Stabilization of Red Mud Using Ground Granulated Blast Furnace Slag by Geopolymerization Technique

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ABSTRACT: Red mud is an alkaline by-product which is generated during the processing of bauxite. Generally red mud is considered as a waste material which is disposed into large lagoons. Red mud contains large amount of Fe_2O_3, Al_2O_3 and small amounts of CaO, SiO_2 and some valuable metals such as titanium however it devoid of reactive alumino-silicates. As red mud is highly alkaline, it is possible to stabilize red mud by adding industrial waste materials rich in alumino-silicates by geopolymerization. The main principle involved in geopolymerization is the chemical reaction between alumino-silicate materials with highly alkaline solution to form amorphous to semi crystalline inorganic polymers. In the present research work an attempt has been made to stabilize red mud using ground granulated blast furnace slag. The amount of slag is varied as 0%, 10%, 20%, 40%, 60% and 80% by weight of the red mud-slag mixture. For each combination of red mud-slag the Atterberg's limits, pH value, differential free swell value, compaction characteristics corresponding to light compaction and heavy compaction energies and unconfined compressive strength (UCS) are determined. Further additional doses of sodium hydroxide (NaOH) as an alkali activator varying as 2%, 4%, 8%, 12% of dry mass of the above red mud-slag mixes were given to accelerate the geopolymerization process. The UCS values of specimens were determined after curing periods of 0, 3, 15, 30 and 60 days. It is observed that mere addition of slag to red mud, without any alkali activator, improves the unconfined compressive strength substantially. An addition 4% NaOH with 40% slag gave a compressive strength of 14 MPa after a curing period of 60days. Hence it can be concluded that red mud can be stabilized effectively by the addition of little amount of alkali and ground granulated blast furnace slag.

INTRODUCTION

Rapid industrialization and infrastructure development produces enormous waste materials which in turn require large area and safe disposal. During past decades more concern is shown towards the utilization of industrial wastes and by-products in Civil engineering works. Utilizing the waste is a partial solution to ecological and environmental problems. If the industrial wastes are used in production of cement, concrete and in some other construction materials as a replacement to conventional materials then the manufacturing/project cost will be reduced and reduces the land fill area. Geopolymerization technique is an alternative in which an alkali activated alumino-silicate material is used as the binder. The major processes involve the reaction between an alumino-silicate source such as fly ash, metakaolin or blast furnace slag and an alkaline solution which leads to final hardening of the matrix by exclusion of excess water and the growth of an inorganic polymer. Red mud is a solid waste generated from aluminium industry in the process of alumina production by Bayer's process. For every ton of alumina one tonne of red mud produced. Due to its alkaline nature, it may cause serious environmental issues. Red mud contains large amount of oxides of iron and aluminium; and small amount of oxides of calcium and silicon; and some valuable metals such as titanium however it devoid of reactive alumino-silicate materials. Blast furnace slag is formed from the manufacture of pig iron. It mainly contains silicates, aluminosilicates and calcium. So, addition of blast furnace slag to red mud may have substantial influence on its index and engineering properties. Furthermore, addition of small amount of alkali may accelerate the geopolymerization process thus improves the engineering properties.

Researches have been made to stabilize red mud either by addition of admixtures or by suitable chemicals. He et al. (2013) has developed a new kind of geopolymer from red mud with rice husk ash and compressive strength ranging from 3.2 to 20.5 MPa was obtained. Hajjaji (2013) has developed a new geopolymer from metakaolin and red mud by sodium silicate solution as alkali activator and concluded that lesser amount of red mud with longer curing period gave more compressive strength. Rai et al. (2013) studied feasibility of reducing the alkaline nature of red mud by sintering using fly ash as an additive via Taguchi methodology. A pH of 8.9 was obtained at 25–50% of red mud and 50–75% fly ash with water and temperature of 1100^{o}C. Deelwal (2014) studied the effectiveness of red mud stabilized by lime with gypsum. The results showed that 12% lime and 1% gypsum gave more UCS value at 7 days curing. Singh (2014) stated addition of higher percentage of cement kiln dust (CKD) has shown higher values up to 8% addition further addition of CKD does not play any vital role in increasing the strength of red mud-CKD mix. Zhang et al. (2014) derived geopolymers from red mud and class F fly ash and found 28 days unconfined compressive strength of about 11.3 to 21.3 MPa. Kaya et al. (2016) investigated the behavior of red mud and metakaolin based geopolymers. Red mud is added in the range of 0 to 40% by weight of red mud-metakaolin mixture. 51.5 MPa was the maximum compressive strength for metakaolin based geopolymer.

