Stabilization of Red Mud using Mineral Precursors by Geopolymerization Process

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Abstract. Red mud (RM) is an alkaline industrial waste product generated during the processing of bauxite by Bayer's process. Red mud is high alkaline, exceedingly caustic and harmful to soil and biological forms posing a significant disposal challenge. The alkalinity of red mud can be successfully utilized to initiate geopolymeric reaction with industrial waste materials rich in alumino-silicates to stabilize the red mud. In this study using mineral precursors like granulated blast furnace slag (GBFS) and rice husk ash (RHA), an attempt has been made to stabilize red mud. The quantity of GBFS and RHA is varied as 0, 5, 10, 15and 20% by weight of the RM-GBFS and RM- RHA mixes. Further additional doses of alkali (NaOH) solutions of 1, 2 and 4 M concentrations are added to accelerate the geopolymerization process. The plasticity properties, compaction characteristics, swelling and strength properties of treated red mud were determined at different curing periods. A noticeable increase in strength was observed with addition of mineral precursors, doses of alkali and curing period. Mineralogical analysis endorses the formation of geopolymeric products which improve the geotechnical properties in addition to encapsulating the metallic ions present in virgin red mud. Atomic absorption spectroscopy (AAS) analysis also confirms reduction in the concentration of metals in leachate of stabilized red mud.

Keywords: *Red mud, Mineral precursors, Geopolymerization, Stabilization, Strength characteristics, Mineralogical and Microstructural characteristics.*

1 INTRODUCTION

Urbanization, rapid industrialization and the development of modern infrastructure produces huge amount of waste material which requires large area for disposal and storage. In recent decades, it has been clear that the use of industrial by-products in civil engineering projects has become a major issue. As a result, its use provides a partial answer to both ecological and environmental issues. Red mud is an industrial waste leftover that results from Bayer's bauxite alumina refining process. It is a type of solid waste that is naturally alkaline. On an average, 1.5 tonnes of RM are created from 1 ton of alumina, however due to its chemical composition, high alkalinity, and heavy metals content, its use in the real world is severely limited. Furthermore, it needs a considerable amount of space for storage and disposal, posing a serious environmental danger in terms of pollution of the surrounding land, air, and water, as well as human health. As a result, thorough treatment and research into the usage of this resource are required. The recovery of valuable elements presents in red mud, such as Fe, Ca, Al, Ti, V, Cr, Ni, Na, K, Mn, Zn, and others, has also been explored as part of the treatment processes. RM is also used as an adsorbent to absorb pollutants from the air and water, as well as to enhance fertility of soil. RM is high in Si, Al, Fe, and Ca, which can be utilized to make a geopolymer that, can be used to make cement, pottery, concrete, and bricks. Various studies on the use of RM in construction industris have been carried out. According to additional research, red mud can be used as a base material with higher strength by mixing it with various proportions of other industrial wastes rich in alumina and silica to create a new product using the geopolymerization method, which has significant economic and environmental benefits. Despite the fact that RM contains some toxic minerals that harm the environment, neutralization and de-alkalization technology is presently used. RM is mixed with rice husk ash gives an advantage of using in subgrade material with good strength properties (Deewa1 et.al. 2018). Also, synthesis and characterization of red mud and rice husk ash based geopolymer composites are used in various construction materials is performed in various studies (Jian et al. 2013). Further studies state that the strength development of solely ground granulated blast furnace slag geopolymers creates a huge impact on industrial site (Ikmal Hakem et al. 2020).

A geopolymer is a novel type of green gelation material created by the chemical interaction of natural minerals silica and alumina in the presence of an alkaline activator. At room temperature, the Si-O and Al-O bonds in the raw resources are broken and then rearranged by the alkaline catalysts (Duxson et al. 2007). Three processes are involved in the geopolymerization reaction mechanisms that are dissolution-recombination and solidification. The SiO_4 and AlO_4 from the first step the alumino-silicate materials are immersed in alkaline solution, then monomers are dehydrated and lead to alumino-silicate oligomers, resulting in the formation of a gel. Alumino-silicate polymeric gel is created by draining excess water from the gel phase. The polymerization of a geopolymer is a difficult process that is influenced by a variety of parameters such as raw material reactivity, Si/Al ratio, alkaline solution concentration, and curing conditions. The mechanical and microstructural properties of geopolymer are affected by this component. RM can be used with other highly active materials such as FA, GBFS, Metakaolin, RHA, and others for improved results. Geopolymer has the advantage of not requiring water for cure. Curing also takes place at normal temperature or below it. In the synthesis and characterization of geopolymer, the curing duration is critical. Further the microstructure, mechanical and chemical studies define the factor affecting red mud based geopolymer (Manjusha and Yashida 2021).

2 MATERIALS AND METHODOLOGY

2.1 MATERIALS

The experimental study includes stabilizing red mud with mineral precursors such as GBFS and rice husk ash (RHA), and assessing the geopolymer-based product formed in terms of physical, chemical, mineralogical, and morphological aspects, as well as comparing it to untreated red mud. The second section compares the behavior of experimental ways to stabilize red mud utilizing various ratios of RM-GBFS and RM-RHA mixes, as well as the addition of alkali activator at various quantities. Red mud (RM) was brought from Vedanta Aluminum Limited, Lanjigarh, Odisha. The red mud was air dried, homogenized, and crushed to powder to increase geopolymerization reaction and reduce compositional error in the final product. The granulated blast furnace slag (GBFS) was obtained from the Rourkela Steel Unit's (RSP) slag granulation plant in Sundargarh, India. It is produced during the pig iron manufacturing process. Silicates, alumino-silicates, and calcium are the primary components. The waste products were dried in the oven to remove the moisture in the raw material. RHA was obtained from Haripriya Agro Industry in M. Rampur, Kalahandi, India. It's also an industrial by-product generated by burning of rice husk to produce electricity, which is a renewable biomass energy source. Because RHA is composed of porous particles, it has less unit weight and a large external surface area. Growing environmental concerns and a demand for long-term biomass energy have led to a practical and cost-effective solution.

