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Development of construction materials from the geopolymerization of red clay and coal fly ash

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ABSTRACT

Red clay contains solid aluminosilicate has been shown to be reactive in the presence of an alkaline activator. The addition of coal fly ash and lime has shown improvements in their mechanical and physical properties of the geopolymer products. FTIR analysis and SEM images of the product have shown the formation of aluminosilicate gel in the geopolymeric product. The maximum compressive strength of the geopolymer products GP-RFL was achieved to be 15.92 N/mm² having water absorption of 10.47 % and bulk density 2.81 g/cm³. These results indicated that geopolymer mortars made from red clay, coal fly ash and lime could be used as an alternative construction material.

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1. Introduction

Red clay is found in Banepa, Beltar, Chidika, Gaighat, Gultar, Guttu, Lamasure, Manna Buddhuk, Panchkhal, Salghari and Sunkada areas of Nepal. Red clay is widely used in house painting in the rural areas of Nepal. The presence of high alumina and iron content in red clay has been proved suitable as an additive material to produce cement. 10300.1 m³ of red clay in the fiscal year 2015/16 have been utilized in the cement industries [1].

In the construction industry, Portland cement is the leading material for concrete. The cement industry contributes about 8 % of the global CO₂ gas emissions and it also produces about 5 % of greenhouse gas emissions [2]. This causes several environmental issues due to the high carbon foot print during cement production. Due to environmental concerns, readily available commercial byproducts as a source of aluminosilicate such as fly ash, blast furnace slag and red mud have been used rather than

naturally available materials such as metakaolin, red soil to meet these demands. Geopolymer concrete is one of the building materials that have become popular since it is environmentally friendly [3, 4].

The formation of geopolymer at low temperature generally below than 100 °C, consists of chains of mineral molecules joined with covalently with a three dimensional polymeric chain consisting of Si-O-Al-O bonds [5, 6]. The high strength development is considered due to the presence of chemical charge-balancing species located in the tetrahedral sites, i.e. the part of the structural network. Mössbauer spectroscopy demonstrates that Fe^{3+} is included in the geopolymer structure, i.e., Fe^{3+} is the equivalent of Al^{3+} in the alumino-silicate network, yielding a ferro-silico-aluminate sequence (-Fe-O-Si-O-Al-O-), i.e., ferro-sialate[7].

The tetrahedrons of silicon and aluminum are connected by oxygen bridges to form the high-connectivity chain or ring network structures. Such high-connectivity molecular structures of the products perform excellent in terms of strength and durability [8]. Geopolymers are characterized by higher durability and greenness relative to conventional OPC. These products have distinct cementitious and ceramic like formulation with good mechanical strength and chemical properties and have gained much attentions recently as a promising partial substitute to OPC [6, 9, 10]. Light weight geopolymer concretes are found as good insulators and fire-resistant and therefore applicable for high-rise buildings and in the areas of high earthquake risk [11].

Global Warming concerns will inevitably lead to the decrease of coal burning for the production of electricity and consequently to the exhaustion of this ultimate waste, which have been utilizing largely for the production of geopolymer and PPC cement [12]. The

recent discovery of ancient red geopolymer sandstone monuments in South America (Tiwanaku/ Pumapunku, Bolivia) have shown the extraordinary long-term durability of this [Fe-O-Si-O-Al-O-] geopolymer molecule withstood at least 1400 years of archaeological burial. These artificial red sandstone megaliths contains in the form of ferro-sialate matrix [13].

The aim of this study was to optimize the condition of geopolymerisation behavior of red clay and coal fly ash in the presence of lime.

2. Material and methods

Materials

The red clay (RC) was collected from Banepa and coal fly ash (CFA) was collected from brick factory of Satungal, Kathmandu. It was then grounded into a powder and dried at 120 °C for 2 hours to remove the moisture content. Calcium oxide was prepared by heating calcium hydroxide at 580 °C for 2 hours. The powder form of sample was weight and mixing was done in different proportion.

Activator Solution

Laboratory grade of NaOH (97 %), liquid sodium silicate (Na_2O : 8.6 %, SiO_2 : 28.0 % and H_2O : 63.4 % Lobe Chemme, India) were used. 4 M NaOH was prepared 24 h before mixing with liquid sodium silicate to prepare 1:1 activator solution. The use of 4 M NaOH solution was found to develop higher compressive strength [14].

