

Sulfate Resistance of Concretes Containing Rice Husk Ash

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Abstract

Deterioration of concrete structures in sulfate environments is a well-known phenomenon. Cement chemistry is an important parameter in coping with sulfate attack. C_3A and $Ca(OH)_2$ leading to expansion, cracking and strength reduction. The use of pozzolans such as fly ash, silica fume, natural pozzolans and Rice Husk Ash (RHA) can improve the sulfate resistance of concrete. It was observed that the sulfate resistance of blended cements was significantly higher in sulfate environments. This study investigates the effect of RHA replacing by cement on the durability of concrete due to sulfate attack. Three RHA replacement levels which are 7%, 10% and 15% were considered in the study by weight of cement. After specified initial moist curing period (28 days) concrete specimens were immersed in sodium sulfate & magnesium sulfate solution. The degree of sulfate attack was evaluated by measuring compressive strength reduction of concrete cubes and their weight losses. Expansions observed in ordinary Portland cement mortar prisms were larger than expansion that for RHA mortar prisms when tested according to ASTM C 1012. Sulfate performance of concrete depends primarily on permeability. RHA replacement of cement is understood to reduce the rate of diffusion of aggressive ions such as sulfates.

Keywords: RHA, sulfate attack, Durability, Expansion

1 Introduction

Sulfate attack is one of the most aggressive environmental deteriorations that affect the long-term durability of concrete structures. The sulfate attack of concrete leads to expansion, cracking, and deterioration of many civil engineering structures exposed to sulfate environment such as piers, bridges, foundations, concrete pipes, etc. The sulfate ions in solution, which come from the soil, ground water, and seawater, are found in combination with other ions such as sodium, potassium, magnesium and calcium ions. The sulfate ions react with C_3A and $Ca(OH)_2$, to produce expansive and softening types of deterioration. The sulfate attack in marine environment gives rise to expansive ettringite, gypsum, and brucite and sometimes is associated with calcite formation. The attack of sodium sulfate on concrete is due to two principal reactions: the reaction of Na_2SO_4 and $Ca(OH)_2$ to form gypsum and the reaction of the formed gypsum with calcium aluminate hydrates to form ettringite. In addition, it is noticed that $MgSO_4$ reacts with all cement compounds, including C-S-H, thus decomposing cement, and subsequently forming gypsum and ettringite. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. In addition to the formation of ettringite and gypsum and its subsequent expansion, the deterioration due to sulfate attack is partially caused by the degradation of calcium silicate hydrate (C-S-H) gel through leaching of the calcium compounds. This process leads to loss of C-S-H gel stiffness and overall deterioration of the cement paste matrix.

To control the cement chemistry, American Standards suggest a limit on the (C_3A) and ($2C_3A + C_4AF$) contents of sulfate resistant, type V, cements as 5% and 25%, respectively. On the other hand, cements with low C_3A and C_4AF compounds generally tend to have a higher C_3S/C_2S ratio, and an increase in the C_3S content of cement generates a significantly higher amount of calcium hydroxide, as the hydration of C_3S produces nearly 2.2 times more calcium hydroxide (CH) than the hydration of C_2S . CH is known to be responsible for the formation of gypsum, and gypsum is known to be the first step of the formation of ettringite, which can be considered as the principal cause of deterioration. Irassar et al. found mortar bars containing a low C_3A and low C_3S cement showed 10 times less expansion than those with a low C_3A and a high C_3S content.

To control the permeability of concrete, lower w/c ratio and pozzolans are recommended. Effect of various pozzolans on the resistance of cements to external sulfate attack has also been studied by other researchers. Pozzolans reduce not only the permeability but also the C_3A amount if they are a partial replacement of cement. Moreover, use of pozzolans or use of blended cements, in general, reduces the quantity of CH due to the pozzolanic reactions which would otherwise react with sulfates to form gypsum. So, the deterioration of concrete due to sulfate attack is considered a complex problem and it depends on many factors:

- Factors related to concrete properties like type of Portland cement, W/B ratio, CH content, pore structure of the formed hydrates and using of mineral admixtures such as fly ash, slag, SF, RHA, etc.
- Factors related to aggressive medium like type of salt, concentration and presence of more than one kind of aggressive ions.
- Factors related to environmental conditions like temperature and drying–wetting cycles.