2.2 METHODOLOGY

In order to synthesis geopolymer, the red mud is mixed with mineral precursor like GBFS, rice husk ash, fly ash etc. In this research RM is mixed with GBFS and RHA with varying fractions ranging from 0% to 20% of the dry mass of the mixture at 5% increments. These mixes are termed as RM, RM-S1, RM-S2, RM-S3, RM-S4 and RM-R1, RM-R2, RM-R3, RM-R4 for GBFS and RHA respectively. Also desired amount of NaOH solution is added in quantity of 1M, 2M and 4M with these mixtures to form the geopolymer. The unconfined compression strength (UCS) tests were conducted on specimens compacted to their respective maximum dry density (MDD) at Optimum moisture content (OMC) and left for 0, 7, 14, and 28 days curing at constant temp of 27±2 ^{0}C. The physical, chemical, morphological and mineralogical properties of cured specimens were evaluated. This includes the GSD (Grain size distribution), SG (Specific gravity), LL (Liquid limit), PL (Plastic limit), Y_d (Dry density), OMC (Optimum moisture content), UCS (Unconfined compressive strength). All these tests were conducted as per the provisions of Indian Standards code of practice. The pH values are determined using an electronic pH meter.

3 RESULTS AND DISCUSSION

3.1 INDEX AND ENGINEERING PROPERTIES

The specific gravity of the RM, GGBS, RHA and RM-GGBS, RM-RHA mix are studied according to IS-2720 part-3(1980). The GGBS has the specific gravity (G_s) value of 2.84, which is higher than conventional earth material. However, the specific gravity of RM is found to be 3.24. This is found to be higher than that of GGBS (2.84) and RHA (2.16) due to the presence of higher percentage of iron. The specific gravity of RM mix with 5, 10, 15 and 20% GGBS or RHA are found to decrease with increase in GGBS and RHA as shown in Figure-1.

The PH of red mud and RM mixed with different fractions of GBFS and RHA is presented in Figure-2. It has been seen that after adding GBFS and RHA, the pH of the mixture is reduced because of the low pH value of GBFS and RHA.

Table-1. Index and engineering properties of raw materials

PHYSICAL PROPERTIES	**RED MUD**	**GBFS**	**RHA**
Colour	Red	Grey	Black
Specific gravity	3.24	2.84	2.16
pH	10.43	10.24	7.12
Liquid Limit (%)	29		Non-Plastic
Plastic Limit (%)	25	Non-Plastic	
Coefficient of uniformity (Cu)	11.88	1	---
Coefficient of curvature (Cc)	0.345	6	---
Optimum moisture content (OMC)	27.3%	19%	---
Maximum dry density (MDD)	1.65 g/cc	16.9 g/cc	---
DFS value (%)			

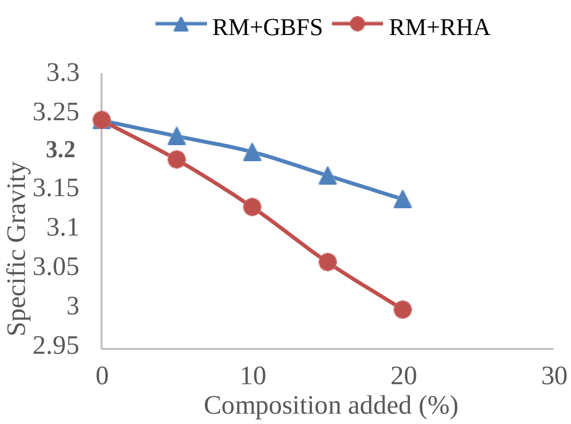

Fig.1. Specific gravity of RM- GBFS/RHA mixes

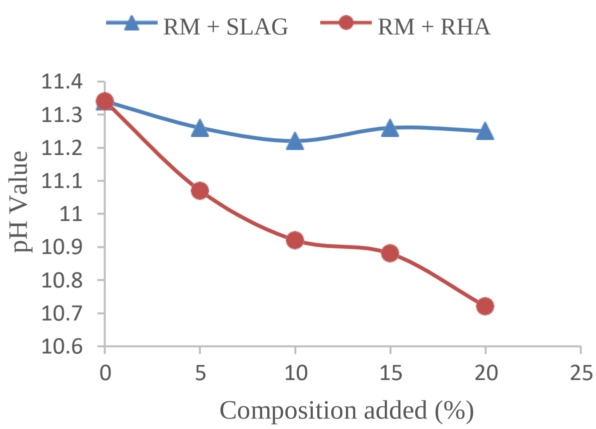

Fig.2. pH value of RM- GBFS/RHA mixes

The plasticity properties of red mud show that it has a low plasticity, with a liquid limit of 29% (<50%) and plastic limit of 25% and plasticity Index was found to be 4%. However, slag and RHA are found to be non-plastic material. The mixture of RM, GBFS and RHA with different fraction and its LL, PL are listed and the variation with GBFS and RHA is shown in Figure 3 (a) & (b) respectively. These tests were conducted as per IS-2720 part-5(1985).