Synthesis of Geopolymer

The red clay and coal fly ash (0 - 20 %) were dry mixed in different composition and then mixed with activator solution to prepare the geopolymer product. After the selection of CFA %, the amount of CaO was varied to prepare the geopolymer product. Finally two geopolymer products GP-RF (90 % red clay, 10 % coal fly ash and activator solution) and

GP-RFL (mixture of 90 % red clay and 10 % coal fly ash was mixed with of 2 % of lime and activator solution) were considered for study. Thus prepared clay paste was then casted in a wooden mould (2.5 cm × 2.5 cm × 2.5 cm) and cured at 60 °C in oven for 2 hours followed by curing at room temperature for 7 – 28 days, schematically represented as:

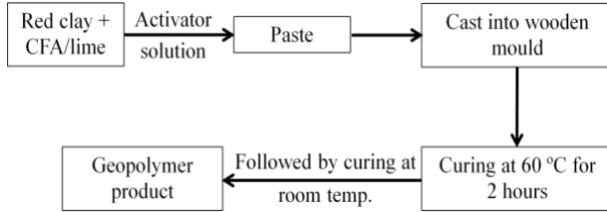


Fig. 1. Schematic diagram of geopolymer synthesis.

Curing at temperature at 60 °C was found dominant compared to higher temperature and requires less energy consumption [15, 16].

Characterization of the raw materials and Geopolymer products

Chemical composition of the raw materials was obtained by using EDX spectrophotometer (EDX-8000, shimadzu) available at Department of Custom, Tripureswor, Kathmandu. Phase analysis of the powdered raw materials and the geopolymer products were carried out by X-Ray Diffractometer (D2 Phaser Diffractometer, Bruker, Germany) using CuK α radiation available at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur. Fourier transform infrared Spectrophotometer (IR Tracer 100, Shimadzu, Japan) was used for structural characterization of geopolymers. FTIR spectra were obtained in the frequency range of 4000 to 400 cm⁻¹ by mixing the samples with KBr, available at the Central Department of Chemistry, Tibhuvan University, Kirtipur. Morphological characterization of the fractured samples was carried out by SEM (S4800 10.0kV 7.9 mm × 2.5k SEM, LAO) at NIMS, Japan.

Mechanical and Physical Properties

Compressive strength values were taken as the average of three consecutive measurements of geopolymer products and were measured using SLF 9 Load frame machine at Central Material Testing Laboratory, Institute of Engineering Pulchowk Campus, Tribhuvan University. Physical properties: apparent specific gravity, and bulk density, porosity and water absorption were measured as per ASTM C373 [17].

3. Results and Discussion

Chemical composition of raw materials

The chemical compositions of the raw materials red clay (RC) and coal fly ash (CFA) were analyzed and are shown in the following Table 1:

Table 1. Chemical composition (mass %) of the raw materials

Oxides (%)	RC	CFA
SiO ₂	42.39	39.14
Fe ₂ O ₃	28.72	24.95
Al ₂ O ₃	17.85	1.27
K ₂ O	7.34	0.80
CaO	-	0.94
TiO ₂	-	1.11
SO ₃	-	28.54
Others	3.69	3.25

Characterization of Raw Materials and the Geopolymer Products

X- Ray Diffraction patterns

X-ray diffraction patterns of red clay, coal fly ash and its geopolymer product are shown in the following Figure 2:

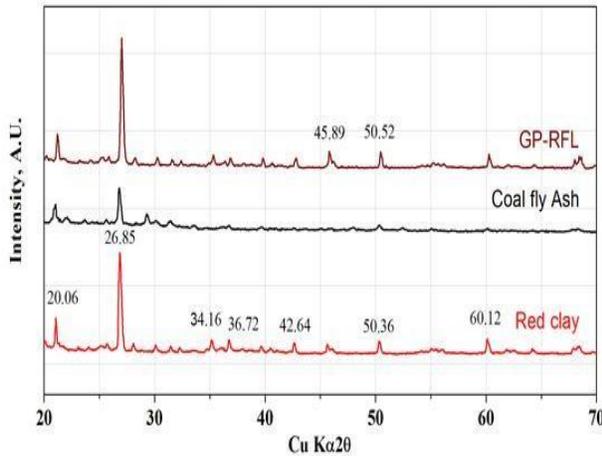


Fig. 2. XRD Pattern of raw materials and the geopolymeric product

Major peaks of the sample at 2θ values equal to 20.06, 26.85, 34.16, 36.72, 42.64, 45.63, 50.36 and 60.12 ° mainly represents quartz (silica). These entire peaks are present in the both raw materials and its geopolymer products.

