Rheological and strength behaviour of red mud - slag geopolymer composites

Sreelekshmi S¹,², Remya S Chandran¹, Sera Rachel Varghese¹, Naeem¹, Thushara Raju¹ and Ramaswamy K P¹

¹Department of Civil Engineering, TKM College of Engineering, Kollam, Kerala, India.
²Email: sreelekshmi2802@gmail.com

Abstract. Alkali activated concrete (AAC) is accepted as impending alternatives to conventional Ordinary Portland cement concrete in order to limit CO₂ emissions as well as beneficiate a number of wastes into useful products. This study aims to explore the possibilities of using red mud, which is a waste product of aluminum manufacturing industry, as a geopolymer solid binder. The fresh properties such as setting time, workability and penetration resistance and the hardened properties like compressive strength and ultra-sonic pulse velocity (UPV) test of various red mud mixes along with fly ash (FA) and slag are found out. Also some of the specimens were immersed in water to check if there is any leaching. From the study it was identified that the mix with 25% red mud and 75% slag gives a better workability and strength characteristics.

1. Introduction
Ordinary Portland cement (OPC) is among one of the most consumed materials in the construction industry, which is highly energy consumed and their production causes intensive pollution to the atmosphere [1]. Therefore the replacement of OPC from concrete is likely indispensable. Alkali activated materials are identified as cost effective alternatives and they have a potential to be used as a major component of a sustainable future global construction material. They are not expected for the complete replacement of Portland cement across its applications, for reasons like those related to supply chain limitations, practical challenges in some modes of application, and the need for improved quality control of formulation and curing. Fly ash containing high amounts of unburnt carbon, slag and red mud with high alkalinity are waste materials with less reuse rate, which can be effectively utilized to make green concrete by using it in developing geopolymer systems.

Geopolymers are amorphous alumino-silicate synthesized by the polycondensation of geopolymeric precursor and alkali polysilicates. It involves a chemical reaction between Silicone (Si)-Aluminium (Al) minerals under alkaline conditions that results in a 3D polymeric chain and ring structure with Si-O-Al-O bonds. It uses industrial by-products and waste products like fly ash, ground granulated blast furnace slag (GGBFS), rice husk ash, metakaolin, red mud, etc. A combination of sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) is the most common alkali activator used for the process. Geopolymer concrete (GPC) is one such eco-friendly and novel alternative to cement concrete with satisfactory strength and durability characteristics [2].

Based on alumina silicate sources, there are about 6 groups of GPC, viz, Fly Ash-based, Metakaolin-based, Slag-based, Rice Husk Ash-based, high calcium wood ash-based and a combination of any two of the aluminosilicates [3]. The advantages of using class F fly ash when compared to
unmodified Portland cement are many, like an increase in the late compressive strength (after 28 days), an increase in the resistance to alkali silica reaction, sulphate attack resistance, workability, pore refinement and less heat generation during hydration and decreased water demand. But a well-defined range of values cannot be provided – to describe the environmental savings in a global scenario, which might be achieved only through the use of alkali-activated materials (full utilization of fly ash) instead of conventional cements and concretes. So it is necessary that the development and optimizations of both one part and two-part binder systems are done based on an ever broader range of raw materials and activators [4]. Also, there is no any specific binder combination which will have all the desired properties at once, therefore the ground breaking research is the only path forward to reach large scale deployment of this technology [5].

GGBFS is a by-product from the iron and steel industry, using blast furnace, obtained as a glassy, granular product which is then dried and ground into a fine powder. GGBFS-FA blends were recommended for AAC as a commercially promising and viable alternative to Portland Cement Concrete. The incorporation of GGBFS into AAC decreases the susceptibility to sulphate acid attack [6]. Slag is highly cementitious and contains calcium silicate hydrates (CSH) which enhances strength and improves the durability of concrete [7]. Depending on the amount of GGBFS in the cementitious material, the setting time of GGBFS cement becomes more than that of OPC. Use of GGBFS has many advantages like reduction in the risk of damage caused by alkali-silica reaction, higher resistance to chloride ingress, reduction in the risk of reinforcement corrosion and higher resistance to attacks by sulphate and other chemicals. Thus, the use of slag in conventional systems is proven but the use is often limited to 50% and these limitations can be overcome in geopolymer systems.

