Incorporation of Ultrafine Rice Husk Ash (URHA) in Geopolymer Concrete

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Abstract- Rice husk ash (RHA) is the byproduct of rice mills which is left after the production of thermal energy (bio-mass energy) from the husk (rice hull). India is the second largest producer of rice around the globe, about 30-40 million tons of RHA is annually produced which becomes a severe environmental threat from last few decades as it is not biodegradable. RHA is a gray-black inorganic material containing more than 90% silica of its mass and therefore could be used as a precursor for geopolymers. The current study has been focused to investigate the behavior of ultrafine rice husk ash (URHA) modified fly ash – blast furnace (FA-BFS) based geopolymer concrete prepared and cured in ambient temperature conditions. X-ray diffraction (XRD), X-ray fluorescence (XRF), particle size analysis (PSA) and scanning electron microscope (SEM) analysis were done for characterization of the source materials viz. - FA, GGBS and URHA. The workability, strength and durability (sulfate resistivity) of the URHA based GPC has been studied and it is found that 5% URHA could be used in place of fly ash (FA) in GPC for its property enhancement.

Keywords- Ultrafine rice husk ash (URHA), geopolymer concrete, workability, durability.

1. Introduction

Sustainable industrial solid waste management and the promotion of green technology have been the real challenges of the present time. Significant research and technological breakthrough with ground-level applicability are the need of the hour. Global cement demand for construction is rising with a rate of 5% per year [1]. Cement production is considered as one of the most energy and resource-intensive process as it nearly consumes 4Gj of energy (for 1 ton of cement) and 1.5 tons of limestone (for 1 ton of clinker). Geopolymer concrete is concrete without conventional hydraulic cement; the binding gel inside the concrete is formed by aluminosilicate precursor materials followed by a polymerization process in the presence of alkali metals liquids. Joseph Davidovits invented this method of concrete making in the year 1978 [2]; he coined the term ‘geopolymer’ as the process of formation of polymers (binding gel) inside the concrete follows geochemistry. Rice Husk Ash (RHA) is an agro-industrial waste generated in rice mills during
thermal energy production from rice husk (rice hulls). RHA contains a large amount of reactive silica (SiO2), which makes it a suitable supplementary cementitious material (SCM) in cement concrete applications due to its pozzolanic activity [9]. Some effort has been made to utilize RHA in geopolymer binder synthesis along with GGBS and FA; Inti et al. (2016) studied the viability of RHA utilization and GGBFS in place of FA in geopolymer concrete in elevated temperature conditions (60°C) [3]. They have concluded that 5-10% of RHA of the total FA content could be utilized. Kim et al. (2014) experimented with the RHA utilization in geopolymer mortar using sodium hydroxide based alkaline; their experiments show that geopolymer mortars made with RHA had superior strength and durability characteristics than the conventional cement mortars [4].

2. Objectives

Rice husk ash (RHA) is the byproduct of rice milling industries that is left after the production of biomass energy from the husk (rice hull). India is the second-largest producer of rice around the globe, about 30-40 million tons of RHA is annually produced, which becomes a severe environmental threat from the last few decades as it is not biodegradable. When the Rice husk is burnt at a controlled temperature, it has high SiO2 content, and most of it is in amorphous form. Due to the occurrence of this abundant silica, it shows pozzolanic behavior in a trend similar way to silica fume so it can be used as supplementary cementitious material (SCM) in cement concrete and also as a strength-enhancing material in Geopolymer concrete besides with other source materials (Viz.- Fly ash and GGBS).

Very few research has been carried out by some researchers on the partial replacement of fly ash by Rice Husk Ash (RHA) in Geopolymer concrete for the preparation of energy-saving, sustainable concrete. The experimental investigations indicated an encouraging result with improvement in mechanical and long-term properties like tensile strength, abrasion resistance, total void content, permeability, and chemical resistance properties. However, the effect of URHA in the strength and workability of Geopolymer concrete is yet to be adequately understood. Hence it is proposed to carry out a critical investigation to determine the strength, workability, and durability of the Geopolymer concrete with fly ash, GGBS, and URHA with different proportions.

