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Mitigation of environmental problems using brick kiln rice husk ash in geopolymer composites for sustainable development

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ABSTRACT

Brick kilns uses assorted amount of rice husk as fuel to fire the stacks of soil bricks. In India, the rice husk ash (RHA) created during the burning process of bricks has yet to be properly exploited. The main focus of this study is to enhance the structural properties of geopolymer composites using brick kiln incinerated rice husk ash waste. The Physico-chemical analysis of brick kiln rice husk ash indicates the presence of high silica (88%) content with the evidence of XRD and FTIR analysis, SEM images shows high porous structure and PSD analysis gives a bonding nature of particle size as binding ingredient. The geopolymer mixes were made manually with different percentage of RHA 0%, 10%, 20% and 30% replaced partially in Siliceous Flyash. To identify suitability of the mixture for geopolymer concrete production, properties like workability and fresh density of the mixture was investigated using manually casted cubes having a size of 100 mm and keeping for oven drying at 40° ±2 °C upto 24 h. Compressive strength as destructive structural test method was investigated at the respective duration of curing. The findings led to the conclusion that increasing the percentages of RHA in the combination improves the mixture for geopolymer concrete composites with the increase of curing time. At 10% RHA addition, the optimal compressive strength of 42.19 N/mm^2 was achieved. The compressive strength of the RHA was found to decrease by 0.8% at 10% addition, which is negligible when compared to the control geopolymer mix (i.e., mix with 0% RHA), implying that the RHA from brick kilns can be employed to improve the structural qualities of geopolymer concrete composites.

1. Introduction

Global Cultivation of rice is a principle source for millions of households. Because of the increasing rice demand, the world paddy production was estimated to 782 million metric tons followed by the statistics of Food and Agricultural organization [1]. In 2018 India has become a second productive country by producing about 172.58 million tons of rice [2]of which 20% of rice husk will be generated after milling process which accounts approximately 34.5 million tons per annum [3]. Rice husk is considered as a low density agricultural waste material which are burnt in ambient atmosphere and results in rice husk ash which causes serious issue of global warming [4]. The annual global production of rice husk ash (RHA) is estimated to be around 20 million tonnes and are being disposed for its less commercial awareness succeeding to the plant infertility and environmental pollution [5].

Concrete is versatile abundantly used material in construction industry. As the construction activities are raising up there is a huge demand of finding an alternative to the concrete binding constituent i,e portland cement since it's manufacturing releases approximate greenhouse gas (CO_2) [6]. Hence, many researchers are focusing on improving the quality, strength and control the carbon emission in concrete by using sustainable materials like coal waste, fly ash, graphene, recycled plastic, ground granulated blast furnace (GGBFS) & rice husk ash (RHA) etc. Due to the presence of amorphous silica in the range of 90–95%, rice husk ash has the potential to substitute portland cement, resulting in improved qualities such as durability and impermeability by generating an extra

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Fig. 1. Brick stacks with Agro waste rice husk ash after stabilization.

calcium silicate hydrate gel (C–S–H) in the matrix [7]. Furthermore, RHA is used in various applications such as synthesis of silica gel, activated carbon, zeolites, silicon nitrite, construction chemical (Admixture) and carbide etc. [8].

The issue of greenhouse gas emission with cement production led to the development of geopolymer which is paving path as an alternative binder being first introduced by a french researcher Josef Davidovits, Geopolymers are semi crystalline or amorphous three-dimensional composite formed from silica alumina rich raw materials [9]. Geopolymer precursors includes fly ash [10–12], metakaolin [13–15], silica fume [16,17], rice husk ash [18], ground granulated blast furnace slag (GGBS) [19–21], calcined water treatment sludge [22], pond ash [23] and nano materials [24]. The alkaline solution made of hydroxide with a high concentration (>5 M) that can dissolve the amorphous fraction of solid particles. A sodium/potassium silicate solution provides the appropriate quantity of soluble silica to confront Al oligomers and produce polysilates. These two silicate solutions (KOH/NaOH) are critical for the effective and efficient sustainability of geopolymers [25]. Locally generated sustainable and cleaner geopolymers should be created with renewable resources, with minimal transportation costs, environmental effect, and manufacturing energy requirements, especially for developing nations and the difficulty of waste management. Previous studies have utilised thermal power plant by product as a precursor material for geopolymer concrete production which have great influence. In order to explore and manufacture with agro waste inorganic materials, performance has become increasingly important, effective utilization of rice husk ash obtain from brick kilns are not being done due to the lack of awareness, hence the aim of this study is to see how kiln rice husk ash (KRHA), a byproduct of the brick firing process, affects physiochemical properties and structural qualities of geopolymer matrix following the optimum mix proportion of rice husk ash of produced geopolymer composite.