MATERIALS AND METHODS

Materials

The raw materials used in this investigation are red mud (RM), granulated blast furnace slag (GBFS) and sodium hydroxide. Red mud was collected from NALCO, Damanjodi, India. The red mud was air dried, homogenized and pulverized to powder in order to provide better geopolymerization and minimizes the compositional error in the final product. The granulated blast furnace slag was collected from slag granulation plant of the Rourkela Steel Plant (RSP), Sundargarh, India. The waste materials were dried in oven to remove the water present in raw material. A NaOH flake with 98% purity was obtained from Loba Chemie, Mumbai, India.

The grain size distribution curves from Figure 1 shows that the red mud is well graded whereas the granulated blast furnace slag contains sand sized particles, so it was ground in a ball mill to a Blaine's fineness of $410m^2/kg$ to obtain ground granulated blast-furnace slag (GGBFS) for better reactivity. The index and engineering properties for both RM and GGBFS are tabulated in Table 1. The chemical compositions of raw materials were examined by X-ray fluorescence (XRF) analysis and presented in Table 2. The microstructure of the raw materials was studied by Scanning electron microscopy (SEM) and the SEM images are shown in Figure 2. The SEM image for red mud shows the particles are angular in shape. The microstructure for GGBFS reveals that most of the particles are rough and angular shaped. The chemical compounds present in the raw materials are investigated by X-ray diffraction (XRD) method and the XRD patterns are shown in Figure 3. The red mud majorly composed of iron oxide, alumina oxide, and silicon dioxide. From the XRD test result of slag it is observed that the slag is glassy material.

Methods

The present work is divided into two phases. In the first phase, red mud is stabilized with GGBFS of 10, 20, 40, 60 and 80 % by dry weight of the total mixture. For all these proportions index properties such as Atterberg's limits (liquid limit, plastic limit and shrinkage limit), differential free swell (DFS) value and pH were determined. Furthermore, engineering properties like optimum moisture content (OMC) and maximum dry density (MDD) and unconfined compressive strength were determined. The second phase of work includes additional alkali to accelerate the geopolymerization process. For the above proportions of red mud-slag, NaOH is added in the percentages of 2, 4, 8, and 12% of dry mass to red mud-slag mixes and unconfined compressive strength for different curing periods of 0, 3, 15, 30 and 60 days were determined. All the experiments have been conducted following IS 2720.

RESULTS AND DISCUSSION

pH Value

From Figure 4, it is observed that pH values are decreasing with the replacement of red mud with slag in red mud-slag mixes. The pH value decreased from 10.43 to 10.24 with the increase of slag content. This is perhaps due to presence of free lime in the slag sample. Both red mud and slag are alkaline, but red mud is more alkaline compared to slag which responsible for decreasing pattern of pH values with the increase of slag percentage.

Atterberg's Limits

From the plasticity characteristics of red mud and GGBFS (Table 1), it is seen that red mud possesses low plasticity with its liquid limit of 29% (<50%), whereas slag is a non-plastic material. For each combination of red mud-slag, liquid limit, plastic limit and shrinkage limit are illustrated in Figure 5. As the amount of slag in red mud is increased the plastic limit and shrinkage limit reduces. This is due to increase in the percentage of non-plastic material in the mixture. However, the liquid limit is found to be decreased up to slag content of 40% thereafter with further increase in slag content the liquid limit increases marginally. This may be due to change in gradation of the mixture.

Differential Free Swell

Figure 6 shows the variation of DFS values with the slag content. Red mud, slag, and their blends exhibit negative values of differential free swelling. This type of negative DFS values are reported for materials containing pure kaolinite minerals, rock powders, fly ash as these materials occupy high sediment volume in non-polar solvents like kerosene than in water. In the present case it is observed that the addition of slag to red mud reduced the negative DFS value. This indicates the inter particle attraction in the materials is non-existent and the material is dispersive in nature.

Compaction Characteristics

The compaction curves for all mixes of red mud-slag were obtained for compactive efforts of 595 kJ/m^3 and 2674 kJ/m^3. The values OMC and MDD were determined for each combination of red mud and slag. The variations of MDD and OMC values with slag content are shown in Figure 7. In red mud-slag mixture, as the percentage of slag added to red mud is increased, the MDD increases up to 40% slag and further addition of slag resulted in decreased MDD value. Both red mud and slag possess higher specific gravity than the conventional earth material. Change in MDD value of the mixture mainly depends on the specific gravity of the constituent materials and gradation of the mix. As a well graded material possess a high MDD value compared to poorly graded material, observed changes in MDD values may be attributed to the above reason. In red mud-slag mixture (40% slag content) the MDD value obtained in heavy compaction test is 1.07 times than that of light compaction test. The OMC for red mud is higher than that of slag. When slag is added upto 60 % to red mud, the OMC reduced but thereafter with increased slag content, the OMC value increased again. The reduction in OMC is may be due to the reduction in adsorbed water by red mud when replaced by slag.