3. Experimental

3.1. Materials

The materials used to prepare geopolymer concrete were fly ash (FA), ground granulated blast furnace slag (GGBS), ultra-fine rice husk ash (URHA), alkali activators, water and aggregates (fine and coarse). The rice husk ash (RHA) was pulverized to very fine particle size to obtain URHA. The average particle size (d50) of the URHA was found to be 10.57µm. A Class-F fly ash per ASTM C618 [6] has been used in this experimental work containing 0.8% CaO, the GGBS, and RHA were collected from nearer steel plant and rice mills, respectively. Sodium based hydroxide and silicate were used for geopolymeric reaction, and portable drinking water has been used to prepare an aqueous solution of sodium hydroxide. The purity of the used NaOH was 99%, and the Na2SiO3 contained 32.15 % SiO2, 15.85% Na2O, and 58% water. Natural river sand of
Zone-III (as per IS-383) and virgin natural coarse aggregates (CA) (20mm>CA>10mm) were used for the preparation of geopolymer concrete.

3.2. Characterization of Source Materials

Advanced characterization techniques were followed to analyze the morphological, microstructural, and chemical composition of the used source materials, i.e., FA, GGBS, and RHA. Laser scattering particle size analysis was done to understand the particle distribution of the used source materials. Meanwhile, X-Ray diffraction (XRD), X-Ray fluorescence (XRF), and scanning electron microscope (SEM) were done to observe the mineralogical, chemical, and morphological properties respectively.

**Particle Size Analysis (PSA)**

The particle size analysis of each of the source materials was conducted by a laser scattering particle size analyzer (HORIBA LA-960). It is observed that the average particle size (d$_{50}$) of the FA was 17.71µm while the average particle size of URHA, GGBS were found to be 10.57µm and 21.61µm, respectively. The particle size distribution curves of FA, URHA, and GGBFS, were plotted in fig.-1, it can be observed that the URHA particles are finer than that of both FA and GGBS. Most of the URHA particles were under 45µm whereas the FA and GGBFS have comparatively larger particles than that of URHA.

![Particle size distribution curve of URHA, FA and GGBS](image-url)
X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF)

XRD and XRF analysis are done for understanding the material’s chemical composition. The XRD analysis of GGBS, FA, and URHA was done with X’Pert HighScore Plus (PANalytical) and given in fig.-2, 3, and 4, respectively. In fig.1, the GGBS diffractograph reveals the presence of SiO₂, CaCO₃, and Al₂O₃ throughout its mass; the same can be observed in the XRF results of GGBS in table-2. The FA majorly consists of silica (SiO₂) and alumina (Al₂O₃), as found from XRF analysis, and the same is confirmed by the XRD analysis (fig.-3). The URHA XRD patterns (fig.-4) were quite different from that of FA and GGBS; from its shape, it can clearly be observed that it's in amorphous form. As the XRF analysis results always show the elements present in the materials in oxide form, the XRF of URHA unveiled that 96% of its mass is silica (SiO₂), and rest is of Al₂O₃, CaCO₃ and other trace elements (in oxides).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>K₂O</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGBS</td>
<td>36.281</td>
<td>8.076</td>
<td>20.383</td>
<td>0.050</td>
<td>0.380</td>
<td>1.554</td>
<td>6.640</td>
<td>0.377</td>
<td>1.022</td>
<td>24.12</td>
</tr>
<tr>
<td>FA</td>
<td>60.342</td>
<td>0.548</td>
<td>30.834</td>
<td>0.522</td>
<td>0.082</td>
<td>0.103</td>
<td>3.346</td>
<td>0.022</td>
<td>1.268</td>
<td>0.801</td>
</tr>
<tr>
<td>URHA</td>
<td>96.235</td>
<td>0.269</td>
<td>0.281</td>
<td>0.361</td>
<td>0.054</td>
<td>0.202</td>
<td>1.366</td>
<td>0.091</td>
<td>0.454</td>
<td>0.578</td>
</tr>
</tbody>
</table>

Table-1. Chemical composition of source materials by XRF

Fig.2. X-ray Diffractogram of GGBS
Fig. 3. X-ray Diffractogram of FA

Fig. 4. X-ray Diffractogram of URHA
**Scanning Electron Microscope analysis (SEM)**

Microscopic observations are very much essential to understand any material’s surface morphology, structural arrangements, particle shapes & sizes, and distribution characteristics. The scanning electron microscope analysis has been done to understand the various essential characteristics, as mentioned above. GGBS, FA and URHA powder were observed under SEM, and the corresponding images were given in fig.-5, 6 and 7. In fig.-1, the SEM image of GGBS is shown, the particles are angular with sharp edges, and most of the particles are above 100 microns. The fig.2 shows the particles of fly ash; the particles are of spherical shape and are of less than 100 microns. The URHA particles are irregular in size, but they are different from GGBS particles, they have a spongy microstructure with pores inside its structure. The size of the URHA particles is very small and falls under 100 microns; moreover, some URHA particles are tiny and falls in a range of 10-20 microns, which can be observed from the SEM image.

