap water for use in mixing concrete in the developing world [15]. Most people, especially from peri-urban settings will use any available water for this purpose, such as that obtained from boreholes, sewages and swamps [15]. Some of the water from these environments may be contaminated and can be a source of aggressive ions on concrete, which can result in a reduced service life of structures due to expansion, cracking, spalling and loss of compressive strength [15].

No work was found on the resistance of Anthill Soil (AHS) replaced concrete to sulfate attack. This work investigated the performance of AHS-replaced concrete in sulfate solutions.

III. METHODS

The sulfate elongation tests conformed to [16]. Cubic prismatic samples measuring 160 mm x 40 mm x 40 mm and cubes measuring 100 mm x 100 mm x 100 mm for sulfate elongation and strength deterioration tests respectively were prepared and cast with a 30% AHS replaced concrete mix. The 0% replacement, also referred to as the control was used as the point of reference from which all performances were measured [1].

The moulds were covered with a plastic plate and placed in a sealed curing container to prevent evaporation. They were then placed in an oven for 23½ hours at 35°C, after which they were removed from the container and demoulded. Two cubes were crushed to ensure that the concrete had achieved compressive strengths of 20.0 N/mm². The lengths of test specimens were taken before they were immersed in 5% Na₂SO₄, 5% MgSO₄, and 5% Na₂SO₄ and MgSO₄ solutions at laboratory temperatures of 23°C.

A pH of 6 to 8 was maintained on the sulfate solutions throughout the test period. Length changes were measured using veneer calipers at 1, 2, 3, 4, 8 weeks, and 4, 8, and 9 months, and worked out by using (1) to [16].

$$\Delta L = \frac{L_x - L_i}{L_g} \times 100 \quad (1)$$

Where;

ΔL = percentage change in length at measuring age,
 L_x = reading of specimen at measuring age,
 L_i = reading of specimen at immersion,
 L_g = 160 (nominal length between the innermost ends of the moulds used).

Strength deterioration was assessed using the Strength Deterioration Factors (SDFs), which were calculated by using (2) after [4].

$$SDF = \frac{f_{cw'} - f_{cs'}}{f_{cw'}} \times 100 \quad (2)$$

Where $f_{cw'}$ is the compressive strength of control specimen cubes and $f_{cs'}$ is the compressive strength of sulfate immersed specimen cubes.

To ensure repeatability, a total of three specimens were cast for each test and the average of elongation and SDF was reported [16]. Surface deterioration was observed at 9 months. The C₃A content of AHS was calculated by using (3), which was obtained from the Bogue calculation [17]

$$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3 \quad (3)$$

IV. RESULTS AND DISCUSSIONS

A. Chemical analysis

From the chemical analysis shown in Table I, AHS contained a low ratio of CaO to SiO₂, which according to [2] removes Ca(OH)₂, thereby improving sulfate resistance. Also, a high level of SiO₂ and a low level of Fe₂O₃, and a low ratio of SO₃ to Al₂O₃ contained in AHS were reported by [2] to be an indication of high sulfate resistance. C₃A in AHS was calculated by using (3).

B. Elongation

Tables IV, V and VI, and Figs. 4, 5, and 6 show the elongation of AHS specimens in the Na₂SO₄, MgSO₄, and the mixed solutions of Na₂SO₄ and MgSO₄ respectively. A standard deviation of 0.04 was calculated across the range of tests.

The elongations of AHS specimens were higher than those of the control specimens in the Na₂SO₄ solution. These results were not consistent with [4] who reported lower expansions in the Na₂SO₄ solution for SF replaced specimens, and attributed it to the pozzolanic reaction which helps in resisting sulfate attack through the refining of pores, dilution of C₃A and removal of Ca(OH)₂ by converting it into the C-S-H gel, thereby reducing the quantities of gypsum formed [2].

Even though AHS contained a high level of SiO₂ and a low level of Fe₂O₃, as well as a low molar ratio of SO₃ to Al₂O₃, which were reported by [2] and [18] as being an indication of high sulfate resistance, its poor performance in the Na₂SO₄ solution could be attributed to the high contents of Al₂O₃ and C₃A, which was calculated at 50.2%. According to [19], the content of Al₂O₃ should not exceed 14%, and if it does, C₃A should not be above 10% for good sulfate resistance.

Although according to [4] and [7] sulfate attack that is

associated with $MgSO_4$ is not characterised by expansion, elongation was recorded on specimens that were immersed in both the $MgSO_4$ and the mixed solution of Na_2SO_4 and $MgSO_4$, with AHS specimens showing higher expansions than those of the control specimens. Park, et al. [20] also reported higher expansions on SF specimens in the $MgSO_4$ solution.

Consistent with [4] elongation was observed to increase with immersion time.

