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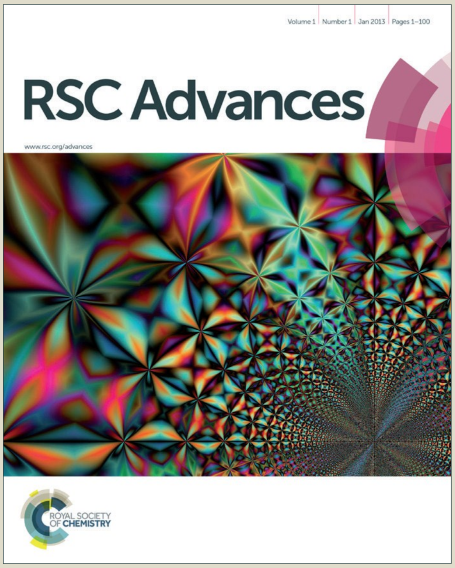

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Geopolymerization with bagasse bottom ash and china clay, Effect of Calcination temperature and silica to alumina ratio

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Abstract

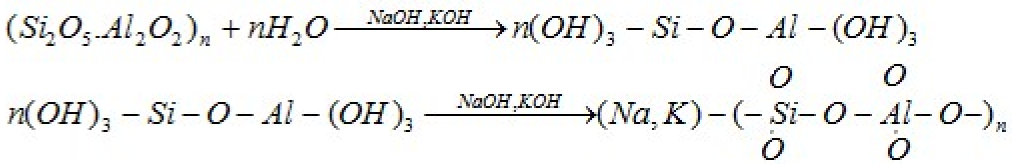
The object of this work is to study the Geopolymerization using bagasse ash and china clay at the most appropriate calcination temperature and the ratio of silica to alumina. Bagasse ash from sugar industries and china clay from shah dheri swat Pakistan was used in this work. Both the raw materials were characterized using XRF, FTIR and XRD. Clay was calcined at a temperature range of 600-1000 °C. The resulting amorphous material was reacted with bagasse ash and sodium silicate in different ratios of silica to alumina ranging from 2-4. The reaction was carried in strongly alkaline solution of sodium hydroxide to produce geopolymer cement whose compressive strength and setting time was studied. Geopolymer cement specimens were characterized using XRF, XRD and SEM. Highest compressive strength of geopolymers 16.64 MPa was obtained from the mix having SiO_2/Al_2O_3 ratio of 2.7 and clay calcined at a temperature of 900 °C

Key words: China clay, Thermal activation, Bagasse bottom ash, Geopolymer, Calcination temperature, Silica to alumina ratio

1. Introduction

Presently Portland cement is the most common among all the hydraulic binders in the present era but its production is highly energy intensive process as well as causes the release of high amount of greenhouse gases to the environment[1,2]. Portland cement production faces two basic problems, on one side, it needs 1450 °C in cement kiln which is achieved by the burning of Coal, gas or furnace oil, making the cost of production very high, due to high prices of fuel, while on the other side huge amount of greenhouse gases are released to the environment. Production of one ton of cement results in the release of approximately one ton of carbon dioxide, both due to calcination of limestone and burning of fuel. Portland cement contains 60-65% CaO which is obtained by the calcinations of $CaCO_3$. In order to address these problems, researchers have been trying to design new binders alternative to the existing cement, which substitute the Portland cements, and also be manufactured in a way as to safeguard our environment. Comparing with ordinary Portland cement, Geopolymer is a well-known binding material for its excellent characteristics, including its higher strength[3,4], low shrinkage[5], good acid resistance and fire resistance[3,5] comparatively low emission of greenhouse gases[3], high thermal resistivity[5], tremendous immobilization of heavy metal[6], high thermal stability[7], and low cost of production[8]. Due to such properties the potential applications of such material in the construction industry include fire proof[9], biomaterials[10] and waste treatment[11].

Geopolymerisation is a geo synthetic reaction of alumino-silicate minerals in a stongly alkaline medium at low temperatures[12]. Geopolymerization is a complex procedure which is not fully understood till the present time. A simple reaction mechanism involve condensation polymerization of ortho-sialiate ions which are considered as hypothetical monomers. The mechanism was proposed by Davidovits[13] as follows



$$(Si_2O_5.Al_2O_2)_n + nH_2O \xrightarrow{NaOH,KOH} n(OH)_3 - Si - O - Al - (OH)_3$$

$$n(OH)_3 - Si - O - Al - (OH)_3 \xrightarrow{NaOH,KOH} (Na,K) - (-\overset{O}{\underset{O}{Si}} - O - \overset{O}{\underset{O}{Al}} - O -)_n$$

Eqution 1 shows the synthesis of geopolymer having silica to alumina ratio (Si/Al) = 1. This ratio may be different depending upon the composition of alumino-silicate material and alkaline activator. Usually, geopolymerization process involves dissolution, transportation and polycondensation[14]. It is anticipated that geopolymer gel may diffuse among the interstitial spaces of particles. On the hardening of gel, the separate alumino-silicate particles are consequently bound together, resulting the matrix poses good mechanical performance like compressive strength. In the early research works, metakaolinite, (calcined kaolinite) has been utilized as the main source in geopolymerization[15,16].