Another effective waste material that can be used to make the AAC is red mud. Disposal of red mud possess several environmental problems due to its high pH, underground water contamination due to alkali percolation, issues with safe storage, alkaline airborne dust emissions, requirement of vast land area for disposal, the presence of minor and trace amounts of heavy metals and radio nuclides and their subsequent seepage into ground water. It is reported that the addition of red mud to fly ash increases the alkalinity of the environment and results in the dissolution of silica and aluminium from the solid phases resulting in the promotion of the polycondensation process and thereby increasing the unconfined compressive strength [8]. The addition of red mud densifies the pore structure and contributes to the strength development of Controlled low strength material (CLSM), called as flowable fill, which is a kind of weak flowable mix used in the construction for non-structural elements like backfills and road bases. Red mud optimizes the microstructure by acting as microfiller and provides alkalis which in turn increases the pH value of pore solutions as well as accelerates the hydration of binary binders [9].

It is noted that the red mud - slag mixes require further researches and studies to know about their geopolymerisation properties and their subsequent use as a green building material. For this, the fresh properties, mechanical and durability characteristics of the developed alkali activated composites are to be investigated. This paper presents the fresh and strength properties of various mixes prepared from slag, fly ash and red mud.

2. Materials and methods
2.1. Materials
In this study, the materials used were Class F fly ash (FA), GGBFS, red mud, and alkaline solution. Low-calcium fly ash conforming to IS: 3812-2010 and GGBFS having a chemical composition of CaO (40%), SiO₂ (35%), Al₂O₃ (13%) and Mg(OH)₂ (8%) obtained from Astra Chemicals, Chennai were used for preparing the geopolymer mix. For this study, slag was collected and sieved through IS sieve 90 micron, and the physical properties were obtained as, specific gravity of 2.9 and bulk density 1200 kg/m³. Red mud, from HINDALCO, Belgaum, generated in the production of alumina from bauxite in the Bayer process with Fe₂O₃ (30-60%), Al₂O₃ (10-20%), SiO₂ (10-20%), Na₂O (2-10%), CaO (2-8%) and TiO₂ (0-25%) were used in this study. Mortar was prepared using uniformly graded manufactured sand passing IS 2 mm sieve. 8 Molar sodium hydroxide solution along with sodium silicate solution
was used as alkali activators and alkaline solution to binder ratio adopted was 0.60. The water to solid ratio was 0.28, alkali silicate to alkali hydroxide ratio was 2.50 and activator modulus of 1.31.

2.2. Mix proportion
For preparing 8M NaOH solution, the solid NaOH pellets were mixed with distilled water and cooled at room temperature, and the Na$_2$SiO$_3$ solution was added to the mix, then properly stirred, and allowed to rest for a period of 24 hours before adding to the mixer. A Hobart mixer was used to mix the geopolymer solid binders along with the alkaline solutions for three minutes to get the proper mix. For this study, five types of mixes were used, which are shown in Table 1.

| Types of mix | Material proportion (%) |
|--------------|-------------------------|
| SGP          | 100% GGBFS              |
| FSGP         | 50% FA + 50% GGBFS      |
| R25S75GP     | 25% Red mud + 75% GGBFS |
| R50S50GP     | 50% Red mud + 50% GGBFS |
| R75S25GP     | 75% Red mud + 25% GGBFS |

3. Experimental investigations
This study was carried out in two phases. The first phase of the study was conducted on paste to determine the rheology and fresh properties, which includes mini slump cone test for workability, setting time test to determine initial and final setting times and penetration resistance test. The work was continued on mortar in the second phase to evaluate the performance of mortar, which contains flow table test, compressive strength test (3, 7, 28 days), dynamic modulus of elasticity using ultrasonic pulse velocity (28 days) and pH test.

