Evaluation of Sulfate Resistance of Portland Cement Mortars Containing Low-Carbon Rice Husk Ash

Harish Kizhakkumodom Venkatanarayanan¹ and Prasada Rao Rangaraju, P.E., M.ASCE²

Abstract: In this study, a low-carbon rice husk ash (RHA) was used as a supplementary cementing material in cement mortars to evaluate its sulfate resistance in sodium and magnesium sulfate solutions. The sulfate resistance of these mixtures in terms of expansion and loss of compressive strength was determined using the standard test method. The water to cementitious material (w/cm) ratio and RHA dosage in the mortars varied from 0.40 to 0.57 and 0 to 15% (by mass), respectively. The results from this investigation suggest that all mortars with a w/cm ratio of 0.40 showed little deterioration, indicating their high sulfate resistance. For mortars with a w/cm ratio of 0.48 and 0.57, the control mortars showed more deterioration than those with RHA. For mortars at any given w/cm ratio, the sulfate resistance decreased with an increase in the RHA dosage. Though both sodium and magnesium sulfates caused significant deterioration in the specimens, the former caused increased expansions in the test specimens while the latter caused significant loss in compressive strength. The sulfate resistance of RHA mortars was comparable with that of silica fume mortars. DOI: 10.1061/(ASCE)MT.1943-5533.0000868. © 2014 American Society of Civil Engineers.

Author keywords: Low-carbon rice husk ash; Sulfate resistance; Durability; Sustainability; Supplementary cementing material.

Introduction

Sulfates are naturally present in significant amounts in soil, groundwater, industrial effluents, and wastes from chemical and mining industries, and sea water. Many portland cement concrete (PCC) structures, which are either constructed in the previously mentioned regions or in close proximity to such sources, have shown severe premature deteriorations (Kalousk et al. 1972; Vladimir 1987). Sulfates present internally in concrete due to the use of sulfate-rich aggregates, cement containing excess gypsum and sulfate bearing water, can also cause deteriorations; however, appropriate screening of ingredients and test procedures before concrete production can avoid such internal sulfate attack (Chengsheng et al. 1988; Yan et al. 1997). Of the different sulfates such as sodium, magnesium, calcium, and ammonium sulfates that cause deterioration in concrete, the first two have been found to be the most common ones, with the magnesium sulfates causing more destruction than any others (Cohen and Bentur 1988; Bonen and Cohen 1992a, b).

The mechanism of attack of portland cement binder by the sodium and magnesium sulfates is primarily due to two reasons: (1) the formation of gypsum due to the reaction of sulfates with the calcium hydroxide produced from cement hydration, and (2) the formation of ettringite due to reaction between the gypsum and monosulfates or calcium aluminate hydrate (Cohen and Bentur 1988; Mehta 1983; Santhanam et al. 2002, 2003; Hekal et al. 2002). In the case of mortars or concretes subjected to magnesium sulfate attack, the decalcification of calcium-silicate-hydrate (C-S-H) gel into a mushy paste occurs in addition to the previously mentioned chemical reactions (Cohen and Bentur 1988; Santhanam et al. 2002; Hekal et al. 2002). Because the effect of sulfate attack is the weakening of the cement paste, thereby leading to premature failure of concrete, the sulfate resistance of concrete is an important durability consideration. The sulfate resistance in concrete can be provided by using portland cements that are low in their C₃A content, such as ASTM C150 (ASTM 2012a) Type II cement (moderate sulfate resistance) or Type V cement (high sulfate resistance). In situations in which such sulfate-resistant portland cements are not readily available, ordinary portland cement can be used along with pozzolans such as fly ash, silica fume, slag, or metakaolin at appropriate cement replacement levels to minimize deteriorations due to sulfate attack (Hooton 1993; Akhras 2006; Frearson 1986; Tikalsky and Carrasquillo 1992). However, the sulfate resistance of the blend depends greatly on the chemistry of the pozzolan used and its replacement level. In particular, the ability of the pozzolan to reduce permeability of matrix is essential to improving the sulfate resistance (Mindess et al. 2003).

In recent decades, the utilization of sustainable and environmentally friendly materials such as rice husks (after refining) to reduce the carbon footprint of concrete has gained significant attention. Rice husks are agrowaste materials from the rice industry that are available in significant quantities around the world [Food and Agriculture Organization of the United Nations (FAO) 2007]. The problems associated with the disposal of rice husks include land nonreusability, its nonbiodegradable nature in soil, its negligible protein content and inability to be used as animal fodder, and environmental concerns regarding open heap burning of rice husk (Mehta and Pitt 1976). Hence, several environmentally friendly and controlled combustion processes [R.K. Vempati, “Composition and method of forming low-carbon, amorphous siliceous ash from siliceous waste material, U.S. Patent No. 6, 44, 186 B1 (2002); Nehdi et al. 2003; Salas et al. 2009; Muthadi and Kothandaram 2010] are being invented to safely dispose of the

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agrowaste to the atmosphere and produce biogenic ash that can be potentially used as a pozzolan to improve the strength and durability of concrete (Zhang and Malhotra 1996; Mahmud et al. 2004; Harish et al. 2010; Sensale 2010; Chatveera and Lertwattanaruk 2011).

