Research Article

Hydrochloric Acid Aggression in Groundnut Shell Ash (GSA)-Rice Husk Ash (RHA) Modified Concrete

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Abstract: This paper presents the findings of an investigation on the resistance of Groundnut Shell Ash (GSA)-Rice Husk Ash (RHA) modified concrete to hydrochloric acid aggression and a regression model of the concrete resistance to hydrochloric acid environment. The GSA and RHA used were obtained by controlled burning of groundnut shell and rice husk, respectively in a kiln to a temperature of 600 °C, and after allowing cooling, sieved through sieve 75 µm and characterized. A total of fifteen 100 mm cubes of GSA-RHA-Concrete grade 20 mixes at replacement levels of 0, 10, 20, 30 and 40 %, respectively by weight of cement were cast, cured in water for 28 days and exposed to attack from 10 % concentration of diluted solution of hydrochloric acid (HCl) and the concrete resistance was also modeled using Minitab statistical software to establish regression model. The results of the investigations showed that the resistance of OPC concrete against HCl aggression was better than that of blended GSA-RHA concrete. The weight loss of OPC concrete after 28 days of exposure was 18.5 % as opposed to an average loss of 36.8 % for GSA-RHA concrete. The regression model of GSA-RHA-Concrete resistance against hydrochloric acid was developed with R² value of 0.683 and was adequate for prediction of the sensitivities of pozzolanic activity of GSA-RHA in hydrochloric acid environment.

Keywords: Concrete, GSA-RHA, Hydrochloric acid, Model, Resistance

INTRODUCTION

Compressive strength is generally used to determine the quality of concrete, and this would fairly reflect on the durability of the concrete to a certain extent, but it is not entirely true that strong concrete is always durable, owing to some failures observed of concrete of high compressive strengths due to environmental conditions [1]. The durability of concrete is an important property which significantly determines the service life of concrete structures [2]. According to [3], durability of concrete is its ability to resist chemical and physical attacks that lead to deterioration of concrete during its service life. These attacks include leaching, sulphate attack, acid attack, carbonation, alkali-aggregate reaction, freezing-thawing and abrasion.

Acidic attack usually originates from industrial processes, but it can even be due to urban activity. Ref. [2] reported that the strength of the acid, its dissociation degree in solution, and mainly the solubility of calcium salts formed are dependent on the chemical character of anion. The acidic attack is affected by the processes of decomposition and leaching of the constituent of cement matrix [4]. Acids react with alkaline components of the binder (calcium hydroxide, calcium silicate hydrates and calcium aluminate hydrates) lowering the degree of alkalinity. The degradation of concrete due to acids occur gradually and leads to loss of alkalinity, loss of mass, loss of strength and rigidity [2].

Supplementary cementing materials have been found in literature to improve the mechanical and durability properties of concrete apart from the main benefits of saving natural resources and energy as well as protecting the environment through the use of the main mineral admixtures [5]. However, there are varying opinions on the resistance to acidic attack on pozzolanic cements in technical literature. According to [6], pozzolanic cement has better durability characteristics against acid attacks, but [2] and others claimed vice versa. Ref. [7] reported that the resistance to acid attack on pozzolanic concrete varies with the acid in consideration.

The use of Groundnut Shell Ash (GSA) as a supplementary cementing material in concrete has been reported in [8], [9] and [7]. They suggested that up to 10 % GSA content could be used as a partial substitute of cement in structural concrete. Ref. [7] also indicated that GSA improved the resistance of concrete against
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sulphuric acid degradation, but concrete containing GSA was more susceptible to nitric acid attack. In another study [10] suggested that 15 % would be considered as the optimum percentage replacement of cement with GSA blended with 10 % Rice Husk Ash (RHA) to act as a retarder suitable for hot weather concreting, mass concrete and long haulage of ready mixed concrete and also to improved the resistance of concrete against sulphuric and nitric acids aggression. However, there is need to also investigate the durability of the GSA-RHA modified concrete exposed to a common and more aggressive acidic environment such as hydrochloric acid.

MATERIALS AND METHODS

Materials

Ordinary Portland cement manufactured in Nigeria as Dangote brand, with a specific gravity of 3.14 was used. The oxide composition of the cement is shown in Table 1. Sharp sand from river Challawa, Kano, Nigeria, with a specific gravity of 2.62, bulk density of 1899.50 kg/m$^3$ and moisture content of 2.50 % was used. The particle size distribution of the sand shown in Fig. 1, indicate that the sand used was classified as zone -1 based on [11] grading limits for fine aggregates. The coarse aggregate is crushed granite of nominal size of 20 mm with a specific gravity of 2.7, moisture content of 1.30 percent and bulk density of 1500.0 kg/m$^3$. The particle size distribution is also shown in Fig. 1.

