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Synthetic Aluminosilicates for Geopolymer Production

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The use of geopolymer has been studied as a potential substitute for Portland cement due to lower CO_2 emission and improvements on structural properties. Some of the major raw materials used in the manufacture of the geopolymer are: steel slag, fly ash and metakaolinite. Due to the impurities contained in these raw materials, the present study uses high purity synthetic aluminosilicates made from the sol gel process for production of geopolymers. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR). The results showed that the synthetic aluminosilicates have similar behavior to metakaolinite (reference). It was found that the coordination of Al in the synthetic aluminosilicate changed from VI to IV and V from 300 °C, with the highest intensity at 900 °C. Temperature at which the highest mechanical strength of the geopolymer was also observed.

Keywords: *Synthetic aluminosilicates, geopolymer, sol-gel process, metakaolinite.*

1. Introduction

Portland cement concrete is a versatile material with relatively low costs, becoming one of the world's most consumed materials. Nevertheless, major drawbacks are attributed to the production of this material, such as high CO_2 emission rates to the atmosphere [1]. The concrete lifespan is another inconvenience due to limitations concerning its porous nature. These restrictions foster the need of alternative materials to Portland cement such as geopolymers. In a pioneer study by Joseph Davidovits in 1970 [2], this term was introduced to describe a class of solid materials synthesized by the reaction of powdered aluminum silicate with an alkaline solution, forming an inorganic polymer [3,4].The application of geopolymers is not limited to the use in civil construction, having potential to be used as: fireproof material, refractory, composites for repair of toxic and radioactive waste reservoir, decorative artifacts [2], electrical conductors [5], biomaterials [6], storage and gas capture [7] and others.

The geopolymer is a hydrated aluminosilicate mineral with a polymeric structure. It consists of materials with activated Si and Al in solutions with medium to high alkalinity. The reaction between Si and Al forms a precursor that bind to other activated molecules provided that the alkaline medium is maintained. The result is a network formed by covalent bonds in a three-dimensional structure [2]. The chaotic spatial configuration obtained between the sialates make the structure predominantly amorphous [2].

Several materials can be used as raw material for geopolymer production, such as: fly ash [8-12]; metakaolin [13-17]; blast furnace slag [18,19] and even Portland cement [9]. But these materials have substances other than the aluminosilicate required for the geopolymerization reactions, interfering with the reactions, such as other oxides besides those associated with Al and Si. In order to produce a high purity material in this study, a synthetic aluminosilicate (S-AS) was produced by the sol-gel process. The use of the sol-gel process for the production of aluminosilicates, in addition to allowing partial control of the granulometry and variation of the composition, allows changes in the molar ratios, especially Si and Al, which will have a direct influence on the final properties of the geopolymer. This work aimed at the production of a synthetic aluminosilicate with Si/Al molar ratios similar to that of some kaolinites, but without common oxides found in natural materials (such as Fe_2O_3, CaO, MgO, K_2O, TiO_2).

The powder was then submitted to a chemical activation for the geopolymerization process using a sodium hydroxide solution. The characteristics of the synthetic powders and the geopolymers produced from these powders were studied by means of XRD, SEM and NMR [2,15,20-26]. NMR spectra are generally considered the most important test for characterization of raw materials for the production of geopolymer, specifically the ^{27}Al spectrum. From this technique it is possible to evaluate the coordination of Al, an essential factor in the evaluation of the potential of activation of the raw material.

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2. Experimental

2.1 Materials

The synthetic aluminosilicate powder was obtained by the sol-gel process using aluminum tri-sec-butoxide and tetraethyl orthosilicate (TEOS) as Al and Si precursors, respectively. Ethanol and ammonia were mixed with the following molar proportions were: Si/Al = 1, EtOH/SiO_2 = 24 and SiO_2/H_2O = 16 and H_2O/NH_4OH = 8. Reagents were mixed and maintained at room temperature under stirring for 12 h and at rest for additional 12h. The solution was further vacuum filtered and dryed at 100 °C for 24 h. Then the powder was heat at temperatures varying within 200 - 1000 °C for 2 h. The metakaolim (Metacaulim do Brasil) was used as reference material and its composition was analyzed using of X-ray fluorescence for the quantification of the material necessary for the production of the samples. The results were, in mass % : SiO_2= 53.40; Al_2O_3 = 40.61; Fe_2O_3 = 2.77; TiO_2 = 1.55; K_2O = 1.27; MgO = 0.22; CaO= 0.11; SO_3 = 0.06; PbO = 0.01 and CuO = 0.01.