2. Experimental methodology

Methodology compiles selection of materials & its preparation, characterization of various chemical & physical properties, design synthesis and structural properties of this new class of agro industrial waste material. Also, the relationships of brick kiln rice husk ash (BKRHA) content with the destructive strength of different mix compositions are discussed.

2.1. Materials

The major raw material used in this study was Siliceous Fly Ash (SFA), a highly active mineral substance with a specific gravity of 2.08 g/cm^3 calculated using kerosene and a le chatelier flask in accordance with IS 4031 part 11 and rice husk ash is incorporated as supplementary binding material. Rice husk ash (RHA) was procured from a brick kilns of N S Brick Industry located at channapatna, Ramnagaram. The RHA manufacturing process with 0.4% amorphous carbon is narrated as follows, the rice husk as fuel stabilizer is filled between the stacks of bricks in intermittent kilns which was maintained in an aerobic condition. Bricks are fired in batches upto 15 days by maintaining the temperature approximately 600°–800 °C then the fire is allowed to die out and the bricks are allowed to cool after they have been fired. The RHA residence time in the furnace was 15 days, at this stage the process will results in the unground rice husk ash which is an amorphous reactive inorganic material [33] and industrial waste dumping on the landsides. Fig. 1 represents the rice husk ash produced from brick kiln.

2.2. Materials preparation

The resulted unground amorphous brick industrial rice husk ash was grinded using high pressure suspension grinder mill to make fine powder less than 90 μm approximately, aiming to the usage as supplementary cementious material. Rossella et al. [26] says that the finer particle with higher grinding time will improve the concrete properties. The supplementary precursor sizes varies from 1 μm to 350 μm to assimilate the role of raw materials in geopolymer matrix development.

2.3. Characterization of brick kiln rice husk ash (BKRHA)

The most extensively utilised instrument by researchers is X-ray diffraction (XRD), which is a non-destructive technique. The crystal structure of metal-alloys, minerals, inorganic compounds, polymers and organic materials can all be determined using this instrumental analysis. The powder diffractometer method was used to record the X-ray diffraction patterns of powdered samples, which has various applications including qualitative phase analysis and quantitative phase analysis. In this study, P A Nalytical's X-ray Diffractometer using Cu Kα (λ = 0.15405 nm) radiation with nickel filter is used for determining the various diffraction pattern of BKRHA and Class F Flyash. The patterns of XRD were recorded at a scan rate of 2 deg min^{-1} with an angular resolution of 0.005°.

2.4. Scanning electron microscopy (SEM)

The most versatile technique to investigate the microstructure, morphological surface and topology [27]. The inorganic materials should be coated with gold using auto fine gold coater and microstructure was recorded with TESCAN-VEGA3 LMU Scanning Electron Microscope (SEM) by depositing a little amount of powdered sample on carbon tape. At least four locations were observed for each sample, and overall morphological features were considered for comparison.

2.5. Particle size distribution (PSD)

Malvern Mastersizer 2000 laser diffractometer were used to analyze the particle size distributions (PSD) of the brick kiln rice husk ash (BKRHA) samples. The PSD analysis were conducted a 20 s by swirling at 2600 rpm with isopropanol (refractive index 1.378). For PSD calculations, the BKRHA samples refractive indexes were 1.544 and 1.68 respectively. It is to be noted that PSD analysis neglects RHA porous structure. It has been verified that grinding RHA to a finer PSD does not always imply increased reactivity, owing to the loss of its mesoporous structure. As a result, RHAs with finer PSD do not always suggest increased ash reactivity.