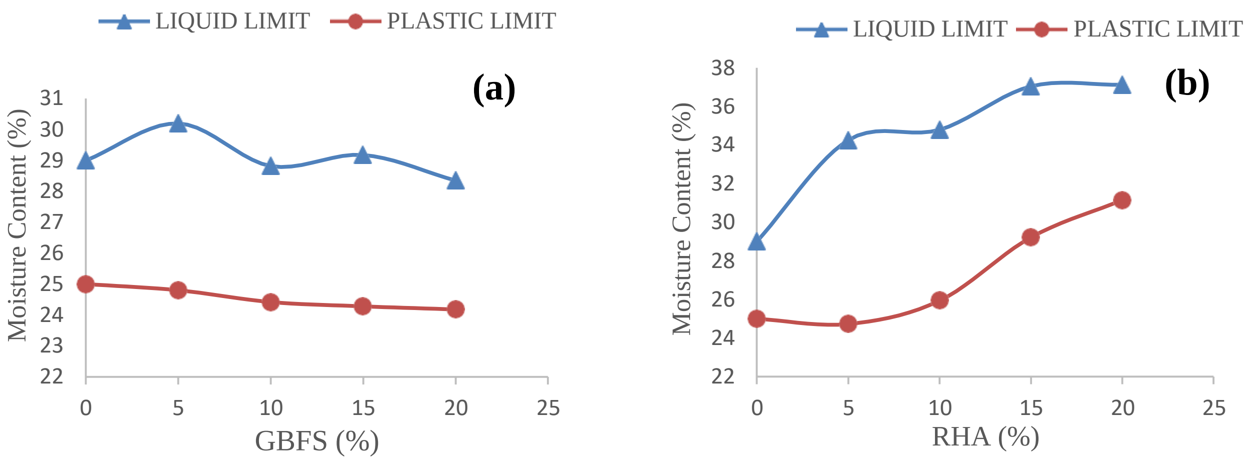

Fig.3**.** LL and PL of RM in addition with (a) GBFS and (b) RHA

The grain size distribution for RM, RHA and GBFS are made as per IS-2720 Part-4 (1985). The gradation curve of these materials is presented in Figure 4. From the grain size distribution and plasticity properties RM is categorized as low compressible silt (ML) as per IS-1498(1970).

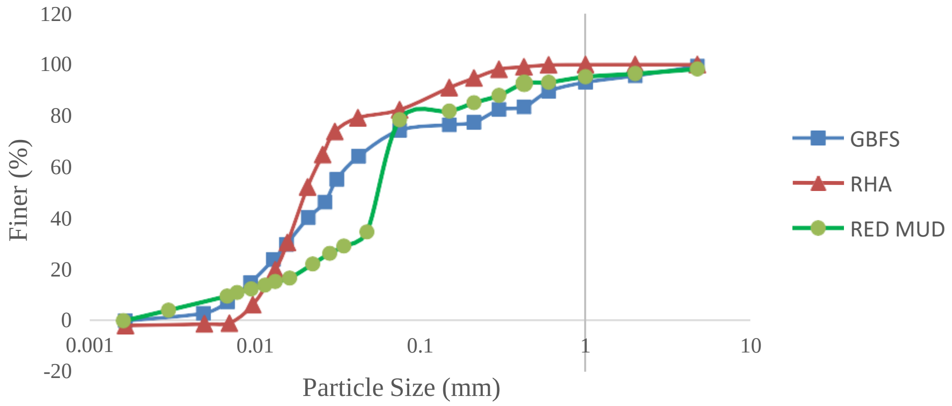

Fig.4. Grain size distribution curve of RM, GBFS and rand RHA

The differential free swell (DFS) value of raw materials that is RM, GBFS and RHA is presented in Table-1. It is observed that DFS values of these materials are negative in nature. Further, the DFS values of RM-GBFS and RM-RHA mixes are also negative. Materials like fly ash, rock powder, pure kaolinite minerals occupy a higher sediment volume in non-polar solvents like kerosene than in water and thus observed to have negative DFS values. This shows that there is no inter-particle attraction in the substances and that they are dispersive in nature. Figure 5 (A) & (B) show the values and change in DFS of RM-GBFS and RM-RHA mixes respectively.

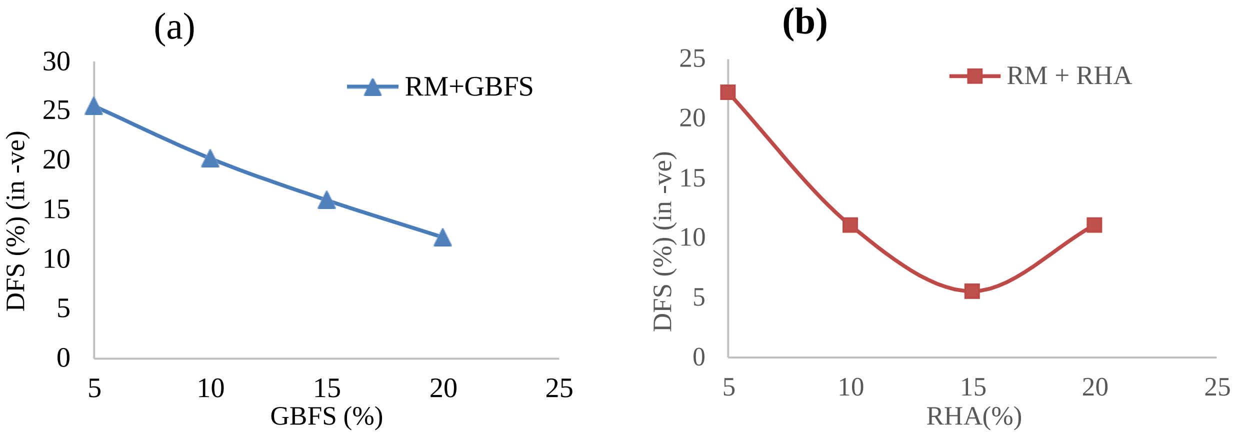

Fig.5**.** DFS values of (A) RM-GBFS and (B) RM-RHA mixes

Compaction tests were conducted on RM-GBFS and RM-RHA mixes using compactive efforts of 595 kJ/m3 and 2674 kJ/m3 as per IS-2720 part-7(1980) and the compaction curves were obtained. For each combination of RM-GBFS and RM-RHA, the OMC and MDD values were determined from the compaction curves. Figure-6 shows how MDD and OMC values change with GBFS content and RHA content. The MDD increases and the OMC falls in RM-GBFS mixtures as the proportion of slag added to red mud increases. Addition of GBFS results in change in gradation of the mix and reduces the plasticity values. This causes a well packing of particles during dynamic loading thus increasing the dry density. The decrease in OMC could be related to the loss of adsorbed water when red mud is replaced by slag. As the amount of RHA added to RM is raised, the MDD drops and the moisture content increases in the red mud RHA combination. The rise in OMC with RHA is due to the inclusion of RHA, which reduces the amount silt sized fraction and increases clay and colloidal sized particles with higher specific surface areas, requiring more water to lubricate the particle surface. This also implies that additional water would be required for greater compaction of the soil and RHA mixture. Figure 7 and Figure 8 show the moisture content and dry density relationship of RM-GBFS and RM-RHA mixture.