Unconfined Compressive Strength

The unconfined compressive strength (UCS) for all the RM-GGBFS mixtures was obtained for different curing periods without and with addition of the chemical activator that is the NaOH solution.

Stabilization without NaOH activation

The variation in compressive strength of specimens with different GGBFS contents and cured for different periods are shown in Figure 8. For 60% red mud and 40% slag, maximum strength of 5.2MPa is obtained. The strength increment is due to the formation of calcium silicate hydrate (CSH) gel as the GGBFS has a high amount of calcium which gets activated by the alkali content of the red mud. However, a decreased strength is observed with further addition of slag which might be explained by the fact that the amount of sodium hydroxide present in red mud became insufficient to react with alumino silicates present in slag. For all red mud-slag mixes, compressive strength at 0 days curing is very less which increases from 0.22 MPa to 0.26 MPa with the addition of 40% slag. For the mix 60% red mud and 40% slag, strength increased about 20 times from 0 days to 60 days curing period.

Stabilization with NaOH activation

The results from Figure 9 show that compressive strength was significantly influenced by the increase of sodium hydroxide content. For all red mud-slag mixtures, the compressive strength increment is achieved for an optimum NaOH content. In case of red mud, maximum compressive strength of 0.63 MPa was obtained when activated with 2% NaOH for 60 days curing period. Further increment in NaOH content resulted in a reduction of the compressive strength. This might be due to the lubricating effect of excess NaOH. Whereas, 60% RM+40% GGBFS with 4% NaOH achieved the highest compressive strength of 14.02 MPa at 60 days curing period and other red mud-slag mixtures with higher slag content showed relatively less significant strength gain.

CONCLUSIONS

Experiments are carried out to investigate the geo-engineering properties of red mud treated with slag. The effects of slag, NaOH and curing period on the strength were investigated. Based on the experimental finding the following conclusions are arrived.

1. Plastic limit and shrinkage limit reduces with increased slag content but the liquid limit is found to be decreases up to 40% slag content thereafter with further increase in slag content the liquid limit increases marginally.
2. Red mud-slag mixes exhibits negative differential free swell values indicating that these materials are dispersive in nature.
3. Red mud shows moderate decrease in pH values with increase in slag content.
4. The maximum dry density increases upto 40 % slag content in red mud-slag mixture whereas the optimum moisture content decreases upto 60% slag content.
5. Addition of slag to red mud without any additional alkali increases the UCS value up to slag content of 40%. Further addition of slag beyond 40% results in reduction in unconfined compressive strength value. Virgin red mud possesses UCS value of 0.22 MPa which is increased to 5.2MPa with the addition of 40% slag at curing period of 60 days.
6. Addition of alkali i.e. NaOH solution enhances the strength remarkably for red mud-slag mixes. With the addition of 40% slag and 4% NaOH, red mud attains an unconfined compressive strength of 14.02 MPa at 60 days of curing
7. Red mud is a highly alkaline material which can be stabilized effectively by addition of slag through geopolymerization process. It reduces the

environmental pollution and it can be used in the construction works such as embankments, structural fills, road base and sub-base courses etc.

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TABLES

Table 1. Index and engineering properties of raw materials

Properties	RM	GGBFS
pH	10.43	10.24
Specific gravity	3.3	2.84
Liquid limit (%)	29	Non-plastic
Plastic limit (%)	23	
Coefficient of uniformity	2.45	1
Coefficient of curvature	20	6
Optimum moisture content (%)	23	19
Maximum dry density (kN/m^3)	17.88	16.9
Unconfined compressive strength (MPa)	0.22	0.09

Table 2. Chemical compositions of raw materials

Composition (%)	RM	GGBFS
MgO	0.020	9.52
Al_2O_3	16.07	21.06
SiO_2	8.25	30.82
K_2O	-	1.04
CaO	1.48	32.02
Fe_2O_3	53.75	1.37
Na_2O	3.82	0.088
MnO	0.157	0.14
TiO_2	4.24	1.04
SO_3	-	0.66
V_2O_5	0.148	-
Loss on Ignition	11.83	1.81