2.6. Fourier transform infrared spectroscopy (FTIR)

The material's FTIR spectra were obtained in KBr pellets on a Perkin Elmer FTIR instrument (with a resolution of 4 cm^{-1}). The solid sample of each micro particle was finely crushed with pure and dry KBr and it was pressed in a hydraulic press to form a thin transparent pellet. The solid samples are extremely finely divided and mixed well to get pellet with uniform composition, the spectrum of the pellet was noted in the range of 4000–400 cm^{-1}.

Table 1
Proportions of different geopolymer mixes.

GCM's (kg/m^3)	SFA	BKRHA	NaOH	Na_2SiO_3	12 mm CA	CSD	L/S
10FAG100	449.5	0	74.10	185.25	1099.2	589.9	0.59
10FRG9010	404.5	44.95	74.10	185.25	1099.2	589.9	0.59
10FRG8020	359.6	89.9	74.10	185.25	1099.2	589.9	0.59
10FRG7030	314.65	134.85	74.10	185.25	1099.2	589.9	0.59

2.7. Thermo gravimetry analysis (TGA)

Thermo gravimetry analysis were performed in a Shimadzu TGA-50 thermo balance under 50 ml/min of Nitrogen and 10 °C/min of heating rate at a room temperature of 800 °C.TGA & DTA analysis was used to inspect the thermal stability of the sample.

2.8. Design synthesis and proportions

The scientific approach of mix design was developed by quantity mass method to illustrate the industrial waste geopolymer concrete to achieve suitable workability and strength. Fly ash a by-product of thermal power plant which is accessible in Raichur Thermal Power Station (RTPS), Karnataka. This material has favourable characteristics to produce geopolymer concrete and hence in this study siliceous fly ash is considered as a primary source [34,35]. The secondary binder is assigned to the rice husk ash obtained from brick industry kilns to be used as a supplementary binder in siliceous flyash. Sodium based alkaline activators are utilised for making the three dimensional polymorph with silico alumina rich materials. The reason of selecting sodium hydroxide as alkali activator because of its economy and accessibility compared to potassium hydroxide where 99% purity was found in the form of pellets and flakes. In this study 10 M (10 M) solution was prepared by adding 400 g of NaOH flakes in 1 L of double distilled water. The water glass or silicate of sodium solution mass ratio (SiO_2 to Na_2O) is 1.76 (SiO_2 = 29.52%, Na_2O = 16.8% and water = 53.68%). The liquid solution of sodium based silicate and hydroxide are equilibrated to room temperature of 27 ± 1 °C before using in the mixture. Crushed stone dust (CSD) confirming to zone 2 was used as fine aggregate with specific gravity of 2.56, fineness modulus of 2.92 and 1.95% of water effective absorption. The employed coarse aggregates was 12 mm down size crushed basalt jelly with specific gravity of 2.65 and 0.92% of water absorption. Aggregates were taken in saturated surface dry condition to enhanced uniformity in the mix. The four geopolymer concrete mixes (GCMs) were made by alkaline activating siliceous fly ash with different volumes of brick kiln rice husk ash by maintaining a constant liquid to solid ratio (L/S) of 0.59. The siliceous fly ash was replaced with 0% (FAG100), 10% (FRG9010),20% (FRG8020) and 30% (FRG7030) of industrial rice husk ash obtained from brick kilns. The design and composition of several blends for 10 M compositions are shown in Table 1; 10 cm cubic specimens were used for the destructive strength and physical appearance measurements. All prepared samples were initially cured at oven temperature at 40 °C for 24 h before demoulding and then demoulded specimens were subjected to further curing at a standard room condition of 27 ± 1 °C and 70 ± 2% relative humidity until testing durations.

Fig. 2. Slump cone setup as per BIS 1199.

Fig. 3. Compression testing machine of 3 Tons capacity.