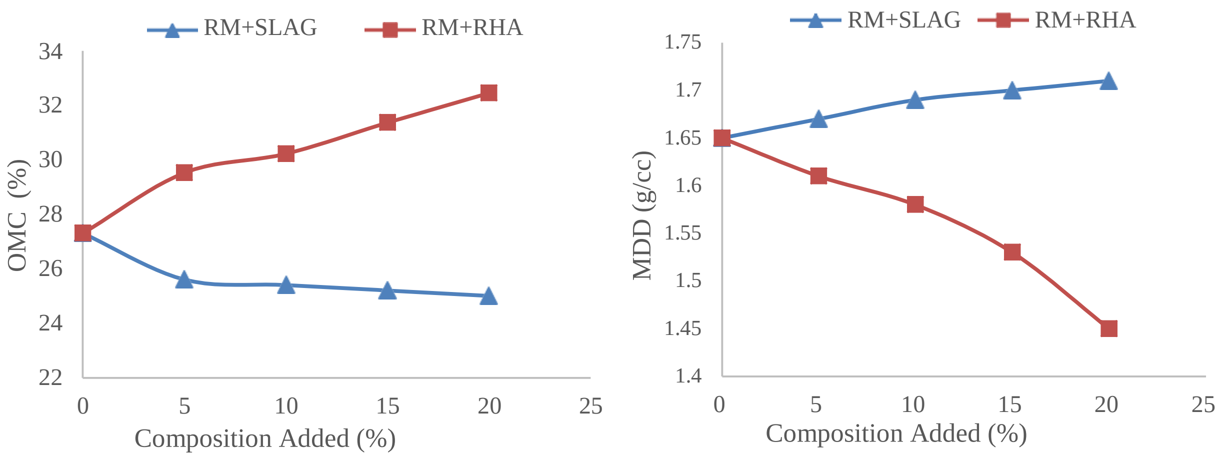

Fig.6. Variation in OMC and MDD with addition of GBFS and RHA

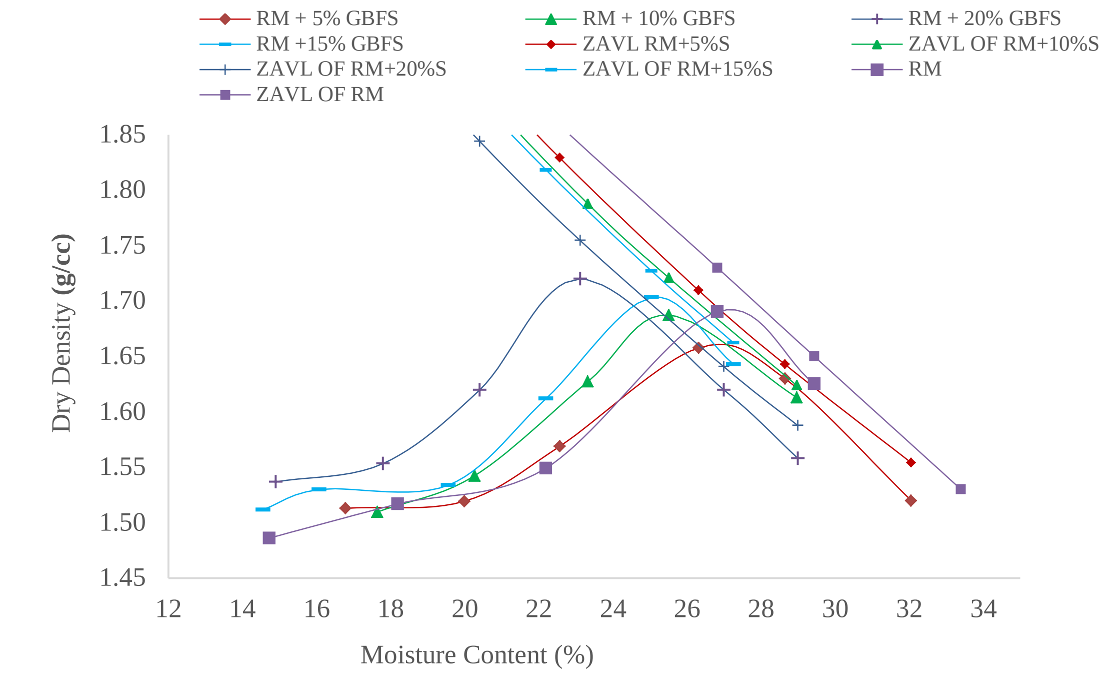

Fig.7. Compaction curves of RM-GBFS mixes

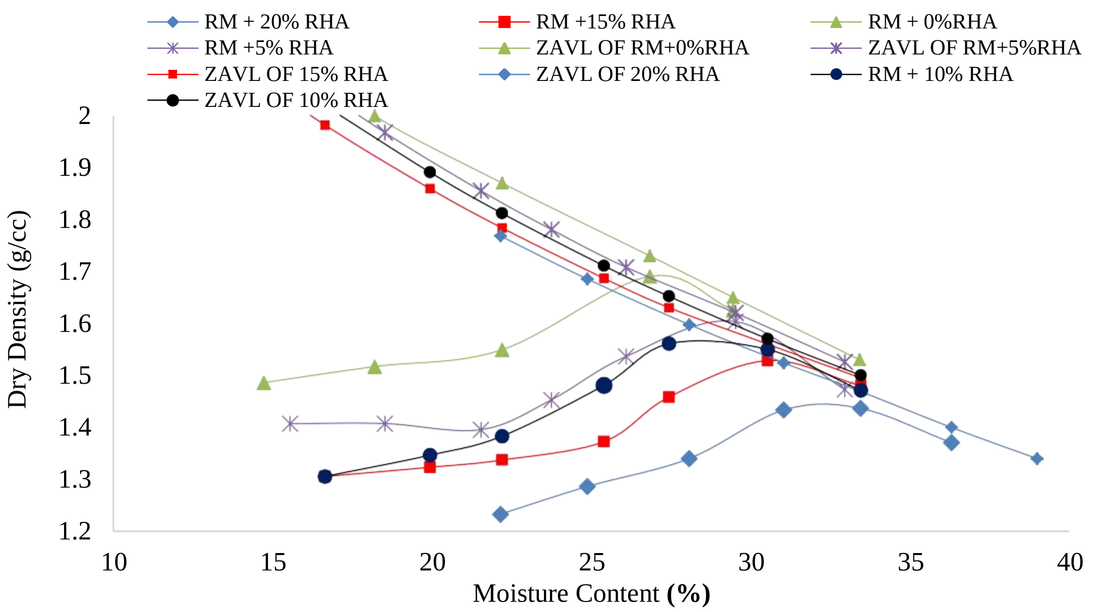

Fig.8. Compaction curves of RM-RHA mixes

Unconfined compressive strength (UCS) tests were carried out on RM-RHA and RM-GBFS mixes compacted to their respective MDD at OMC. These tests were conducted as per IS-2720 part-10(1991) code provisions with a loading rate of 1.25 mm/min. UCS test specimens were wax coated and cured at an average temperature of 30 ºC for 0, 7, 14, and 28 days. For each test conditions