TABLE IV: ELONGATION OF AHS REPLACED SPECIMENS IN THE SODIUM SULFATE SOLUTION (MM)

	Control	AHS
Week 1	0.0208	0.0042
Week 2	0.0260	0.0208
Week 3	0.0302	0.0333
Week 4	0.0417	0.0333
Week 8	0.0042	0.0917
4 months	0.0692	0.2667
8 months	0.2583	0.3104
9 months	0.4854	0.7792

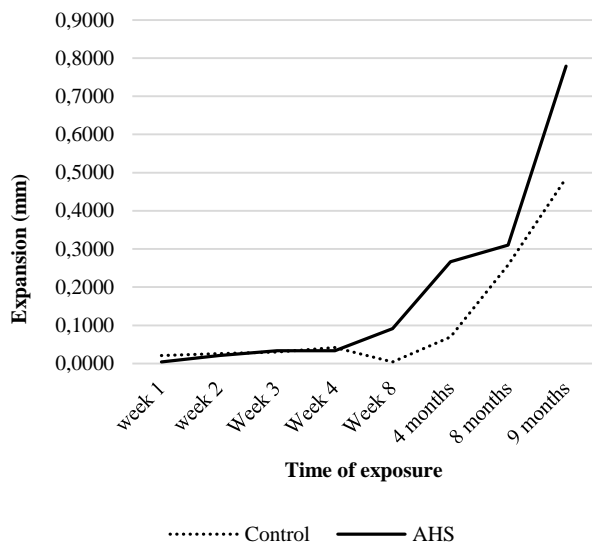


Fig. 4. Elongation of AHS replaced specimens in the sodium sulfate solution against time (mm).

However, the expansions for all specimens in the Na_2SO_4 solution were higher than those of specimens immersed in the $MgSO_4$ and mixed sulfate solutions, consistent with [4] who reported only a small change in length in the $MgSO_4$ and the mixed sulfate solutions for all the specimens, compared with the Na_2SO_4 solution. Moon, et al. [4] attributed the expansion in the $MgSO_4$ solution to the lower alkalinity that is associated with the formation of brucite in the cement matrix due to the presence of magnesium ions.

TABLE V: ELONGATION OF AHS REPLACED SPECIMENS IN THE MAGNESIUM SULFATE SOLUTION (MM)

	Control	AHS
Week 1	0.025	0.0167
Week 2	0.0027	0.0208
Week 3	0.0029	0.0042
Week 4	0.0042	0.0042
Week 8	0.075	0.0208
4 months	0.1833	0.0417
8 months	0.1854	0.05
9 months	0.1875	0.3125

Expansion of AHS specimens in $MgSO_4$ solution against time (mm)

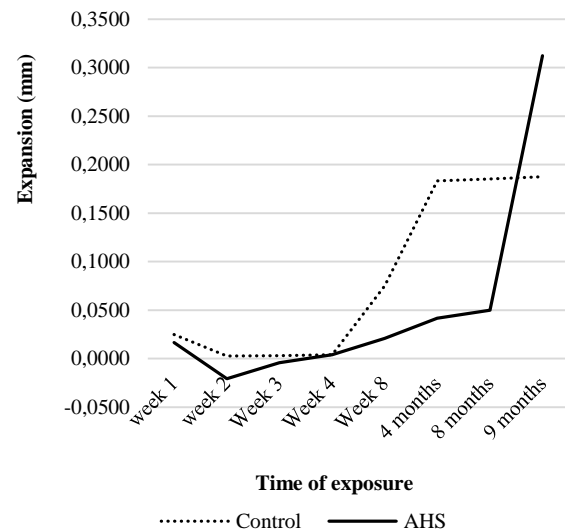


Fig. 5. Elongation of AHS replaced specimens in the $MgSO_4$ solution against time (mm).

TABLE VI: ELONGATION OF AHS REPLACED SPECIMENS IN THE MIXED SOLUTION OF SODIUM AND MAGNESIUM

	Control	AHS
Week 1	0.0052	0.0917
Week 2	0.0135	0.1292
Week 3	0.0177	0.1333
Week 4	0.0129	0.1469
Week 8	0.1417	0.2292
4 months	0.200	0.3000
8 months	0.1500	0.3333
9 months	0.3500	0.6042

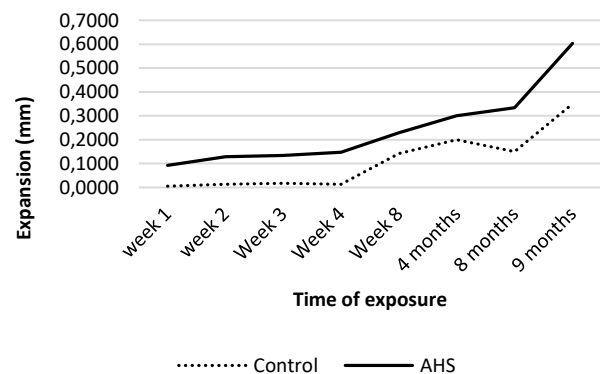


Fig. 6. Elongation of AHS replaced specimens in the mixed solution of Na_2SO_4 and $MgSO_4$ against time (mm)

C. Strength deterioration

TABLE VII: STRENGTH DETERIORATION FACTOR (SDF) OF AHS SPECIMENS IN SODIUM, MAGNESIUM AND MIXED SULFATE SOLUTIONS

Specimens	Na_2SO_4	$MgSO_4$	$Na_2SO_4 + MgSO_4$
Control	8.6	17.7	26.9
AHS	2.4	31.7	16.8