Geopolymerization is mainly divided in to three steps as reported by a number of researchers[17]. In the first step silica and alumina source material are dissolved in alkaline solution, in the second step re-organization and dispersion of dissolved ions take place with the formation of small coagulated arrangement while the third step involves the poly-condensation of soluble species and formation of hydrated products.

Geopolymerisation may be carried out through sol-gel method, in which the most common raw material may be rich in alumina and silicate like natural pozzolan, fly ash, blast furnace slag, and thermally activated kaolinite clays. On thermal activation the kaolinite is transformed in to an anhydrous alumino-silicate which is the essential part of geopolymer. On thermal activation the kaolinite is converted in to its disordered structure, and possesses an enormous reaction potential when treated in a strongly alkaline medium like sodium hydroxide[18] or aqueous solution of calcium hydroxide[10]. Studying the Literature on geopolymer, it become clear that a number of researchers have thermally treated kaolinite clays at different levels of temperatures. Davidovits and Davidovits[19] activated a kaolinite clay at a temperatures like 500, 650, 700 and 750 ^{o}C and concluded that 750 ^{o}C is the optimum one for thermal activation. Palomo et al[20] reported 600-700 ^{o}C temperature range for the clay calcination as the optimum one, while Cioffi et al[21] activated the clay at 500, 550, 650 and 750 ^{o}C respectively. Zhang and Sun-Wei[22] used 700 ^{o}C while Zibouche et al[23] converted kaolinite into metakaolinite in the clay at 800 ^{o}C. Chareerat et al[24] thermally activated a kaolinite clay at various temperatures like 400-800 ^{o}C at the interval of 100 ^{o}C for different durations like 2, 4 and 6 h respectively and reported 600 ^{o}C as the best calcination temperature. Geopolymer was synthesized employing a mixture of 20% of meta-kaolinite and 80% of ash. All these researchers synthesized geopolymers with different properties.

In the present work geopolymerization was performed using bagasse bottom ash, a waste of sugar industry and china clay activated at different temperatures and different silica to alumina ratio and the effects of these parameters on the properties of geopolymer composite and mortar were studied. Moreover the effect of alkali concentration on the geopolymer properties has also been reported in this paper. Geopolymer cement pastes were also characterized with XRD (BRUKER), FTIR and scanning electron microscopy.

2. **Material and methods**

2.1. Collection of raw materials

For the synthesis of geopolymer bagasse bottom ash, china clay, sodium silicate, sodium hydroxide and de-ionized water were used. Bagasse bottom ash was collected from Premier Sugar mill Mardan KPK Pakistan, China clay was collected from Shah Dheri at District Swat, Sodium silicate was purchased from local glass industry at industrial estate Hayat Abad Peshawar. Chemical composition of bagasse ash and china clay are given in table 1. Sodium hydroxide of the Merck Company was purchased in the local market. De-ionized water was obtained from PCSIR Labs Peshawar. 3 M aqueous solution of sodium hydroxide and sodium silicate in the ratio of 1:1 by weight was used as basic solution. Sodium hydroxide solution was prepared by dissolving dried pellets of 99% pure sodium hydroxide in distilled water. Aqueous solution of sodium silicate was made with a ratio of 28.7% SiO_2, 8.9% Na_2O and 62.4% H_2O by weight.

2.2. Thermal treatment of china clay

Five samples of china clay were dried in oven at 105 ºC for one hour. The dried clay samples were crushed using mortar and pestles and sieved to 80 μm. All samples were calcined in a programmable electric furnace for 10 hours with a heating rate of 5 ºC/min at temperatures of 600, 700, 800, 900 and 1000ºC and were named as C_1, C_2 C_3 C_4 and C_5 respectively. All the clay samples were stored in air tight plastic bottles to avoid moisture capture.

2.3. Synthesis of Geopolymer composite

Different geopolymers mixes were prepared with silica to alumina ratio (SiO_2/ Al_2O_3) of 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.16, 3.28 and 3.5 and polymer obtained were named as GP_1 GP_2 GP_3 GP_4 GP_5 GP_6 GP_7 GP_8 and GP_9 respectively. The detail of the mixes is given in Table 2. For this purpose thermally activated china clay at optimum temperature (900 ˚C) was mixed with bagasse ash and Sodium silicate at proper ratio (tables 2). Raw mixes were thoroughly mixed in laboratory blender and slurry was made using 3 M

Sodium hydroxide solution. Slurry after thorough mixing was added into iron mold of internal diameter of 50 mm cubic mold in accordance with ASTM C109 and kept in oven at 60˚C for 24 hours and then de-molded. The de-molded samples were again kept in the oven at 60˚C for 7 days.