three identical specimens were tested and the average value is reported in Figure 9. Again, an extra additional dose of 1M, 2M and 4M NaOH solution were added to the RM-RHA and RM-GBFS mixes to accelerate the geopolymerization reaction. The UCS of these specimens was also determined after curing periods of 0, 7, 14 and 28 days. These results are presented in Figure10, 11 and 12 respectively.

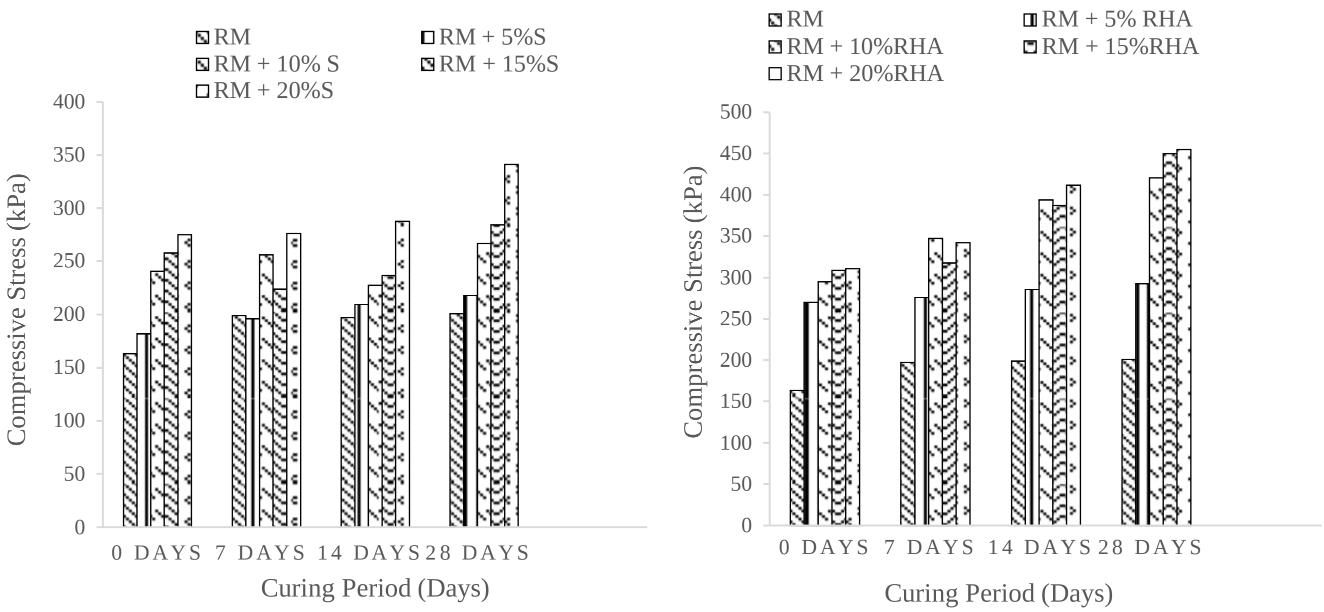

Fig.9. UCS of RM-GBFS and RM-RHA mixes at different curing periods

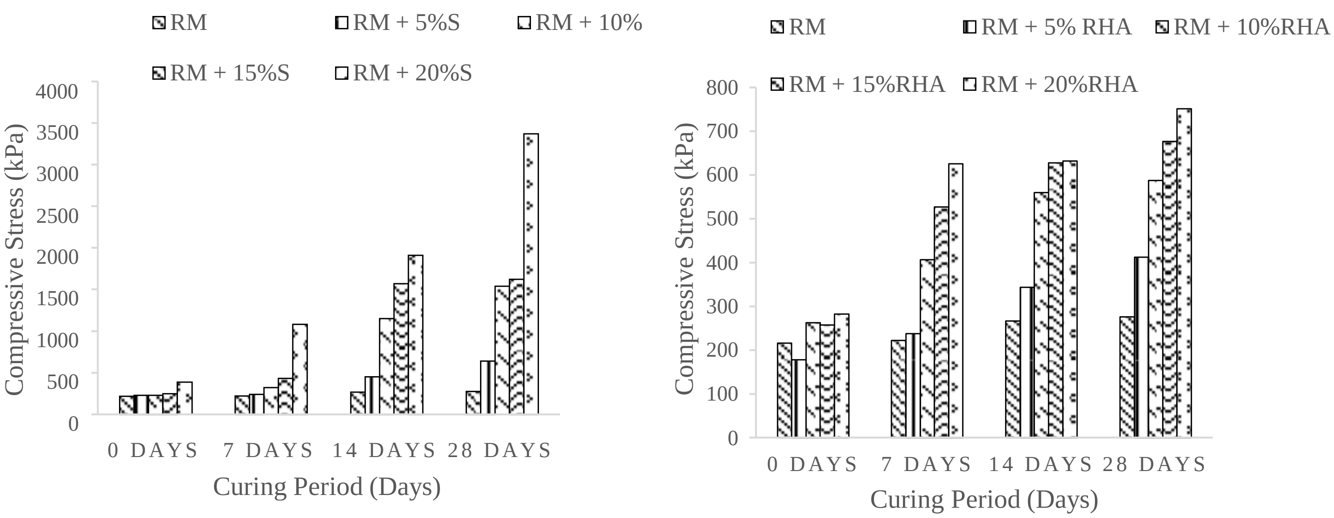

Fig. 10. UCS of RM-GBFS/RHA mixes with an addition of 1M NaOH solution at different curing period