2.2 Geopolymer synthesis

For geopolymer production, initially the solutions containing water, silicate and sodium hydroxide were prepared. These solutions remained at rest and at room temperature for 24 hours. Subsequently, the solution was mixed with the synthetic aluminosilicate calcined in a vessel kept in an ice bath to minimize the effects of temperature because the temperature accelerates the reactions of geopolymerization, making it difficult to mold the pastes. The molar ratio of the components were: Na_2O/SiO_2 = 0.68; SiO_2/Al_2O_3 = 3.2 e H_2O/Na_2O = 6.7

For mechanical tests, the geopolymer slurry was poured into cylindrical molds after mixing for one minute. The dimension of the specimens used to evaluate the compressive strength was 5 x 10 mm in order to maintain the ratio of 1:2, as recommended in the standards NBR 7215 - 1996 [27] and ASTM C39 - 2016 [28]. After the molding process, the mold was sealed and placed in an oven for 24 hours at a temperature of 60 °C. Subsequently, the specimens were removed from the molds and kept at room temperature (23 °C ± 2 °C) until the final curing age. For the other analyzes, the same conditions of cure were maintained, however, without concern for the shape of the specimens.

2.3 Characterization

The solid structure of the powders calcined at different temperatures and of the geopolymer was analyzed by X-ray diffraction (XRD) (Empyream Panalytical, radiation with copper tube and xenon detector). The infrared spectroscopy (Perkin Elmer - Paragon 1000) was performed with analysis range from 4000 cm^{-1} to 400 cm^{-1}, 128 scans and resolution of 2 cm^{-1}.

The morphology analysis of the powders and of the geopolymer was performed using a scanning electron microscope (Quanta FEG 3D FEI). The compressive strength of the geopolymer was assessed by an universal test machine (Instron, model 5882) with loading speed of 0.5 mm/min, as adopted by other authors [23].

The MAS NMR spectra of ^{27}Al and ^{29}Si isotopes of the synthetic aluminosilicates and the geopolymer were obtained using an Avance III 400WB HD spectrometer. Frequencies of 14 kHz for Al and 10 kHz for Si were used.

3. Results and Discussion

3.1 XRD analysis

XRD diffractograms (Figure 1) show that the peaks attributed to the synthetic aluminosilicate (S-AS) samples range from 22° to 25°, while the peak of the geopolymer sample cured at 60 °C occurs at approximately 28°. The samples show peaks in the region within 15° and 35°, similar to observed in the XRD spectrum of metakaolinite [2]. The lack of intense peaks indicates amorphous structure in all samples. Peaks with 2θ values of 46° and 67° on the XRD spectrum of the samples heat treated at 1000 °C confirm initial crystallization. It is also noted that, unlike that of kaolinite (structure of metakaolin before heat treatment), which is crystalline at 100 °C, the aluminosilicate of the present work is amorphous at that temperature.

The structure of synthetic materials is typically amorphous, with absence of an atomic structure and its structure is similar metakaolinite [2]. However, according to the Scherrer equation, the change in the angle 2θ may be due to the increase of the ordered molecular structure with the temperature increase [5]. Thus, after heat treatments, the short-range of Al_2O_3-$2SiO_2$ is exported to be more ordered than in the samples before heat treatment.

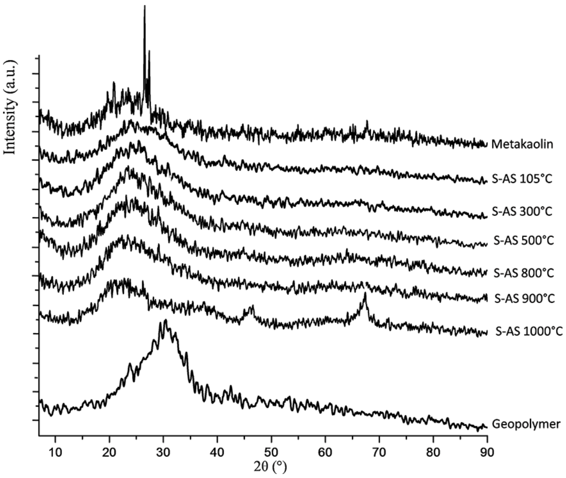

Figure 1. XRD pattern of the geopolymer, the synthetic powders at different heat treatment temperatures and metakaolin.

3.2 Morphological analysis

Figure 2 illustrates SEM micrographs of the synthetic aluminosilicate heat treated at 900 °C. The Figure 2a shows an irregular layer structure, different from what was observed in metakaolin [5], which has many particle agglomerates. It is also observed in the Figure 2b the presence of the spherical particles indicating the presence of pure unreacted silica.

3.3 FTIR analysis

Figure 3 represents the FTIR spectra of synthetic aluminosilicate and natural aluminosilicate (metakaolin), while Figure 4 shows the spectra of synthetic aluminosilicate and geopolymers made with the power heat treated at 900 °C.

In Figures 3 and 4 bands at 3450 cm^{-1} show a broad band which is attributed to the overlap of the O-H group, with stretching of water molecules bond by hydrogen (H-O-H) and silanols groups, SiO-H, bound to the molecular water, observed in the non-heat treated samples.

The band at 1640 cm^{-1} is also characteristic of hydroxyl group. At 1380 cm^{-1}, the band can be attributed to the / group due to the presence of ammonia (used in sol-gel process), which is removed after the heat treatment at temperatures above 400 °C. At 1100 cm^{-1} and 1040 cm^{-1}, the intense bands correspond to the asymmetric stretches and vibrations of Si-O-Si and Si-Al-O, respectively.