3.1. Tests on paste
The mini slump cone is just a mini version of the slump cone, used to determine the workability of cementitious paste. It is a truncated conical mould with dimensions as: 19 mm top diameter, 38 mm bottom diameter and a height of 57 mm, and is shown in Figure 1. The mould was placed in the centre of a circular piece of glass and filled with sample paste. The cone was then lifted, allowed one minute for spreading the paste, and then the average spread of paste was measured along any three diagonals and the average of the three values is taken as the final diameter of the paste. The workability in terms of % spread was then obtained by using the equation (1).

\[
\text{% spread} = \frac{(\text{Final diameter} - \text{Initial diameter})}{\text{Initial diameter}} \times 100
\]  

Figure 1. Mini slump cone.
The initial setting time of paste is considered as the time period elapsed between the moment the water is added to the binders to the moment when the paste starts losing its plasticity. Vicat apparatus conforming to IS: 5513-1976 was filled to the brim of the mould with the prepared paste and the surface was levelled and the mould was gently shaken to expel the air, if any. The test block was immediately placed on the non-porous resting plate, under the initial setting needle. The rod with the needle was lowered and quickly released to penetrate into the paste in the mould. At first, the needle completely penetrated into the paste and then the procedure was repeated at regular intervals till the needle failed to penetrate the mould for 5±0.5 mm. The time duration between the times of adding water to the binders to the time when the needle failed to penetrate the mould by 5±0.5 mm was recorded as the initial setting time of the paste and the time duration required for the annular ring to fail to make an impression on the wet paste was recorded as the final setting time.

3.2. Tests on mortar
The flow table test was conducted to get an idea about the workability of mortar. The flow table apparatus used in the study is shown in the Figure 2, and the top of the table and inside portion of mould were wetted with oil and cleaned before starting the test.

![Figure 2. Flow table apparatus.](image)

The mould was placed on the centre of table and filled it with mortar sample in three layers and compacted by tamping 25 times with a tamping rod of 16 mm diameter. After that, the top of the layer was levelled with a trowel and then the mould was removed from the mortar by a steady upward pull and the diagonals of the spread was measured after giving 25 blows to the apparatus in 15 seconds. The diameter of flow was measured along 3 directions and the average final diameter was obtained. Then the % flow of mix was obtained by using the equation (2).

\[
\% \text{flow} = \frac{\text{average diameter} - \text{original base diameter}}{\text{original base diameter}} \times 100
\]  

(2)

The mortar specimens prepared for testing compressive strength are shown in Figure 3. The cylindrical specimens of size 25mm diameter and 50mm height were used. The strength test was carried out on multi speed loading frame of 50kN capacity and the machine was modified by fixing a test rig. A loading rate of 0.5 kN/sec, starting load of 1 kN and stop load of 40% of starting load was used as the test settings. Before conducting the test, the exact dimensions and mass of the air cured specimens were measured, noted and given as input to the test. The load was applied gradually until the failure of the specimen and the load at the failure point were noted down. The load was released and the process was repeated for 3 specimens from each mix and the 3rd day, 7th day and 28th day mortar compressive strength were obtained.
The strength and quality of mortar was also assessed by finding the velocity of an ultrasonic pulse passing through the specimen. Good quality specimens exhibit higher velocities which is also an indication of the quality of the material, while a specimen with cracks and voids might exhibit slower velocities. In this study, the transducer (of 150 kHz frequency) was held in contact with one surface of the specimen after 28th day, under test. After travelling a fixed path length L, the ultrasonic pulse was converted into an electrical signal by the second transducer which is kept in contact with the other surface of the specimen and an electronic timing circuit enables the transit time (T) of the pulse to be measured. The pulse velocity (V) was obtained by using the equation (3)

\[ V = \frac{L}{T} \]  

(3)

The dynamic modulus of elasticity of material \( E_d \) was found using the equation (4)

\[ E_d = \frac{\rho(1+\mu)(1-2\mu)}{(1-\mu)} V^2 \]  

(4)

Where \( \rho \) is the bulk density of the mortar in kg/m\(^3\), \( \mu \) is the Poisson’s ratio (assumed value of 0.17 for mortar) and \( V \) is the ultrasonic pulse velocity in m/s. The bulk density was computed from the weighed mass and volume of each specimens. Also, the pH tests were conducted using a digital pH meter to know about the pH variations of the water in which the specimens are immersed to check for any leaching of alkali ions from the specimen.