FIGURES

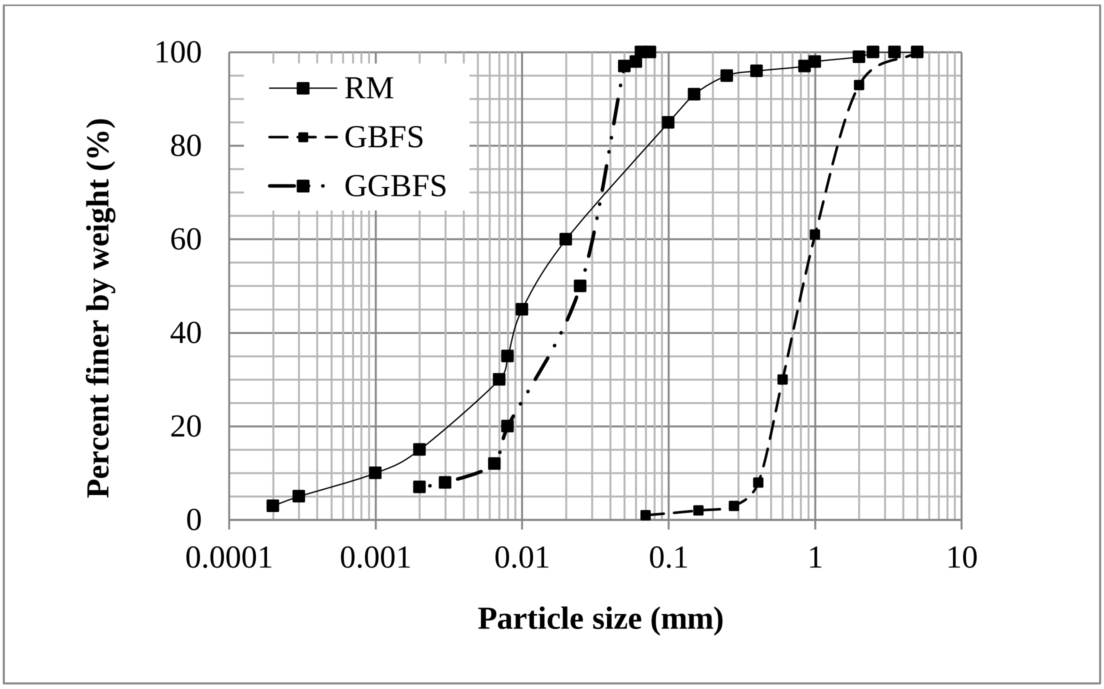


FIG. 1. Grain size distribution for raw materials

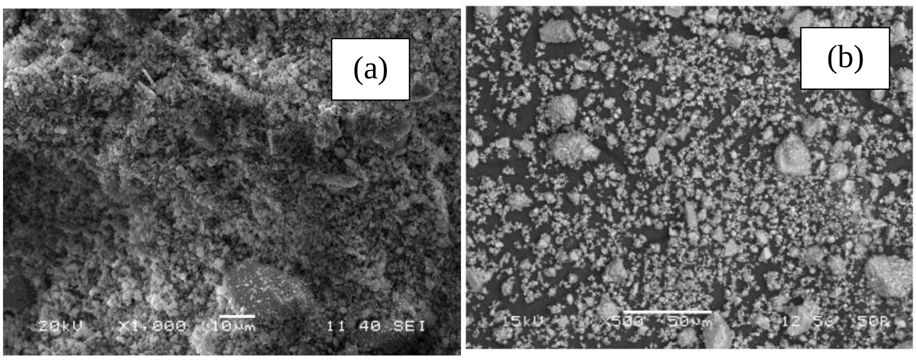


FIG. 2. SEM images for (a) RM and (b) GGBFS

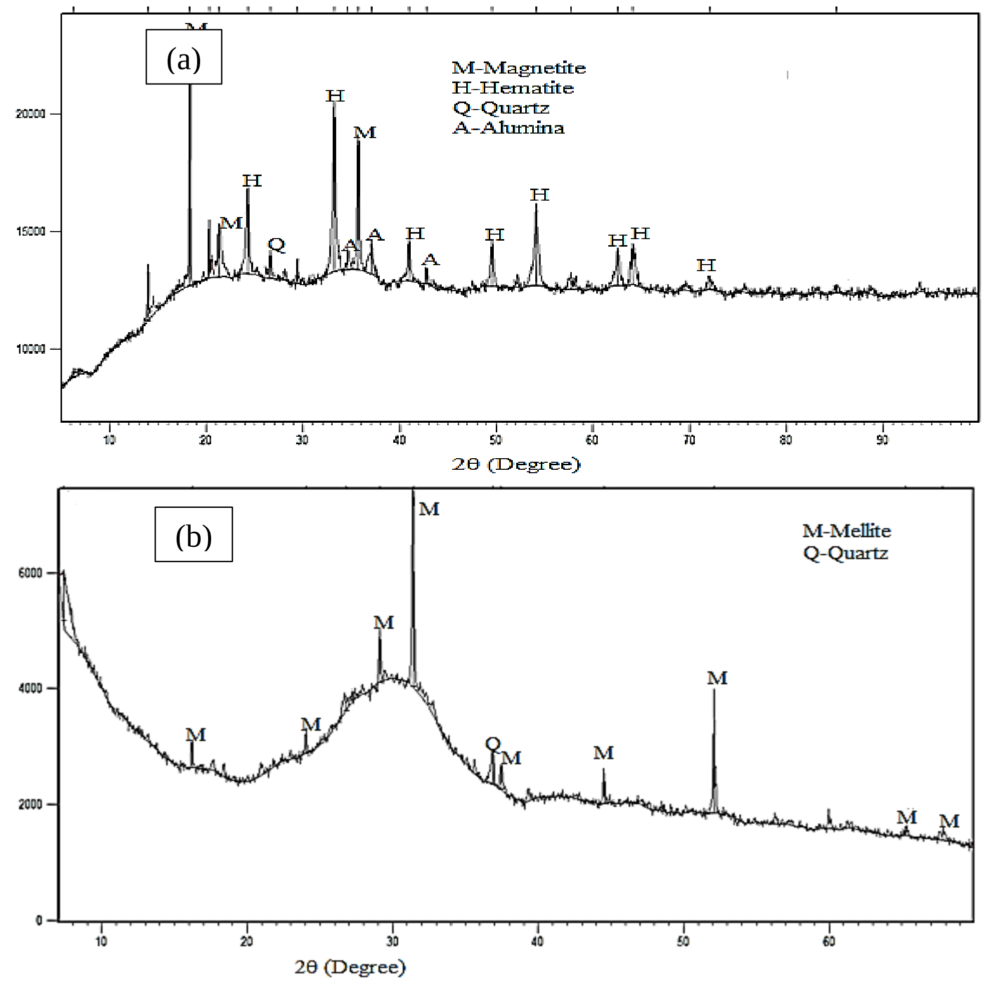