Groundnut shell and rice husk were obtained from Yakasai village and Bunkure town, respectively, Kano State, Nigeria. The Groundnut Shell Ash (GSA) and rice husk ash (RHA) were obtained by a two-step burning method [12], where the shell and husk were burnt to ash and further heating the ash to a temperature of about 600 °C in a kiln and controlling the firing at that temperature for about two and five hours, for GSA and RHA respectively, and the ashes were allowed to cool before sieving through 75 µm sieve. The GSA is of specific gravity of 2.12, bulk density of 835 kg/m$^3$ and moisture content of 1.60 %, while the RHA is of specific gravity of 2.03, bulk density of 368.50 kg/m$^3$ and moisture content of 2.0 %. The grain size distributions of GSA and RHA is shown in Fig. 1. The oxide composition of GSA and RHA was conducted using X-Ray Flouresence (XRF) and the result is shown in Table 1.

Table 1: Oxide Composition of OPC (Dangote Brand), GSA and RHA

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>TiO$_2$</th>
<th>MnO</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>18.0</td>
<td>3.10</td>
<td>4.82</td>
<td>68.37</td>
<td>1.48</td>
<td>0.35</td>
<td>0.32</td>
<td>1.82</td>
<td>0.35</td>
<td>0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>GSA</td>
<td>20.03</td>
<td>2.00</td>
<td>4.03</td>
<td>13.19</td>
<td>1.82</td>
<td>38.80</td>
<td>-</td>
<td>-</td>
<td>1.08</td>
<td>0.68</td>
<td>0.20</td>
</tr>
<tr>
<td>RHA</td>
<td>75.30</td>
<td>2.73</td>
<td>2.30</td>
<td>2.34</td>
<td>0.37</td>
<td>4.70</td>
<td>0.53</td>
<td>0.63</td>
<td>0.16</td>
<td>0.37</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>V$_2$O$_5$</th>
<th>P$_2$O$_5$</th>
<th>ZnO</th>
<th>Cr$_2$O$_3$</th>
<th>NiO</th>
<th>CuO</th>
<th>SrO</th>
<th>ZrO$_2$</th>
<th>Cl</th>
<th>L.o.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>1.27</td>
</tr>
<tr>
<td>GSA</td>
<td>0.03</td>
<td>1.90</td>
<td>0.08</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.02</td>
</tr>
<tr>
<td>RHA</td>
<td>-</td>
<td>9.87</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.41</td>
</tr>
</tbody>
</table>

Groundnut shell and rice husk were obtained from Yakasai village and Bunkure town, respectively, Kano State, Nigeria. The Groundnut Shell Ash (GSA) and rice husk ash (RHA) were obtained by a two-step burning method [12], where the shell and husk were burnt to ash and further heating the ash to a temperature of about 600 °C in a kiln and controlling the firing at that temperature for about two and five hours, for GSA and RHA respectively, and the ashes were allowed to cool before sieving through 75 µm sieve. The GSA is of specific gravity of 2.12, bulk density of 835 kg/m$^3$ and moisture content of 1.60 %, while the RHA is of specific gravity of 2.03, bulk density of 368.50 kg/m$^3$ and moisture content of 2.0 %. The grain size distributions of GSA and RHA is shown in Fig. 1. The oxide composition of GSA and RHA was conducted using X-Ray Flouresence (XRF) and the result is shown in Table 1.

Fig. 1: Particle Size Distribution of GSA, RHA, Fine Aggregates and Coarse Aggregates
Methods
Concrete mix design
Concrete grade 20 was designed with a target mean strength of 33 N/mm², slump range of 10-30 mm, and a water-cement ratio of 0.55 for a mix proportion of GSA-Cement: Fine Aggregate: Coarse Aggregate of 1: 2.2: 3.9 by weight of cement. Five mixes were used, CMI-00 is the control mix and CMI-10, CMI-20, CMI-30 and CMI-40 are mixes containing GSA blended with 10 % RHA at combined replacement levels of 10, 20, 30, and 40 %, respectively.

Test of GSA-RHA-Concrete in Hydrochloric Acid Medium.
Grade 20 concrete with stated mix proportion was used to determine the influence on GSA-RHA-Concrete to exposure in hydrochloric acid environment. Five mixes were used, CMI-00, CMI-10, CMI-20, CMI-30 and CMI-40. Concrete was mixed and cast in steel cube moulds of 100 mm during the casting of cubes for compressive strength test. A total of fifteen (15) cubes were cast and cured in water for 28 days. At the end of every curing regime, three samples were air dried, then weighed before subjection in 10 percent concentration of diluted solution of hydrochloric acid (HCl). The concrete cubes were weighed after subjection in acid environments at 7 days interval until the 28th day to determine the weight of the samples after the acid degradation. The behaviour of GSA-RHA-Concrete resistance to exposure to hydrochloric acid environment is shown in Fig. 2.

