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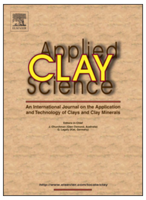

Research Paper

Synthesis and characterisation of geopolymer from Nigerian Clay

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ABSTRACT

Nigerian Ikere-clay has been characterised for its possible use in synthesis of geopolymer binder. The significance of endothermic peaks at the dissolution/hydrolysis stage on alkaline reactivity of the clay and geopolymer strength development was also investigated. The clay, which was of kaolin type, was thermally treated to convert it into amorphous metakaolin which is more reactive precursor for geopolymer synthesis. Geopolymer has been synthesised at ambient temperature using sodium hydroxide and/or sodium silicate solution. The characteristics of clay and clay derived geopolymer were evaluated using x-ray fluorescence (XRF), x-ray diffraction (XRD), Fourier transform infra-red spectrometry (FTIR), laser particle size analyser and scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX). The reactions occurred during geopolymerisation were monitored using isothermal conduction calorimeter. FTIR revealed the existence of Al-O and Si-O stretching vibrations of amorphous alumino-silicate network for clay and geopolymers. SEM-EDX images confirmed the presence of reaction product corresponding to NASH ($N = NaO$, $A = Al_2O_3$, $S = SiO_2$, $H = H_2O$) gel. Attempts were made to correlate the microstructure with strength development. The maximum compressive strength of 28.2 MPa was obtained for geopolymer that was synthesised with $NaOH/Na_2SiO_3$ solution and cured at 27 °C for 28 days. The samples with good compressive strength showed compact microstructure. The results demonstrated the suitability of Nigerian kaolinitic clay for synthesis of geopolymer at ambient temperatures.

1. Introduction

Clay minerals are naturally occurring alumino-silicate hydrates with varying amounts of iron, magnesium, alkali metals and alkaline earths. Bergaya and Lagaly (2013) alluded to the fact that clay and clay minerals will be recognised as the material of the twenty-first century due their environment friendliness, widespread availability and low cost when compared with other raw materials. The clay group of minerals is classified into different group depending on the ratio of silica to alumina and layering of their sheets. The sheets may be layered on a 1:1 to form tetrahedral-octahedral where silica and alumina sheets form a layer by sharing oxygen atoms and held together by hydrogen bonding. Kaolin group is an example of clay minerals with SiO_2/Al_2O_3 ratio = 1.

Traditionally, clay is used in pottery, ceramics, environmental remediation and construction due to its inertness, stability, rheological properties and reactivity (Harvey and Lagaly, 2013). One of the emerging applications of clay is the production of geopolymer. The term geopolymer is used for inorganic polymer produced by alkali activation of alumino-silicate precursors such as slag, clay and coal fly ash (Davidovits, 1991; Rickard et al., 2011; Kuenzel et al., 2013; Kumar et al., 2013). The most widely investigated clay groups for geopolymer synthesis is kaolin (Davidovits, 1991; Alonso and Palomo, 2001a; Phair and Van Deventer, 2001; Provis et al,. 2009). This is due to the fact that kaolin transforms to metakaolin on thermal treatment which is a good source of amorphous silica (SiO_2) and alumina (Al_2O_3). The amorphous alumino-silicate material reacts with alkali hydroxides or alkali silicates under high pH conditions to form an inorganic polymer with 3 dimensional structure. The term geopolymer was coined by Davidovits (1991) for {poly(sialate), –Si–O–Al–O– with Si/Al = 1}or {poly(sialate– siloxo), –Si–O–Al–O–Si–O– with Si/Al = 2} or{poly(sialate–disiloxo), –Si–O–Al–O–Si–O–Si–O–, with Si/Al = 3}. Synthesis of geopolymer requires less amount of energy and generates less CO_2 when compared to Portland cement. Furthermore, geopolymer binder possesses excellent physico-chemical and mechanical properties such as high strength, micro- or nano-porosity, thermal stability, high surface hardness, and fire and chemical resistance (Dimas et al., 2009).