3. Tests methods

3.1. Workability and fresh density

Workability is a composite property where the fresh blend can be moulded into any desired shape. In accordance to BIS 1199, the slump cone test was used to measure the mixability of fresh geopolymer concrete. The cone dimensions were compiled with a bottom diameter of 200 mm, a top diameter of 100 mm, and a height of 300 mm. The cone was eccentrically placed on the non-absorbent metal sheet and the fresh geopolymer concrete (GPC) was filled in three layers following the uniformity by tamping each layer 25 times with a sufficient tamping pressure. Then after, the top surface of cone is wiped and levelled. The prepared cone mould is lifted instantly which allows the concrete to subside and the subsidence is referred as slump of geopolymer concrete as shown in Fig. 2.

The fresh concrete unit weight was determined using ASTM C138. The unit weight of concrete was measured by considering 100 mm cubic mould as per BIS 10086. The cubic mould volume should be known. The fresh geopolymer mixture was filled, levelled with the plainer and vibrated using table vibrator for 30 Seconds. The weight of the empty mould and the weight of the concrete filled mould were measured separately. Below equation describe the formula to calculate the fresh density.

$$\text{Unit Weight} = (F_m - E_m)/V$$

where, 'F_m' is mass of concrete filled mould in 'kg' and 'E_m' is empty mould mass in 'kg' and 'V' is the volume of mould i,e 1×10^{-3} m^3.

3.2. Compressive strength

Compressive strength of any material is characterised as its resistance to failure when subjected to compressed loading and determining its

Table 2
Chemical composition of binder.

Modules		SFA	BKRHA
Chemical Composition in oxides (%)	Silica (SiO_2)	62.2	88.84
	Alumina (Al_2O_3)	24.9	0.81
	Iron (Fe_2O_3)	5.2	0.83
	Magnesium (MgO)	1.6	0.44
	Sulphur (SO_3)	0.75	0.35
	Calcium (CaO)	2.80	1.68
	Sodium (Na_2O)	1.20	0.18
	Potassium (K_2O)	0.3	2.06
	Loss on ignition (30 min)	1.05	2.73

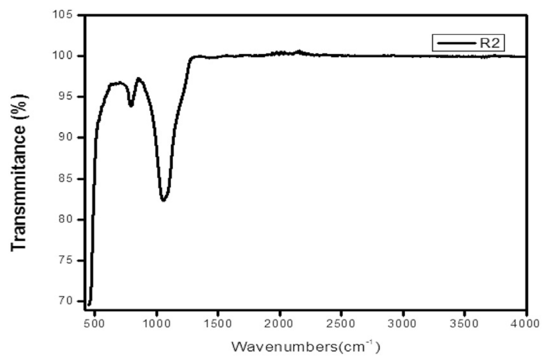

Fig. 4. Absorption spectra in the infrared region of BKRHA.

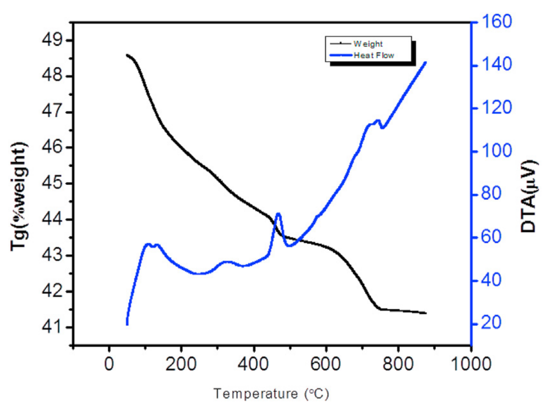

Fig. 5. TGA & DTA plots of BKRHA.

efficiency in operation. This test was performed as per IS 516 specification on the prepared GPC samples of different compositions. The test was performed on 100 mm cubic samples at respective days of curing using a 3000 kN digital Compression Testing Machine manufactured by AIMIL as shown in Fig. 3. The application of load should be done without shock and taken as 140 kg/cm^2/min.