2.4. Preparation of Geopolymer mortar

Three types of mortars M_1, M_2 and M_3 in the ratio of 1:1, 1:2 and 1:3 of geopolymer to sand respectively were prepared. Cubes of the mortars were prepared in the same way as that of geopolymer composites and compressive strength was studied in the same way.

2.5. Characterization of the materials

For characterization of raw material X-Ray fluorescence spectrophotometer (XRF) PW 2582/00 (Philips), X-Ray Diffractometer (XRD) JDX-3532 (JEOL Japan) working on 40KV and 30mA and Scanning Electron Microscope (SEM)JSM-5910 (JEOL Japan) working 20 KeV were and Fourier transform infrared spectroscopy (FTIR) IR-AFFINITY-1 (SHIMADZU Japan) were used.

2.6. Compressive strength of geopolymer composites and mortars

Compressive strength of geopolymer composites and mortars was determined using Universal Testing Machine (UTM) UTM-100 TON/1000 KN (SHIMADZU Japan) at the curing age of 7 days.

3. Results and discussions

3.1. Characterization of raw material

Chemical composition of the bagasse ash as determined by XRF is shown in the table 1. Bagasse bottom ash contain as high quantity of silica as 78% along with other major components like Al_2O_3, Fe_2O_3, CaO and MgO. The sum of silica and alumina in the studied ash is 84% which is in good agreement with ASTM designation for the pozzolana. The loss on ignition (LOI) was recorded as zero, it means that no moisture content present in the ash and no side reaction take place by heating.

Chemical composition of china clay represent 46% silica and 33.595% alumina as the major components while some CaO, MgO and Fe_2O_3 are also present in comparatively small quantities (table 1). China clay also exhibits the properties of natural pozzolana per ASTM. 14% loss of ignition is due to significant weight loss which corresponds to the loss of water during the conversion of kaolinite in to meta- kaolinite.

XRD pattern of bagasse ash is shown in figure 1, which indicate the major diffraction peaks at 20º and 40º indicating the amorphous nature of silica. Two major peaks are shown in the XRD pattern i.e. mullite and quartz. XRD patterns of uncalcined and calcined clay are represented in figures 2a and 2b respectively. Study of the pattern for untreated clay shows that all the characteristics peaks are due to the kaolinitic clay and on calcination these peaks were reduced and mostly disappeared (figure 2b), showing that clay become amorphous on thermal treatment. The main object of thermal activation is to convert metakaolinite into kaolinite which is confirmed from the XRD pattern of calcined clay.

3.2. Characterization of the geopolymer

3.2.1. XRD study

The XRD diffractogram of geopolymer composite synthesized at optimum conditions (clay calcined at 900 °C and silica to alumina ratio 2.7) is shown in figure 3. Although the geopolymer obtained seems to be amorphous at initial stage but the formation of zeolitic phase can also be observed. The alkali activation of bagasse ash may also give rise to the formation of crystalline phase as sodium chabazite and hydroxyl sodalite type zeolites represented from the peaks marked as A. The peaks of a low broad peaks (19-25°) represent the presence of meta-kaolinite[30]. The presence of kaolinite is confirmed from the characteristic peaks of clay at 800 °C which seems not sufficient to convert kaolinite into amorphous meta-kaolinite. Peaks for kaolinite vanishes absolutely in the geopolymer containing clay calcined at 900 °C endorsing the complete transformation of kaolinite into meta-kaolinite. At this temperature some peak amorphous alumino-silicate phase also appears in the geopolymer materials[9].

The appearance of peaks for quartz in XRDs of geopolymer samples indicate that quartz can’t be dissolved during geopolymerization.

The SEM micrographs of the geopolymers synthesized from clay calcined at 800 and 900°C with silica to alumina ratio of 2.7 are shown in figure 4a and 4b respectively.

The SEM image of geopolymers obtained at 800 °C have a spongy nature while that obtained at 900 °C has a compact nature indicating that geopolymer synthesis is more significant in the clay calcined at 900 °C than that at 800 °C. Some small cracks are seen on the micrograph of geopolymer matrix. For SEM analysis solid sample of geopolymer was cut into reasonable size pieces and was coated with silver to make it conductor. These cracks may have come either during cutting or coating with silver or may be due to some instrumental error. Some unreacted particles can also be identified which may be due to the incomplete reactions during geopolymer formation.

