CHARACTERIZATION OF GEOPOLYMERS OBTAINED BY ALKALINE ACTIVATION OF METAKAOLIN WITH HIGH IRON CONTENT

ERICA A. S. VASSALO, ADRIANA G. GUMIERI, and MARIA TERESA P. AGUILAR

*Dept of Materials Engineering and Construction, School of Engineering,
Federal University of Minas Gerais, Belo Horizonte, Brazil*

The use of activated alkali aluminosilicate has been shown to be an economically-viable alternative that decreases the environmental impact of building construction material. Geopolymers are a type of activated alkali aluminosilicate that are rich in SiO_2 and Al_2O_3, and harden within alkaline solutions. In this study, geopolymers obtained by alkaline activation of metakaolin with high iron content were characterized. The activation process used sodium hydroxide solutions at molarities of 12, 15, and 18 mol. The geopolymers were oven-dried at 85°C and at room temperature. The results identified the physicochemical and microstructural properties of the geopolymers and elucidated the activation process using the techniques: XRF, XRD, DTA, TG, DTG and DSC analysis. The results of the dynamic recrystallization indicated the presence of quartz, kaolinite, hematite, and muscovite in the samples. The DSC analyses showed an immediate reaction between the precursor material and the activator. The DTA results showed that the reactions began at low temperatures, where the dissolution of Si and Al occurred. The peaks that appear between 45°C and 60°C indicate that polymerization occurred through the condensation of Si and Al.

Keywords: Portland cement, Alkali aluminosilicate, Construction materials, Microstructure, Cementitious materials.

1 INTRODUCTION

Portland cement is the most widely used civil construction. The production of 1 ton of clinker generates 0.95 tons of carbon dioxide (Davidovits 2013). Geopolymers are alkali-activated materials that are rich in alumina and silica. Because the production of geopolymers does not require high-temperature calcination, as is the case with Portland cement, geopolymers can greatly help sustainable development.

Feng *et al.* (2012) defined geopolymers as structures produced by the condensation of tetrahedral units of aluminosilicate, where alkaline metal ions balance the charges associated with the tetrahedral aluminum structures Zeolite, a mineral of hydrated aluminosilicates, and the polymers are the result of the reaction (Palomo *et al.* 1999). Davidovits (1991) and Maia *et al.* (2007) showed the production of type A zeolites ($Na_{12}Al_{12}Si_{12}O_{48}27H_2O$) and hydroxysodalite ($Na_6Al_6Si_6O_{24}8H_2O$) in geopolymers. The sources of aluminosilicates (precursors) are materials rich in Si and Al in proportions that vary according to the final product obtained. The activators are soluble alkaline metals that are generally based on Na or K, where the most commonly used activator is

(NaOH) or (KOH), which are combined with sodium silicate or potassium silicate (Wallah 2006). Davidovits (2012) potentiated iron and patented a new type of geopolymer, known as iron-metakaolinite (Fe-MK-750), where 25% of the Al is substituted for Fe. The new ligand has a molecular structure where part of the Fe atoms (tetrahedral Fe) is included in the geopolymeric structural sequence of Ferro-Sialate (Fe-O-Si-O-Al-O). The reddish color is due to the high concentration of iron (Na, K, Ca) and poly (ferro-sialate), and the resulting concretes are similar to ceramic bricks. In this study, geopolymers obtained through alkaline activation of metakaolin with high iron content are characterized. The activation process was performed using NaOH solutions at different molarities.

2   METHODOLOGY

High-performance metakaolin was used in this study and is commercially available in Brazil. Sodium hydroxide (NaOH) in the shape of flakes was used as an activator (96% to 98% purity) in addition to water. Geopolymers were created via an alkaline activation of metakaolin with a sodium hydroxide solution at molarities of 12, 15, and 18 mol. The solutions were rested for 24 hours. Afterwards, the metakaolin was mixed with the activating solution. Immediately after activation, samples of the mixture were subjected to thermographic tests. Almost all of the entire sample was subjected to manual molding, where the paste was compacted in PVC molds with dimensions of 2.7 x 5.4 cm. After molding, the geopolymers were cured under room temperature and in an oven at a temperature of $85 \pm 3°C$A quantitative analysis using energy-dispersive X-ray fluorescence was performed with an EDX-720 instrument from Shimadzu, with approximately 10 g of powdered sample under a vacuum. X-ray diffraction was performed in an X-ray diffractometer, model XRD-7000, from Shimadzu (3 kW of power, scanning with an angular velocity of 0.05 to $25°\theta/s$, counting time of 1s, and return velocity of $500°$ θ/min). For the thermogravimetric analysis (TGA), and differential thermal analysis (DTA), DTG-60 equipment from Shimadzu was used, which simultaneously performed the differential thermal analysis and TG analysis under a controlled atmosphere. The differential scanning calorimetry test was performed in a Grace AdiaCal calorimeter.