4. Results and discussions

4.1. Chemical characterization of BKRHA

Brick kiln rice husk ash (BKRHA) and Siliceous flyash chemical compositions of both samples were analysed by wet chemical method (silica, sulphate, calcium, magnesium, iron and aluminium etc. by gravimetric method, following chloride by titration method) as per BIS 1727–1963 reaffirmed 2018, results shown in Table 2, indicates that BKRHA contains high amount of silica content compare to the Flyash, aluminium is 0.81%, loss on ignition is 2.73% respectively, other constituents is very low percentage compare to class F flyash. The

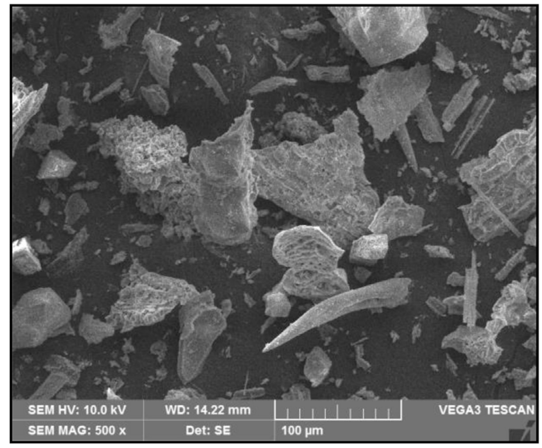

Fig. 6. Morphology of brick industrial rice husk ash.

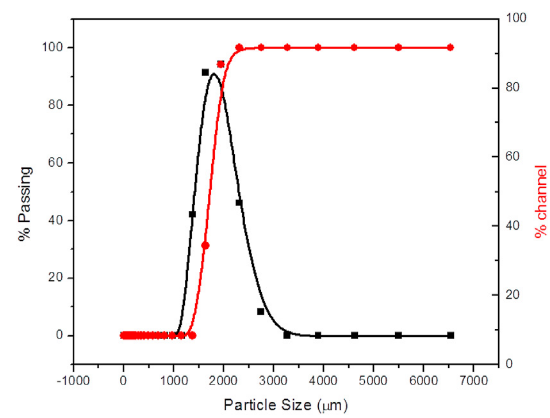

Fig. 7. Particle size distribution of RHA.

characterization of BKRHA indicates that high amount of Silica in the amorphous and high porous content. Hence, BKRHA material is used as construction binder in the partial replacement of low calcium Flyash. The present study was performed by replacing 10 to 30% of BKRHA waste to impart in geopolymer application and the results are shown below.

The FTIR spectra of BKRHA material is shown in Fig. 4. Stretching of Si–O–Si bonds in amorphous Silica is responsible for the strong band at 1056 cm^{-1}. The Si–O symmetric stretching and bending vibrations are correlated to the band at 797. The FTIR spectra indicate that the BKRHA includes a majority of silica content in terms of oxides (Si–O–Si), and also calcium, magnesium, iron and aluminium oxides are very small amount present in the BKRHA material.

There are two main thermogravimetric phenomenon's in the graph as shown in Fig. 5. The first occurrence (I) corresponds to the loss of mass related to the moisture content from room temperature to 105 °C. The loss of mass can be divided into three stages. The first is between 35 °C and 70 °C where the moisture present is evaporated in pores above 0.08 μm. The second (II) is between 200 °C to 400 °C which tends to the loss of organic impurities and the third phenomenon (III) corresponds to de at about 400 °C upto 600 °C indicates the presence of silica content.

The rough surface of rice husk ash before grinding under higher magnification and also fineness of before grinding is between 300 μm to 350 μm, it can be observed that large pores and needle like protrusion contributes to the surface roughness. After grinding, BKRHA particles have a relatively smoother surface and irregular shape as shown in Fig. 6. Large distinctive pores of rice husk ash are destroyed during the process of grinding. However, particles tend to retain their porous surface through minute pores. The non-spherical shapes and porous morphology

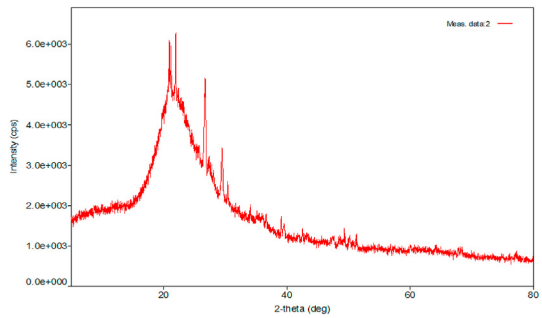

Fig. 8. XRD pattern of BKRHA.

