Study on the Influence of Processed Rice Straw Ash as a Binder on Compressive Strength and Water Absorption of Alkali Activated Mortar

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Abstract

Major concern today with cement production is its environmental issues. For the sustainable development the usage of cement is reduced day by day in the construction sector. The alkali activated binders (AAB) are eco-friendly and they do not cause any environmental effects which can be used as one of the alternatives to cement. AAB is a hardened cementitious paste made of industrial pozzolanas such as Fly Ash and GGBS, and alkaline solutions like sodium hydroxide and sodium silicate. Currently Fly Ash is the most commonly used AAB; but fly ash may become scarce because coal-fired power plants are declining due to the increasing popularity of renewable energy.

Rice straw ash (RSA) is an agricultural waste which has the pozzolanic characteristics and contains about 70%-80% of amorphous silicon dioxide (SiO2) when burnt at 650°C. Rice straw can be used as replacement of fly ash in Alkali Activated Mortar (AAM) by burning it at 650°C and milling it for 10 minutes, 20 minutes and 30 minutes. The specimens are casted for Rice Straw based AAM and compressive strength and water absorption are studied for 7.5, 10, 16 molarity of NaOH and also RSA milled for 10, 20 and 30 minutes and SEM EDX is studied for the hardened specimen at 28 days.

The RSA has significant positive effects on performance of AAM. The replacement of RSA by 20% has shown greater results and as the milling time of RSA is raised the surface area of RSA is increased which in turn resulted in improved strength and as the molarity of NaOH is increased the AAM at 3, 7, 28 and 56 days has the higher Compressive Strength and lower Water absorption.

Keywords: RSA (Rice Straw Ash), AAM (Alkali Activated Mortar), AAB (Alkali activated Binder), Fly Ash.

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Introduction

Nearly 1 tone of carbon dioxide (CO2) is released into atmosphere for generating 1 tone of ordinary portland cement. Around 3.5 billion tons of cement is produced in this world yearly. Hence, the equal amount of carbon dioxide is released into the air due to cement production. The solution to reduce the harmful effects due to portland cement alkali activated technology can be used. So, alkali activated binders can be used in the place of cement to make concrete without cement and as a binder. The alkali activated binders are environmentally friendly and they do not produce any harmful gases during its manufacturing as the materials used here are the waste that is generated in the industries. Such waste materials are GGBS, fly ash, metakaolin these materials have the ability to produce the binder which is capable of replacing cement mortar and produce alkali-activated mortar. The three-dimensional structures from amorphous to the semi crystalline silico-aluminate of poly (sialate) (-Si-O-Al-O-), orpoly (sialate-siloxo) (Si-O-Al-O-Si-O) are known as Geopolymers. The materials used here consists of aluminum and silica which go through the stages like this integration, gel development, setting and hardening in generation of geopolymers. The aspects affecting the characteristics of alkali activated mortar are NaOH concentration, Sodium silicate, aluminates, Calcium ratio, curing type and many more. Durability characteristics of these polymers have been increased by the utilization of fly ash. Waste materials such as GGBS consist of more amount of calcium oxide which helps in reducing the curing time at ambient temperature. Due to the presence of GGBS in geopolymer gives rise to the precipitation of Calcium-Silicate-Hydrate (C-S-H) and calcium-alumino–silicate–Hydrate(C-A-S-H) gels in alkali-activated concrete and mortar cured at 27°C.
Other supplemental materials which can be used as a replacement to fly ash in alkali activated binders are ashes from agricultural wastes. Agricultural waste mainly contains straw, fruit shells, bagasse, seeds, and shells. All these wastes can be used with proper treatment in development of sustainable building materials. Biomass is used as a replacement to fossil fuel due to its high calorie value in recent days. Some ashes produced contain pozzolanic properties so they can be used as a construction material. One of the wastes from agriculture is rice straw (RS), the production of rice straw is 731 million tones worldwide in 2008 (Abdel-Rahman et al., 2015) while Asia produces larger amount of Rice Straw about 620 million tons. About 1-1.5 kg of RS is generated for every 1 kg rice produced. RS is the waste which is generated within a less period of time in a given year and it is burnt in the field in which it is cultivated generally. But there is less research going on the characteristics of RSA and its applications. The research of obtaining silica by rice straw was done and the results have shown that about 65% of silica which is not crystalline form. We know that the roots of the plants absorb silicon element which will be in the form of silicic acid, which is carried through vascular system and store as opal or hydrated amorphous silica (SiO$_2$·nH$_2$O). Farmers think that this helps in destroy of fungal spores, bacteria, and weed seeds and also it may help in gain of some nutrients in soil. But this may cause serious health issues and may cause environment damage. Due to the burning of RS several gases are released such as carbon dioxide (CO$_2$), methane (CH$_4$), nitrogen oxide (NO$_x$), sulfur oxides (SO$_x$), hydrocarbons, dioxides, and some particles of nature. Prescribed burning and enhancement of use of ash can be a solution to the problems. Various ashes generated from agricultural waste have been validated in their possibility in concrete industry for the replacement of cement and fly ash for production of new building materials. RS is created by leaves, stems and roots formed by fibrous cellulose which has more silica content.