The effectiveness of rice husk ash (RHA) to serve as a pozzolan in portland cement concrete is primarily dependent on its silica content and the nature of silica present in RHA. For instance, the concretes containing RHA with high amorphous silica content showed higher compressive strength and lower permeability than those RHAs containing crystalline silica (Nehdi et al. 2003). This may be because the high quantity of amorphous silica in RHA attributes to quicker depletion of calcium hydroxide especially at early ages, thereby resulting in enhanced strength and reduced permeability (Mehta 1977; Harish et al. 2010). Incidentally, RHA with crystalline silica typically contain high unburnt carbon, resulting in high loss on ignition. Other disadvantages of using high-carbon RHA include the high demand for air entraining agents (Nehdi et al. 2003; Zhang and Malhotra 1996) and unpleasant color (Ferraro et al. 2010). While several investigations suggest the beneficial use of low-carbon RHA with amorphous silica to improve specific durability property of portland cement concrete (Mahmud et al. 2004; Sensale 2010; Chatveera and Lertwattanaruk 2011), very few have performed research to understand the effectiveness of RHA in improving the sulfate resistance property of mortars or concrete (Chindarprasit et al. 2007; Chatveera and Lertwattanaruk 2009). In this study, the performance of a low-carbon RHA in improving the sulfate resistance of portland cement mortars was investigated. The RHA was used in the as-obtained or unground form instead of the ground form primarily to avoid the cost involved in the grinding process and to explore the possibility of using unground RHA (URHA). In addition, Harish et al. (2010) involving fundamental investigations with unground RHA for use in cementitious mortars has shown low permeability values. Because high sulfate resistance can be obtained using materials that provide less permeable matrices, unground RHA was chosen for this study.

**Objectives**

The principal objectives of this research study are as follows:

- To evaluate the sulfate resistance of mortars containing low-carbon RHA;
- To determine the effect of the water to cementitious material (w/cm) ratio on the sulfate resistance of RHA mortars;
- To compare the sulfate resistance of low-carbon RHA and silica fume mortars at a specific w/cm ratio; and
- To compare the extent of deteriorations caused in RHA mortars by the sodium and magnesium sulfate solutions.

**Experimental Program**

In this study, a total of 10 mortars (M1 to M10) were prepared at three different w/cm ratios, namely, 0.40, 0.48, and 0.57. For mortars having w/cm ratios of 0.48 and 0.57, three RHA replacement levels of 0% (control with no RHA), 7.5%, and 15% were used, whereas for mortars having a w/cm ratio of 0.40, only two replacement levels (0 and 7.5%) were used because of workability restrictions at higher dosage levels of RHA. The sulfate resistance of mortars was studied by immersing test specimens in 5% sodium sulfate and 5% magnesium sulfate solutions separately. In order to compare the sulfate resistance of mortars containing RHA with that of mortars containing silica fume, mortars were prepared at a constant w/cm ratio of 0.48 with two different silica fume replacement levels of 7.5 and 15%. The material properties, mixture proportion, curing procedure, and methods adopted are discussed.

**Properties of Materials**

The materials used to prepare cement mortars include portland cement, low-carbon RHA, silica fume, and sand. The cement used was a high alkali ASTM C150 (ASTM 2012a) Type I cement having an alkali content of 0.82% NaOeq, the chemical composition of which is provided in Table 1. The particle size distribution and chemical composition of the as-obtained low-carbon URHA and the densified silica fume (SF) particles are shown in Fig. 1 and Table 1, respectively. As Fig. 1 shows, the URHA is a coarser material than SF, with the former having an average particle size (∼29.90 μm) larger than that of the latter (∼7.37 μm). The specific gravity of the unground low-carbon RHA and densified silica fume were 2.19 and 2.20, respectively.

The microstructure of the URHA particles as seen through a scanning electron microscope (SEM) is shown in Figs. 2(a and b). As can be seen, the URHA particles are broadly distributed containing RHA with that of mortars containing silica fume, mortars were prepared at a constant w/cm ratio of 0.48 with two different silica fume replacement levels of 7.5 and 15%. The material properties, mixture proportion, curing procedure, and methods adopted are discussed.