3.2.2. FTIR spectra study

FTIR spectra of geopolymer containing clay treated at 800 and 900 °C are shown in Figure. 5. Spectrum of 800 °C, indicates that this temperature is not appropriate to breakdown the crystalline kaolinite and its transformation into meta-kaolinite. The characteristic absorption bands of kaolinite appears at 3700-3625 cm^{-1} [25]. The absorption band at 1450-1400 cm^{-1} is regarded as to the stretching of Carbon-Oxygen bond in sodium carbonate. This may bring efflorescence in geopolymer[26]. The bands at 3450-3470 and 1650 cm^{-1} may corresponds to the stretching and deformation of oxygen hydrogen bond of water molecule respectively[27]. The peaks observed at 1070 and 760 cm^{-1} are accredited to the A-symmetric and symmetric vibration of Si-O-Al and Si-O-Si in tetrahedral geometry of AlO_4 and SiO_4 respectively[28]. The absence of 920 cm^{-1} band in the composite containing clay calcined at 900 °C confirm the complete reaction of meta-kaolinite in geopolymerization.

3.2.3. Setting time

The relation of setting time with calcination of china clay at 600-1000 ºC is shown in Figure. 6. The geopolymer cement having china clay at 800 ºC shows a little high setting time and showed efflorescence. This may be due to the presence of kaolinite as confirmed from the X-ray diffractogram. It is therefore clear that the clay heating at 800 ºC, is not sufficient for the calcination and its transformation into meta-kaolinite. From the results, it seems that setting time decrease upon increasing the calcination temperature upto 900 ºC which corresponds to the amount of amorphous nature of meta-kaolinite. Consequently during the calcination process of clay at 900 ºC, highest dis-orderness within the meta-kaolinite structure occur. During geopolymerization the state of disorder in meta-kaolinite assure the reactivity. So the increase in setting time is attributed to the increase of dis-orderness in meta-kaolinite.

3.2.4. Compressive strength.

The influence of calcination temperature of clay on the compressive strength of geopolymer composite is reported in figure 7. From the figure it is clear that compressive strength increases from 600 to 900 ^{o}C and then decrease is observed on further increase in calcination temperature. It is obvious that when de-hydroxylation of kaolinite occur, structure of the resulting meta-kaolinite comes in disorder state, which depends upon the calcination temperature. The highest disorder state is attained at around 900 ^{o}C. The greater is the dis-orderness, the better is the quality of geopolymer. Calcination of kaolinitic clays above 900 ^{o}C decreases the tendency of dis-orderness within the structure of meta-kaolinite, which give rise to less performant geopolymer products.

The ratio of silica to alumina (Si/Al) has a great impact on the compressive strength of resulting geopolymer composite. Compressive strength of geopolymers having different Si/Al is shown in figure. 8. Comparing the strength of different composites i.e. GP_1 GP_2 GP_3 GP_4 GP_5 GP_6 GP_7 GP_8 and GP_9 containing china clay calcined at 900 ^{o}C (C_3) shows that compressive strength of geopolymer having silica to alumina of 2.7, is the highest as compared to all other composites, which may be regarded due to the stoichiometric ratio of silica to alumina in the geopolymer while the smaller strength for other ratios is attributed to the fact that excess silica affects the bonding between silica and alumina in geopolymer.

Concentration of sodium hydroxide also play very important role in the synthesis and developing strength of geopolymer. The effect of sodium hydroxide on the compressive strength of geopolymer composite is shown in Figure. 9. From the table it is clear that the highest compressive strength of geopolymer composite is observed with 3M NaOH. Further increase in alkali concentration the compressive strength goes on decreasing. The decrease in strength may be due to the presence of excess amount of NaOH above the stoichiometric value and due to its hygroscopic nature.

Compressive strength of geopolymers mortars is given in table 3. Three types of mortar have been studied ranging in the polymer to sand ratio of 1:1, 1:2 and 1:3 respectively. For all these mortars the silica to alumina ratio was kept as 2.7, as it is the optimum ratio for maximum strength. It is clear from the table that compressive strength decreases with the proportion of sand in the mortar. Highest strength was recorded for mortar of 1:1 of polymer to sand respectively.

4. Conclusion

China clay samples were calcined at different temperatures and used as an aluminosilicate material for the synthesis of geopolymer binder. The effect of calcination temperature on the parameters of geopolymer including setting time and compressive strength showed that geopolymer pastes obtained from china clay calcined at 600-900 ^{o}C showed the drop in setting time and increase in the compressive strength increases. Above 900 ^{o}C, an increase in setting time and decrease in compressive strength is observed. From these results it is concluded that when the de-hydroxylation of kaolinite clays takes place, the dis-orderness in the structure of meta-kaolinite occurs which changes with calcination temperature. This maximum dis-orderness is attained at 900 ^{o}C. An increase in the dis-orderness in meta-kaolinite promotes better characteristics of geopolymer. Above this temperature, the dis-orderness again decreases. Moreover silica to alumina ratio of 2.7, and 3M NaOH was found as the optimum for achieving highest compressive strength.