Roselló et al. chemical composition of ashes of different parts of RS: rice leaf ash (RLA), rice leaf sheath ash (RLSA) and rice stem ash [1]. The main oxide present in all the ashes was SiO$_2$, but rice stem ash has the more percentage of SiO$_2$. K$_2$O, CaO are the other oxides present in it. Sung et al. studied replacement of Portland cement with RSA [2]. Properties such as density, compressive strength and flexural properties, durability and ultra-sonic pulse velocity have been evaluated. Mechanical properties are high at 5% RSA but the durability properties are good at 15% RSA. Munshi et al. studied cement mortars, RSA as a pozzolanic material and observed an increase of 12.5% in compressive strength by replacing 10% of cement by RSA [3]. The authors suggested that RSA satisfies as pozzolanic material. They have also studied RSA burnt at different temperatures and have obtained a better pozzolanic activity at 600 and 750°C.

The objective of this study is to prepare pozzolanic material from one of the agricultural wastes that is Rice Straw to reduce its effects on environment and to increase the properties of construction material. The effect of grinding of RSA has been studied in this project. Rice straw can be used as replacement of fly ash in Alkali Activated Mortar (AAM) by burning it at 650°C and milling it for 10 minutes, 20 minutes and 30 minutes. The specimens are casted for Rice Straw based AAM and compressive strength, mechanical properties are high at 5% RSA but the durability properties are good at 15% RSA. Munshi et al. studied cement mortars, RSA as a pozzolanic material and observed an increase of 12.5% in compressive strength by replacing 10% of cement by RSA [3]. The authors suggested that RSA satisfies as pozzolanic material. They have also studied RSA burnt at different temperatures and have obtained a better pozzolanic activity at 600 and 750°C.

Constituents of alkali activated mortar
Constituents of Alkali Activated Mortar consist of cementitious materials (fly ash, GGBS, Rise Straw Ash), Alkaline activators (NaOH, Na$_2$SiO$_3$), Fine Aggregates (Sand).

Fly ash
Fly Ash is a material obtained from thermal power plants, which is a byproduct. The flue gases generated at the time of combustion of coal have been separated from the fly ash. The main constituents of fly ash are SiO$_2$, Al$_2$O$_3$, and CaO with some amount of MgO, SO$_3$, Na$_2$O, and K$_2$O. Fly ash has the shape of spherically glassy. The surface area of fly ash is 2500-5000 m$^2$/g.