In many states in Nigeria, kaolin clay is in abundance and can be sourced through inexpensive mining. However, scanty information is available on the characteristics of Nigerian clays as precursor for geopolymer synthesis (Ogundiran and Ikotun, 2014). Furthermore, chemical reactions that characterise geopolymer formation involve heat change and this is measured with isothermal conduction calorimeter (Alonso and Palomo, 2001b; Pacheco-Torgal et al., 2008; Kumar and Kumar, 2011). In calorimetric studies of alkaline geopolymerisation of metakaolin, several authors have identified two peaks with a dormant period in between (Alonso and Palomo, 2001b; De Silva et al., 2007; Zuhua et al., 2009; Kuenzel et al., 2013). The dissolution/hydrolysis stage was characterised by the first exothermic peak while

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the geopolymerisation stage was characterised by the second exothermic peak. However, the significance of endothermic peak which is associated with the dissolution/hydrolysis stage was less emphasised. Therefore, the aim of the present work was to characterise Nigerian Ikere-clay and study its reactivity under different alkaline conditions and its suitability for the synthesis of geopolymer. Isothermal conduction calorimetry has been used to elucidate the effect of reactivity on reaction and consequently microstructure evolution. Attempts were made to correlate the microstructure with compressive strength.

2. Materials and Methods

2.1. Material

The Nigerian raw clay used in the study was originally extracted from Ikere, in Ekiti state of Nigeria. This was sourced from the Federal Institute of Industrial Research Oshodi (FIIRO), Lagos. The clay was thermally treated in a laboratory programmable furnace at a constant rate of 7.8 °C/min from ambient to 700 °C for 6 hours. The optimum condition of thermal treatment was determined in a previous study (Ogundiran and Ikotun, 2014).

2.2. Material characterisation

The chemical composition of calcined clay (CC) was measured by X-ray fluorescence (XRF) spectroscopy (Table 1). Raw clay (RC) and (CC) were characterised for their chemical, mineralogical and structural properties. The mineralogical phases present in the RC and CC were identified by Bruker X-ray diffractometer (D8 Discovery, US). Samples were analysed using 2θ range from 15 to 90^0 with a scan rate of 0.02^0/0.5 sec. The CuKα radiation (= 1.5418) was generated at 40 kV and 40 mA. The XRD patterns presented in Fig. 1 were analysed using Diffrac. EVA V2.1 software. Absorption spectra of the bonding characteristics of the samples were determined by Fourier transformed infrared spectroscopic method (Nicolet 5700 FTIR, Thermo Electron Corporation) and are shown in Fig. 2. The particle size distribution of both raw and calcined clays was determined with laser particle size analyser (MASTERSIZERS, Malvern, UK).

2.3. Determination of reactivity of raw and calcined clay

Effects of sodium hydroxide (NaOH) and NaOH/sodium silicate (NaS) activators at different concentrations on the clay reactivity were measured as a function of heat released with time for 24 hours using an eight channel isothermal conduction calorimeter (ICC) (TAM AIR, Thermometric AB, Jarafalla, Sweden) at 27.0 °C. Sodium hydroxide activators were prepared by dissolving NaOH pellets (EMPARTA, India) in deionised water and allowed to cool to room temperature. Alkaline activators were prepared by mixing 6 M, 8 M, 10 M NaOH solutions individually with sodium silicate (1:1) about 24 hours before use. 7 g of CC was thoroughly mixed with 5 mL each of 6 M, 8 M, 10 M NaOH solutions and the mixtures before loading into the calorimeter. The reactivity of RC was also investigated by mixing 7 g of it with 5 mL 8 M NaOH/NaS and subjected to the same ICC.

