Introduction
Red clay is widely used in house painting in rural areas of Nepal. Due to the presence of high alumina and iron content, red clay has been proved suitable as an additive material to produce cement. Red clay is found in Lamasure, Beltar, Gaighat, Salghari, Manna Buddha, Banepa, Panchkhal, Chidika, Sunkada, Guttu and Gultar areas. The production of red clay for its use in cement industries was recorded to be 10300.1 m$^3$ in the year 2015/16 [1].

Concrete is one of the most commonly used construction materials and Portland cement is the leading material for concrete. Cement industries contribute about 5% of greenhouse gas emissions and it also produces about 8% of the global CO$_2$ emissions [2]. Huge consumption of cement caused several environmental issues worldwide due to the high carbon footprint during cement production.

Due to the environmental concerns, readily available commercial by-products as a source of aluminosilicates such as fly ash, blast furnace slag and red mud have been used rather than naturally available materials such as metakaolin and red soil to meet these demands. Geopolymer concrete is one of the building materials that have become more popular in recent years due to the fact that it is significantly more environmentally friendly [3, 4].

Geopolymers are a member of the family of inorganic polymers and are chain structures formed on a backbone of Al and Si ions. The chemical composition of this geopolymer material is similar to that of natural zeolitic materials, but they have an amorphous microstructure instead of crystalline [5]. The polymerization process involves a substantially fast chemical reaction under the highly alkaline condition of Si-Al minerals that results in a three-
dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [6].

The formation of geopolymer at a low temperature generally below than 100 ºC, consists of chains of mineral molecules joined with covalent bonds [7]. Geopolymers synthesized from fine volcanic ash withstand very good compressive strength. A chemical charge-balancing consideration requires it as located in the tetrahedral sites, i.e. the structural network developing the high mechanical strength. Mössbauer spectroscopy demonstrates that the inclusion of iron Fe$^{3+}$ in the geopolymer structure, yielding a Ferro-silico-aluminate sequence (-Fe-O-Si-O-Al-O-), i.e. Ferro-sialate [8].

The tetrahedrons of Si and Al are connected by oxygen bridges to form the high-connectivity chain or ring network structures. Thus, such high-connectivity molecular structures of the products can perform excellently in terms of strength and durability [9]. Geopolymers are characterized by higher durability and greenness relative to the conventional OPC. These products have distinct cementitious and ceramic-like formulations with good mechanical strength and chemical properties and have gained much attention recently as a promising partial substitute to OPC [7, 10 and 11]. 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 [12]. The effect of temperature on brick powder-based geopolymer has shown an increase of compressive strength of 29.78 %, 61.47 % and 19.28 % with every increase of 10 ºC at 50 ºC, 60 ºC and 70 ºC respectively [13].

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 has been utilized largely for the production of geopolymer and PPC cement. Rock-based geopolymer is the solution [14]. The recent discovery of ancient red geopolymer sandstone monuments contain Ferro-sialate matrix, in South America (Tiwanaku/Pumapunku, Bolivia) has shown the extraordinary long-term durability of [Fe-O-Si-O-Al-O-] geopolymer molecule withstood at least 1400 years of archaeological burial. [15].

Sandstone is a sedimentary rock composed of quartz grains and a clay binder. Electron microscopic analysis of red sandstone of Pumapunku proves that the composition of the sandstone could be artificial (a Ferro-sialategeopolymer) and manufactured to form cement [16].

The aim of the study was to optimize the condition of geopolymerisation behaviour of red and calcined white clay.

**Materials and Methods**

**Raw materials**
The Red Clay (RC) and white clay (WC) were collected from Kavrepalanchok and Palpa districts of Nepal respectively and then these were dried and ground into a powder and dried at 120 ºC for 2 hours to remove the moisture content. White Clay was heated at 700 ºC for 2 hours [17]. Calcium oxide was prepared by heating calcium hydroxide at 580 ºC for 2 hours. The powder form of sample was weight and mixing was done in different proportion.

**Activator solution**
Laboratory grade of NaOH (97%) and liquid sodium silicate (Na$_2$O: 8.6%, SiO$_2$: 28%) were used. Four molar NaOH was prepared 24 h before mixing with liquid sodium silicate to prepare a 1:1 activator solution. The use of 4 M NaOH solution was found to develop higher compressive strength [18].

