Behaviour of metakaolin-based geopolymers incorporating sewage sludge ash (SSA)

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ABSTRACT

In recent years, geopolymers have become a widely researched binding material. There are technological and environmental advantages to using this type of binder instead of Portland cement. In this study, binary systems of geopolymers were produced by using mixtures of metakaolin (MK), a well-known aluminosilicate raw material, and a residue from sewage sludge incineration: sewage sludge ash (SSA). This ash was used to partially replace the metakaolin in proportions of 0–20%. The mixtures were activated with alkaline solutions and they were cured by using two different conditions: at room temperature (25 ºC) and in a thermal bath (65 ºC). The samples were assessed by X-ray diffraction, scanning electron microscopy (pastes) and compressive strength (mortars). The results from these studies showed zeolite formation (faujasite) in geopolymers cured in the thermal bath, which caused a decrease in the compressive strength of the alkali-activated mortars. Replacement of MK with SSA caused a lower reduction in the compressive strength of mortars cured at 65 ºC. However, at room temperature, similar mechanical strength was observed for the MK and MK-SSA systems. These results demonstrated that SSA is a suitable mineral precursor for partial replacement of MK in geopolymer production.

KEY WORDS: alkali-activated binder, microstructure, residue, X-ray techniques

1. INTRODUCTION

Geopolymers are a new class of material obtained by a chemical reaction of an aluminosilicate material and a highly concentrated alkaline solution [1]. This binding material can be used as a construction material due to their high strength and durability, replacing Portland cement (OPC) in concrete [2].

Metakaolin (MK) is usually used as the aluminosilicate source in geopolymers [3-5]. Previously studies on metakaolin-based geopolymers have shown high compressive strength after a few hours of curing at temperatures ranging from 40 to 95 ºC [3]. However, research has shown that some geopolymers, especially metakaolin-based ones cured at high temperatures, tend to form crystalline structures: zeolites [6-9]. These crystalline phases significantly reduce the compressive strength of geopolymers, a critical behaviour for building materials [2,9].

In this sense, the combination of different raw materials containing silicon and/or aluminium oxides on their composition are being carried out (binary systems) in order to reduce the zeolite formation [10,11]. Sewage sludge ash (SSA), a waste generated in large amounts (1.7million tons per year) has been studied extensively in blended Portland cements [12-14]. The first study related to the use of SSA in geopolymers were reported by Yamaguchi et al. where authors used fly ash/SSA yielding the maximum flexural strength (about 5.5 MPa) for mixture containing 75%SSA [15].

In this paper is presented the influence of SSA on the mechanical strength and on the crystallization process (zeolite formation) of metakaolin-based geopolymers. Specimens were cured at both high-temperature and 25 ºC and they were assessed through compressive strength, X-ray diffraction and scanning electron microscopy.

2. MATERIALS AND METHODS

2.1 Materials and Equipment

Metakaolin was supplied by Metacaulim do Brasil®. Sewage sludge ash was obtained from an auto-combustion process of sewage sludge from São José do Rio Preto city (São Paulo-Brazil). The chemical composition of MK and SSA are shown in Table 1. The mean particle diameter, d_{50} and d_{90} of MK were

23.90, 18.16 and 53.96 µm, respectively; and for SSA they were 20.28, 11.77 and 52.45 µm, respectively. For mortar preparation, siliceous sand (Castilho city, São Paulo-Brazil) with a fineness modulus of 2.05 and specific gravity of 2.67 ton/m³ was used. Sodium hydroxide (98% purity) and sodium silicate (18% Na_2O, 63% SiO_2) were used for the preparation of alkaline solutions (both supplied by Dinâmica Química).

X-ray diffraction (XRD) patterns for raw materials and geopolymeric pastes were obtained using a Shimadzu XRD-6000 system. The 2θ range was 5–60° using Cu-Kα radiation and a Ni filter, at a voltage of 30 kV, a current intensity of 40 mA, an angle step of 0.02°, and a step time of 1.20 s/step. Scanning electron microscopy (SEM) images of fractured surface pastes were obtained using a ZEISS model EVO LS15. The compressive strength of mortars was measured in an EMIC Universal machine with a 200-ton load limit.