**Table 1. Chemical Composition of Cement and Pozzolan**

<table>
<thead>
<tr>
<th>Oxide or compound</th>
<th>Cement</th>
<th>URHA</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.78</td>
<td>92.46</td>
<td>93.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.98</td>
<td>0.26</td>
<td>0.50</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.13</td>
<td>0.30</td>
<td>2.10</td>
</tr>
<tr>
<td>CaO</td>
<td>61.84</td>
<td>1.63</td>
<td>0.80</td>
</tr>
<tr>
<td>Alkali (Na₂Oeq,%)</td>
<td>0.82</td>
<td>1.24</td>
<td>0.10</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.15</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>2.54</td>
<td>0.38</td>
<td>—</td>
</tr>
<tr>
<td>Carbon</td>
<td>—</td>
<td>0.54</td>
<td>—</td>
</tr>
<tr>
<td>Tricalcium silicate (C₃S)</td>
<td>51.66</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Dicalcium silicate (C₂S)</td>
<td>17.74</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)</td>
<td>7.90</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tetracalcium alumino ferrite (C₄AF)</td>
<td>9.52</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Fig. 1. Particle size distribution of pozzolans**
over a wide size range and have irregular, vesicular, and porous microstructure. It must be remembered that the larger cellular URHA particles tend to create water demand in fresh concrete and produce additional porosities in hardened concrete by remaining unreacted in the matrix (Nehdi et al. 2003; Zhang and Malhotra 1996). To account for the high water demand, a high-range water reducer of polycarboxylic-ether-based type was used. The dosage of the water reducer was determined from flow studies conducted as part of Harish et al. (2010). Sand used in this study was natural river sand from a local source and its specific gravity was 2.50.

Mixture Proportions
A total of 10 mortar mixtures were prepared, which included three control mixtures, five low-carbon RHA mixtures, and two silica fume mixtures. These 10 mixtures were studied at three different water to cementitious material ratios of 0.40, 0.48, and 0.57. In these mixtures, the cement is replaced with pozzolans at 0, 7.5, and 15% dosage levels by mass. The mortar mixture proportions chosen based on the ASTM C1012 (ASTM 2012b) specifications are shown in Table 2. In all the mixtures, the fine aggregate to cementitious material ratio was 2.75.

Casting and Curing of Test Specimens
The ingredients were weight batched and mixed using a specific procedure similar to that stated in the ASTM C192 (ASTM 2013a) specification. Accordingly, a portion of the URHA was added to the solution mixture containing the mix water and adequate high-range water reducer, while the remaining portion was added to cement. After mixing each portion separately, the (cement + URHA) mixture was added to the fine aggregates and dry mixed well, and the (URHA + superplasticizer + water) mixture was finally added to this dry mixture. The entire quantity was thoroughly mixed to obtain a wet homogenous mixture, with which mortar bars (25 × 25 × 285 mm) and cubes (50 × 50 mm) of standard dimensions were prepared for sulfate resistance test as per the ASTM C1012 (ASTM 2012b) test procedure. The wet mortars after vibration, sufficient compaction, and finishing were moist cured for a 24-h period before demolding. The specimens were then cured in lime water for a period mentioned in the ASTM C1012 (ASTM 2012b) test procedure before immersion in the sulfate solutions.

Experimental Test Methods
Mortar Bar Length Change Exposed to Sulfate Solution (ASTM C1012)
The sulfate resistance of RHA mortars was determined by measuring the expansion of the mortar bars exposed to sulfate solution as per the ASTM C1012 (ASTM 2012b) method. In this procedure, the mortar bars were cured in lime water along with cube specimens after demolding until the specimen reached a compressive strength of 20 MPa. The details of the lime water curing period for the mixtures are shown in Table 3. This time period was determined by conducting compression test on mortar cubes every day after demolding. When the strength of a mortar cube reached 20 MPa, initial length readings of the mortar bars were taken using a standard comparator before immersing bars in 5% sodium sulfate and 5% magnesium sulfate solutions in order to evaluate the sulfate resistance of the RHA mortars in each type of solution. The length measurements were recorded at regular intervals of time until 360 days (~1 year) and the expansions were calculated using the formula specified in the test procedure. The sulfate soak solutions were replaced with fresh stock solution at frequent intervals of 2 months from the date of immersion until 12 months.

Table 2. Mixture Proportions of Mortars at Various w/cm Ratios

<table>
<thead>
<tr>
<th>Mortar number</th>
<th>Mortar identification</th>
<th>Quantity of materials (g)</th>
<th>w/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Control</td>
<td>Cement 500, RHA 0, Sand 1375, Water 200</td>
<td>RQ 0.40</td>
</tr>
<tr>
<td>M2</td>
<td>RHA-7.5%</td>
<td>Cement 462.5, RHA 37.5, Sand 1375, Water 200</td>
<td>RQ 0.40</td>
</tr>
<tr>
<td>M3</td>
<td>Control</td>
<td>Cement 500, RHA 0, Sand 1375, Water 242</td>
<td>RQ 0.485</td>
</tr>
<tr>
<td>M4</td>
<td>RHA-7.5%</td>
<td>Cement 462.5, RHA 37.5, Sand 1375, Water 242</td>
<td>RQ 0.485</td>
</tr>
<tr>
<td>M5</td>
<td>RHA-15%</td>
<td>Cement 425, RHA 75, Sand 1375, Water 242</td>
<td>RQ 0.485</td>
</tr>
<tr>
<td>M6</td>
<td>SF-7.5%</td>
<td>Cement 462.5, RHA 37.5, Sand 1375, Water 242</td>
<td>RQ 0.485</td>
</tr>
<tr>
<td>M7</td>
<td>RHA-15%</td>
<td>Cement 425, RHA 75, Sand 1375, Water 242</td>
<td>RQ 0.485</td>
</tr>
<tr>
<td>M8</td>
<td>Control</td>
<td>Cement 500, RHA 0, Sand 1375, Water 285</td>
<td>RQ 0.57</td>
</tr>
<tr>
<td>M9</td>
<td>RHA-7.5%</td>
<td>Cement 462.5, RHA 37.5, Sand 1375, Water 285</td>
<td>RQ 0.57</td>
</tr>
<tr>
<td>M10</td>
<td>RHA-15%</td>
<td>Cement 425, RHA 75, Sand 1375, Water 285</td>
<td>RQ 0.57</td>
</tr>
</tbody>
</table>