Ground granulated blast furnace slag
Iron ore, coke, and limestone are used in the furnaces in iron industries and are subjected to higher temperatures. At the higher temperatures iron is produced from iron ore and all the elements left are turned into slag. This slag is extinguished to get Blast furnace slag and then it is grounded to acquire GGBS. Its surface area is 350 m$^2$/Kg. It mainly consists of CaO, silica, alumina, and small amount of magnesia.

Rice straw ash (RSA) preparation
Rice straw had been collected from Kurnool. First the RSA was burnt in the open air which has uncontrolled temperature under the sun light and the RSA has been turned into ashes (RSA0). The ashes formed by open air burning of RSA were again subjected to a controlled calefaction of 650°C for 1 hour duration in muffle furnace. It has been noticed that the color of RSA was changed from black to grey due to the burning. To reduce the size of the particles of RSA the RSA is grinded in Ball mills for 10 minutes, 20 minutes, and 30 minutes and produced 3 different samples of RSA with 3 different surface areas and are given the notation RSA0 (RSA which is
burnt in muffle furnace), RSA1 (RSA burnt at 650°C and grinded for 10 minutes), RSA2 (RSA burnt at 650°C and grinded for 20 minutes), RSA3 (RSA burnt at 650°C and grinded for 30 minutes) (see Figure 1).

![Figure 1](image)

**Figure 1.** Three different samples of RSA: rice straw in field (a), RSA burnt in open field (b), RSA burnt at 650°C (c)

**Alkaline activator**

Alkaline Activators plays an important role in the polymerization process and strength. Sodium Hydroxide or potassium hydroxide combined with sodium silicate or potassium silicate is usually used. The mixture of sodium silicate along with sodium silicate has more rate of reaction. NaOH has higher capacity of dissolution compared to KOH so NaOH is used along with Na₂SiO₃.

**Fine Aggregates**

Fine aggregates occupy about 60%-70% of the total volume. Locally available Aggregates were used.

**Mixture proportions**

Different mixes were developed with the replacement of fly ash with RSA from 0% to 35% for 7.5, 10 and 16 molarity of NaOH. Mix design with 0% RSA is shown in Table 1.

The compressive strength of mortar mix with 20% replacement of RSA1, RSA2, and RSA3 is higher and for replacement above 20% and it is considered as optimum values and all the tests were conducted at 20% replacement of RSA1, RSA2 and RSA3 using 7.5, 10 and 16 molarity NaOH.

**Table 1.** Mix design with 0% RSA

<table>
<thead>
<tr>
<th>Na₂SiO₃ (kg/m³)</th>
<th>NaOH (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>FlyAsh (kg/m³)</th>
<th>GGBS (kg/m³)</th>
<th>Fine Aggregate (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.9</td>
<td>86.5</td>
<td>107</td>
<td>303.8</td>
<td>130.2</td>
<td>1609.6</td>
</tr>
</tbody>
</table>

**Notations for mixes:**

7.5R0- Mix with 0%RSA and 7.5M NaOH
7.5R1- Mix with 20%RSA1 and 7.5M NaOH
7.5R2- Mix with 20%RSA2 and 7.5M NaOH
7.5R3- Mix with 20%RSA3 and 7.5M NaOH
10R0- Mix with 0%RSA and 10M NaOH
10R1- Mix with 20%RSA1 and 10M NaOH
10R2- Mix with 20%RSA2 and 10M NaOH
10R3- Mix with 20%RSA3 and 10M NaOH
16R0- Mix with 0%RSA and 16M NaOH
16R1- Mix with 20%RSA1 and 16M NaOH
16R2- Mix with 20%RSA2 and 16M NaOH
16R3- Mix with 20%RSA3 and 16M NaOH

**Sample preparation**

Three cubes of size 50mm×50mm×50mm were used for each mix for each day of testing for compressive strength and 100mm dia×50mm depth were used for water absorption which are tested at 3, 7, 28 and 56 days. All the specimens casted are kept for ambient curing. SEM images are taken for hardened samples and are analyzed.