2 Experimental Program

2.1 Materials

Locally available ordinary Portland cement (ASTM Type I) was used in the study. The physical properties and chemical composition of the cement are presented in Tables 1, respectively. On the other hand the coarse aggregate used was crushed limestone. The coarse aggregate had a maximum aggregate size of 19 mm, water absorption of 1.7%, bulk specific gravity of 2.58. Also the fine aggregate used was natural silica sand. The sand had a bulk specific gravity of 2.56, a fineness modulus of 1.8, and water absorption of 2.5%.

Homogeneous rice husk ash produced by the special designed furnace at 650°C and 60 minutes burning time. Table 1 shows the physical and chemical characteristics of RHA (RHA-650-60) and cement. It is in grey color, average silica (SiO_2) content of 90%, and Blaine fineness of 3,800 cm^2/gr . The physical properties and chemical composition of the RHA are presented in Tables 1, respectively. Also the super plasticizer was used is based on polycarboxylate.

Table 1. Results of XRF on Rice Husk Ash Samples and Cement.

			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	LOI
temperature and time duration	550	60min	75.22	0.05	0.14	0.57	0.37	0.36	0.07	1.47	0.51	0.01	21.01
		90min	80.76	0.03	0.09	0.66	0.23	0.43	0.05	1.72	0.79	0.01	14.95
	600	60min	80.55	0.02	0.24	0.59	0.34	0.39	0.06	1.65	0.44	0.02	15.33
		90min	85.60	0.06	0.15	0.87	0.22	0.41	0.06	1.53	0.48	0.02	9.81
	650	30min	76.21	0.08	0.22	0.86	0.21	0.31	0.08	1.69	0.52	0.01	19.53
		60min	89.61	0.04	0.22	0.91	0.15	0.42	0.07	1.58	0.41	0.02	5.91
		90min	90.21	0.06	0.27	0.85	0.25	0.49	0.08	1.51	0.56	0.02	5.48
	700	30min	81.35	0.09	0.15	0.77	0.18	0.33	0.08	1.72	0.53	0.02	14.53
		60min	89.93	0.06	0.11	0.88	0.14	0.39	0.09	1.48	0.55	0.02	6.01
		90min	92.19	0.09	0.10	0.71	0.09	0.41	0.05	1.64	0.41	0.01	4.14
	750	30min	84.22	0.09	0.18	0.54	0.17	0.38	0.06	1.35	0.61	0.02	12.09
		60min	93.11	0.08	0.27	0.67	0.11	0.44	0.06	1.69	0.63	0.02	2.67
	1100	a few min	95.31	0.04	0.11	0.78	0.11	0.41	0.09	1.61	0.45	0.01	0.84

3 Test Methods

A total of 4 concrete mixtures were made; one corresponding to a control concrete (CTL) and three others with 7%, 10% and 15% RHA replaced with cement by weight. Table 2 lists the mix proportions of concrete. Slumps were kept constant at 70 ± 10 mm. Super plasticizer was used at very low percentages according to the results obtained for the slumps. Concrete test specimens were compacted by external vibration and kept protected after casting to avoid water evaporation. After 24 hour they were demolded and cured in lime-saturated water at $23 \pm 2^\circ\text{C}$ to prevent possible leaching of $\text{Ca}(\text{OH})_2$ from these specimens. Concrete cubes of $100 \times 100 \times 100$ mm dimension were cast for compressive strength and water penetration tests. The results obtained are reported as an average of three tests. The sulfate exposure testing procedure was conducted by immersing concrete specimens after the specified initial curing in a water tank containing 5% sodium sulfate and 5% magnesium sulfate solution at $23 \pm 2^\circ\text{C}$ (ASTM C1012-04). Some control concrete cubes were kept in the lime-saturated water solution tank at $23 \pm 2^\circ\text{C}$ for the compressive strength reduction determinations. In addition, $50 \times 50 \times 50$ mm mortar samples were prepared for the pozzolanic activity test. All specimens were moist cured until the time of testing.