**Synthesis of geopolymer**
The red clay and calcined white clay (5-20%) were dry mixed in different compositions and then the mixture was further mixed with activator solution to prepare the geopolymer product (RCW). After the selection of CWC percentage, the amount of CaO was varied to prepare the geopolymer product (RWL). Thus prepared clay paste was then cast in a wooden mould (2.5 cm × 2.5 cm × 2.5 cm) and cured at 60ºC in an oven for 2 hours followed by curing at room temperature for 7 to 28 days, schematically represented as:
The effect of curing temperature at 60 °C was found dominant compared to the higher temperature and requires less energy consumption, therefore the condition was selected [13].

**Mechanical and physical properties of the geopolymer products**

The mechanical property of the geopolymer products was determined by measuring the compressive strength. 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 such as water absorption, porosity, apparent specific gravity and Bulk density were measured as per ASTM C373 [19]. These properties are widely used in the evaluation and comparison of product quality and as part of the criteria for the selection and use of refractory products in a variety of industrial applications. Durability properties such as chloride resistance test were carried out by using the geopolymer samples to severe environmental conditions using 5 % hydrochloric acid solution, the specimens were analyzed by the change in compressive strength values at 7, 30 and 60 days at the room temperature (25 °C).

**Characterization of the raw materials and geopolymer products**

For the chemical composition of the raw materials, Energy Dispersive X-Ray Fluorescence (EDX) analysis was performed using an EDX spectrophotometer (EDX-8000, Shimadzu, Japan) available at the Department of Customs, Tripureshwor, Kathmandu. The raw materials and the geopolymer products were powdered and analyzed by X-Ray Diffractometer (D2 Phaser Diffractometer, Bruker, Germany) using CuKα radiation available at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur. Fourier Transform Infrared (FTIR) analyses were carried out using FTIR Spectrophotometer (IR Tracer 100, Shimadzu, Japan) in the frequency range of 4000 to 400 cm$^{-1}$ available at the Central Department of Chemistry, Tribhuvan University, Kirtipur. Morphological characterization of the fractured samples was performed by scanning electron microscope (S4800 10.0kV 7.9 mm × 2.5k SEM, LAO) at NIMS, Japan.

**Results and Discussion**

**Chemical composition of raw materials**

Chemical compositions of the raw materials such as red clay (RC) and calcined white clay (CWC) are shown in Table 1:

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>RC</th>
<th>CWC</th>
</tr>
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<tbody>
<tr>
<td>Si</td>
<td>34.42</td>
<td>57.37</td>
</tr>
<tr>
<td>Fe</td>
<td>34.89</td>
<td>21.46</td>
</tr>
<tr>
<td>Al</td>
<td>16.41</td>
<td>8.09</td>
</tr>
<tr>
<td>K</td>
<td>10.59</td>
<td>7.19</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>2.36</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>2.23</td>
</tr>
<tr>
<td>Others</td>
<td>0.73</td>
<td>1.30</td>
</tr>
</tbody>
</table>

**Physical properties of the geopolymer products**

Water absorption tests on the bricks are conducted to determine the durability and quality of the masonry unit. The pores present in the brick increases the water absorption. The lower the value of water absorption indicates higher resistance to water infiltration and to environmental damage. The water absorption value of less than 17% is applicable in masonry units. Water absorption, porosity, apparent specific gravity and
bulk density test were carried out at 28 days as per ASTM C373 standards and mentioned in Table 2:

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>RCW</th>
<th>RWL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption of water (%)</td>
<td>8.52</td>
<td>8.01</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>22.06</td>
<td>19.65</td>
</tr>
<tr>
<td>Apparent specific gravity</td>
<td>3.32</td>
<td>3.37</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.58</td>
<td>2.66</td>
</tr>
</tbody>
</table>

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

**X-ray diffraction patterns**

X-ray diffraction patterns of RC, CWC, and its geopolymer product are shown in Figure 2.

Major peaks of the sample have 2θ values = 31.34, 26.84, 35.21, 42.66, 50.37 and 60.13° mainly representing quartz (silica). These entire peaks are present in both raw materials and their geopolymer products.

**FTIR analysis of raw materials and the geopolymer products**

FTIR spectra of the raw materials (RC and CWC) and its geopolymer product RWL are shown in Figure 3. The absorption band appeared at 2361, 1000, 909, 791, 745, 525 cm⁻¹. The bands in the range of 950 to 1100 cm⁻¹ are assigned to the asymmetric stretching vibrations of Si–O–Si and/or Si–O–Al [20]. The spectra in the frequencies between 800 and 480 cm⁻¹ correspond to the symmetry of the Si-O-Si stretching vibration [21]. The absorption band at around 2361 is attributed to bending vibrations of H-O-H [22]. In the product, all the main characteristics band gets broadened showing the substitution of Si with Al forming the geopolymeric network.