Note: RQ = required quantity to obtain sufficient flow; SP = superplasticizer.
Compressive Strength (ASTM C109)

As explained previously, companion cube specimens were cast along with the bar specimens to determine the loss of compressive strength due to immersion in the sulfate solutions. The cube specimens were cured in the same way as the bar specimens and immersed in the sodium sulfate and magnesium sulfate solutions after reaching a compressive strength of ∼20 MPa. The compression strength of the cubes was determined after regular immersion periods (28, 150, 270, and 360 days) in sulfate solution until 360 days using the ASTM C109 (ASTM 2013b) test procedure.

Results and Discussions

Expansion due to Sulfate Attack

Expansion Behavior of RHA Mortars in Sodium and Magnesium Sulfate Solutions

The expansion behavior of RHA mortars with varying w/cm ratios when soaked in sodium sulfate solution is shown in Figs. 3(a–c). In these figures, the mortar bar expansion increases with an increase in the period of immersion, indicating that sustained exposure to sodium sulfate causes continuous deterioration in mortars.

**Fig. 3.** Expansion behavior of RHA mortars at different w/cm ratios in sodium and magnesium sulfate solution: (a) Na$_2$SO$_4$ solution, w/cm = 0.40; (b) Na$_2$SO$_4$ solution, w/cm = 0.48; (c) Na$_2$SO$_4$ solution, w/cm = 0.57; (d) MgSO$_4$ solution, w/cm = 0.40; (e) MgSO$_4$ solution, w/cm = 0.48; (f) MgSO$_4$ solution, w/cm = 0.57
For mortars having a w/cm ratio of 0.40 as shown in Fig. 3(a), the expansion of control mortar subjected to sodium sulfate solution was found to be well below the 0.10% expansion limit at 1 year as indicated by the ASTM C1115 (ASTM 2011) specifications for high sulfate resistance cement. This may be primarily due to the low permeability of the cement matrix at such low w/cm. Past research has shown that concrete having low permeability possesses better sulfate resistance than those having high permeability, and both permeability and chemical resistance of binder are important considerations governing the sulfate resistance of concretes (Khatri and Sirivivatnanon 1997). It appears that the portland cement binder by itself can resist the sulfate attack due to reduced permeability, and hence the use of pozzolan is not essential at low w/cm ratios. In addition, it can also be observed that the RHA-7.5% mortars, which showed slightly lower expansion than that of the control mortars (without RHA) up to an immersion period of 270 days, showed significantly lower expansion at an immersion period of 360 days, indicating the beneficial effects of RHA addition in the long term.

For mortars having w/cm ratio of 0.48 and 0.57 as shown in Figs. 3(b and c), respectively, their expansion behaviors were found to be approximately similar, with the former showing slightly lower expansion than the latter. At both w/cm ratios, the control mortars registered higher expansions than RHA mortars and the 360-day expansion was found to be above the 0.10% limited expansion, indicating that the control mortars require a mitigation measure against sulfate attack. Not only did the use of RHA at a 7.5% replacement level decrease the mortar bar expansions significantly at all ages, but it also reduced the 360-day expansion below the 0.10% expansion limit. Similarly, the use of RHA at a 15% cement replacement level further reduced the expansions, indicating the improved performance of RHA at higher replacement level.

The expansion behavior of RHA mortars with varying w/cm ratios when soaked in magnesium sulfate solution is shown in Figs. 3(d–f). As these figures show, the expansion behavior of each mortar series (at specific w/cm ratio) soaked in magnesium sulfate solution was similar to the expansion behavior of that soaked in sodium sulfate solution. In these tests, the RHA mortars registered lower expansions than their respective control mortars, and the expansions decreased with increase in the RHA replacement level. In addition, not only were the expansions of the control mortars at any w/cm low but also their 360-day expansion was below the 0.10% expansion limit. Based on the previous expansion results, it is unwise to arrive at a conclusion that portland cement by itself may have resisted the attack by magnesium sulfate because previous studies have shown that magnesium sulfate attack can cause very severe deterioration, despite the mortar bars registering lower expansions (Chatveera and Lertwattanaruk 2009). One possible reason may be because magnesium by itself participates during the mechanism of magnesium sulfate attack to form magnesium hydroxide (brucite) and magnesium silicate hydrate (Hekal et al. 2002); the production of these compounds may have lesser tendency to increase expansions in concrete while decalcifying the cementitious paste at a faster pace resulting in increased loss of compressive strength. Other investigators have also demonstrated the deteriorations caused by magnesium sulfate from the loss of compressive strength values rather than from the expansion values (Cohen and Bentur 1988; Hekal 2002; Mehta and Montiero 2006). In addition, the visual observation of the bars revealed that significant damage and debonding of the paste or C-S-H gel from the cement matrix had occurred.