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Figure captions

Figure 1. XRD Pattern of the bagasse ash

Figure 2. XRD Pattern a. uncalcined china clay b. calcined china clay

Figure 3. XRD of geopolymer containing a. clay calcined at 800 ^{o}C b. clay calcined at 900 ^{o}C.

Figure 4a. SEM micrograph of geopolymer containing a. clay calcined at 800 ^{o}C.

Figure 4b. SEM Picture of geopolymer containing clay calcined at 900 ^{o}C

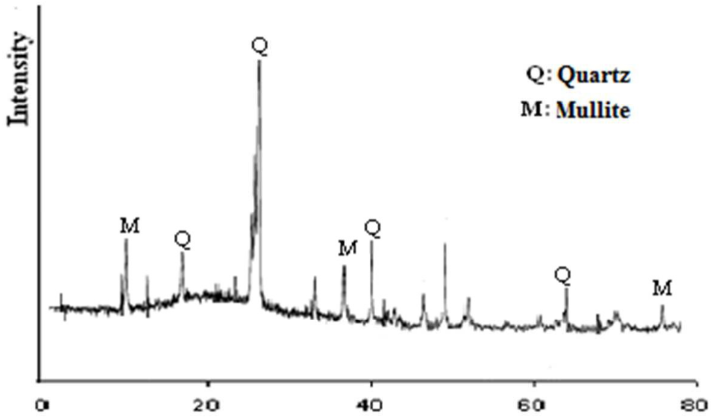
Figure 5. FTIR spectra of geopolymer containing a. clay calcined at 800 ^{o}C b. clay calcined at 900 ^{o}C.

Figure 6. Effect of calcination temperature of clay on the setting time of geopolymer.

Figure 7. Effect of calcination temperature of clay on the compressive strength of geopolymer.

Figure 8. Effect of silica to alumina ratio on the compressive strength of geopolymer.

Figure 9. Effect of alkali concentration on the compressive strength of geopolymer.



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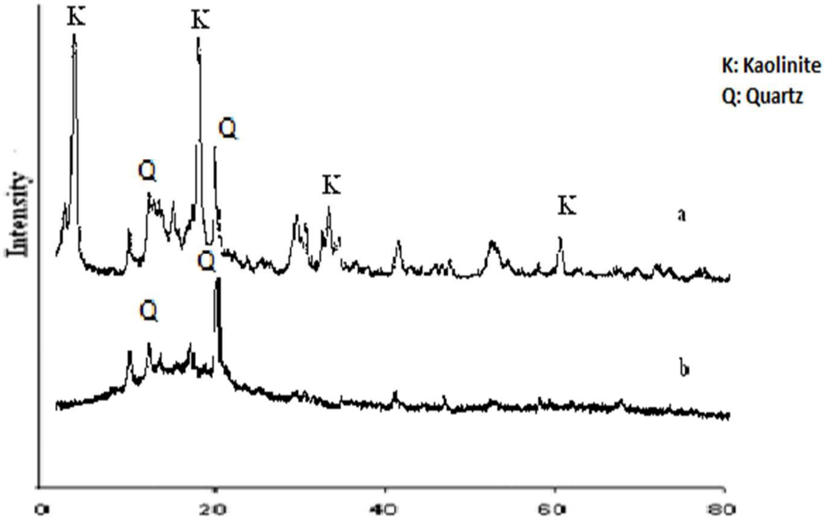