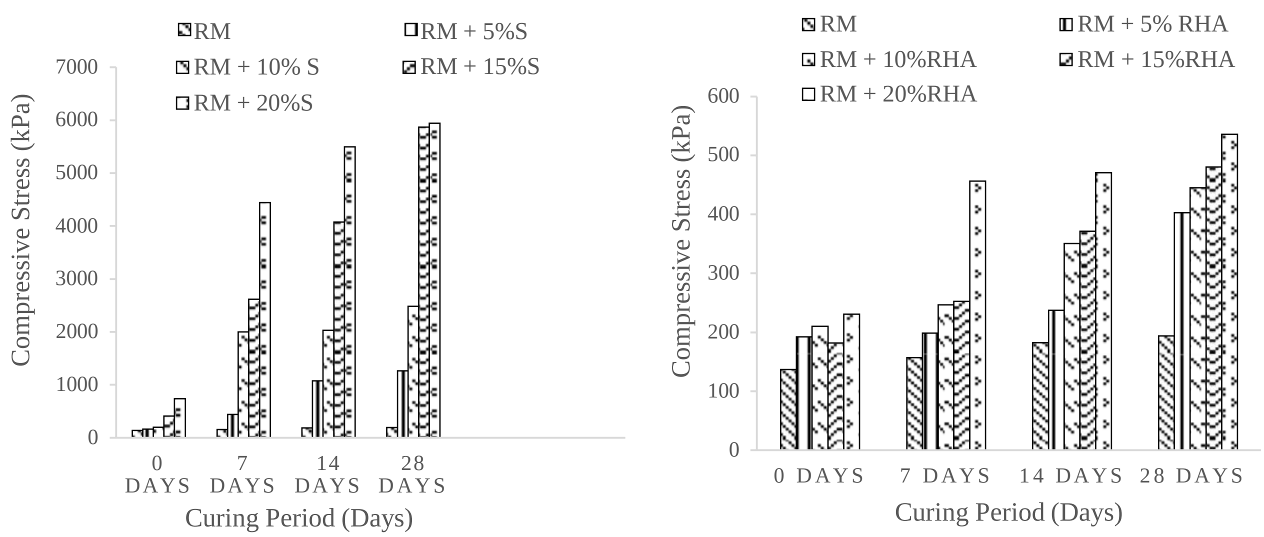

Fig. 11. Variation in UCS of RM with GBFS and RHA and an addition of 2M NaOH with curing period

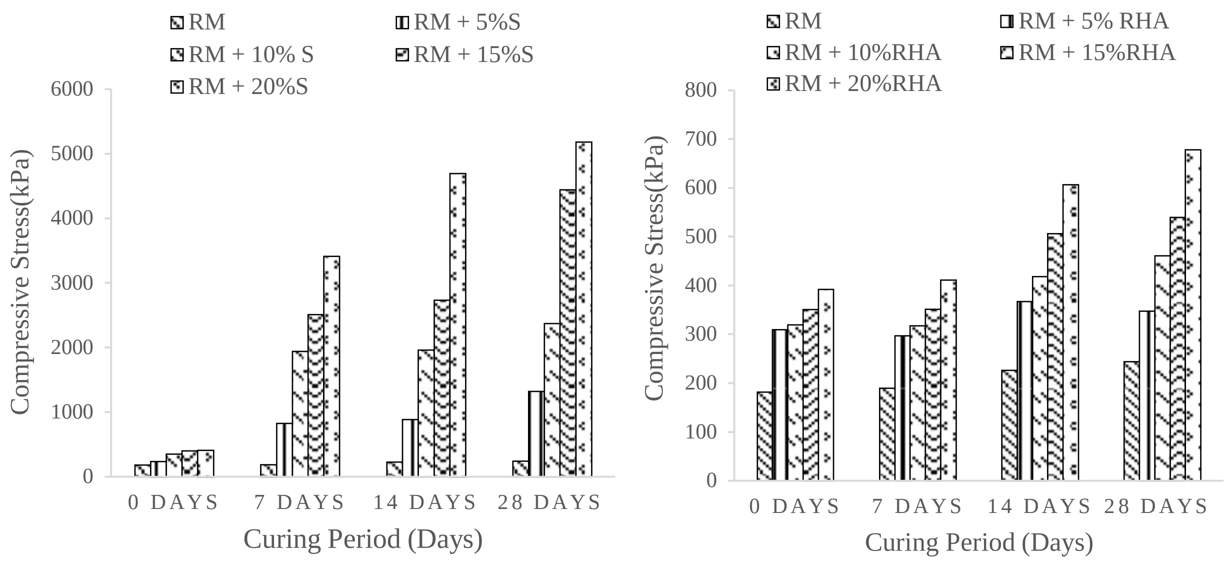

Fig. 12. Variation in UCS of RM with GBFS and RHA and an addition of 4M NaOH with curing period