FIG. 3. XRD patterns for (a) RM and (b) GGBFS

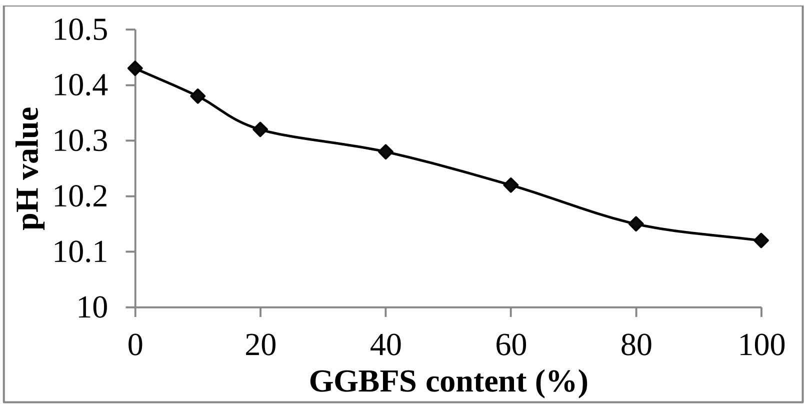


FIG. 2. Variation of pH value with slag content

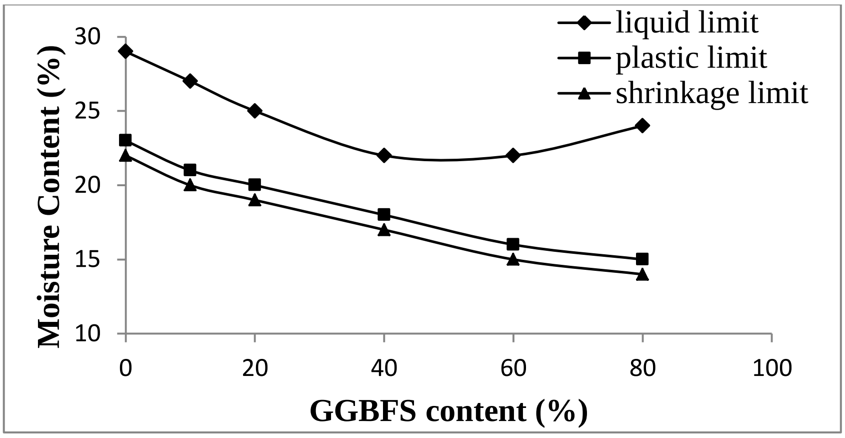


FIG. 3. Variation of Atterberg's limits with slag content

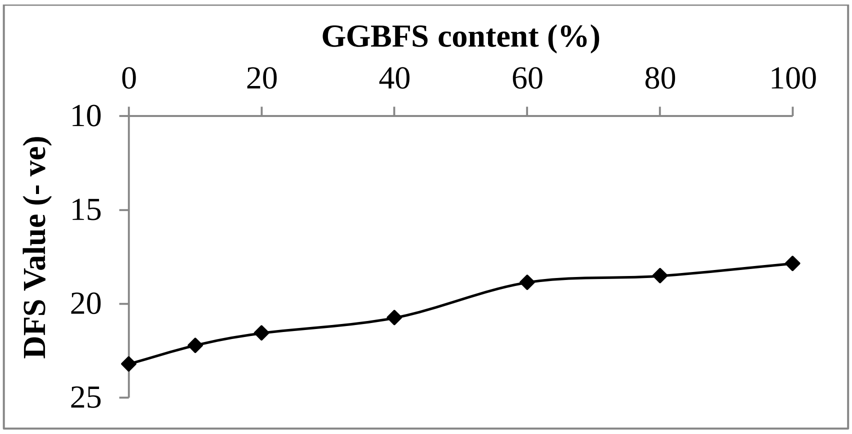