Table 3
Physical properties of Geopolymer binders.

Modules		SFA	BKRHA
Physical Properties	Specific gravity	2.08	1.9
	Particle retained on 45μ Sieve	1.3%	29.7%
	Specific surface area (m^2/kg)	488	339

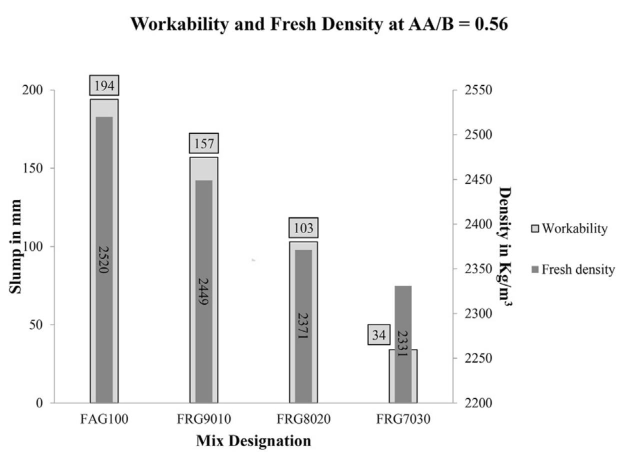

Fig. 9. Slump and fresh unit weight of GPC mixes.

of rice husk ash can have an adverse effect on flow ability of BKRHA blend cement composites.

Particle size distribution of rice husk ash after grinding is shown in Fig. 7. BKRHA particles the fineness is less than 90μ. The mass median diameter (d50) and d90 of BKRHA particles were 4–6 and 8–20 μm, respectively. The large particle size of mortar constituents results in blockage or clogging of the nozzle.

The X-ray diffraction patterns of BKRHA shown in Fig. 8. The crystallinity of SiO_2 can be qualitatively assessed by comparing the peaks around $2\theta = 20^\circ$–30° of BKRHA. A broader peak of brick industrial rice husk ashes around $2\theta = 22^\circ$ indicates the presence of amorphous silica (SiO_2), confirms the presence of quartz, mullite and hematite. This indicates that BKRHA are partially crystalline in nature.

4.2. Physical characterization

The physical properties of SFA and RHA were listed in Table 3 following specific surface area (SSA), specific gravity and 45 μm retention, the SSA could be one of the valuable reason for the ultra-high reactivity of RHA owing to the larger contact area between particles.

The workability test was created to investigate the effects of rice husk ash properties on siliceous fly ash and in the present scenario the degree of flow was considered as very high. Flow is made up of several proportions, including plasticity, consistency, and cohesion. Plasticity and

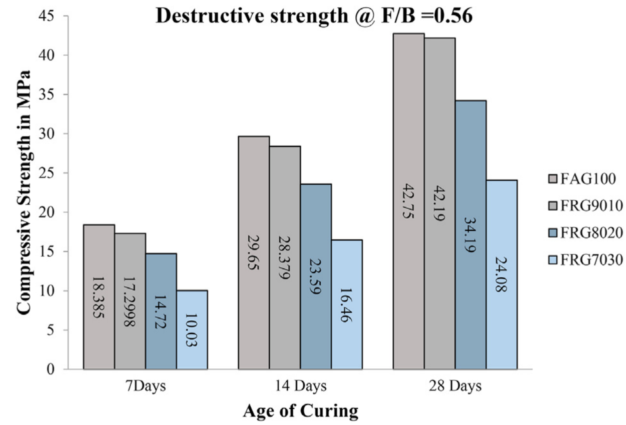

Fig. 10. Compressive strength values of GPC mixes at respective ages.