Figure 13 (A), (B) & (C) show the XRD patterns of the RM, RHA and GBFS respectively and Figure 14(D) & (E) show cured RM–GBFS and RM-RHA geopolymers. The presence of hematite and calcite in RM is detected with sharp peaks. The lack of apparent broad humps in the RM pattern implies that the amorphous phases are either absent or present in small amounts. For geopolymerization, the RM offers primarily NaOH and Al in the form of amorphous Al_2O_3 or dissolved $NaAlO_2$, but little Silica. In fig-13(B) as seen in XRD plot of RHA, at 10–35°, the RHA pattern has one sharp peak overlaid on a broad hump. Cristobalite, a high-temperature silica polymer, is responsible for the steep peak. Amorphous silica, a significant component of RHA, is responsible for the very broad hump. The RHA contains mostly amorphous silica with cristobalite and trace crystalline quartz. According to its chemical makeup the XRD pattern of GBFS powder is shown in the Figure 13(C). It has a board hump that ranges from 30 to 40 degrees. The presence of an amorphous (glassy) phase accounts for this hump. The XRD pattern of the GBFS powder matches that of prior studies conducted by other authors. A quantitative XRD investigation previously determined that 97.7% of this GBFS is amorphous in nature, with minor crystalline content, with one sharp peak superimposed over a broad hump at 10–35° diffraction angles. Cristobalite, a high-temperature silica polymer, is responsible for the steep peak.