Figure 2. XRD Pattern a. uncalcined china clay b. calcined china clay

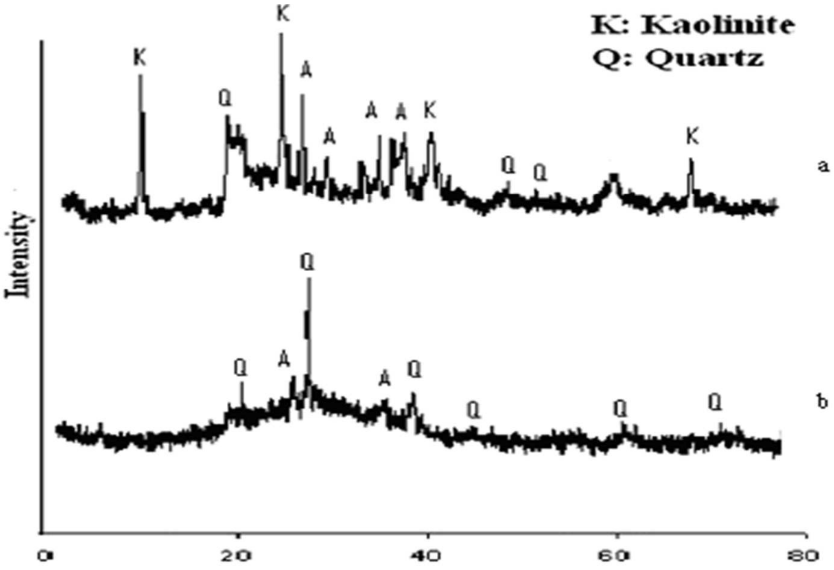


Figure 3. XRD of geopolymer containing a. clay calcined at 800 °C b. clay calcined at 900 °C.

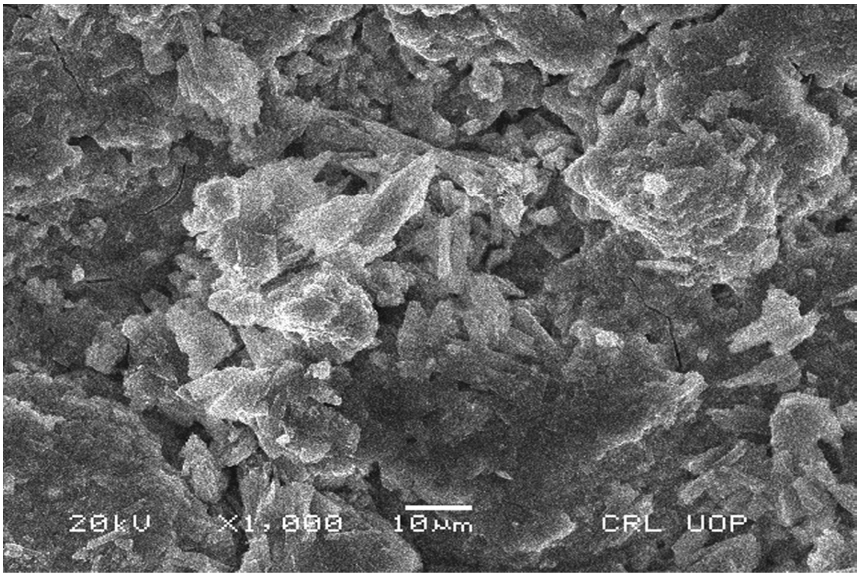


Figure 4a. SEM micrograph of geopolymer containing a. clay calcined at 800 °C.

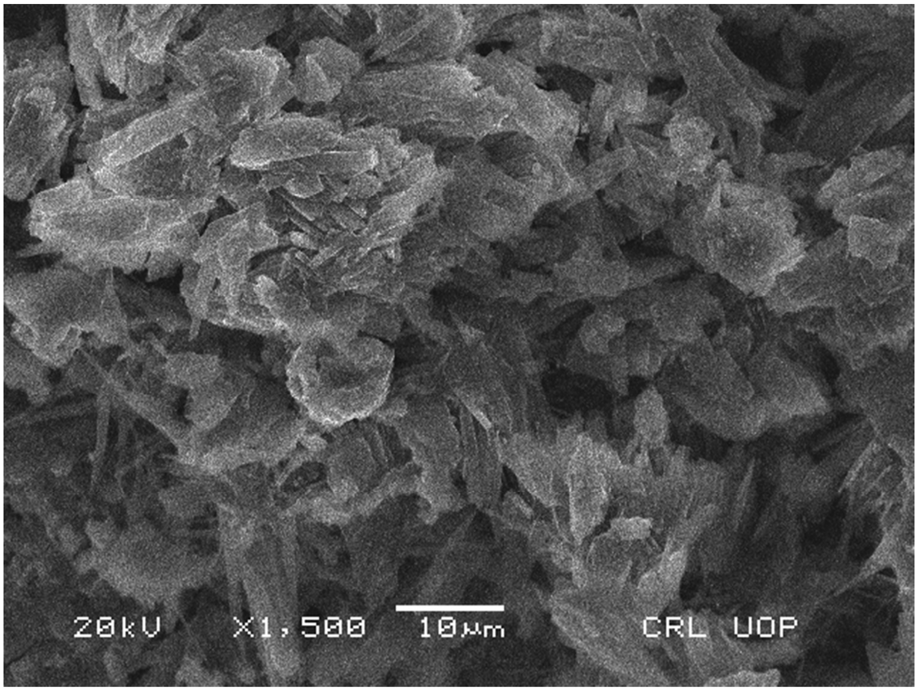
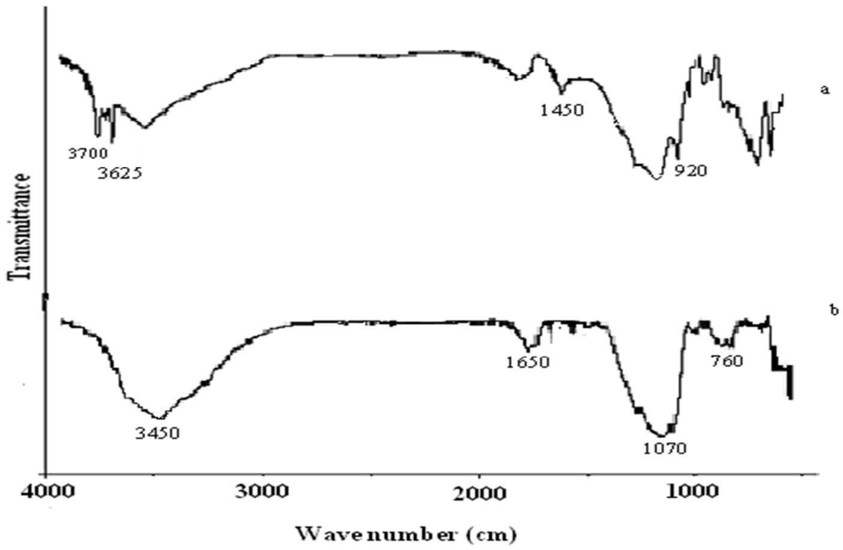