Table 2. Mix proportions of concrete.

	RHA (kg/m^3)	cement (kg/m^3)	Aggregate (kg/m^3)		water (kg/m^3)
			fine	coarse	
CTL	0	350	960.29	795.66	175
7%RHA	24.5	325.5	960.29	795.66	175
10%RHA	35	315	960.29	795.66	175
15%RHA	52.5	297.5	960.29	795.66	175

Moreover, From each mortar mixture, mortar bars ($25 * 25 * 285$ mm) and cubes ($5 * 5 * 5$ cm) were prepared. After casting and finishing, the molds were covered with plastic sheets and stored for 24 h in a moist room (relative humidity: above 95% and temperature: 35 ± 3 °C). After the initial curing period, the specimens were demolded and cured in lime saturated water ($23 \pm 2^\circ\text{C}$) until the mortar cube specimens gained a compressive strength of 20 MPa as described by ASTM C 1012. Upon reaching a compressive strength of 20 MPa, the performance of cements under sulfate attack were determined weekly through expansion measurements of mortar bars following the ASTM C 1012 standard. Mortar bars, however, were subjected to five different exposure regimes, as shown in Fig. 1, for expansion measurements weekly. First regime is 5% sodium sulfate, second one is 5% magnesium sulfate, third one is 10% sodium sulfate, fourth one is 10% magnesium sulfate, and fifth is 5% mix sulfate (2.5% sodium sulfate and 2.5% magnesium sulfate).

4 Test Results

4.1 Compressive Strength and Water Penetration

The compressive strength of the concrete specimens at ages 3, 7, 28, 56 and 90 days were tested. RHA specimens had higher compressive strength at various ages and up to 90 days when compared with the control concrete. Results of the compressive strengths of concretes are given in Figure 1.

In addition, investigations of water permeability were carried out. In this test, water was forced into the concrete samples from one side for three days and under constant pressure of 0.5 MPa. Then, the samples were split in a plane parallel to the direction of water penetration, and the greatest depth of water penetration into the concrete sample was measured. The depth of water penetration of concrete incorporating RHA specimens is shown in Figure 2. As expected, depth of water penetration of concrete specimens decreased significantly with an increase in RHA content and curing period.

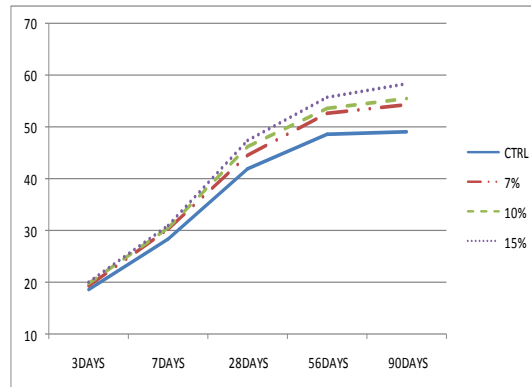


Figure 1. Compressive strength (MPa) at various ages for control (CTL) & RHA.