Effect of Water to Cementitious Material Ratio on the 360-Day Sulfate Attack Expansions
The 360-day expansion of cementitious mortars prepared at different w/cm ratios when soaked in sodium and magnesium sulfate solutions are shown in Figs. 4(a and b), respectively. As Fig. 4(a) shows, the 360-day expansions of the control and RHA-7.5% mortars significantly increase with an increase in the w/cm ratio from 0.40 to 0.48. Such a steep increase in the mortar bar expansion may be due to the corresponding increase in the permeability of concrete. Beyond a w/cm ratio of 0.48, the 360-day expansions of both control and RHA-7.5% mortars tend to slowly level off. It is likely that at a w/cm ratio of 0.48, the concrete is sufficiently permeable to allow the external sulfates to cause sustained deterioration. The extent of this deterioration beyond w/cm ratios of 0.48 is governed more by the composition of the binder, rather than by a further increase in w/cm ratio. In the case of RHA-15% mortars, their 360-day expansion was found to be the smallest compared with others and was not much influenced by the variation in the w/cm ratio used. Such a behavior is attributed to the presence of high

![Fig. 4. Effect of water-to-cementitious material ratio on the resistance of the mortar bar in different sulfate solutions: (a) sodium sulfate attack 360-day expansions versus w/cm; (b) magnesium sulfate attack 360-day expansions versus w/cm](image-url)
amounts of reactive silica in the mixture at early ages, which helps in significantly reducing the permeability of concrete by depleting the calcium hydroxide from cement hydration to form calcium silicate hydrate (C-S-H) gel of low C/S ratio (Mehta and Monteiro 2006). In addition, Harish et al. (2010) had shown that the mortars containing unground RHA have low to very low permeability depending on the replacement level used, when evaluated based on rapid chloride permeation ion values. The significantly low permeability in the RHA-15% mixture prevents the external sulfates from entering into the matrix and causing deteriorations. These trends suggest that at high RHA replacement levels, the reduction in permeability offered by the pozzolanic activity of the RHA far exceeds the influence of w/cm ratio.

In the case of magnesium sulfate attack, with an increase in the w/cm ratio from 0.40 to 0.57, the 360-day expansion of the control mortars uniformly increased, which may be attributed to the increase in the permeability of these mortars. In the case of RHA-7.5% and RHA-15% mortars, there is only a slight increase in the expansion with increase in the w/cm ratio. It appears that the addition of RHA in the portland cement mortar there is very minimal. At any specific w/cm, the expansions of RHA mortars were typically lower than 0.05% (~50% below the 0.10% expansion limit), clearly indicating the benefits of adding RHA.

**Comparison of Sulfate Resistance Performance of RHA and Silica Fume Mortars**

In order to evaluate the effect of replacement level of RHA and SF on the sulfate resistance of mortars, the 360-day expansions of the control mortars at a constant w/cm ratio of 0.48 was considered as 100% and the 360-day expansions of mortars containing RHA and SF mortars were normalized to this value. Figs. 5(a and b) show the effect of replacement level of RHA and SF on the normalized 360-day expansion of cementitious mortars in different sulfate solutions.

As Fig. 5(a) shows, the normalized 360-day expansion of mortars soaked in sodium sulfate solution decreases with an increase in the replacement level of both RHA and SF as expected. A reduction in the 360-day expansion of 52 and 69% was observed, respectively, for RHA and silica fume mortars, with an increase in the replacement level of each pozzolan from 0 to 7.5%. With further increase in the replacement level up to 15%, the expansion of the RHA and SF mortars decreased to 78 and 84%, respectively. At any fixed replacement level, the normalized expansion of the SF mortars was only slightly lower than that of the RHA mortars.

The normalized 360-day expansion of mortars soaked in magnesium sulfate solution as shown in Fig. 5(b) was similar to the normalized 360-day expansion of that soaked in sodium sulfate solution, i.e., the expansion decreases with an increase in the replacement level of the pozzolans. Specifically, the normalized 360-day expansion of mortars containing RHA and SF at a 7.5% replacement level decreased by 42 and 52%, respectively, while the same at a 15% replacement level decreased by 71 and 76%, respectively.

**Compressive Strength of Mortars subjected to Sulfate Solutions**

**Compressive Strength Behavior of Mortars in Sodium and Magnesium Sulfate Solutions**

In order to obtain the compressive strength behavior of mortar cubes immersed in different sulfate solutions as per the ASTM C1012 (ASTM 2012b) test procedure, the mortars were immersed in the sulfate solution as soon as they reached a compressive strength of ~20 MPa. The mortar cubes were then tested after specific immersion periods until 360 days. The compressive strength behavior of mortars prepared at different w/cm ratios and soaked in sodium and magnesium sulfate solutions are shown in Figs. 6(a–c) and Figs. 6(d–f), respectively.