Figure 4b. SEM micrograph of geopolymer containing clay calcined at 900 °C



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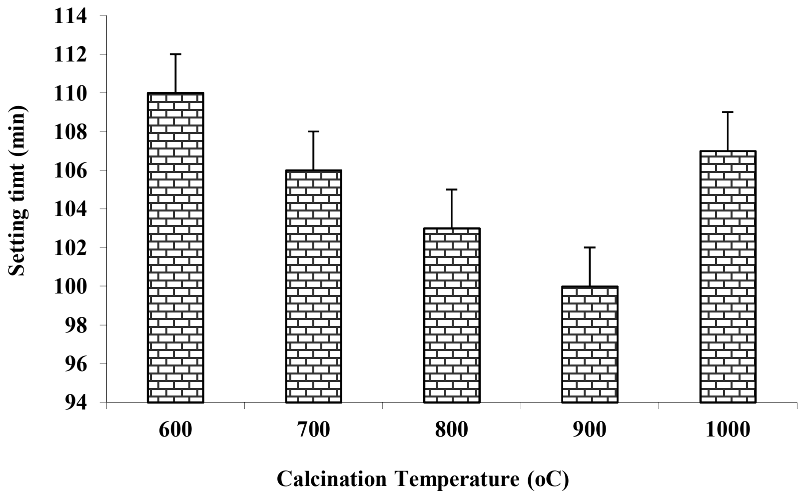

Figure 6. Effect of calcination temperature of clay on the setting time of geopolymer.

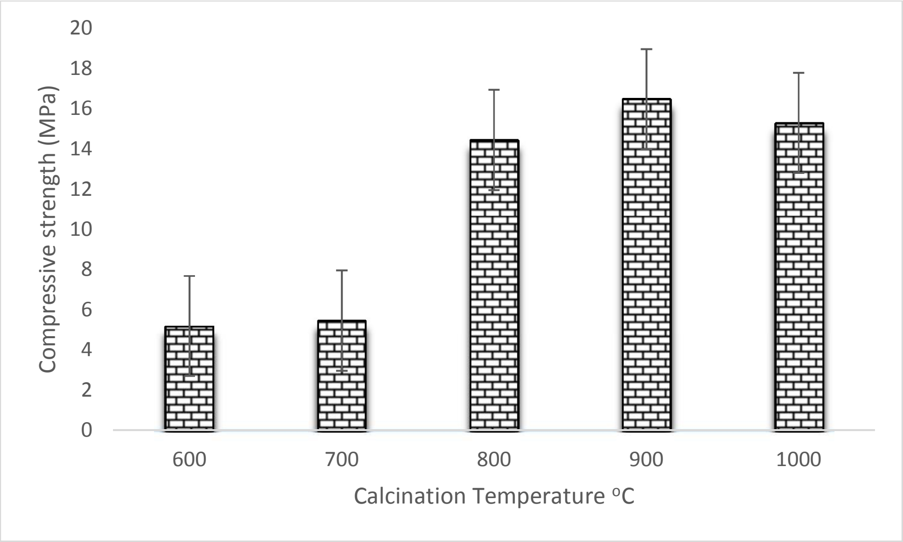

Figure 7. Effect of calcination temperature of clay on the compressive strength of geopolymer.