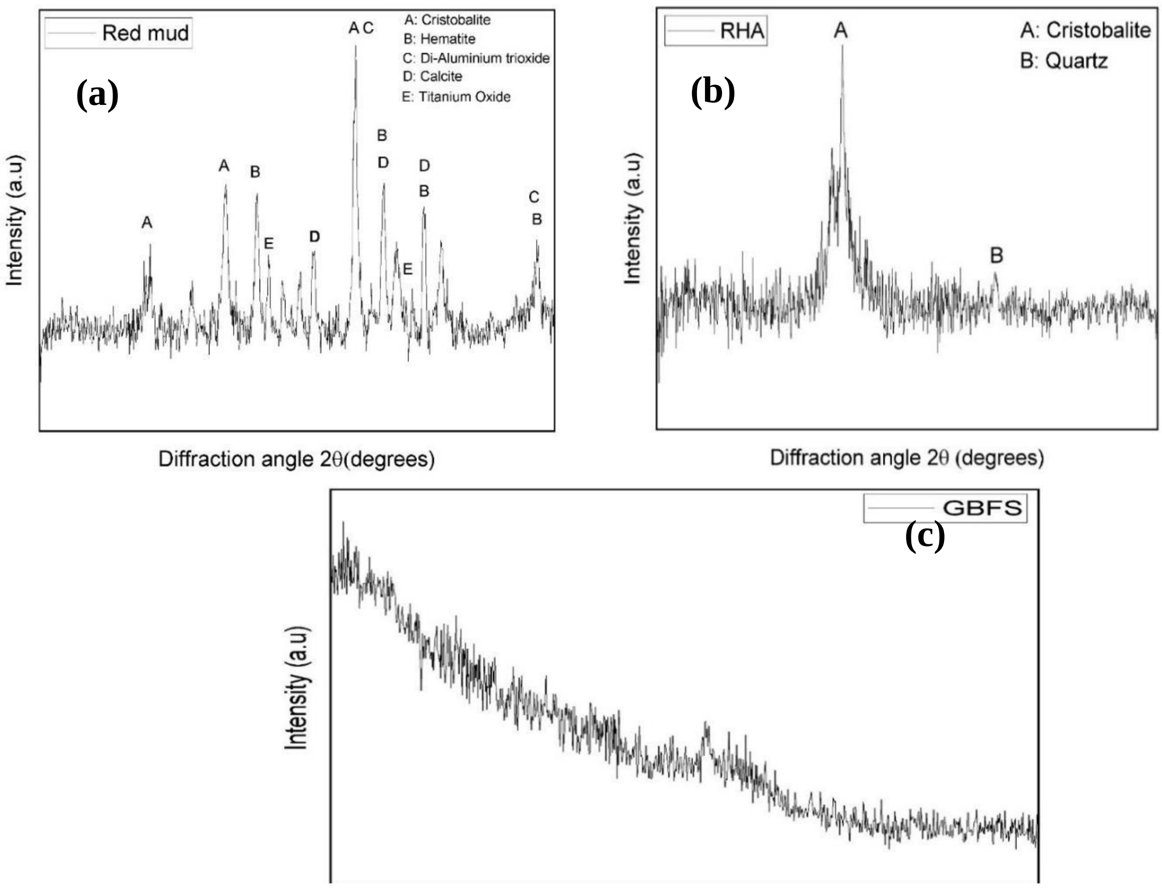

Fig. 13. XRD micrograph of (a) Red mud, (b) RHA and (c) GBFS

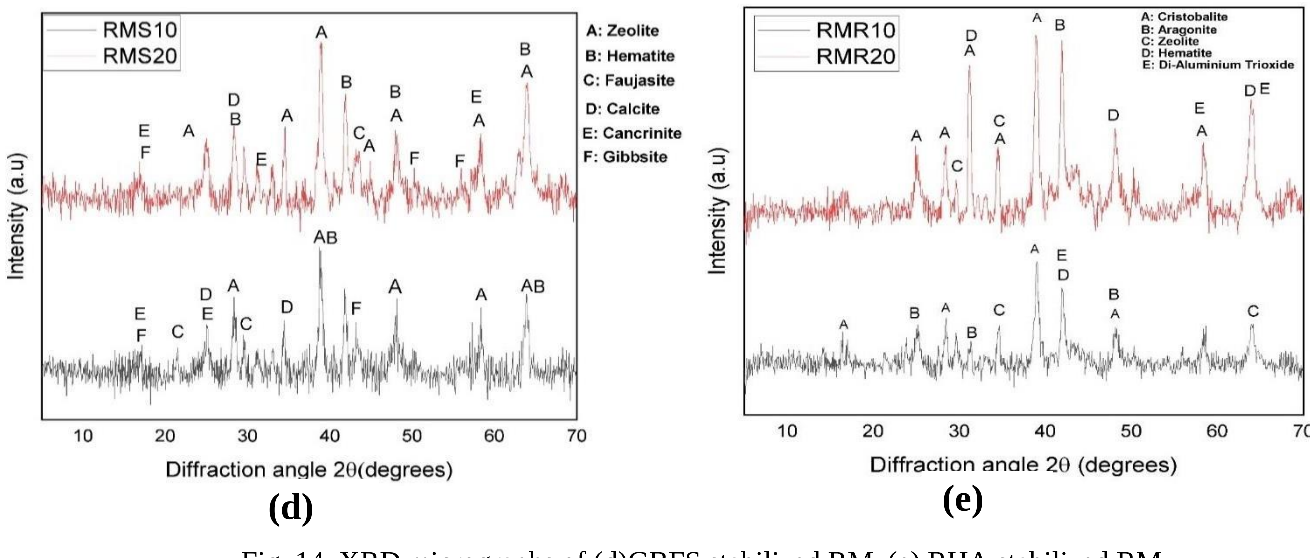

Fig. 14. XRD micrographs of (d)GBFS stabilized RM, (e) RHA stabilized RM

Table-2 shows the real concentration, which is based on the average concentration of three specimens. The dangerous heavy metals designated by the EPA for toxicity characteristics (As, Cr, Pb, Ni, Hg) are high in the red mud within tolerable values. It has been observed that stabilizing red mud with activated GBFS can stop Hg from leaching. Other heavy metal leaching, on the other hand, increases after stabilization but remains within permitted limits. According to the study report, the chromium in the red mud is present as Cr+3, which is not a health danger. The silent increase in pH caused by the use of NaOH as an activator may be to blame for the increased leaching. Although the heavy metal concentration is within the permitted thresholds for toxicity characteristics, it is beyond the WHO's recommended drinking water standards. As a result, the water quality of the surrounding drinking water source must be investigated anytime this material is utilized as a geotechnical material.

Table 2 Heavy metal concentrations in the leachate (ppm)

	RM			GBFS			RHA	
	Mean	SD		Mean	SD		Mean	SD
Na	2	0.388		1.256	0.0159		1.309	0.0166
K	6.573	0.1015		55.19	0.148		255.1	1.39
Ca	0.013	0.0048		27.37	0.088		0.148	0.0135
Fe	2.686	0.0284		0.207	0.087		0.142	0.045

4 CONCLUSIONS

This work uses geopolymerization to convert three industrial wastes, red mud (RM), granulated blast furnace slag (GBFS), and rice husk ash (RHA) into valuable construction materials, resulting in a new type of RM-GBFS and RM-RHA geopolymer composites. NaOH was the sole non-waste substance employed in this study. The degree of geopolymerization and its influence on mechanical, chemical, and microstructural properties were determined using a variety of synthesis parameters, including GBFS/RM and RHA/RM ratios, alkalinity condition, and curing period. The following conclusions can be taken from the experimental findings.

- From result it has seen that there is a change in liquid limit and plastic limit of RM upon addition of RHA or GBFS. Graph shows that by adding GBFS there is a slight decrease in LL and PL in case of GBFS and an increase in LL and PL in case of RHA.
- The OMC decreases and MDD increases by adding GBFS to RM however by adding RHA it was found that OMC increases and MDD decreases.
- RM, GBFS, RHA and their mixes exhibit negative differential free swell indicating that they are dispersive in nature. The dispersive percentage of RM is found to be 54.5% by double hydrometer method and also by crumb test it was found that after adding GBFS and RHA the depressiveness reduces.
- Addition of GBFS and RHA in RM shows an increase in UCS up to 20% by the quantity of RM-GBFS and RM-RHA mixture. Maximum UCS value is recorded in the mix composition containing 20% GBFS or RHA at curing period of 28 days. Additional doses of alkali showed a tremendous improvement in UCS value up to 4 M NaOH concentration.
- At high pressure, more amorphous silicate gel polymers and zeolite structures are formed, according to XRD data. This data shows that the geopolymer reaction is more powerful. The geopolymers have good mechanical characteristics as their porosity decreases and their structure densifies.
- The toxic heavy metals (As, Cr, Pb, Ni, Zn and Hg) as identified by EPA for toxicity characteristics was found to be increased after stabilization but within permissible limit.

5 REFERENCES

1. Deewa1 et.al. (2018), "Influence of rice husk ash source variability on road subgrade properties", Nigerian Journal of Technology (NIJOTECH) Doi:10.4314

2. Duxson, P., Fernandez-Jimenez, A., Provis, J. L., Lukey, G. C., Palomo, A., and Van Deventer, J. S. J. (2007). "Geopolymer technology: The current state of the art." *J. Mater. Sci.*, 42(9), 2917–2933.
3. Ikmal Hakem A Aziz, Mohd Mustafa Al Bakri Abdullah, M A A Mohd Salleh, Emy Azimi. Jitrin Chaiprapa and Andrei Victor sandu (2020), "Strength development of solely ground granulated blast furnace slag Geopolymers", Construction and Building Material, DOI: 250, 118720
4. IS 2720 part 10 (1991): Methods of test for soils, Part 10: Determination of unconfined compressive strength, Bureau of Indian Standards, New Delhi.
5. IS: 2720 (part 3 / sec. 1), 1980. Determination of specific gravity, Bureau of Indian Standards, New Delhi.
6. IS: 2720 (part 4), 1985. Grain size distribution of soil, Bureau of Indian Standards, New Delhi.
7. IS: 2720 (part 5), 1985. Determination of liquid limit, plastic limit and shrinkage limit, Bureau of Indian Standards, New Delhi.
8. IS: 1498, 1970. Classification of soil, Bureau of Indian Standards, New Delhi.
9. IS: 2720 (part 7), 1980. Determination of water content-dry density relation using Light compaction, Bureau of Indian Standards, New Delhi.

10 Jian He, Yuxin Jie, Jianhong Zhang, Yuzhen Yu and Guoping Zhang (2013), "Synthesis and characterization of red mud and rice husk ash based geopolymer composites", Cement and concrete composites, doi: 10.1016/j.cemconcomp.2012.11.010.

11 Manjusha, M., and Yashida, N., (2021), "Factors affecting the mechanical properties and microstructure of geopolymers from red mud and granite waste powder", Ceramic International, doi:10.1016, 2021.02.009