As these figures show, the compressive strength of all the cubes was found to initially increase from the day these cubes were immersed in the sulfate solutions until an immersion period of approximately 28 days. This initial strength increase is because of the continued hydration of portland cement and of pozzolans immediately after immersion in sulfate solution before significant effects of sulfate attack are manifested. It is believed that the deteriorations caused by the sulfate solutions do not dominate during the initial immersion periods. However, beyond an immersion period of 28 days, the compressive strength of mortars decreased most likely due to the deterioration caused by the sulfate solutions. In a similar research conducted by Chatveera and Lertwattanaruk (2009), the compressive strength of the cubes was found to constantly decrease with increase in the period of immersion in sulfate solutions, which appears to be very different from that obtained in this study. This may be due to the use of higher w/cm ratio in their research, variation in the cement characteristics, and the use of higher curing
It can be observed from these figures that the control mortars containing no RHA registered lower compressive strength throughout the period of test compared with mortars that contained RHA. The control mortars after the 360-day immersion period were found to possess strengths equal to or lower than 20 MPa, indicating that significant deterioration has occurred as a result of exposing the cubes to sulfate solution. The ability of the control mortars to retain their initial strength after an immersion period of 360 days is dependent on the w/cm ratio. However, in the case of mortars containing RHA, the compressive strengths were found to be well above or slightly below 20 MPa throughout the duration of the test. In addition, the compressive strength of the cubes increased with an increase in the replacement level of RHA. The compressive strength behavior of the cubes immersed in sodium and magnesium sulfate solutions were approximately similar, though the percentage increase or decrease in compressive strengths varied at specific immersion periods.

**Loss of Compressive Strength due to Sulfate Attack**

It is generally known that the detrimental action of sulfates in portland-cement-based mortars and concretes is to cause expansion and cracking, with loss of cementing ability of the matrix.
Table 3. Curing Time to Reach the Required Compressive Strength of Mortars at 20 MPa

<table>
<thead>
<tr>
<th>Mortar number</th>
<th>Mortar identification</th>
<th>Curing time in saturated lime water (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Control</td>
<td>2</td>
</tr>
<tr>
<td>M2</td>
<td>RHA-7.5%</td>
<td>2</td>
</tr>
<tr>
<td>M3</td>
<td>Control</td>
<td>4</td>
</tr>
<tr>
<td>M4</td>
<td>RHA-7.5%</td>
<td>4</td>
</tr>
<tr>
<td>M5</td>
<td>RHA-15%</td>
<td>4</td>
</tr>
<tr>
<td>M6</td>
<td>SF-7.5%</td>
<td>4</td>
</tr>
<tr>
<td>M7</td>
<td>RHA-15%</td>
<td>4</td>
</tr>
<tr>
<td>M8</td>
<td>Control</td>
<td>6</td>
</tr>
<tr>
<td>M9</td>
<td>RHA-7.5%</td>
<td>6</td>
</tr>
<tr>
<td>M10</td>
<td>RHA-15%</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4. Compressive Strength Test Results of Mortars Immersed in Different Sulfate Solutions for 28 Days

| Mortar number | Mortar identification | Compressive strength of mortars after lime curing for specified period* (MPa) | Compressive strength of mortars after immersion in sulfate solution for 28 days (MPa) | Loss of compressive strength due to different sulfate attack (%)
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sodium Magnesium</td>
<td>Sodium Magnesium</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>sulfate sulfate</td>
<td>sulfate sulfate</td>
</tr>
<tr>
<td>M1</td>
<td>Control</td>
<td>35.8</td>
<td>34.2 34.5</td>
<td>4.4 3.6</td>
</tr>
<tr>
<td>M2</td>
<td>RHA-7.5%</td>
<td>39.3</td>
<td>38.2 37.9</td>
<td>2.8 3.7</td>
</tr>
<tr>
<td>M3</td>
<td>Control</td>
<td>30.0</td>
<td>29.4 29.8</td>
<td>2.1 0.8</td>
</tr>
<tr>
<td>M4</td>
<td>RHA-7.5%</td>
<td>34.9</td>
<td>33.2 32.9</td>
<td>4.8 5.6</td>
</tr>
<tr>
<td>M5</td>
<td>RHA-15%</td>
<td>35.2</td>
<td>38.4 32.5</td>
<td>–9.1 7.6</td>
</tr>
<tr>
<td>M6</td>
<td>SF-7.5%</td>
<td>33.2</td>
<td>31.3 26.1</td>
<td>5.8 21.5</td>
</tr>
<tr>
<td>M7</td>
<td>RHA-15%</td>
<td>33.8</td>
<td>32.6 27.9</td>
<td>3.4 17.2</td>
</tr>
<tr>
<td>M8</td>
<td>Control</td>
<td>25.2</td>
<td>24.6 22.2</td>
<td>2.3 11.8</td>
</tr>
<tr>
<td>M9</td>
<td>RHA-7.5%</td>
<td>30.1</td>
<td>28.5 28.6</td>
<td>5.3 5.1</td>
</tr>
<tr>
<td>M10</td>
<td>RHA-15%</td>
<td>33.1</td>
<td>31.9 32.6</td>
<td>3.5 1.5</td>
</tr>
</tbody>
</table>

*The specified periods were 30, 32, and 34 days for mortars having w/cm ratio of 0.40, 0.48, and 0.57, respectively.