2.4. Synthesis of clay-based geopolymers

The clay sample was mixed with 6 M, 8 M and 10 M NaOH at liquid/ratio of 0.48 and 6 M, 8 M, 10 M NaOH/NaS at liquid/ratio of 0.46 to form geopolymer pastes. Geopolymer could not be produced with 10 M NaOH/NaS because clay reacted very fast and set before the proper mixing. The pastes were cast into 25 × 25 × 25 mm^3 cubic moulds and vibrated to remove entrapped air. Two sets of samples were prepared, first, the samples cured at ambient temperature (27 °C) and second, the samples cured at 60 °C for 48 hours followed by curing at 27 °C. Compressive strength were measured at 7 and 28 days using an automatic compression test machine (ACT-COMPTEST 2000 AIMIL INDIA LTD). Three samples were tested for each measurement and the mean values for the closest two were determined.

Table 1
Chemical composition of calcined clay (Wt. %).

SiO_2	Al_2O_3	CaO	MgO	P_2O_5	TiO_2	Na_2O	K_2O	Fe_2O_3	ZrO_3	LOI
55.8	27.4	0.11	0.06	0.09	1.24	0.23	0.17	1.10	0.11	1.27

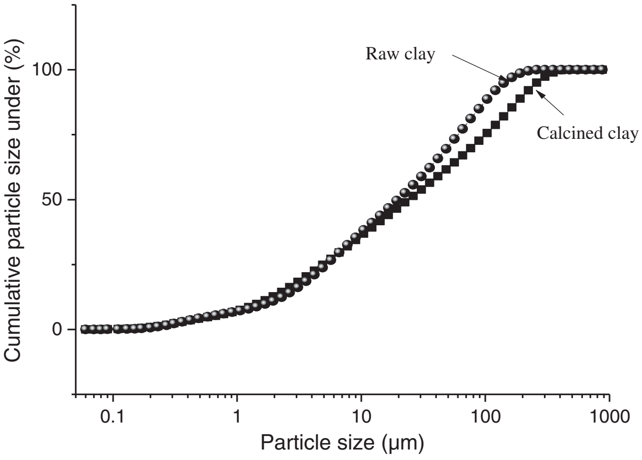

Fig. 1. Particle size distribution for raw and the resulting calcined clay.

2.5. Geopolymer characterisation

The geopolymerisation of the samples was stopped by crushing and immersing in isopropyl alcohol overnight and dried at 60 °C for 8 hours to remove adsorbed water. The dried samples were pulverised separately to pass a 200 μm sieve. XRD was used to identify the mineralogical changes in the geopolymer. The structural re-ordering and bonding characteristics of the geopolymers were studied using FTIR. Microstructural information and changes in elemental composition of the geopolymers were obtained using Field emission gun-scanning electron microscope (Model FEI 430) fitted with energy dispersive X-ray spectrometer (SEM/EDX) and operated at 15.0 KV.

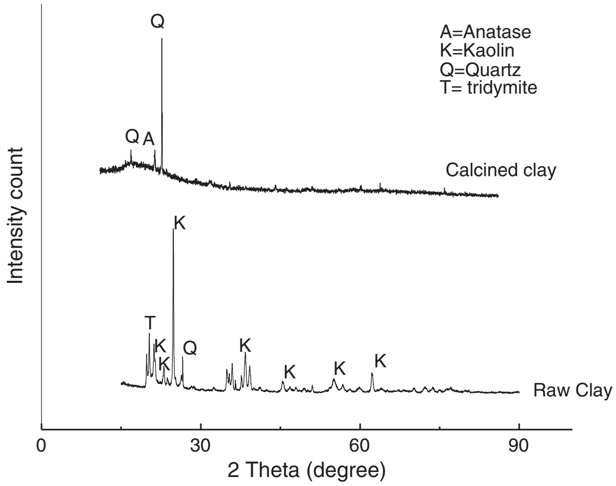

Fig. 2. XRD spectra of raw and calcined clay.

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