Statistical Modeling of GSA-RHA Modified Concrete Resistance in Hydrochloric Acid Environment
A statistical model was developed from experimental data using MINITAB 11 software to predict resistance behavior of GSA-RHA modified concrete. The model was also used to analyze the sensitivity of pozzolanic activity of GSA blended with 10 % RHA in the resistance to hydrochloric acid attack. In developing the resistance prediction model of the GSA-RHA modified concrete, two effects were considered; influence of ash content and influence of duration of exposure on weight of concrete sample retained. The software generates model equation and graphs that would best fit the experimental data. A comparison is then made between the experimental data and data generated by the model and the error difference evaluated.

ANALYSIS AND DISCUSSION OF RESULTS
Groundnut Shell Ash (GSA) and Rice Husk Ash (RHA)
The oxide composition of Groundnut Shell Ash (GSA) and rice husk ash (RHA) indicate a combined SiO₂, Al₂O₃ and Fe₂O₃ content of 26.06 and 80.33 %, respectively. This shows that the GSA is a low reactive pozzolana, while the RHA is very reactive [13]. The CaO content (13.19 %) in GSA also shows that it has some self cementing properties. The chemical composition also indicated a high content of K₂O (38.80 %) and P₂O₅ (9.87 %) in GSA and RHA, respectively which may adversely affect their reactivities.

Effect of Hydrochloric Acid on GSA-RHA-Concrete
The effect of hydrochloric acid on GSA-RHA modified concrete shown as weight retained, in Fig. 2 shows that Ordinary Portland cement concrete offered better resistance to HCl aggression than GSA-RHA modified concrete. The weight loss of OPC concrete after 28 days of exposure was 18.5 % as opposed to an average loss of 36.8 % for GSA-RHA concrete. The poor resistance of GSA-RHA-Concrete to HCl attack when compared with control can be attributed to higher porosity of GSA-RHA-Concrete due to incomplete formation of calcium silicate hydrate gel during hydration, consistent with [14] and [15] reports on RHA-Concrete.
Regression Model for GSA-RHA Modified Concrete Resistance in Hydrochloric Acid Environment

The regression model equation for GSA-RHA-concrete weight retained in HCl environment is given in equation 1.

\[ M_{C1} = 112.67 - 4.83 \text{GR} - 7.28 \text{E} \quad \cdots \cdots \cdots \quad (1) \]

Where: \( M_{C1} \) is concrete weight retained in HCl, GR and E are GSA-RHA content at 0, 10, 20, 30, 40 % replacement and exposure duration of 0, 7, 14, 21, 28 days of samples, respectively.

At 0.05 level of significance, from the regression analysis, \( P \)-value = 0.000 for both GSA-RHA content and exposure duration in HCl and shows that both variables are highly significant (\( P < 0.05 \)) signifying that the variation in the concrete weight retained in HCl is caused by GSA-RHA content and exposure duration.

The coefficient of determination, \( R^2 \) of the model is 68.3 %. This indicates that the variation of concrete weight retained is significantly dependent on the variations of GSA-RHA content and exposure duration in HCl. The residual and normality plots (Fig. 3 and 4) were drawn for the GSA-RHA-concrete weight retained in HCl to further examine how well the model fits the data used. It was observed that there were few large residuals [16] and [17] and limited apparent outlier [18]. This confirms that the model is adequate for prediction of the sensitivity of pozzolanic activity of GSA admixed with 10 % RHA in hydrochloric acid environment.

![Fig. 3: Residual Vs Fitted values for Weight Retained of GSA-RHA-Concrete in HCl](image)

![Fig. 4: Normal Probability of Residuals for Weight Retained of GSA-RHA-Concrete in HCl](image)

CONCLUSIONS

i) GSA is a low reactive pozzolana, while the RHA is more reactive as indicated in the combined SiO\(_2\), Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) content of GSA and RHA of 26.06 and 80.33 %, respectively.

ii) The resistance of OPC concrete against HCl aggression was better than that of blended GSA-RHA concrete.
The regression model for GSA-RHA modified concrete weight retained after exposure in HCl with R² values of 0.683 was adequate for prediction of the sensitivity of pozzolanic activity of GSA admixed with 10 % RHA in acidic environment.

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