Loss of compressive strength, SL (%) = \[
\frac{f_c - f_{c1}}{f_c} \times 100 \quad (1)
\]

where \(f_c\) = compressive strength of mortar cured in lime water for specific period (30, 32, and 34 days for mixtures having a w/cm ratio of 0.40, 0.48, and 0.57, respectively); and \(f_{c1}\) = compressive strength of mortar at any specified immersion period in sulfate solution.

The extent of deterioration due to sulfate attack by sodium and magnesium sulfate solutions in terms of percentage loss of compressive strength in the mortar cubes are shown in Figs. 7(a–c) and Figs. 7(d–f), respectively.

As these figures show, there is only slight variation in the loss of compressive strength at early immersion periods up to 180 days for all mortars prepared at any specific w/cm ratio. Beyond this immersion period, the control mortars registered the maximum strength loss, indicating that the portland cement mortar is more susceptible to sulfate attacks than RHA mortars. Such a behavior was observed in mortars prepared at all w/cm ratios. One possible reason for such improved behavior of RHA mortars is due to the presence of C-S-H gel having low C/S ratio obtained from pozzolanic reaction. The low permeability of these mortars prevents the sulfates from entering into the cementitious matrix. In addition, though some RHA mortars at specific w/cm ratio gave slightly higher loss of strength than the control mortars at early immersion periods, all the RHA mortars registered a significantly lower strength loss values at later immersion periods.

The approximate strength loss for the control, RHA-7.5%, and RHA-15% mortars after the 360-day immersion period in sodium sulfate solution was found to be in the range of 42–51%, 22–36%, and 22–32%, respectively, depending on the w/cm ratio used. Similarly, the approximate strength loss of the control, RHA-7.5%, and RHA-15% mortars after the 360-day immersion period in magnesium sulfate solution was found to be in the range of 45–58%, 26–38%, and 22–36%, respectively. It can also be observed from these calculated percentage values that the loss in strength decreases with an increase in the replacement level of RHA, indicating the beneficial effects of RHA in improving the sulfate resistance of portland cement mortars.

Comparison of Deterioration of Mortars Immersed in Sodium and Magnesium Sulfate Solutions

Figs. 8(a and b) show the comparison of the expansion and loss of strength of mortar specimens immersed in different sulfate

However, this deterioration can also be accomplished by significant reduction in compressive strength. Because an increase in the compressive strength of all mortar cubes was observed after immersion in sulfate solution for 28 days as explained in the previous section, it is not appropriate to calculate the strength loss of mortars at any immersion period due to sulfate attack by considering 20 MPa as the initial strength. Also, a definite loss of mortar strength after 28 days of immersion in sulfate solution was observed. In order to determine accurately the strength loss of mortars due to the initial 28-day immersion in sulfate solution, parallel series of mortar cubes (control, RHA-7.5%, and RHA-15%) having a w/cm ratio of 0.40, 0.48, and 0.57 were cast, cured in lime water for a period of 28 days, beyond the initial curing age required to achieve 20 MPa strength. As a result, the total curing age for the mortars ranged between 30 and 34 days, depending on the w/cm ratio and the RHA content. The compressive strength test results of these mortars and the loss of strength due to immersion in sulfate solution for a period of 28 days is shown in Table 4. It can be observed from these tables that there is only a small decrease in the compressive strength of the mortars due to an initial 28-day immersion in sulfate solution. In addition, because most of the cement hydration is expected to occur within the first 28 days of curing, the strength of specimens cured in lime water for the specified periods (30 to 34 days) were considered as the initial strength for the respective w/cm ratio mixtures.

The percentage loss of compressive strength at any immersion period (after 28 days) was calculated by using the formula:

\[
\text{SL} (%) = \frac{f_c - f_{c1}}{f_c} \times 100
\]

where \(f_c\) = compressive strength of mortar cured in lime water for specific period (30, 32, and 34 days for mixtures having a w/cm ratio of 0.40, 0.48, and 0.57, respectively); and \(f_{c1}\) = compressive strength of mortar at any specified immersion period in sulfate solution.

The extent of deterioration due to sulfate attack by sodium and magnesium sulfate solutions in terms of percentage loss of compressive strength in the mortar cubes are shown in Figs. 7(a–c) and Figs. 7(d–f), respectively.

As these figures show, there is only slight variation in the loss of compressive strength at early immersion periods up to 180 days for all mortars prepared at any specific w/cm ratio. Beyond this immersion period, the control mortars registered the maximum strength loss, indicating that the portland cement mortar is more susceptible to sulfate attacks than RHA mortars. Such a behavior was observed in mortars prepared at all w/cm ratios. One possible reason for such improved behavior of RHA mortars is due to the presence of C-S-H gel having low C/S ratio obtained from pozzolanic reaction. The low permeability of these mortars prevents the sulfates from entering into the cementitious matrix. In addition, though some RHA mortars at specific w/cm ratio gave slightly higher loss of strength than the control mortars at early immersion periods, all the RHA mortars registered a significantly lower strength loss values at later immersion periods.