4. Results and discussions

4.1. Flow behaviour of geopolymer paste

The flow of paste for various mixes measured, and the results are displayed in Table 2. The result suggests that as the content of red mud increases there is a massive decrease in the spread of paste. This might be due to the fact that the finer particles of red mud require more water molecules to wet and wrap the particles causing less free water molecules to exist in the paste, and the fluidity becomes less [10]. Slag paste and paste blended with slag and fly ash showed high % flow (296% and 300% respectively).

Setting time tests for paste mixes were carried out and the initial and final setting time of mixes were recorded. The setting time values of mixes obtained are shown in Table 2. From the study, it was found that both initial and final setting time increases tremendously with increase in the content of red mud. The higher Si content will catalyse the geopolymerization reaction and small amounts of calcium in red mud lowers the calcium hydration reaction, which will prolong the setting time [11]. The initial setting time of all the mixes were found to be greater than 30 minutes, which is optimum for the transportation and placing of mixes. The final setting time of the mix R25S75GP was found to be more than 1 hour and that of R50S50GP, R75S25GP and FSGP was found to be greater than 2 hours which are satisfactory for working with these mixes. It is also seen that the mix sets quickly when the
slag content is high. Thus, incorporation of red mud is found to be beneficial in delaying both the initial and final setting times of paste.

The penetration resistance tests for the paste mixes were conducted along with the setting time tests and the penetration of the initial setting time needle at different times were noted and were plotted against time. It was found that the most resistive mix to penetration was SGP and the least resistive mix was found to be R75S25GP. Among the red mud mixes, R25S75GP was found to show satisfactory penetration resistance. The penetration resistance curves of various mixes are shown in Figure 4. The stiffening process of various paste mixes can be understood from Figure 4. It can be seen that the rate of stiffening for SGP and R25S75GP mixes are very fast whereas the stiffening rate is moderate for the mixes FSGP and R50S50GP.

| Mixes    | Setting time | Mini slump test |
|----------|--------------|-----------------|
|          | Initial setting time (min) | Final setting time (min) | Spread (%) |
| SGP      | 43           | 57              | 296.47     |
| R25S75GP | 57           | 70              | 260.27     |
| R50S50GP | 120          | 160             | 255.95     |
| R75S25GP | 205          | 285             | 170.27     |
| FSGP     | 122          | 150             | 300.00     |

**Table 2. Setting times of geopolymer paste.**

![Figure 4. The penetration resistance curves of various mixes.](image)

4.2. Behaviour of geopolymer mortar

The workability of various mortar mixes were found from the mortar flow table test. The flow of mortar observed for the various mixes obtained after conducting the test are shown in the Figure 5, and the flow results are shown in Table 3. Among all the mixes, it was found that the mixes R25S75GP, R50S50GP and the mix FSGP have good workability and satisfies 110 ± 5% as per IS 4031. From the test results and visual observations, the flow of the mix was found to be decreased with increase in the percentage of red mud. These observations were in alignment to the results from the mini slump cone test on paste. The decrease in flow of mortar with the inclusion of red mud may be due to its small particle size [10] and higher absorption of water.
Table 3. Flow of geopolymer mortar mixes.

| Mixes       | Spread or flow (%) |
|-------------|--------------------|
| SGP         | 75                 |
| R25S75GP    | 108                |
| R50S50GP    | 105                |
| R75S25GP    | 50                 |
| FSGP        | 115                |

Figure 5. The flow pattern of various mortar mixes. (a) SGP, (b) R25S75GP, (c) R50S50GP, (d) R75S25GP, (e) FSGP.