FIG. 4. Variation of DFS value with slag content

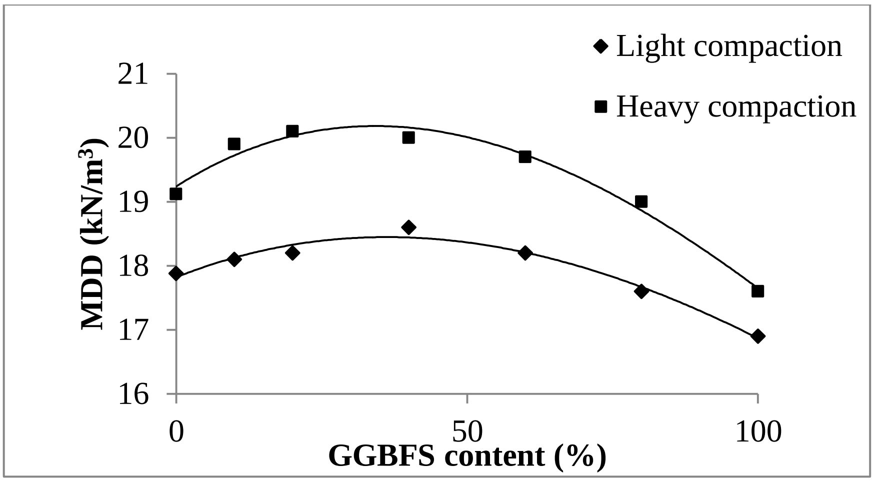


FIG. 5(a). Variation in MDD with slag content

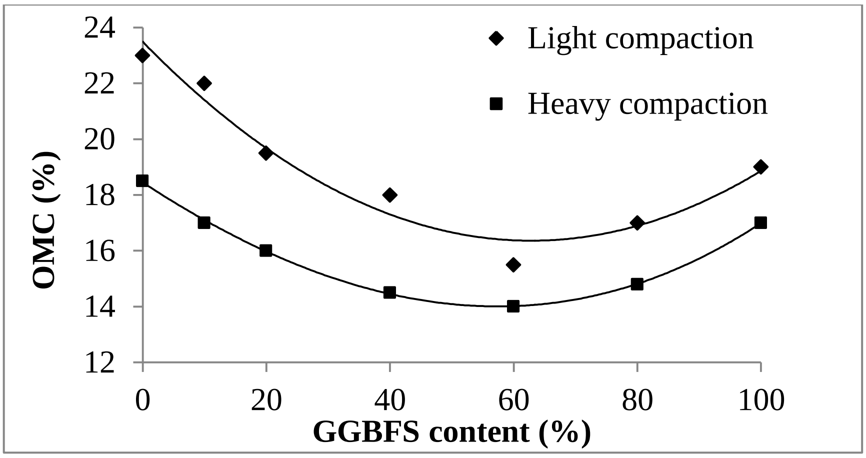


FIG. 5(b). Variation in OMC with slag content