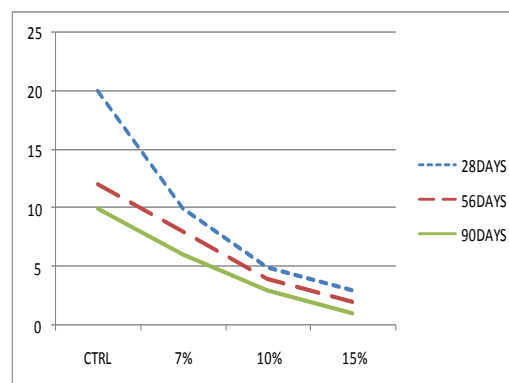


Figure 2. Depth of water penetration (mm) at various ages for control (CTL) & RHA mixtures.

4.2 Compressive Strength Reduction

The compressive strengths computed as an average of three cubic specimens subjected to a 5% Na_2SO_4 solution are presented in Table 3. As seen in that Figure, when subjected to continuous sulfate exposure all specimens showed an increase in compressive strength up to 2 months. In cubic specimens subjected to a 5% Mg_2SO_4 solution all specimens showed an increase in compressive strength up to 2 months except control specimens which was not significant. This was attributed to the hydration of calcium silicates and to the pozzolanic reactions of blended cements. However, in following weeks we expect, the compressive strength of the OPC mortars began to decrease drastically for all specimens. This was an expected result, as ettringite formation leading to an expansion, cracking and drastic reduction in the strength and gypsum formation leading to a reduction of stiffness and strength were the major form of deterioration of mortars containing cements with a high C_3A content.

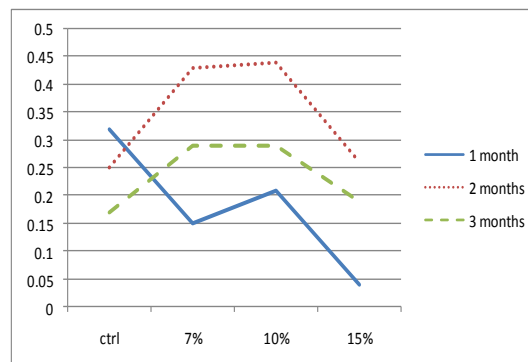
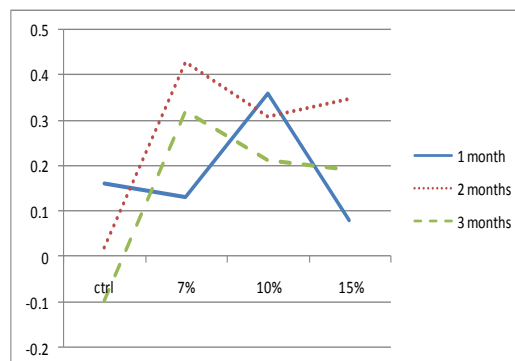
RHA cubes resulted in the highest strengths at all ages and did not show significant strength loss. This was possibly due to the filling of the pores by the reaction products of sulfate attack. The beneficial effect of pore filling to strength can be considered for OPC specimens too. However, the reduction in strength of OPC specimens shows that the destructive effect of reaction products (gypsum and ettringite) dominated their contribution to strength. When the blended cements are considered, they do not show any significant strength loss until 2 months of continuous exposure (Table 3).

Table 3. Compressive strength in lime saturated Water and sulfate exposure.

Compressive strength of specimens after 2 months sulfate exposure (MPa)			
	28 days	2 months	2 months
	Curing	In 5%Na ₂ SO ₄	In 5%MgSO ₄
CTRL	41.92	41.58	45.5
7%	44.61	49.78	50.28
10%	46.19	51.40	55.49
15%	47.46	47.74	52.16

4.3 Weight Loss

Subsequently, the disruption of the hydrated cementitious matrix by these expansive reaction products resulted in a decrease in the weight of specimens, thus increasing the weight loss with immersion period. The weight of specimens without RHA is reduced by 0.1% after 2 months of exposure in 5% MgSO₄ exposure but other specimens showed increase in weight, while the weight of specimens with RHA replacement of cement is increased by 0.32% for 7% RHA and 0.21% for 10% RHA and 0.19% for 15% RHA after 2 months of exposure in 5% MgSO₄ solution. (Figure 4.) But, all specimens in 5%Na₂SO₄ showed increase in weight after 2 months of exposure (Figure 3).