The approximate strength loss for the control, RHA-7.5%, and RHA-15% mortars after the 360-day immersion period in sodium sulfate solution was found to be in the range of 42–51%, 22–36%, and 22–32%, respectively, depending on the w/cm ratio used. Similarly, the approximate strength loss of the control, RHA-7.5%, and RHA-15% mortars after the 360-day immersion period in magnesium sulfate solution was found to be in the range of 45–58%, 26–38%, and 22–36%, respectively. It can also be observed from these calculated percentage values that the loss in strength decreases with an increase in the replacement level of RHA, indicating the beneficial effects of RHA in improving the sulfate resistance of portland cement mortars.

Comparison of Deterioration of Mortars Immersed in Sodium and Magnesium Sulfate Solutions

Figs. 8(a and b) show the comparison of the expansion and loss of strength of mortar specimens immersed in different sulfate
solutions for a period of 360 days. As Fig. 8(a) shows, the 360-day mortar bar expansion due to sodium sulfate attack is significantly higher than that caused due to magnesium sulfate, with the control mortar showing the maximum difference. This difference may be primarily due to the differences in the mechanism involved in sodium and magnesium sulfate attacks as explained previously. The control mortar immersed in sodium and magnesium sulfate solution registered a 360-day expansion higher and lower than 0.10%, respectively. The use of RHA at 7.5% and 15% replacement level clearly reduced the expansions well below control mortar bar expansions.

As Fig. 8(b) shows, the compressive strength of the control mortars immersed in sodium sulfate solution was found to be lower than that immersed in magnesium sulfate solution, indicating that the strength reduction of mortars immersed in the latter is higher than that in the former. However, the compressive strength of the RHA mortars immersed in both solutions was approximately the same and well below that of the control mortars. The observations seen in the loss in compressive strength for mortars well support that observed in their expansion.

Fig. 7. Loss in compressive strength of RHA mortars at different w/cm ratio immersed in different sulfate solutions: (a) Na$_2$SO$_4$ solution, w/cm = 0.40; (b) Na$_2$SO$_4$ solution, w/cm = 0.48; (c) Na$_2$SO$_4$ solution, w/cm = 0.57; (d) MgSO$_4$ solution, w/cm = 0.40 (e) MgSO$_4$ solution, w/cm = 0.48; (f) MgSO$_4$ solution, w/cm = 0.57
Though the control and RHA mortars had the same compressive strength after immersion in sulfate solution, the latter maintained higher compressive strength than the former after immersion in sulfate solutions. With increase in the replacement level of RHA, the compressive strength of mortars immersed in sulfate solutions was found to be higher. The pozzolanic reactivity of RHA along with the reduced permeability of the matrix is responsible for the improved performance of RHA mortars.

- From the different sulfate attack studies conducted, both sodium and magnesium sulfate caused significant deteriorations to portland cement mortars. The deteriorations caused by sodium sulfate attack were clearly witnessed from both the expansion and loss of compressive strength, whereas the deteriorations caused by magnesium sulfate attack were more evident from the loss of compressive strength rather than from increase in the mortar bar expansion.

Overall, it can be understood that the addition of RHA improves the sulfate resistance of portland cement mortars.

**Acknowledgments**

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**References**


**Fig. 8.** Comparison of expansions and loss of strength of mortars in sodium and magnesium sulfate solutions: (a) 360-day expansion; (b) loss of compressive strength after 360-day immersion in sulfate solution

**Conclusions**

From the studies conducted to determine the sulfate resistance of mortars containing low-carbon RHA, the following conclusions can be drawn:

- The use of low-carbon RHA in mortars significantly reduced the mortar bar expansions when exposed to sodium sulfate and magnesium sulfate solutions. The sulfate resistance of mortars improved with increasing replacement levels of low-carbon RHA from 0 to 15%.
- The expansions of both control and RHA mortars increased with increase in the w/cm ratio used. Severe deterioration was observed in control mortars having higher w/cm ratio.
- The performance of RHA and silica fume at any given replacement level was comparable, with the latter performing slightly better.
- Though the control and RHA mortars had the same compressive strength (~20 MPa) before immersion in sulfate solution, the latter maintained higher compressive strength than the former after immersion in sulfate solutions. With increase in the replacement level of RHA, the compressive strength of mortars immersed in sulfate solutions was found to be higher. The pozzolanic reactivity of RHA along with the reduced permeability of the matrix is responsible for the improved performance of RHA mortars.
- From the different sulfate attack studies conducted, both sodium and magnesium sulfate caused significant deterioration to portland cement mortars. The deteriorations caused by sodium sulfate attack were clearly witnessed from both the expansion and loss of compressive strength, whereas the deteriorations caused by magnesium sulfate attack were more evident from the loss of compressive strength rather than from increase in the mortar bar expansion.

Overall, it can be understood that the addition of RHA improves the sulfate resistance of portland cement mortars.