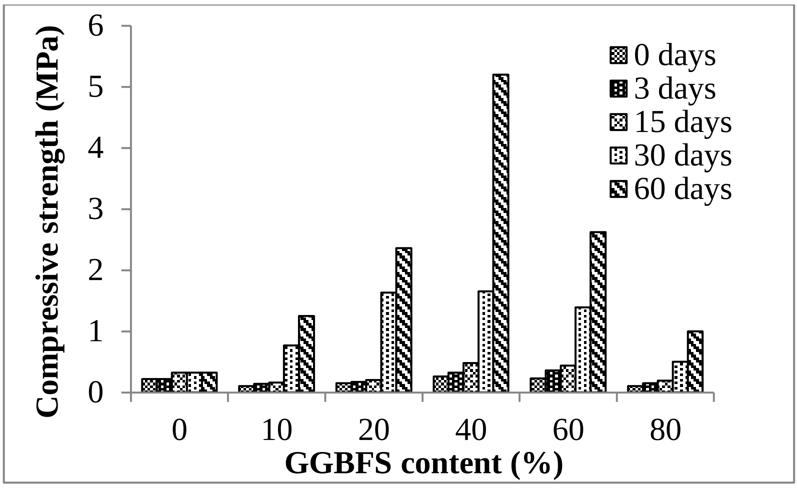
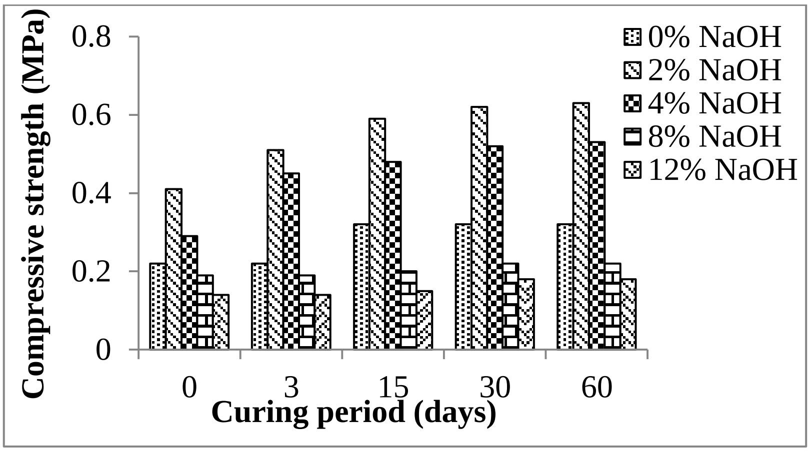
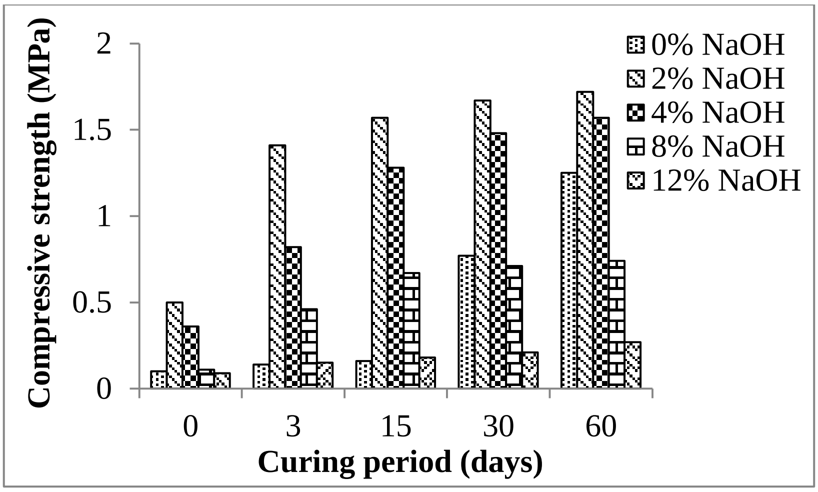


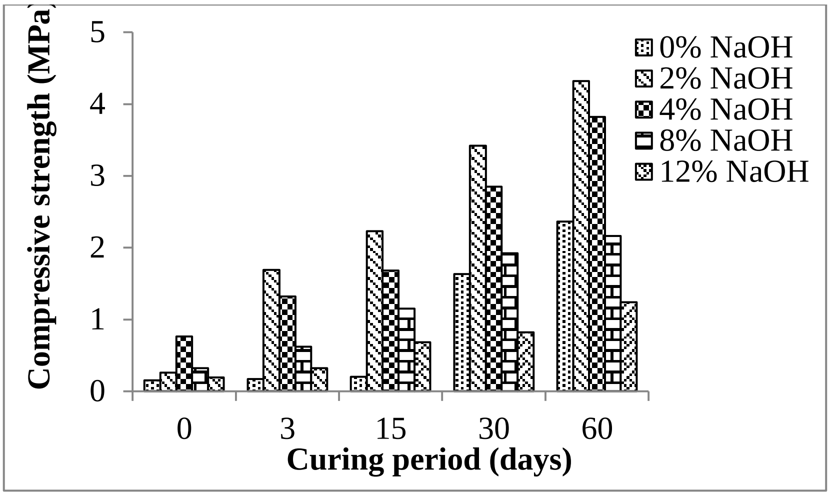
FIG. 6. Variation in UCS value with slag content for different curing periods