**Figure 3.** Relative mass change (%) In 5% Na₂SO₄.**Figure 4.** Relative mass change (%) In 5% MgSO₄.

4.4 Prism Mortars Expansion

This result is consistent with the results of mortar bar expansions, where RHA specimens are found to be highly resistant to the sulfate exposure. Control specimens demonstrated higher expansion. RHA specimens did not deteriorate and develop any significant crack after the 13 weeks continuous exposure period.

This may be due to lower C_3A content and lower C_3S/C_2S ratio of this cement than those of the other cements. It should be noted that expansions of blended cements decrease by the amount of RHA replacement by cement weight. The expansions of 15% RHA prisms are nearly three to four times less than that of the mortar prepared from ordinary portland cement. However, it is known that pozzolan addition will improve the sulfate resistance of cements.

Thus, at the time of exposure, which seems to be immediately after casting of the specimens, the durability and impermeability of mortar mixtures prepared from the blended cements are better than that of OPC mixture. This makes the blended cement containing mixtures more durable to sulfate attack.

Regardless of rate of cement, all mortar bars showed a decreasing rate of expansion with decrease of sodium sulfate ion (Figure 5,6). This may be in part, due to strength gaining characteristics of cements and in part, due to progressive reduction in gypsum concentration of the system upon ettringite formation.

At the end of 13 weeks large expansions were observed in OPC containing prism mortars, respectively. All RHA mixtures showed better performance against sulfate expansion. (both Na_2SO_4 and $MgSO_4$) The data exhibit a less expansion in 5% Na_2SO_4 than 5% $MgSO_4$ for all specimens (Figure 5,7) , while rate of expansion is not much different in 10% Na_2SO_4 and 10% $MgSO_4$ (Figure 6-8).

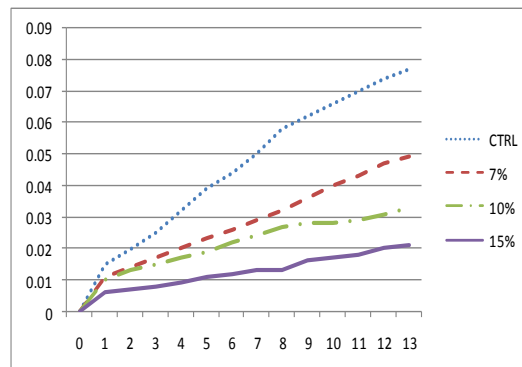


Figure 5. Expansion of mortar prisms in 5% Na_2SO_4 .

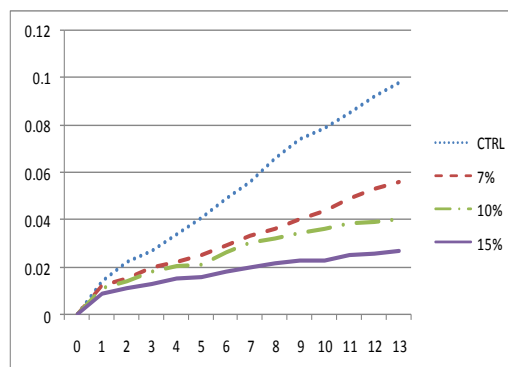


Figure 6. Expansion of mortar prisms in 10% Na_2SO_4 .

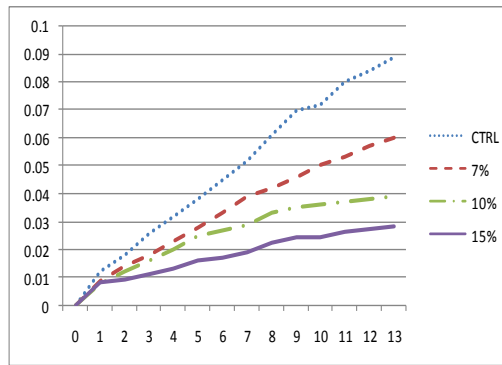


Figure 7. Expansion of mortar prisms in 5% MgSO₄.