cohesion are difficult to assess on site but consistency, on the other hand is usually utilised as a metric of workability [28,29]. The ash content of rice husks and the material properties have a significant impact on the workability of geopolymer concrete. Fig. 9 shows the values of workability and fresh density of geopolymer concrete with different designation of mixes. The brick kiln rice husk ash has a great effect on workability of geopolymer concrete. It was noticed that geopolymer concrete mix containing class F flyash (FAG) or siliceous fly ash have higher workability than other types of mixes, Due to rice husk ash fineness and lower specific surface area the grading of mix affected the flow of geopolymer concrete. The 100% FA geopolymer concrete (FAG100) and 90% FA with 10% BKRHA geopolymer concrete (FRG9010) shows higher flow than the considerations taken. FRG8020 are within the limit by 4.761% more than the minimum value of considered flow and FR7030 shows 70% less flowability than the minimum consideration, hence it needs more alkaline activator or additional chemical admixture (Super plasticizer) to achieve a good flow compared to other grades. Fresh density or fresh unit weight properties of geopolymer concrete was conducted directly after mixing and is measured for all four mixtures as shown in respective Fig. 9. The density of the fresh unit weight was in significant decrease due to the increase of BKRHA content. FAG 100 exhibits a maximum density and other supplementary mixture exhibits a reduction in fresh unit weight which is due to the light weight of supplymentary material. The results made into observations that the sufficient unit weight has been achieved in all mixes and it is more than 2300 kg/m^3 which satisfy the needs of non-structural applications.

4.3. Effect of BKRHA contents on the mechanical performance of siliceous flyash based geopolymer concrete

Compressive strength is considered as most precise test to conduct the brittle load carrying capacity of the material. The destructive strength of geopolymer cubic specimens of size 100 mm × 100 mm × 100 mm were tested in compressive testing machine (CTM) at 2.33 Kn/s rate of loading. The graph shown in Fig. 10 demonstrates the compressive strength of FAG100, FRG9010, FRG8020 and FRG7030 geopolymer samples at the ages of 7, 14 and 28 days respectively. It is clearly seen that in all mix proportions, the age of curing results in the increase of compressive strength, this could be due to the presence of about 90% silica in BKRHA and the formation of strong silico bonds (Si–O–Si) rather than silico alumino bonds (Si–O–Al) [30–32]. For the reference FAG100 Mix, the compressive strength at 7 d is 18.385 MPa which incremented to 29.65 MPa at 14d and 42.79 MPa. The compressive strength of FRG9010 mix shows a negligible decreasing value compared with the reference FAG100 mix at the same age. However, it shows a sharply decreasing in compressive strengths at all ages when the addition dosage of BKRHA up to 30% in the intervals of 10%. This indicates that the BKRHA contributes less to the compressive strength development of FRG in comparison to

Fig. 11. Failure of specimen after compressive destruction.

the FAG. It is probable related to the limited availability of Al resource due to the partial replacement of SFA by BKRHA, resulting to this phenomenon. The 28 days strength of Flyash rice husk ash (FR) geopolymer concrete samples containing 10%, 20% and 30% of BKRHA are 42.19 MPa, 34.19 MPa and 24.08 MPa in which 10% of BKRHA is found to be optimal percentage to be used as partial replacement for siliceous flyash at 10 M NaOH concentration, Na_2SiO_3/NaOH of 2.5 and alkali activator to binder ratio of 0.59.

The Hardened concrete density is also one the important aspect of mechanical property where it depends upon the unit weight of constituent materials and volume of void space after the age of curing. The density of FAG100 specimen was 2379 kg/m^3 at the age of 7 days which reached to 2408 kg/m^3 at 14 days and 2473.3 at 28 days respectively. As the curing time increases, the development of mechanical performance was also increases in all geopolymer concrete mixes. But the results made into specific observation that the density decreased constantly with the increase of BKRHA contents, the density reaches 1.06%–1.205% lesser value in contrast to FAG100 at 28 days when BKRHA content replace up to 30%. The reason may also states as the lower density of BKRHA may cause a reduction in density in the geopolymer system.