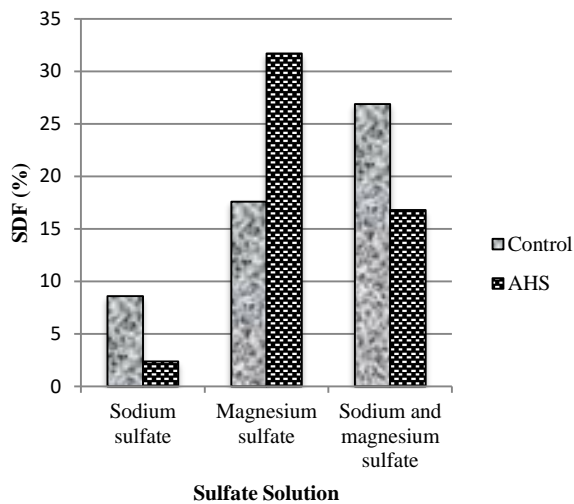


Fig. 7. Strength Deterioration Factor (SDF) of AHS specimens in Na_2SO_4 , MgSO_4 and mixed sulfate solutions

Table VII and Fig. 7 show the percentage Strength Deterioration Factors (SDFs) of specimens that were immersed in solutions of Na_2SO_4 , MgSO_4 and mixed Na_2SO_4 and MgSO_4 solutions. The SDFs of AHS replaced specimens were 2.4, 31.7, and 16.8 while those of the control specimens were 8.6, 17.7, and 26.9 for the Na_2SO_4 , MgSO_4 and mixed Na_2SO_4 and MgSO_4 solutions respectively.

The performances of AHS specimens were lower than those of the control specimens in the MgSO_4 solution. These findings were consistent with literature that MgSO_4 attack manifests itself through the loss of strength of concrete, and is more pronounced in pozzolanic concretes [2], [4], [7]. Also consistent with literature, it was found that the reaction between Na_2SO_4 and C-S-H is negligible; hence the manifestation and evaluation of Na_2SO_4 attack through expansion due to the presence of gypsum and ettringite [2], [4], [7].

The low levels of C-S-H in the control specimens was termed by [4] as the reason for the good performance of control specimens in the MgSO_4 solution, since MgSO_4 attack is controlled by magnesium attack on C-S-H. However, since SCMs contain less $\text{Ca}(\text{OH})_2$ and more C-S-H, MgSO_4 readily reacts with the secondary C-S-H gel, decomposing it to the M-S-H gel, that in turn allows the easy diffusion of sulfate ions into the concrete matrix once the combined layer of gypsum and brucite has peeled off [2]. The good performance of the control specimens in the MgSO_4 solution was attributed by [4] to the pore blocking effect by the formation of the less permeable brucite.

The results were also consistent with [4], who reported lower SDFs on SF-replaced specimens in the Na_2SO_4 solution compared with those of the control, whereas for specimens that were immersed in solutions that contained MgSO_4 , the SDF of SF-replaced specimens were higher than those of the control specimens. Lower SDFs than those of the control specimens were however recorded for the AHS specimens in the mixed sulfate solution, unlike in [4]'s work where higher SDFs were reported for SF-replaced specimens immersed in the mixed sulfate solution compared to those immersed in individual sulfate solutions of Na_2SO_4

and MgSO_4 .

From the SDF results, it can be concluded that AHS could be used in concrete with an advantage over 100% cement in Na_2SO_4 environments and environments of mixed Na_2SO_4 and MgSO_4 .

D. Surface deterioration

TABLE VIII: SURFACE DETERIORATION OF AHS SPECIMENS SUBJECTED TO SULFATE SOLUTIONS [21]

Specimen	Na_2SO_4	MgSO_4	$\text{Na}_2\text{SO}_4 + \text{MgSO}_4$
Control	0	0	2
AHS	0	1	2

Key: Deterioration levels. 0, no damage; 1, minimum visible cracks; 2, mass loss and some disintegration; 3, extensive spalling and softening; 4, wider cracks and extensive spalling; 5, Complete disintegration

Table VIII shows the surface deterioration levels of AHS specimens immersed in 5% MgSO_4 , 5% Na_2SO_4 , and the mixed solution of Na_2SO_4 and MgSO_4 based on [21].

Visual observations showed no damage on both the control and AHS specimens that were immersed in the Na_2SO_4 solution, minimum visible cracks were observed on the AHS specimens immersed in the MgSO_4 solution, while mass loss and some disintegration was observed on both the control and AHS-replaced specimens that were immersed in the mixed solution of Na_2SO_4 and MgSO_4 . The results were consistent with literature that the predominance of the more aggressive MgSO_4 attack over Na_2SO_4 attack is spelled in the mixed sulfate solution [4].

The presence of gypsum and brucite confirmed by [4] from specimens that were immersed in the MgSO_4 solution was considered by the authors as being the cause of deterioration to the surface of specimens.

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