**Results and discussion**
Properties of materials
The specific gravity and surface areas of fly ash, GGBS, RSA0, RSA1, RSA2 and RSA3 are shown in Table 2. As the grinding time is increased the particle size of RSA is decreased so simultaneously surface area is also increased, hence surface area of RSA3 > RSA2 > RSA1 > RSA0. The chemical composition of fly ash, GGBS, RSA are shown in Table 3.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fly ash</th>
<th>GGBS</th>
<th>RSA0</th>
<th>RSA1</th>
<th>RSA2</th>
<th>RSA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>2.14</td>
<td>2.73</td>
<td>1.62</td>
<td>1.76</td>
<td>1.87</td>
<td>2</td>
</tr>
<tr>
<td>Surface area$\text{(m}^2/\text{kg})$</td>
<td>358</td>
<td>459</td>
<td>163</td>
<td>328</td>
<td>544</td>
<td>725</td>
</tr>
</tbody>
</table>

Table 3. Chemical composition of Fly ash, GGBS, RSA.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>63.53</td>
<td>27.40</td>
<td>3.67</td>
<td>1.26</td>
<td>0.35</td>
<td>0.01</td>
<td>0.85</td>
<td>0.19</td>
</tr>
<tr>
<td>GGBS</td>
<td>34.26</td>
<td>11.32</td>
<td>0.61</td>
<td>38.34</td>
<td>7.94</td>
<td>3.84</td>
<td>0.55</td>
<td>0.32</td>
</tr>
<tr>
<td>RSA</td>
<td>71.99</td>
<td>0.67</td>
<td>0.64</td>
<td>4.98</td>
<td>2.65</td>
<td>1.96</td>
<td>13.89</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Compressive Strength
This test is performed using procedure from ASTM C 109/C 109M - 07 [4] 7 days compressive strength of the specimens with 7.5, 10, and 16 molarity of NaOH with replacement of RSA1, RSA2, and RSA3 from 0%-35% was found and has found that 20% replacement of RSA1, RSA2 and RSA3 has the highest compressive strength. The compressive strength of specimens with 7.5 molarity of NaOH with replacement of fly ash by RSA1, RSA2 and RSA3 has been shown in Figure 2. The compressive strength of specimens with 10 molarity of NaOH with replacement of fly ash by RSA1, RSA2 and RSA3 has been shown in Figure 3. The compressive strength of specimens with 16 molarity of NaOH with replacement of fly ash by RSA1, RSA2 and RSA3 has been shown in Figure 4. As the molarity of NaOH is increased the compressive strength is also increased as the concentration of sodium hydroxide is increased as the concentration is increased the dissolution from the leaching of silica and alumina is increased so the polymerization reaction is increased hence 16R0, 16R1, 16R2, 16R3 samples have higher compressive strength compared to 10R0, 10R1, 10R2, 10R3, similarly 10R0, 10R1, 10R2, 10R3 has higher compressive strength compared to 7.5R0, 7.5R1, 7.5R2, 7.5R3. And as the particle size of RSA is decreased the reactivity of RSA is increased and the compressive strength is also increased so 16R3, 10R3, 7.5R3 has more compressive strength compared to 16R2, 10R2, 7.5R2 similarly 16R2, 10R2, 7.5R2 has more compressive strength compared to 16R1, 10R1, 7.5R1. Due to the addition of RSA, there will be an increase in the SiO2 which helps in increase of sialate and orpedly bonds and there will be a slow rate of dissolution and reaction of RSA which makes a part of RSA as filler material and it is the reason to reduction in the compressive strength beyond the addition of 20% of RSA. At each optimum values the compressive strength is found at 3, 7, 28 and 56 days and are shown in Figure 5, 6, 7.

Figure 2, 3 and 4 represents the compressive strength of alkali activated mortar with 7.5 M, 10 M and 16 M of NaOH respectively which is replaced with RSA1, RSA2 and RSA3 from 0% to 35%. As it is observed the compressive strength of alkali activate mortar with 7.5M, 10M and 16M of NaOH replaced with RSA1, RSA2 and RSA3 has higher values at the replacement of 20% of RSA1, RSA2 and RSA3.