Hardened properties like compressive strength and elastic modulus of both ambient cured specimens as well as water immersed specimens were found out. In the case of water immersed specimens, the pH of the water in which the specimens are submerged was monitored at intervals to check for any leaching from the specimens. Compressive strength tests were carried out on the specimens on 3rd day, 7th day and 28th day of curing and it was found that the strength increased with days of curing. It was also found that there is only a slight change in the strengths when the specimens were cured in water. The values of compressive strength obtained are given in Table 4. From the results, it can be seen that the mix with R25S75GP possess the greatest strength, in the range of 50MPa. A substantial decrement in the strength was observed when the red mud content goes beyond 25%. Shrinkage cracks occurred when the red mud content is excess in the AAC mix. The number of cracks increases and become larger when the red mud content exceeds 25%. As the red mud content increases, the amount of inert material which does not participate in polymerization also increases. They may hinder the polymerization reaction creating a weaker matrix. This might be the reason for the decreased strength of geopolymer when the red mud content exceeds 25% [12].

UPV tests were conducted on the specimens on the 28th day, and the dynamic elasticity modulus in GPa was found out using the equation (4). It was found that the elastic modulus of water immersed specimens were greater than that of air dried mixes. Although, normally, saturated specimens are expected to give a slightly higher UPV and $E_d$ value, higher values obtained here (Table 5) may indicate that immersion curing may be more beneficial than air curing. Among the mixes, SGP was found to have the greatest elastic modulus. The mix of R25S75GP was also found to show a high value of elastic modulus, but is slightly lower than that of SGP. These two mixes showed higher compressive strength too.
Table 4. Compressive strength of geopolymer mortar specimens.

| Mixes   | Compressive strength (MPa) | 3rd day | 7th day | 28th day | 3rd day | 7th day | 28th day |
|---------|----------------------------|---------|---------|----------|---------|---------|----------|
| SGP     | 29.11                      | 45.18   | 53.16   | 50.46    | 52.58   | 56.15   |
| R25S75GP| 39.52                      | 42.66   | 48.34   | 58.83    | 59.11   | 59.75   |
| R50S50GP| 19.16                      | 21.33   | 24.42   | 23.91    | 32.41   | 40.36   |
| R75S25GP| 12.85                      | 14.02   | 17.13   | 13.63    | 15.46   | 17.08   |
| FSGP    | 23.09                      | 24.88   | 26.76   | 29.38    | 30.20   | 36.29   |

Table 5. Elastic modulus of mortar specimens.

| Mixes   | Elastic modulus, \( E_d \) (GPa) | Air curing | Immersion curing |
|---------|----------------------------------|------------|-------------------|
| SGP     | 18.90                            | 40.50      |
| R25S75GP| 15.60                            | 30.90      |
| R50S50GP| 1.90                             | 5.30       |
| R75S25GP| 2.50                             | 5.70       |
| FSGP    | 11.60                            | 18.70      |

The pH tests were conducted to determine if there were any leaching phenomena in the water immersed geopolymer mortar specimens. The pH of water was noted every week. Once the readings are taken, the solution was replenished with fresh water (volume equal to 4 times the volume of the specimens). Table 6 shows the pH variations of different geopolymer mixes. From the results obtained, it was found that leaching occurred (pH increased from 5.65 to 11-12) and alkaline substances might have leached out of the specimens into the water. The effect of this, on the microstructure of the specimens, demands another study.