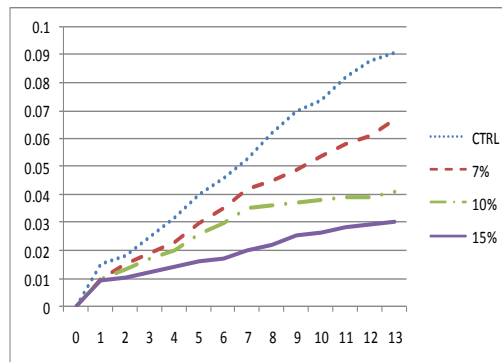


Figure 8. Expansion of mortar prisms in 10% MgSO₄.

4.5 Surface Degradation of Mortar Specimens

Surface deterioration was not clearly identifiable on the concrete cubes immersed in the 5% Na₂SO₄ solution except control specimens. (Fig. 8) However, surface scaling and loss of mass could be identified on the concrete cubes immersed in the 5% MgSO₄ solution, specially in control (Fig. 11) and 7% RHA replacement by cement weight and this effect seemed to increase with time of exposure (Fig. 10). While pozzolanic admixtures tended to significantly reduce expansion due to sulfate exposure, in both sodium and magnesium solutions. In fact, the 7% RHA concrete cubes had surface degradation somewhat better than that of the control OPC concrete cubes. In Figure 8. At first row you can see specimens that submerged for 3 months in lime saturated water. In second and third row there are specimens which subjected to 5% Na₂SO₄ and 5% MgSO₄. In left column you can see control specimens. Respectively from left column in each row are control, 7%, 10% and 15% RHA replacement by cement cubic specimens.



Figure 10. Specimens in lime saturated water, 5% Na₂SO₄ and 5% MgSO₄.



Figure 11. Deterioration on cubic control specimen after 3 months exposure to 5% MgSO₄.

5 Conclusion and Discussion

- 7% RHA replacement in this study, do not guarantee sulfate resistance of concretes in sulfate environments. Blended cements prepared with RHA reduced the potential for the formation of ettringite due to the reduction in the quantity of calcium hydroxide and C3A, and thus improved the resistance of specimens to sulfate attack.
- As seen in Figure 3,4. , when subjected to continuous sulfate exposure all specimens showed an increase in weight up to 2 months. This was attributed to the hydration of calcium silicates and to the pozzolanic reactions of blended cements. However, after 2 months, we observed the mass loss of the OPC concretes began drastically. This was an expected result, as ettringite formation leading to an expansion, cracking and drastic reduction in the strength and gypsum formation leading to a reduction of stiffness and strength were the major form of deterioration of concretes containing cements with a high C3A content.
- The lower expansion in blended cements was attributed to the early consumption of calcium hydroxide through pozzolanic reactions, which thus reduced the potential for the formation of gypsum and ettringite. The secondary C–S–H gel formed as a result of the pozzolanic reactions forms a coating on the alumina-rich and other reactive phases thereby hindered the formation of ettringite.
- All concrete samples showed a continuous increase in compressive strength up to 2 months except control specimens. The first increase in strength may be attributed to two types of reactions: (I) the continuous hydration of unhydrated cement components to form more hydration products in addition to the reaction of RHA (in case of blended cements) with the liberated lime to form more C-S-H leading to increasing compressive strength and (II) reaction of sulfate ions with hydrated cement components to form gypsum and ettringite. At earlier ages, these two reactions lead to a denser structure as a result of precipitation of the products within voids and micropores. Whereas, at later ages, the second type of reactions (sulfate attack) become more dominant leading to formation of microcracks and this decreases strength.

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