Figure 5, 6, and 7 represents the 3-, 7-, 28- and 56-days compressive strengths of alkali activated mortar with 7.5 M, 10 M and 16 M NaOH with 20% replacement of RSA1, RSA2 and RSA3. As the days increased the compressive strength increased due to the polymerization up to 28 days but after 28 days depolymerization may occurred due to which there is a slight decrease in compressive strength at 56 days.

If we compare the compressive strengths of alkali activated mortar with 7.5 M, 10 M and 16 M NaOH the compressive strength of 16 M NaOH alkali activated mortar is high because as the molarity of NaOH is increased the concentration of NaOH is increased which in turn results in less water present in mortar so the strength of mortar is increased and also as NaOH is increased the dissolution of particles is increased so the compressive strength is also increased.
Figure 2. 7 days compressive strength of 7.5M with replacement of fly ash with 10min, 20min, 30min grinded RSA.

Figure 3. 7 days compressive strength of 10M with replacement of fly ash with 10min, 20min, 30min grinded RSA.

Figure 4. 7 days compressive strength of 16M with replacement of fly ash with 10min, 20min, 30min grinded RSA.
Figure 5. Compressive strength of samples of 7.5M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 days

Figure 6. Compressive strength of samples of 10M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 days

Figure 7. Compressive strength of samples of 16M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 days
Water absorption

100mm diameter x 50mm depth cylinders were casted which were ambient cured for 3, 7, 28, and 56 days. These samples were then oven dried for 24 hours at temperature 110°C till mass become constant. The dry weight of the cylinder is noted as \( w_1 \). Then dried samples are immersed in water for 48 hours till the 2 consecutive values of surface dried sample at interval of 24 hours has increment in mass is not less than 0.5%, then the sample is removed from surface moisture using a towel and the weight of the sample is noted as \( w_2 \). This test is done according to ASTM C-642.

Water absorption = \( \left[ \frac{w_2 - w_1}{w_1} \right] \times 100 \)

The water absorption results of the casted samples are presented in Figure 8, 9, 10. The water absorption may be due to the permeability of the mortar which is related to the pore structure. The pore structure depends on many factors one of them is the bond between sand particle and alumina silica gel and it also depends on the quantity of alumina silica gel formed. More water absorption is observed in the samples without RSA due to less quantity of alumina silica gel and may also be due to the presence of unreacted particles of fly ash and GGBS. As the molarity of sodium hydroxide is increased the reactivity of the NaOH more reaction products are formed and filling the pores due to the presence of less water and thus decreasing the permeability of the mortar. Due to the addition of RSA which has more amount of silica which helps in the formation of bonds and reduce the pores and the water absorption up to 20% replacement. Due to the decrease in the particle size of RSA the reactivity is increased which helps in more reaction of the binder and more reaction products like alumino silica gel and C-S-H gel are formed which decreases the pores and increases the density of the mortar. So, the samples with RSA3 have lesser water absorption compared to RSA2, RSA1.

Figure 8, 9, and 10 represents the 3-, 7-, 28- and 56-days water absorption of alkali activated mortar with 7.5 M, 10 M and 16 M NaOH with 20% replacement of RSA1, RSA2 and RSA3. As the days increased the water absorption is decreased due to the polymerization which fills the pores with the alumino silica gel up to 28 days but after 28 days depolymerization may occurred due to which there is a slight increase in water absorption at 56 days.

If we compare the water absorption of alkali activated mortar with 7.5 M, 10 M and 16 M NaOH the water absorption of 16 M NaOH alkali activated mortar is less because as the molarity of NaOH is increased the concentration of NaOH is increased which in turn results in less water present in mortar so the polymerization increases which fills the pores more and reduces the water absorption and the strength of mortar is also increased and also as NaOH is increased the dissolution of particles is increased so the compressive strength is also increased and water absorption is decreased.