3   RESULTS

3.1   Characterization of the Precursor Material

The chemical composition of metakaolin is shown in Table 1. The results indicate a high Fe concentration in the material in addition to Si and Al concentrations. The Si/Al ratio was determined to be 1.64, which agrees with the results obtained by Davidovits (1994), who suggested that a Si/Al ratio between 1 and 3 is required to form a geopolymer. The results also corroborate results obtained by Duxson *et al*. (2005) and Jimenez *et al*. (2006), which suggested a ratio between 1.2 and 2.5. Based on the oxide concentrations, the molar ratio of SiO_2/Al_2O_3 was 3.28, a ratio that is between 3.0 and 5.5, which is considered to be the ideal ratio to produce geopolymers according to Davidovits (1982), Duxson *et al*. (2005). The X-ray diffractogram of metakaolin (Figure 1) shows peaks of crystallinity due primarily to the presence of quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), hematite (FeO_3), titanium (TiO_2), and muscovite

($H_2KAl_3SiO_{12}$). The quartz did not react during the calcination of kaolin. The hematite is responsible for the pinkish color of the sample, and the muscovite is responsible for the potassium concentration. The XRD of the metakaolin confirmed the presence of the oxides identified by the XRF analysis.

Table 1. Chemical composition of metakaolin.

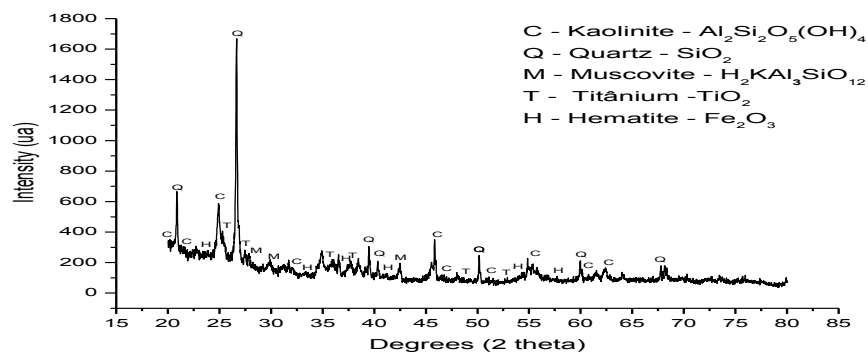| Elements	Si	Al	Fe	K	Ti	S	Others
%	39.091	22.884	18.035	9.325	5.782	1.921	2.962
Oxides	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	SO_3	Others
%	47.1	24.4	14.5	6.3	5.5	2.1	0.1

Figure 1. X-ray diffractogram of metakaolin.

3.2   Thermal Analysis of the Activation Process

Figure 2 shows the results from the calorimetry tests by DSC for samples at molarities of 12, 15, and 18 mol and for the reference sample. Immediate reactions occurred for all of the samples, which indicate that the mixture began to react instantaneously and that exothermic reactions occurred.
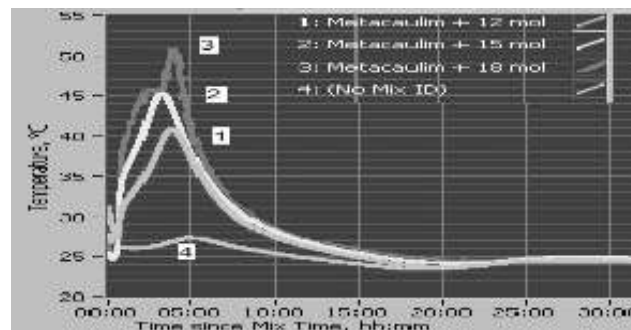

Figure 2. Thermal analysis by differential scanning calorimetry (DSC).