![SEM image of GGBS](image.png)

**Fig.5. SEM image of GGBS**
Fig. 6. SEM image of fly ash

Fig. 7. SEM image of URHA
3.3. Methods and Mixture Proportions

Since there are no international specific standards are available for geopolymer concrete preparation, the existing standards for conventional cement concrete were used developed by the American Society of Testing and Materials (ASTM) and Bureau of Indian Standards (BIS). Both the coarse and fine aggregates were chosen with reference to IS-383 [5], and the fly ash was taken as per ASTM C618 [6]. The concrete mixing procedure was developed by self-observation and literature study, the dry mixing of all the required materials was done for 7-8 minutes and then the prepared alkaline solutions (made before 1 hour of the casting) were mixed; the mixing operation continued for another 3-4 minutes to form a homogenous mixture. A minimal amount of extra mixing water (EW) was added to all the mixtures to enhance the workability; this EW could be added 1 minute after the alkaline liquid addition.

Seven numbers of mixture proportions were designed to check the effect of URHA in GPC properties. The mixture was designed in such a way that the percentage of GGBS was constant, and FA and URHA were varied. FA was being replaced by URHA in 1%, 3%, 5%, 7%, 9%, and 11%, and a standard mixture was prepared with no URHA addition for comparisons; the mixture proportions of casted GPC were given in table-2. Sodium based hydroxide and silicates were used with the source materials for geopolymerization; the aqueous sodium hydroxide (SH) of 14M was mixed with liquid sodium silicate (SS) in a ratio of 1:2 (SH: SS) by volume. The workability test was done by referring to ASTM C143/ C143M [7] to assess the followability of each mixture for workability valuation. The fresh geopolymer concrete was then moulded into 150x150x150 mm cubes for compressive strength test as per IS-10086 [8]. The crushing strength of the GPC samples was tested in 7day, 14 day, and 28-day intervals and the test was conducted with a digital compressive testing machine with a capacity of 2000kN. Optimum mixture and a standard mixture of GPC were also taken for sulfate resistivity rest; an aqueous solution of MgSO4 (5%) solution was used to conduct this test. The cube samples of GPC were immersed in the sulfate solutions for 90 days, and the mass loss, visual changes, and compressive strength of the immersed samples were analyzed in 28, 56, and 90-day intervals.

Table- 2. Mixture proportions of GPC with URHA

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Mix Name</th>
<th>Fly Ash (Kg/m³)</th>
<th>GGBFS (Kg/m³)</th>
<th>URHA (Kg/m³)</th>
<th>Coarse Aggregates (Kg/m³)</th>
<th>Fine Aggregates (Kg/m³)</th>
<th>Alkaline Liquid (L/m³)</th>
<th>Extra Water (L/m³)</th>
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</thead>
<tbody>
<tr>
<td>01</td>
<td>A1</td>
<td>343.00</td>
<td>150.00</td>
<td>3.51</td>
<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
<tr>
<td>02</td>
<td>A2</td>
<td>339.57</td>
<td>150.00</td>
<td>10.50</td>
<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
<tr>
<td>03</td>
<td>A3</td>
<td>332.71</td>
<td>150.00</td>
<td>17.50</td>
<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
<tr>
<td>04</td>
<td>A4</td>
<td>325.85</td>
<td>150.00</td>
<td>24.50</td>
<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
<tr>
<td>05</td>
<td>A5</td>
<td>318.99</td>
<td>150.00</td>
<td>31.50</td>
<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
<tr>
<td>06</td>
<td>A6</td>
<td>308.70</td>
<td>150.00</td>
<td>38.50</td>
<td>1500.00</td>
<td>500.00</td>
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<tr>
<td>07</td>
<td>A7</td>
<td>350.00</td>
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<td>1500.00</td>
<td>500.00</td>
<td>150.00</td>
<td>20.00</td>
</tr>
</tbody>
</table>
4. Results and Discussions

4.1. Workability

The workability of GPC was decreased when URHA was incorporated into the system, and this is due to the high finesse and water absorption of URHA. From SEM observation it can be noticed that the URHA has a unique porous structure similar to honeycomb which could store water inside its structure, this may be one of the reasons of reduction in workability; the high specific surface area (SSA) of RHA leading to high reactivity and high water requirement is also responsible for formation of cohesive GPC mix ultimately reducing the workability. Experimental observation has revealed that more is the URHA percentage in GPC less is its workability. The figure-8 shows the trend of workability reduction of GPC with URHA incorporation.