![Water absorption of samples of 7.5 M NaOH](image)

**Figure 8.** Water absorption of samples of 7.5 M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 and 56 days
Figure 9. Water absorption of samples of 10M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 and 56 days

Figure 10. Water absorption of samples of 16M NaOH with RSA0, RSA1, RSA2, RSA3 at 3, 7, 28 and 56 days

Scanning Electronic Microscope, Energy Dispersive X-Ray Analysis (SEM EDX)

The high-resolution images of the 7.5R0, 10R0, 16R0, 7.5R3, 10R3, and 16R3 sample along with elemental identification is provided in below images. SEM micrographs and EDX analysis of samples 7.5R0, 10R0, 16R0, 7.5R3, 10R3, and 16R3 are presented in this section in Figures 11, 12, 13, 14, 15 and 16.

In the EDX analysis the elemental composition is derived. In the Figure 11(b), 12(b), 13(b) the molarity of NaOH is changed so there is an increase in the Na and there is an increase in the silica content for the samples activated in sodium hydroxide and sodium silicate. It assures that silica is provided to the paste along with Na$_2$SiO$_3$ which results in the formation of C-S-H gel and geopolymer gel. And due to the addition of RSA as results shown in 5(b), 6(b), 7(b) the silica content is increased, and which gives more Si-O-Si and Si-O-Al bonds. The EDX analysis confirms that the major reaction product in alkali activated mortar is aluminosilicate gel.

According to the SEM images shown in Figure 11(a), 12(a), 13(a), 14(a), 15(a), 16(a) FA, GGBS, RSA are stimulated by the NaOH, Na$_2$SiO$_3$ and the closer observation shows some partially and unreacted particles. Increase in NaOH concentration increases the density so the 16R3 has the denser composition as the molarity is high and the particle size of RSA is also small hence it has denser structure thus has more compressive strength compared to other samples with lesser molarity and lesser particle size of RSA.
Figure 11. Image of 7.5R0: SEM (a) and EDX (b)

Figure 12. Image of 10R0: SEM (a) and EDX (b)

Figure 13. Image of 16R0: SEM (a) and EDX (b)
Figure 14. Image of 7.3R3: SEM (a) and EDX (b)

Figure 15. Image of 10R3: SEM (a) and EDX (b)

Figure 16. Image of 16R3: SEM (a) and EDX (b)
Conclusions
As the molarity of NaOH is increased the compressive strength is also increased as the concentration of sodium hydroxide is increased as the concentration is increased the dissolution from the leaching of silica and alumina is increased so the polymerization reaction is increased. As the particle size of RSA is decreased the reactivity of RSA is increased and the compressive strength is also increased.

More water absorption is observed in the samples without RSA due to less quantity of alumina silica gel and may also be due to the presence of unreacted particles of fly ash and GGBS. As the molarity of sodium hydroxide is increased the reactivity of the NaOH more reaction products are formed and filling the pores due to the presence of less water and thus decreasing the permeability of the mortar.

Due to the decrease in the particle size of RSA the reactivity is increased which helps in more reaction of the binder and more reaction products like alumino silica gel and C-S-H gel are formed which decreases the pores and increases the density of the mortar. So, the samples with RSA3 have lesser water absorption compared to RSA2, RSA1.

The EDX analysis confirms that the major reaction product in alkali activated mortar is aluminosilicate gel. Increase in NaOH concentration increases the density so the 16R3 has the denser composition as the molarity is high and the particle size of RSA is also small hence it has denser structure thus has more compressive strength compared to other samples with lesser molarity and lesser particle size of RSA.

In the EDX analysis the elemental composition shows that the molarity of NaOH is changed so there is an increase in the Na, and there is an increase in the silica content for the samples activated in sodium hydroxide and sodium silicate.

References