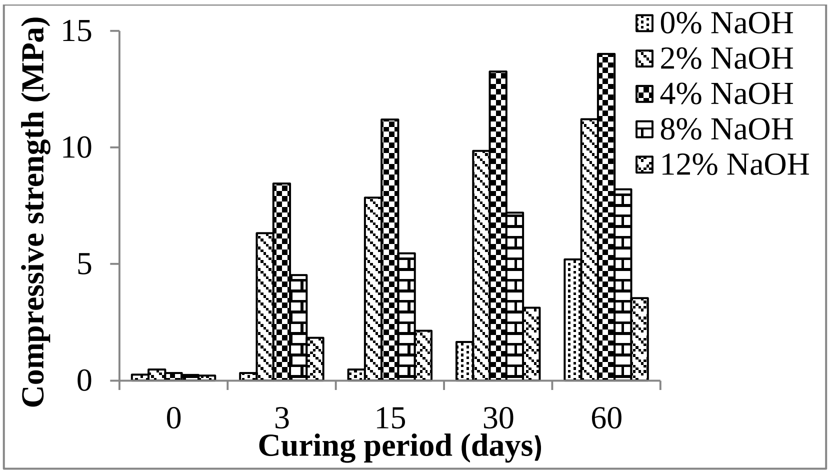
(a) 100% RM + 0% GGBFS



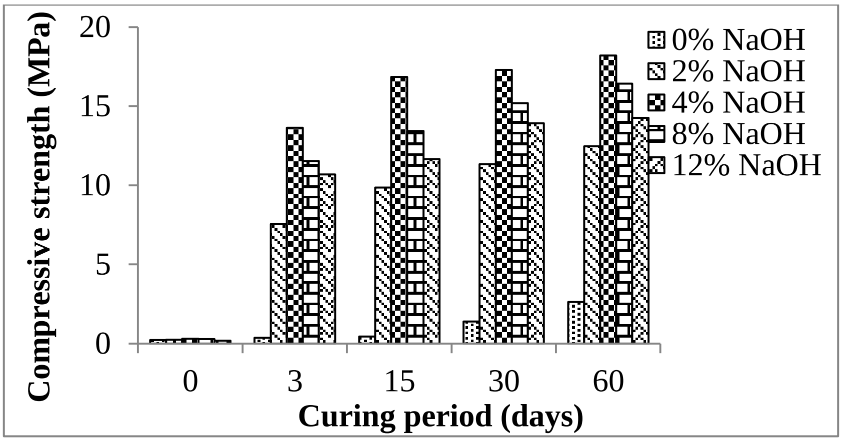
(b) 90% RM + 10% GGBFS



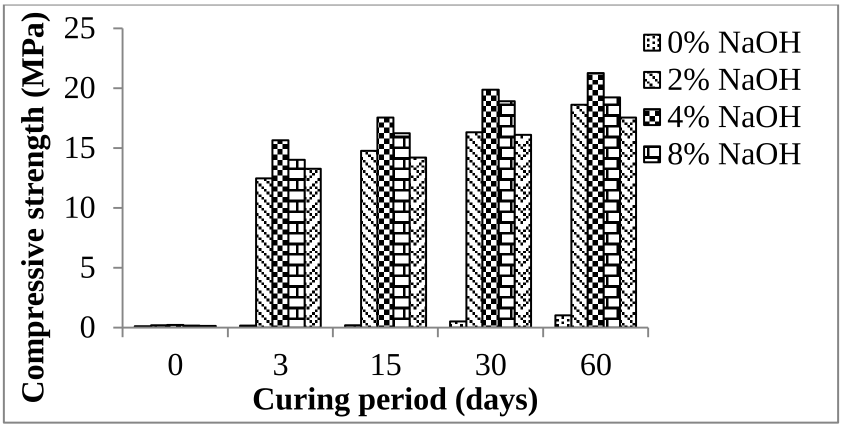
(c) 80% RM + 20% GGBFS



(d) 60% RM + 40% GGBFS



(e) 40% RM + 60% GGBFS



(f) 20% RM + 80% GGBFS

FIG. 7. Variation in UCS value with alkali content for different curing periods