**SEM image of the geopolymer product**

The scanning electron micrograph of the geopolymer product RCW is shown in Figure 4.

The SEM images of the geopolymer product RCW have shown to develop more networking channels which indicate the formation of aluminosilicate hydrate gel. The geopolymer product is expected to high compressive strength value with low porous sites also supported by the water absorption value of the product.
Variation of the amount of RC and CWC

The geopolymer products were prepared from the mixture of RC and CWC (5 – 20%) and mixed 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 as 0.60, 0.67, 0.81, 1.10 and 0.87 MPa for 0, 5, 10, 15 and 20 % of CWC respectively and are shown in Figure 5:

The compressive strength value increased with increasing with increase in the amount of CWC up to 15% but at 20 % compressive strength value was decreased. The increase in compressive strength value may be due to the pozzolanic reactivity of calcined white clay [17].

Effect of curing time on compressive strength of the geopolymer RCW

The geopolymer was prepared from RC (85%), CWC (15%) and the activator solution. The products were then cured at 60 °C for 2 hours followed by curing at room temperature for up to 28 days. The compressive strength values of the geopolymer products were found as 1.10, 1.53, 7.38 and 15.91 MPa at 7, 14, 21 and 28 days respectively and are shown in Figure 6.

The compressive strength value of the geopolymer products was found to increase with curing time. The curing for a longer period of time at low temperature is preferable for the synthesis of geopolymer as the condensation and evaporation of water molecules take place simultaneously preventing the formation of voids and cracks inside the materials thus increasing the compressive strength [23].

Variation of the amount of CaO

After the selection of the amount ratio of RC and CWC (85:15 in %) in the mixture, the amount of CaO was 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 was found to have 6.05, 7.55, 4.05 and 3.37 MPa for 1, 2, 3 and 4 % of CaO respectively and is shown in Figure 7.

![Figure 6: Compressive strength of the geopolymer products RCW with curing time](image)

![Figure 7: Compressive strength of the geopolymer product with variation of CaO](image)
The compressive strength value of the geopolymer product RWL was found to a maximum at 2% of addition of CaO. In ceramics, mechanical strength usually increases with decreases in porosity and same the Behaviour is observed in CWC-based geopolymers.

The introduction of CaO induces rapid setting; the Additional calcium reacts with silica and alumina to form the reaction products within the matrix, resulting in the additional strength development. However, the use of excessive lime disrupts the optimum gels forming structure and therefore a reduction in strength development has been observed [24, 25].

**Effect of curing time on compressive strength of the geopolymer RWL**

The mixture of 85% RC and 15% CWC was dry mixed with 2% of CaO, and then it was mixed with activator solution to make the paste and cast in the mould. The geopolymer product RWL was then cured at constant temperature 60 °C followed by curing at room temperature. The compressive strength values of the geopolymer products were found as 7.55, 10.18, 14.03 and 20.30 MPa at 7, 14, 21 and 28 days respectively and are shown in Figure 8.

![Figure 8: Effect of curing time on geopolymer product RWL](image)

Chloride resistance test

A Chloride resistance test was carried out by dipping the geopolymer product RCW in a 5 % hydrochloric acid solution, to determine the resistance to the severe environmental condition. The change in compressive strength values before exposure at 28 days of curing and dipping the sample in 5 % HCl solution at 7, 30 and 60 days is 15.91, 5.70, 5.00 and 4.05 MPa respectively and are shown in Figure 8.

![Figure 9: Change in compressive strength of the geopolymer product RCW dipped in 5% HCl solution](image)

The compressive strength was found to be reduced, but the degradation on the 7th days and 60th days was found slower. Chlorides in the solution may interact with Calcium Silicate Hydrate (CSH) gel and chemisorbed on the CSH layer. Thus promoting the formation of porous sites and weakening the strength of the product [27].

**Conclusions**

The geopolymerization Behaviour of red and white clays was studied. The compressive strength values of the geopolymer RCW using RC (85%) and CWC (15%) using a 1:1 solution of 4M NaOH and liquid sodium silicate were found to have 15.91 MPa at 28 days of curing. The use of additives such as lime enhanced the compressive strength of 20.30 MPa at 28 days of curing. A Microstructural study of the product has shown the formation of aluminosilicate gel. The mechanical, physical and durable properties of the geopolymer products were studied. These products are suitable for construction activities.
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References


