



## Research paper

# Geothermal clay-based geopolymer binders: Synthesis and microstructural characterization



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## ABSTRACT

Geothermal clay rich in kaolinite was first prepared into geopolymer binders. Preparation conditions of calcination on geothermal clay,  $\text{Na}_2\text{SiO}_3$  and NaOH combination in alkaline activator, and water content were studied. Thermal nature of the geothermal clay was characterized by TG-DSC and XRD measurements, which shows characteristics of kaolinite and cristobalite during calcination. Mechanical property, morphology and microstructure of the geothermal clay-based geopolymers were characterized by compressive strength measurements, SEM observation and NMR spectra analysis. With optimal synthesizing parameters, geothermal clay-based geopolymer possessed a compressive strength of 19.5 MPa, as well as a homogeneous geopolymeric gel with high percentages of  $Q^2(2Al)$  and  $Q^1(1Al)$ . As geothermal clay is supposed to be of intermediate dissolution reactivity in geopolymerization, this synthesis might extend the kinds of raw aluminosilicates in geopolymer formation.

## 1. Introduction

Geopolymer, a three-dimensional amorphous binder material, has attracted extensive attention due to the potential properties in replacement of ordinary Portland cement (OPC), but of low  $\text{CO}_2$  emission in the synthesis process (Davidovits, 1989; Duxson et al., 2007). Chemical reactions in synthesizing geopolymers, namely geopolymerization, are integrated processes involved the dissolution of raw materials in highly alkaline solution to form silicate and aluminate monomers, reorientation and polymerization of these monomers into oligomers and network, and the condensation of the network (Rao and Liu, 2015). In geopolymerization, the dissolution of monomers plays an important role because it forms the precursors for polymerization and condensation. Generally, calcination in the pre-treatment or to choose by-products after calcination is employed to obtain raw materials with high reactivity for the dissolution of monomers. For instance, metakaolin obtained through heating kaolinite in the temperature range among 500–900 °C was studied as exemplary material in geopolymer synthesis (Rahier et al., 1996). Calcination forms an amorphous structure to the kaolinite, in which the  $\text{SiO}_4$  sheets persist but in a distorted form, while the octahedral aluminum sheets are profoundly altered, although some short-range structure is preserved (Wan et al., 2017). Similarly, ore-dressing tailings of bauxite heated at 800 °C for 1 h has been

synthesized into geopolymer of 40 MPa in compressive strength (Ye et al., 2014). Fly ash, which is the other most extensively studied raw material for synthesizing geopolymers, is the by-products of coal combustion (van Jaarsveld et al., 2002). Granulated blast furnace slag, which is the by-products of iron smelting, is also used as raw aluminosilicate in geopolymerization. In addition, mechanical activation has been used to enhance the dissolution activity of raw aluminosilicates. Temuujin et al. (2009) reported that grinding fly ash in a vibration mill with a milling media to powder ratio of 10 led to an 80% increase in compressive strength of the produced geopolymers when compared with geopolymers synthesized directly from raw material. Obviously, calcination and mechanical activation are the opposite of low  $\text{CO}_2$  emission, which is the important advantage of geopolymer synthesis.

Therefore, in pursuing the commercialization of geopolymer as environmental friendly construction material, raw aluminosilicates from industrial waste without pre-treatment are studied extensively. For example, kaolinite, albite and silty clay were used as fine aggregates in the preparation of fly ash-based geopolymers (Xu and van Deventer, 2002; Sukmak et al., 2013). And Ahmari et al. (2012) used waste concrete powder as additive in the synthesis of fly ash-based geopolymer, of which the maximum compressive strength was 35 MPa. Another waste named red mud that produced in alumina refining process was synthesized into geopolymers using rice husk ash (full in  $\text{SiO}_2$ ) and

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NaOH as alkaline activator (He et al., 2013). However, these syntheses rely on the limited industrial by-products (e.g., fly ash), which would be an obstacle in large-scale applications in some countries. Furthermore, oil sands tailings and many mine tailings that contain aluminosilicate minerals as their main constituents have been proposed as raw materials in the syntheses of geopolymers (Rao and Liu, 2015). Zhang et al. (2011) pioneered the preparation of copper mine tailings-based geopolymer bricks, but compression was applied in the bricks formation. Thus to synthesize geopolymers directly from industrial waste is interesting area that can be studied further for selecting the proper raw aluminosilicate.

Clay minerals related to geothermal activity, which is named geothermal clay in this study, are abundant aluminosilicates in geothermal fields. Their properties are not only affected by temperature but also by several factors such as rock and fluid chemistry, time, fluid/rock ratio, the nature of the precursor material or the mechanism of the crystal growth (Mas et al., 2006). Geothermal clay is usual industrial waste after drilling wells in geothermal energy exploitation. Many studies reported the geological characteristics of geothermal clay (Mas et al., 2006), but no application of geothermal clay has been found so far. However, geothermal silica from geothermal power plants, which is an analogous by-product to geothermal clay, is employed as additive in OPC and geopolymer syntheses. For example, Gómez-Zamorano and Escalante-García (2010) prepared Portland cement pastes substituted with 0%, 5%, 10% and 15% of geothermal silica in mass and cured at 10, 20, 40 and 60 °C for up to 540 days. According to calcium hydroxide contents analysis, they found that the geothermal silica showed a strong pozzolanic behavior. Hajimohammadi et al. (2011) used geothermal silica to mix with solid sodium aluminate and sodium silicate solution in the preparation of geopolymers at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 3. In the present study, geothermal clay is studied as raw aluminosilicate in preparing geopolymers, of which the microstructure is characterized. We hypothesize that the clay endured geothermal activity possesses higher reactivity in the dissolution of silicate and aluminate monomers than usual clay. This study might enrich the types of raw aluminosilicates for the synthesis of geopolymers and give a further understanding on geopolymerization reactions.