FTIR analysis

FTIR spectra of the raw materials red clay, coal fly ash and its geopolymer product GP-RFL are shown in the Figure 3. The main absorption bands in RC and CFA were observed at 2361.5, 1025.9, 1001.2, 908.9, 793.7, 747.7, 524.4 and 1047.4, 592.9 cm^{-1} whereas the spectra for GP-RFL: 1001.2, 910.7, 529.5 cm^{-1} wavenumbers.

Absorption band at 2361 cm^{-1} could be attributed to bending vibration of H-O-H group associated with weakly bond water molecules [18]. The bands in the range of 950 to 1100 cm^{-1} assigned to the asymmetric stretching vibrations of Si-O-Si and/or Si-O-Al. The absorption bands at 910.7 cm^{-1} is due to Al-(OH) vibrations [19].

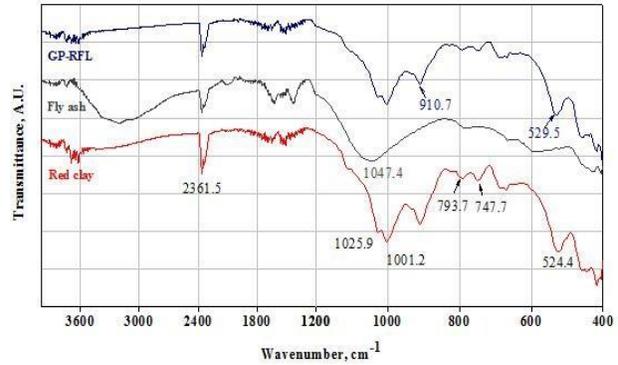


Fig. 3. FTIR spectra of red clay, coal fly ash and its geopolymeric product GP-RFL.

The spectra in the frequencies between 800 cm^{-1} and 480 cm^{-1} correspond to the symmetry of the Si-O-Si stretching vibration [20]. In the geopolymeric product the entire main characteristics band gets broadened shows the substitution of Si with Al forming the geopolymeric network.

SEM analysis

The scanning electron micrograph of the fractured surface of geopolymerization product GP-RFL is shown in the following Figure 4:

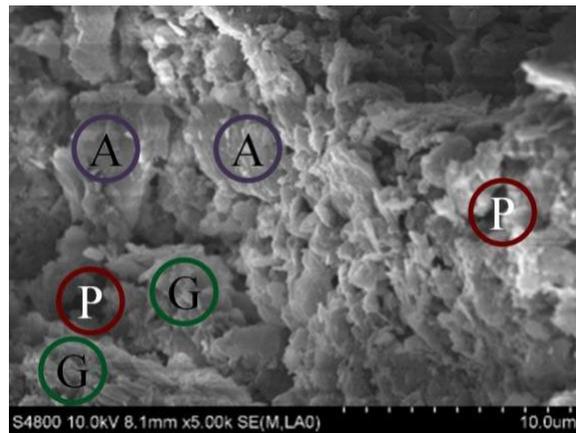


Fig. 4. SEM image of GP-RFL (G-gel, P-porous site, A-aggregate) representing gel formation.

The solid aluminosilicate material present in the powdered mixture are converted into a porous, hydrate gel and are bound through networking channel supported by the high

compressive strength value of the geopolymerization product (GP-RFL).

Variation of the Amount of RC and CFA

The geopolymer products were prepared from the mixture of RC and CFA (5 – 20%) and mixing with the activator solution. The products were then cured at 60 °C for 2 hours followed by curing at room temperature for 7 days. The compressive strength values of the geopolymer products were found to be 0.60, 1.13, 1.75, 0.65 and 0.64 N/mm² for 0, 5, 10, 15 and 20 % of CFA respectively and are shown in the following Figure 5:

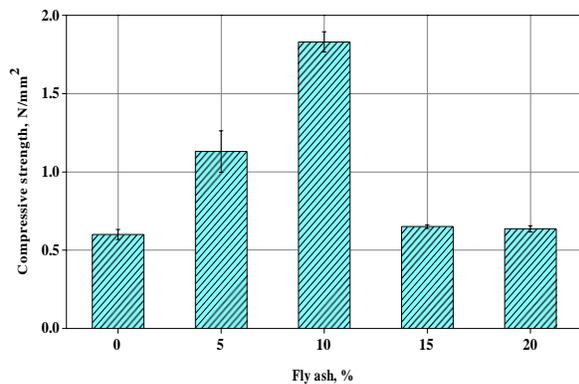


Fig. 5. Compressive strength of the geopolymer products with the variation of fly ash

The compressive strength value increased with increasing with increase in amount of coal fly ash up to 10 %. The increase in compressive strength value may be due to the pozzolanic activity of coal fly ash [21]. As the increases of % of coal fly ash some cracks was observed in the geopolymeric sample, thus compressive strength was decreased.