Table 6. Results of pH test.

| Mixes   | Initial pH | 3rd day pH | 7th day pH | 14th day pH | 21st day pH |
|---------|------------|------------|------------|-------------|-------------|
| SGP     | 5.65       | 10.86      | 11.52      | 11.63       | 11.97       |
| R25S75GP| 5.65       | 11.54      | 11.74      | 12.07       | 12.31       |
| R50S50GP| 5.65       | 11.22      | 11.79      | 11.92       | 12.11       |
| R75S25GP| 5.65       | 11.74      | 11.85      | 11.96       | 12.04       |
| FSGP    | 5.65       | 11.61      | 11.66      | 11.72       | 11.92       |

5. Conclusions

Geopolymers, which are rich in alkali silicates and alkali hydroxides, are being experimented worldwide to develop GPC as an alternative to OPC systems. Red mud is a waste product of aluminium manufacturing industry, which is rich in aluminosilicates, suitable for geopolymerisation. Red mud was chosen for this study as it possesses grave environmental problems as there are no end environment friendly methods for its safe disposal. Based on the study conducted on slag and red mud mixes, following conclusions are drawn.

Based on the experiments conducted, it was found that, as the percentage of red mud increases in slag blended paste/mortar, the flowability of the mix and strength characteristics decreases, while the setting time of paste increases. So it is important that an optimum amount of red mud is to be added in the mix to balance out the workability criteria and strength criteria. Among the mixes, R25S75GP gives satisfactory workability and good compressive strength as well as better dynamic modulus of
elasticity. When the red mud content become more than 25%, the number of cracks augmented and widened, which results in low strength mix and the dosage above 25% are not recommended for construction purposes. Hence this study suggests that the suitable percentage replacement of GGBFS in AAC with red mud is 25%. Further research is required to know about the influence of red mud and slag on the other mechanical properties like tensile strength, flexural strength, etc. so as to ensure the use of such industrial waste products to make green concrete, thereby finding a solution to the environmental problems related to the disposal of waste materials from the industries.

Acknowledgement
The authors thank the Centre for Engineering Research and Development (CERD) for the financial assistance given as part of Students Project in 2019-20.

6. References
[1] Melike E Bildirici 2019 Cement production, environmental pollution, and economic growth: evidence from China and USA Clean Technologies and Environmental Policy 21 783–793
[2] Davidovits J 2005 Geopolymer, green chemistry and sustainable development solutions Proceedings of the World congress geopolymer Institute Geopolymere Saint Quentin France
[3] Ma C K, Awang A Z and Omar W 2018 Structural and material performance of geopolymer concrete: A review Construction and Building Materials 186 90–102
[4] Provis J L 2018 Alkali activated materials Cement and Concrete Research 114 40–48
[5] Provis J L and Deventer J S J 2014 Alkali Activated Materials State of Art Report RILEM TC 224-AAM Springer Publications
[6] Rakhimova N R and Rakhimov R Z 2019 Literature review of advances in materials used in development of alkali-activated mortars,concretes and composites ASCE Journal of Materials in Civil Engineering 31(11) 1-13
[7] Shunxiang Wang and Min Wu 2020 Mechanical strength and durability properties of pervious concretes with blended steel slag and natural aggregate Journal of Cleaner Production 271 1-29
[8] Choo H, Lim S, Lee W and Lee C 2016 Compressive strength of one-part alkali activated fly ash using red mud as alkali supplier Construction and Building Materials 125 21–28
[9] Yuan B, Yuan S, Straub C and Chen W 2020 Activation of binary binder containing fly ash and portland cement using red mud as alkali source and its application in controlled low-strength materials Journal of Materials in Civil Engineering 32(2) 1-11
[10] Jian Zhang, Shucai Li, Zhaofeng Li, Chao Liu and Yifan Gao 2020 Feasibility study of red mud for geopolymer preparation: effect of particle size fraction Journal of Material Cycles and Waste Management 22 1328–1338
[11] El-Kholy, Hasan S A, El Deen H, Asran, Gomaa A, Abd Al-Kader and Al Sayed A 2018 Experimental studies on effect of alkaline solution type on behaviour of zeolite and red mud based geopolymer mortar Life Science Journal, 15(4) 31-39
[12] Smita Singh, Basavanagowda S N, Aswath M U and Ranganath R V 2016 Durability of bricks coated with red mud based geopolymer paste Materials Science and Engineering 149 1-9