Table 1 – Chemical composition of MK and SSA in percentage by mass

Oxide (%)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**SO_3**	**TiO_2**	**Others**	**LOI**
MK	58.39	35.47	2.71	0.01	0.30	-	1.44	-	1.51	0.07	0.10
SSA	38.28	20.72	11.27	5.51	1.91	0.70	0.73	4.18	3.73	9.25	3.72

2.2 Geopolymer preparation

Three different proportions of MK replacement by SSA were assessed in this study: 0% (control), 10% and 20% (by mass). The H_2O/Na_2O and SiO_2/Na_2O molar ratios were maintained constant at 9.26 and 2.00, respectively. For mortars, the sand/binder ratio was 2.5 (the binder amount being the sum of the masses of MK and SSA). Two different curing temperatures were applied at a relative humidity greater than 95%: 25 ºC (room temperature) and 65ºC (using a thermal bath). The compressive strength of the mortars was determined after one, three and seven days of curing. XRD studies were performed on pastes after the same curing times. SEM studies were performed only after three days of curing.

The samples used in this paper are named as MK*c-xx*, where c is the curing temperature (*c*, R: room temperature, B: thermal bath) and xx is the percentage of SSA incorporated (*xx* = 0, 10 or 20).

3. RESULTS AND DISCUSSION

The compressive strengths of the different mortars are shown in Figure 1. For mortars cured at 65 ºC (Fig. 1a), the compressive strength of all mixtures decreased with increasing curing time. Similarly, the strength of the mortars after one day of curing at 65 ºC decreased with increasing replacement of MK by SSA. After three days of curing at 65ºC the compressive strength of the mortars decreased by 34% for MKB-0, 36% for MKB-10 and 37% for MKB-20. The compressive strength of mixtures incorporating 10 or 20% of SSA decreased by a similar percentage as the control (MKB-0, 36%). After seven days of curing, the compressive strength values and their respective percentage loss of compressive strength compared to the values after three days of curing were 20.3 MPa (16.8%), 16.6 MPa (12.6%) and 15.0 MPa (9.1%) for MKB-0, MKB-10 and MKB-20, respectively. These results show that the relative decrease in compressive strength with curing time is lower in mortars containing up to 20% SSA than in the control sample. These results suggest that the use of SSA in the production of metakaolin-based geopolymers stabilizes the compressive strength in mortars prepared with long curing times.

Mortars cured at room temperature (Fig. 1b) behaved differently to samples cured at 65 ºC. At room temperature, mortars did not show a decrease in compressive strength with curing time. After one day of curing at room temperature, the strength decreased when SSA content was increased, similar to the situation for mortars cured at 65ºC. After three and seven days of curing, the compressive strength of MKR-0 increased slightly, whereas samples incorporating SSA presented an important strength gain. After seven days of curing at room temperature, the MKR-10 sample achieved a similar strength to MKR-0 (27.9 and 28.8 MPa, respectively). This result suggests that the use of SSA in metakaolin-based geopolymers may be an interesting possibility.

XRD studies were carried out on MKB-0, MKB-20, MKR-0 and MKR-20 pastes in order to examine the formation of crystalline phases, both at 25ºC and 65ºC (Figure 2). The raw materials MK and SSA show a baseline deviation in the range 16–32º and 18–32°, respectively, which is characteristic of the presence of an amorphous phase. Quartz (SiO_2, PDFcard#331161), kaolinite ($Al_2Si_2O_5(OH)_4$, PDFcard#140164) and muscovite ($KAl_3Si_3O_{10}(OH)_2$, PDFcard#210993) were found in MK, and quartz, anhydrite ($CaSO_4$, PDFcard#371496), anorthite ($CaAl_2Si_2O_8$, PDFcard#411486) and hematite (Fe_2O_3, PDFcard#130534) were found in SSA.