In this study the compressive strength of geopolymer concrete mixtures is related to the density using statistical method. The results of the statistical method generate an equation in analytical form to find the respective geopolymer concrete results of different proportions. It can be seen that the samples with higher densities have a greater compressive strength. In Fig. 12 a linear trend line of all mixes (FAG100, FRG9010, FRG 8020 & FRG7030) with correlation coefficient varies from 0.96 to 0.99 is drawn to find a relation between compressive strength to hardened density which indicates the accuracy of results. The failure pattern of 100 mm cube is shown in Fig. 11.

5. Conclusions

1. The Agro waste brick kiln rice husk Ash contains high amount of silica and can be used as SiO_2 provider for geopolymer materials to increase SiO_2/Al_2O_3 ratio and Si–Al bonding.
2. BKRHA Chemical composition results indicates that high amount of silica content, this is evidenced by other analysis FTIR, XRD pattern of BKRHA partially crystalline in nature, high porous in structure, finesses of the material is d50, d90 is 4–6 μm and 8–20 μm, hence all the results is evidence it is very good material for the replacement of flyash.
3. The hardened density and compressive strength shows an improvement with the RHA addition as increase in the age of curing.
4. The compressive strength of geopolymer mix with rice husk ash was optimised with the value of 42.19 N/mm^2 with 10% replacement at the age of 28 days by maintaining a hardened density of about 2400 kg/m^3.
5. The optimal percentage of brick kiln rice husk ash can be used for the precast paving applications and since the rice husk ash contain less alumina in its chemical composition further studies can be made by using alumina based alkali activators or alumina rich precursors.

Credit author statement

Shaik Numan Mahdi: Investigation and Methodology. **Dushyanth V Babu R**: Project administration and supervision. **Shivakumar M**: Resources and validation. **Mustafa Al Bakri Abdullah**: Conceptualization and Formal analysis.

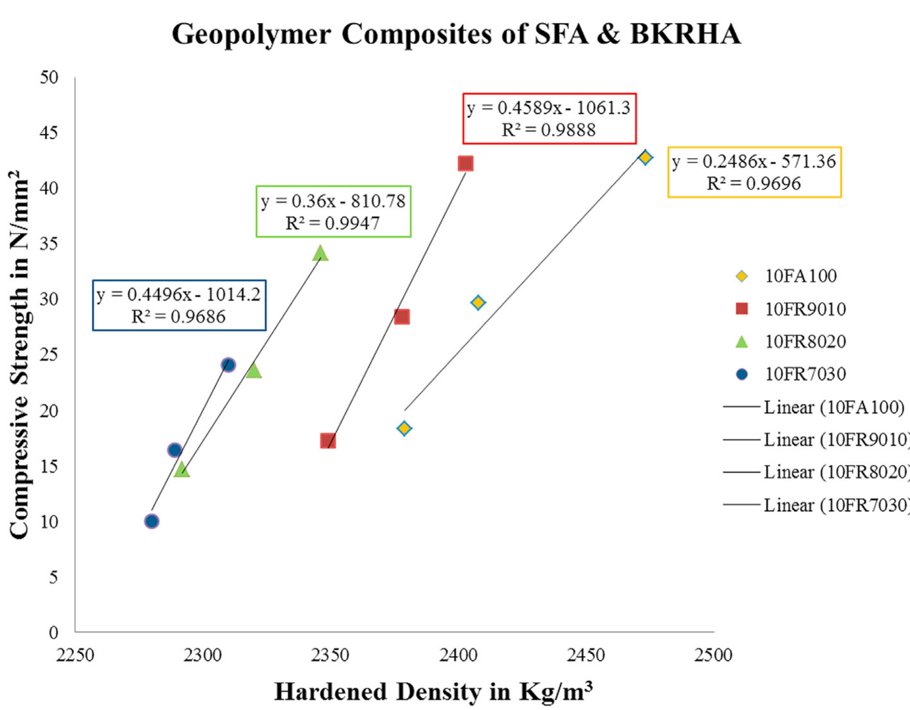

Fig. 12. Linear correlation of hardened density and compressive strength of different GPM's.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crgsc.2021.100193.

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