Variation of the Amount of CaO

90 % red clay and 10 % coal fly ash was mixed and then the amounts of CaO were varied. At first these were dry mixed and then mixed with the activator solution. The geopolymer products were then cured at 60 °C for 2 hours followed by curing at room temperature for 7

days. The compressive strength of geopolymer products were found to be 5.78, 7.73, 5.66, and 4.64 N/mm² for 1, 2, 3 and 4 % of CaO respectively and are shown in the following Figure 6:

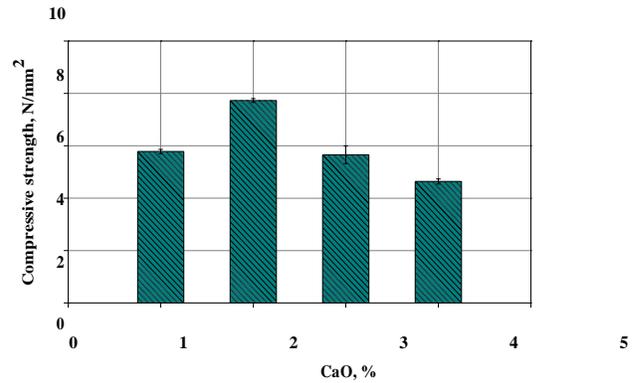


Fig. 6: Compressive strength of the geopolymer product with CaO %

The compressive strength value of the geopolymer product was found maximum at 2 % of addition of CaO. In ceramics, mechanical strength usually increases with decreases in porosity. Similar trend of increase in strength was also observed in case of metakaolin based geopolymer on the addition of small amount of Ca(OH)₂ [22].

Effect of Curing Time

The geopolymer products GP-RF and GP-RFL were then cured at 60 °C for 2 hours followed by curing at room temperature up to 28 days. The compressive strength values of the geopolymer products were measured and are shown in the Figure 7. The compressive strength value of the geopolymer products were found increasing with curing time.

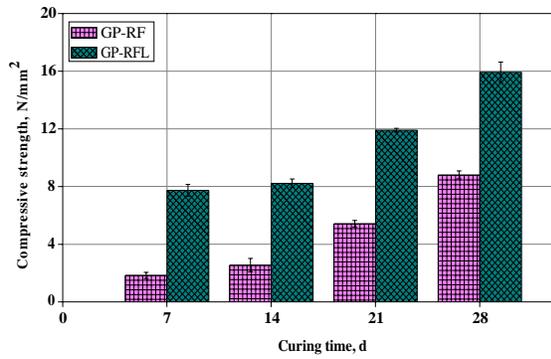


Fig. 7. Compressive strength of the geopolymer products with curing time

The curing for longer period of time at low temperature is preferable for the synthesis of geopolymer as the condensation and evaporation of water molecules takes place simultaneously preventing the formation of voids and cracks inside the materials thus increasing the compressive strength. The adequate curing time accelerates the extent of chemical reaction [23, 24].

Physical properties of the Geopolymer Products

The lower the value of water absorption indicates good quality and has higher resistance to water infiltration and to environmental damage. The water absorption value less than the 17 % are applicable in masonry units. The physical properties of the geopolymeric product measured at 28 days as per ASTM C373 standards are mentioned in the following Table 2:

Table 2. Physical properties of the geopolymer products measured at 28 days.

Physical properties	GP-RFL
Absorption of water (%)	10.47
Porosity (%)	27.56

Apparent specific gravity	3.63
Bulk density (g/cm ³)	2.81
Compressive strength (N/mm ²)	15.92

Apparent specific gravity, bulk density, porosity and Water absorption and compressive strength value indicates these masonry unit can be used as an alternative construction material.

Conclusions

The geopolymerisation behavior of red clay and fly ash was studied. The compressive strength values of the geopolymer GP-RF using RC (90%) and CFA (10%) using 1:1 solution of 4M NaOH and liquid sodium silicate was found to be 8.80 N/mm² at 28 days of curing. Use of 2 % lime as additives enhanced the compressive strength of 15.92 N/mm² at 28 days of curing. Microstructural study of the geopolymeric product has shown the formation of aluminosilicate gel. The mechanical and physical properties of the geopolymer product were studied. These results indicated that geopolymer mortars made from red clay, coal fly ash and lime are suitable for construction activities and can be used as an alternative construction material.

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Department of Chemistry, Tribhuvan University, Kirtipur for FTIR spectra of the samples, Dr. Lok Kumar Shrestha, Scientist, MANA, NIMS, Japan for providing SEM Image of the sample.

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