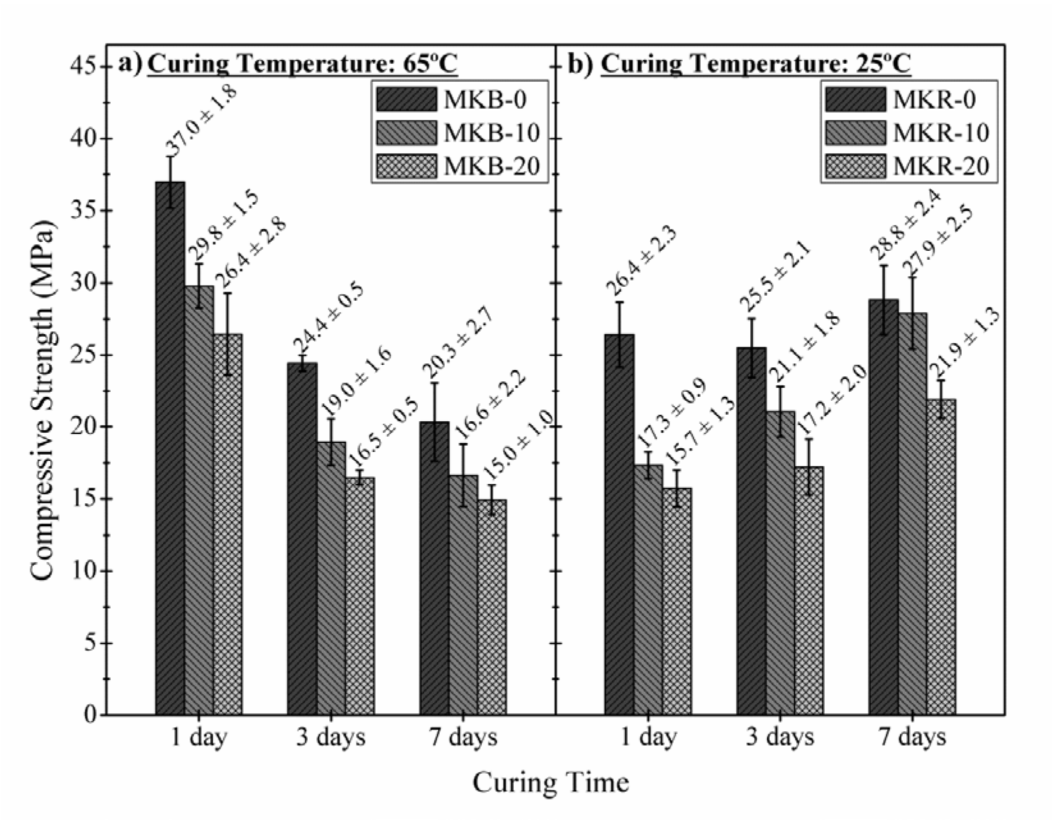

Figure 1 – Compressive strength of mortars: a) cured at 65ºC; and b) cured at 25ºC

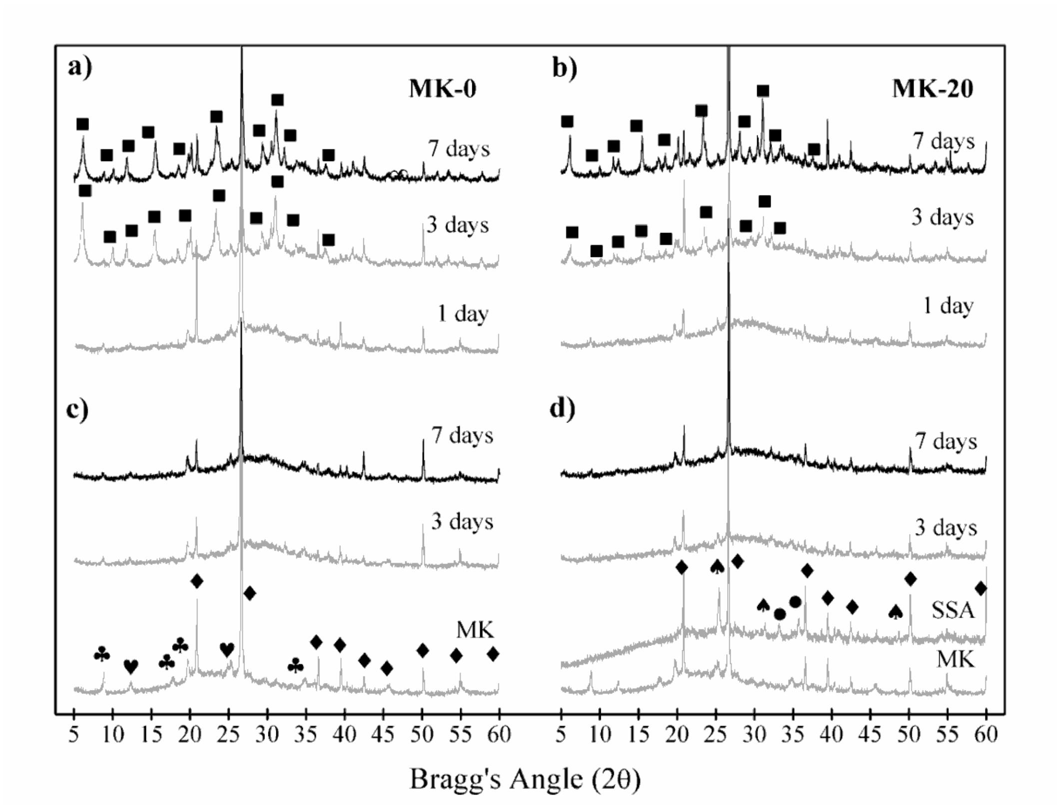

Figure 2 – XRD patterns for MK/SSA pastes: a) MKB-0; b) MKB-20; c) MKR-0; d) MKR-20 (Key: ♦: Quartz; ♥: Kaolinite; ♣: Muscovite; ♠: Anhydrite; ●: Hematite; ■: Faujasite)