Fig.8. Workability variation of GPC with URHA

4.2. Compressive Strength

The compressive strength results of the GPC cubes are given in fig.-9, Where it can be noticed that with the inclusion of URHA the compressive strength of GPC increases to a certain replacement level (i.e-9%) and then decreases (i.e-11%). It can also be observed that the early strength development mechanism of the GPC enhanced when URHA was induced to the system. The strength increment of GPC samples with the inclusion of URHA is due to the presence of highly reactive amorphous silica in URHA, which resulted in a rapid reaction mechanism enhancing the
process of geopolymerization. Due to this mechanism, both the early and later age strength of GPC specimens were comparatively more significant than the standard GPC samples containing only FA and GGBFS. Nevertheless, with a high percentage of URHA, at 11%, the compressive strength of GPC specimens were started decreasing. This happened due to the excessive siliceous material available as a precursor in the presence of a limited alkaline activator. Hence the extra amount of silica inside the matrix was unreacted, resulting in a negative impact on the gel synthesis and gel density; ultimately, it reduces the concrete compressive strength. The highest compressive strength was achieved by GPC samples containing 5% URHA (A3); the mix-A3 has shown 14.96% and 15.72% greater strength in 7 and 28 days, respectively than the GPC without URHA (i.e-A7).

![Compressive strength of GPC with URHA](image)

**Fig.9.** Compressive strength of GPC with URHA

### 4.3. Durability (Sulfate Resistivity)

The sulfate resistance property of the URHA incorporated GPC were studied; this study was done by taking aqueous magnesium sulfate solutions (5% MgSO₄). The GPC cubes (A3 and A7) were immersed in the sulfate solutions for 120 days; the reduction in mass and compressive strength of the concrete were checked. The result showed that both of the concrete mixtures are reluctant to sulfate attack as there is no free lime content inside the concrete matrix. In the case of conventional cement concrete, the free lime (Ca(OH)₂) generated from the hydration process reacts with the sulfate (SO₄) present in the soil or water and forms calcium sulfate (CaSO₄). Due to this phenomenon, the volumetric expansion occurs in hydraulic cement-based concrete; in contradict to this fact, the GPC shows significant sulfate resistance to sulfate attack due to the absence of free
lime (hydration product) in it. Both the GPC (with and without RHA) show unusual behavior as the mass of the GPC samples goes on increasing with time while immersed in a sulfate solution. Though there is no loss in strength of the GPC cubes after 90 days of sulfate ambiance, the mass of both the standard and RHA incorporated GPC increased by 0.89% and 0.92%, respectively. This weight gaining mechanism of the GPC could be due to new compound formation inside the concrete in reaction with the magnesium sulfate (MgSO₄), or this could be due to entrapment of water molecules inside the matrix as it has been submerged in the solution for a prolonged time. Nevertheless, the URHA content does not significantly change the resistivity of GPC against sulfate attack because the gel formation mechanism in both the case was the same, and the nature of the materials is identical; therefore, both the standard and RHA incorporated GPC is found to be sulfate resistant.

Fig.10. GPC specimens immersed in sulfate solution (5%MgSO₄)

5. Future Research Scope

Further experimental should be conducted on the characterization of optimum GPC mixture (A3) and the standard GPC (A7) to study the effect of URHA on gel synthesis mechanism of GPC. Extensive study on the durability of URHA incorporated GPC with different acid environment has to be done for better understanding of the effect of URHA in GPC. The weight gain mechanism of GPC in sulfate environment has to be properly understood by adopting some material characterization techniques such as XRD and FTIR; if new compound has been formed inside the GPC matrix it can observed by such analysis.
6. Conclusions

The experimental investigation results and discussions disclose the following conclusions.

1. Rice husk ash (RHA) is rich in silicon dioxide (silica), which is in amorphous form, and due to this high silica content, RHA could be used in geopolymerization reaction for gel synthesis, and the particle size of RHA plays a vital regarding its reactivity. Ultrafine rice husk ash (URHA) is proven to be highly reactive in geopolymerization along with FA and GGBS in optimum dosages.

2. The GPC with 5% URHA (A3) achieved the highest compressive strength; this is due to the maximum reaction mechanism, which was facilitated by the optimum dosage of additional silica incorporation by URHA in the mixture. Addition of URHA more than 11 percent in binders (in place of FA) for GPC is not recommended as the strength of the GPC reduces than the standard mixture, and the workability of the concrete significantly reduces.

3. The workability of the GPC was reduced with an increasing percentage of URHA inclusion. This was happened due to the high specific surface area (SSA) and porous microstructure of URHA, which increased the water requirement and made the mixture cohesive. At 5% URHA, the GPC mixture showed gentle workability, but beyond 5% URHA incorporation GPC mixture became highly cohesive and not workable.

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