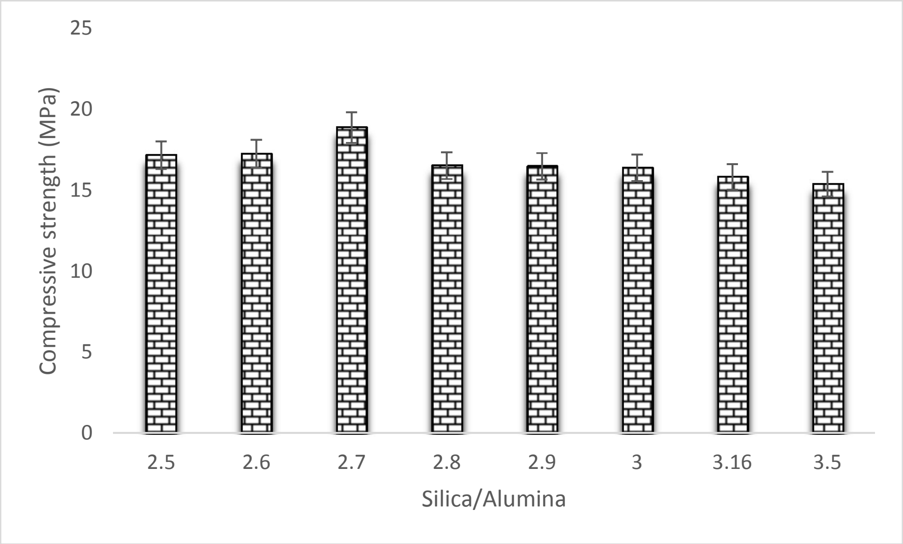

Figure 8. Effect of silica to alumina ratio on the compressive strength of geopolymer.

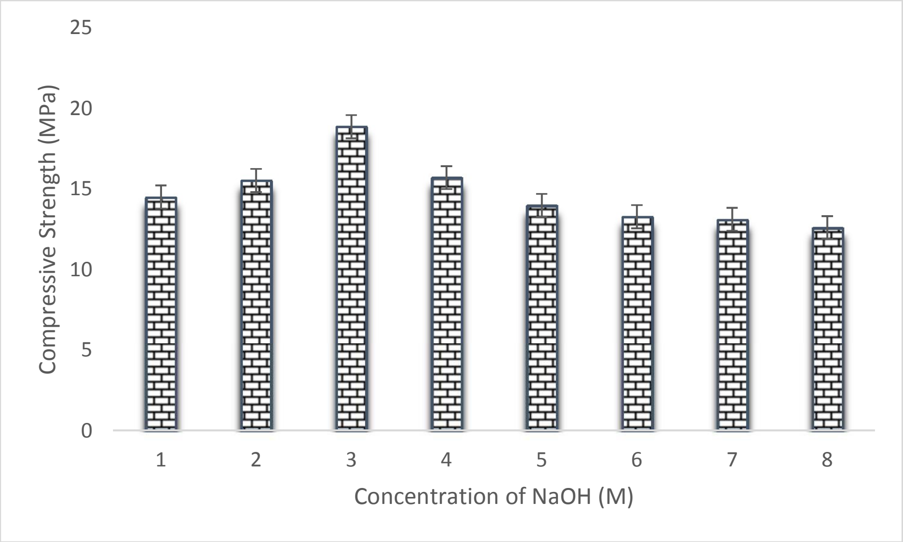

Figure 9. Effect of alkali concentration on the compressive strength of geopolymer.

Table 1. Chemical composition of bagasse ash and china clay

Oxides	Weight (%)	
	Bagasse bottom ash	China Clay
SiO_2	78.046	46.087
Al_2O_3	3.813	33.676
Fe_2O_3	2.012	6.937
CaO	3.975	0.453
MgO	2.245	1.238
K_2O	5.943	4.238
Na_2O	0.377	0.436

Table 2. Proportion of raw material in Geo-polymer having different silica to alumina ratio.

Sample Taken	% Weight Taken								
bagasse ash	36.00	34.00	36.00	38.00	40.00	40.00	41.00	42.00	44.00
china clay	64.00	61.00	59.00	57.00	55.00	53.00	51.00	49.00	46.00
Sodium silicate	0.00	5.00	5.00	5.00	5.00	7.00	8.00	9.00	10.00
SiO_2/Al_2O_3	**2.50**	**2.60**	**2.70**	**2.80**	**2.90**	**3.00**	**3.16**	**3.28**	**3.50**

Table 3. Compressive strength of mortar

Sample ID	Ratio of composite to sand	Compressive strength (PSI)
M_1	1:1	13.41
M_2	1:2	9.70
M_3	1:3	6.42