For the geopolymeric pastes, all samples presented a baseline deviation line between 16 and 40º, which can be attributed to the amorphous phase of the geopolymeric gels. This shift of the baseline to higher 2θ values compared to the MK and SSA amorphous phases due the geopolymerisation reaction has also been observed in others studies [16]. For pastes cured at 65ºC, faujasite ($Na_2Al_2Si_4O_{12}.8H_2O$, PDFcard#391380) formation was observed after three days of curing (Fig. 2a and 2b). However, the presence of SSA influences the zeolite formation, since a lower zeolite peak intensity is observed after three days of curing at 65ºC compared to MKB-0. No signals attributed to zeolites were distinguished by XRD analyses on pastes cured at room temperature, either in MKR-0 (Fig. 2c) or MKR-20 (Fig. 2d), whatever the curing time (three and seven days).

Both geopolymeric gel and zeolite formation are directly related to the reactivity of the raw materials and to the curing temperature [2,17]. For high alkaline environment, high curing-temperatures favours the crystallization of aluminosilicate gels forming zeolite-type structures and, according to Bosnar et al., the crystallization process is sharply reduced with the increase on the SiO_2/H_2O [17]. In this paper, MK presented higher reactivity than SSA, so it was expected that geopolymers with higher amounts of MK would present more intense zeolite formation and, consequently, greater reduction in compressive strength. It is due to the microporous-crystalline structure based on 3D-cage system of zeolites that reduces the compressive strength of mortars when compared to the amorphous structure based on 3D-network of aluminate and silicate tetrahedral of geopolymers [2,18].

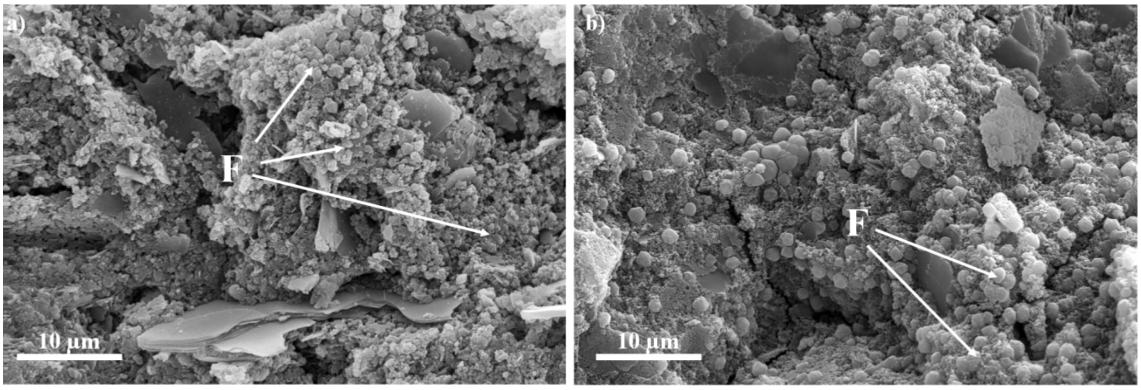

Figure 3 – SEM micrographs of geopolymer fractured surfaces: a) MKB-0; b) MKB-20 (Key: F-faujasite)

Faujasite was also observed in SEM on fractured samples of MKB-0 and MKB-20 after three days of curing (Fig.3). Rounded crystalline particles of 2–4 µm size were formed. Since the raw material mainly contains metakaolin, faujasite was formed in both pastes.

4. CONCLUSION

Metakaolin-based geopolymers with partial replacement of MK with SSA were studied. XRD analysis showed that geopolymers cured at 65 ºC produced faujasite after three days of curing. This zeolite formation caused a decrease in compressive strength with the curing age at 65 ºC. The addition of SSA (up to 20%) to the mixture resulted in a smaller loss of compressive strength in mortars cured at 65ºC when compared to the control without SSA. In addition, in samples cured at 25ºC, those containing 10% SSA presented similar compressive strength as the control mortar after seven days of curing. Thus partial replacement of metakaolin with SSA showed advantages in both curing conditions.

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