## 2. Experimental

### 2.1. Materials

Geothermal clay rock was collected from the Los Azufres geothermal field, Mexico at the depth of 250 m where the temperature exceeds 150 °C. It was measured the particle size at 50% and 85% of cumulative undersize of 26.9 μm and 36.3 μm, respectively from a Shimadzu SALD-1100 laser diffraction analyzer. Table 1 gave the chemical analysis of the whole geothermal clay rock measured by X-ray fluorescence (XRF, PANalytical Axios), in which SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the main components with Si/Al ratio around 3.5. Fig. 1 showed the X-ray diffraction (XRD, Bruker D8) pattern and scanning electron microscopy (SEM, JEOL JSM-5610LV) image of the geothermal clay. The quantitative analysis of XRD pattern gave 47.44% kaolinite, 49.85% cristobalite in mass, and trace amount of tridymite and quartz in the geothermal clay. The SEM image showed kaolinite and cristobalite particles in micrometers, exhibiting platy and granular shapes, respectively. Although other clay minerals (e.g., montmorillonite or illite) were not identified in the XRD pattern of the geothermal clay, they were presumably included according to the components of Table 1.

**Table 1**  
Chemical analysis of the whole geothermal clay rock.

Components	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>	CaO	TiO <sub>2</sub>	ZrO <sub>2</sub>	LOI
Mass %	71.30	17.11	1.80	0.37	0.07	0.03	0.08	0.03	0.055	0.02	9.089

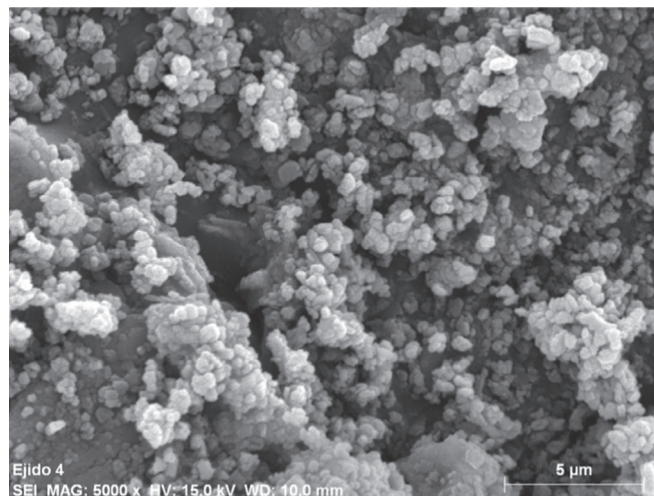
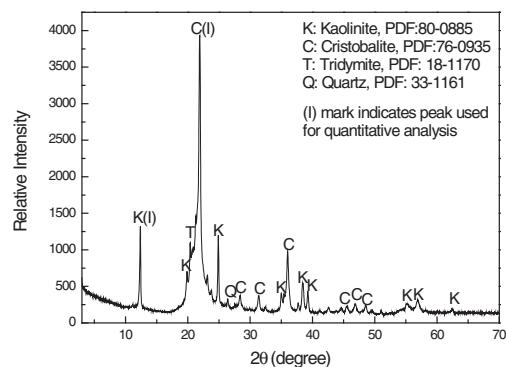


Fig. 1. XRD pattern and SEM image of the geothermal clay.

Sodium hydroxide (NaOH) and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) of analytical reagents of the American Chemical Society (ACS) reagent grade were purchased from Sinopharm Chemical Reagent, China and used as alkaline activator in the synthesis of geopolymers.

### 2.2. Geopolymer synthesis

In a typical synthesis, alkaline solution was first prepared and then mixed with the geothermal clay. The mixture was poured into a cubic steel mold (50 mm × 50 mm × 50 mm) and vibrated on a vibration table for 3 min to liberate the air bubbles. After that, the mold was sealed for the curing process, in which it was first cured at 60 °C for 6 h and continued at room temperature for 7 days. Table 2 gave the preparing regimes of geothermal clay-based geopolymers, of which the variables were the calcination of geothermal clay, the alkaline activator combination and the water dosage. For preparations No. 1–8, geothermal clay sample (222 g) without and with calcination at 200, 400, 450, 500, 550, 600 and 800 °C were used as raw aluminosilicates. The calcination was performed in a muffle stove with heating rate of 15 °C/min. Once the calcination temperature reached the required value, the alumina crucibles with geothermal clay were heated for 6 h more. After that, the samples were left in the furnace to cool down. The alkaline activator solutions were synthesized consistently with 0.5 mol Na<sub>2</sub>SiO<sub>3</sub>, 0.5 mol NaOH and 9 mol H<sub>2</sub>O, making the solid to liquid and Na/Al

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