The first peak occurred at the beginning of the reaction, indicating that NaOH acts as a catalyst of the dissolution reaction of metakaolin in the alkaline solution. This dissolution represents a break in the Si-O-Al-O particles.   The greater the molarity of

the NaOH solution, the greater the temperature of the heat release, and the more rapid the reaction will be. The thermal stability of the samples is achieved in approximately the same period of time, indicating the end of the reaction. Figures 3 (a, b, c) present the curves obtained from the TGA, TG analysis, and the derivation of the TGA results (DTG) after the activation of metakaolin. The TGA and DTG curves were used to evaluate the activation development through the variation in mass during heating, and the DTA curves were used to determine the energy expended during the process.
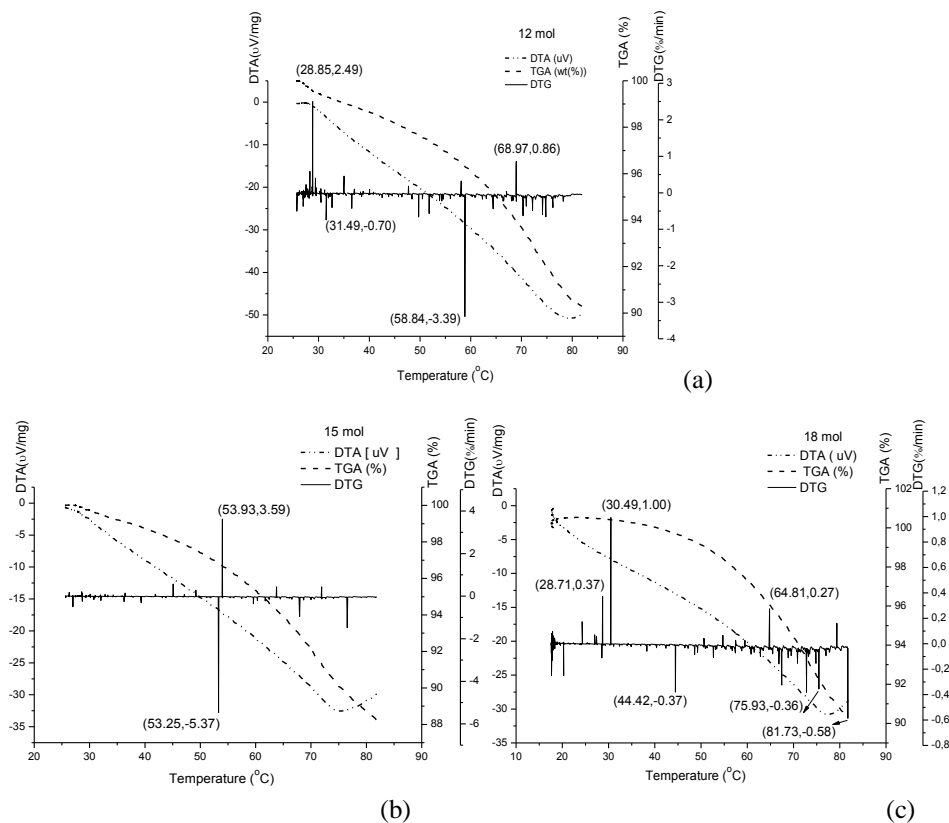

Figure 3. DTA, TGA, and DTG results - (a) 12 mol, (b) 15 mol, (c) 18 mol.

The results show that as the temperature increases, there is a loss of mass throughout the process. However, the rate of mass loss is not constant with the occurrence of peaks, which does vary. Regarding the energy involved in the process (DTA), the results show that the reactions began at low temperatures, at which the dissolution of Si and Al occurred. The peaks appearing in the interval from 45°C -60°C represent the formation of the new phase (polymerization). After 75°C, an endothermic peak is observed, which is most likely associated with the change in the atomic arrangement and saturation of the material obtained. Polymerization occurs through the condensation of Si and Al, where water is expelled and the excess unreacted alkali remains in a liquid phase (Davidovits 1999).

3.3   Characterization of the Geopolymer

Figures 4 (a, b, c) show the XRD diffractograms of the samples cured in an oven at 85°C for 7 days. Quartz peaks were identified for all samples. This mineral was already present in the precursor material (metakaolin) and therefore was not a product of synthesis.

(a)

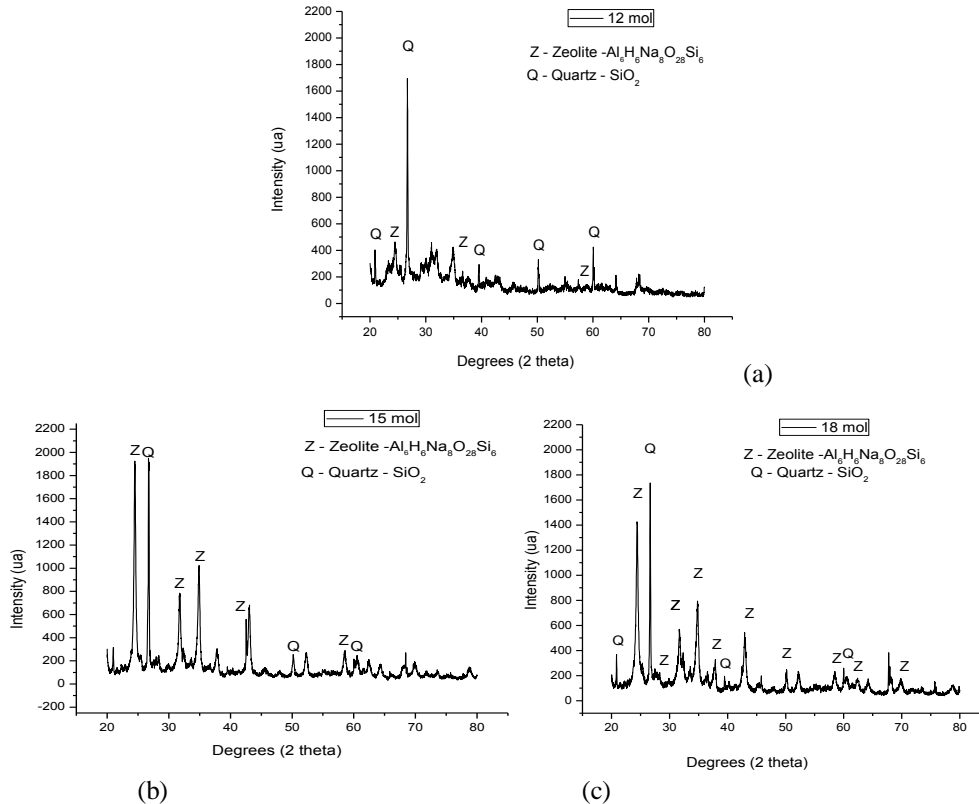
(b)   (c)

Figure 4. XRD of the geopolymer - (a) 12 mol, (b) 15 mol, (c) 18 mol.

Comparing Figures 4(a) and 1, it can be observed that the geopolymer from the solution with 12 mol. maintained a similar structure to that of metakaolin, with crystallinity peaks. In analyzing this result in light of the DSC graph (Figure 2), an immediate reaction between the precursor and the activator material is observed, the final reaction peak occurred at a temperature less than the curing temperature, in this case, 85°C. The similarity of the sample of the precursor material (Figure 1) with the obtained geopolymers (Figures 4) indicates that the temperature during polymerization affects the crystallization behavior of geopolymers. According to Yao *et al.* (2009), this result implies that the crystallization behavior of geopolymers depends not only on the temperature but also on the activator and curing time conditions. In the X-ray diffractograms, a type of zeolite was identified: $Na_8Al_6\ Si_6\ H_6O_{28}$ (hydrated sodium aluminum silicate hydroxide). By comparing the diffractograms, it was verified that the kaolinite peaks present in the metakaolin sample (Figure 1) were transformed into zeolite peaks after activation in the analyzed samples.

4 CONCLUSION

The alkaline activation of metakaolin was performed to identify the primary physical-chemical characteristics and microstructures of obtained geopolymers and their reaction process. The chemical composition and mineralogy of metakaolin indicated the predominance of silica, with the presence of non-crystalline silica (quartz), which is most likely from the kaolin, kaolinite and alumina (source of aluminosilicates), muscovite (source of potassium), and hematite (source of iron). The analysis of the activated samples indicated the presence of quartz, which is inert during the reaction process, and zeolite was identified in the activated samples, which originated from the kaolinite. The DSC analysis indicated that an immediate reaction between the precursor material and the activator occurred. The thermal analyses indicated that the activation reactions are exothermic and accompanied by a loss of mass. The curing process and molar concentration of the activator were shown to be fundamental to the physical, chemical, and structural development of the geopolymers. Although exploratory and preliminary, this study presents results that are coherent with the literature, and thus contribute to the advancement of technological knowledge regarding geopolymers.

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