Covalent bonds reveal the existence of a dense silica network [2], in which oxygen atoms act as bridges between two silicon atoms (Si-O-Si) in asymmetric stretching vibration. The bands with wave number of 874 cm^{-1} in the S-AS 105 °C spectrum can be attributed to the overlapping of the bands typical of the Al(VI)-O and Si-OH vibration bonds. Bands at 914 cm^{-1} indicates Al(VI)-O bonds[29] and the band at 840 cm^{-1} occurs due to Si-OH bonds [2]. The bands at 880 cm^{-1} e 808 cm^{-1} refer to the frequency of Al(V)-O and Al(IV)-O, respectively, on the S-AS 800 °C and 900 °C

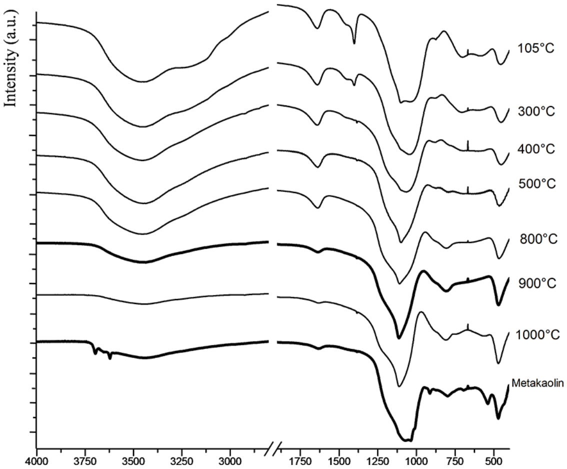

Figure 3. FTIR spectra of powders heat treated at different temperatures and natural metakaolin.

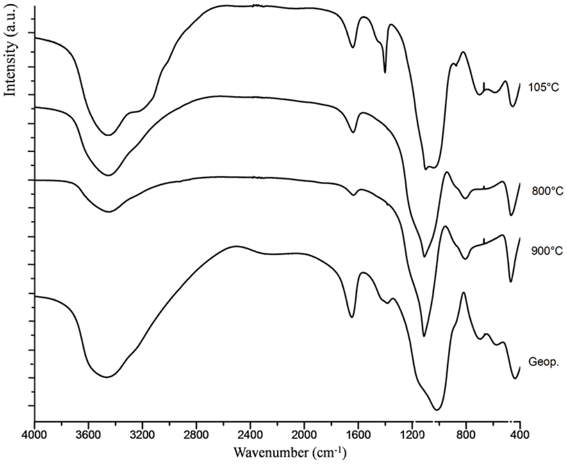

Figure 4. FTIR spectra of powders heat treated at 105 °C, 800 °C, 900 °C and geopolymer.

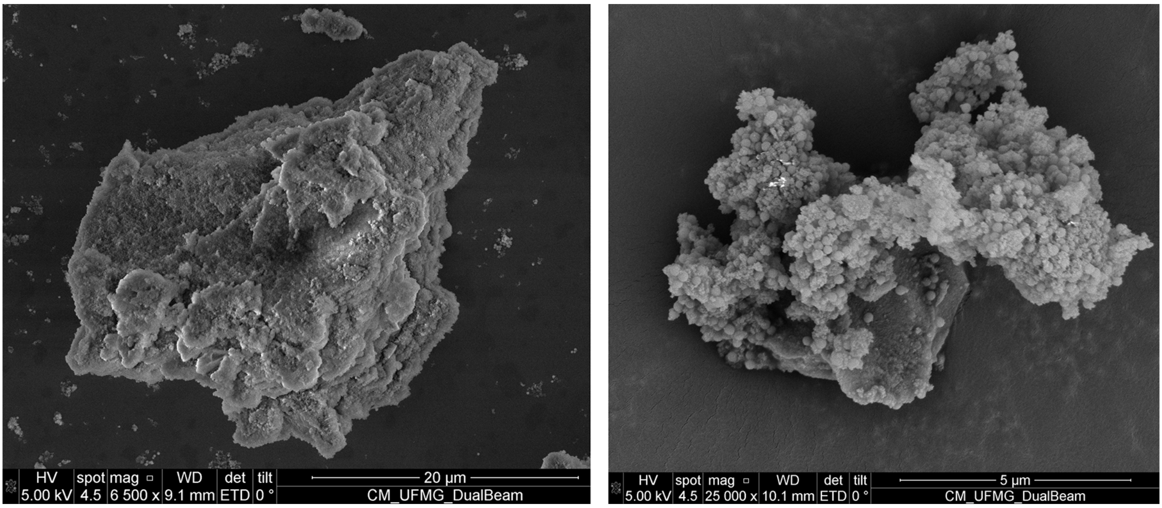

Figure 2. SEM images of synthetic aluminosilicate heat treated of 900 °C by secondary electrons: (a) structure and (b) structure with agglomerated silica.

spectra. This result indicates the alteration of Al coordination from VI at 105 °C for IV e V coordination at 800 °C e 900 °C temperatures. The spectra in the frequencies between 800 cm^{-1} and 480 cm^{-1} correspond to the symmetry of the Si-O-Si stretching vibration. The peaks at approximately 1100 cm^{-1}, 910 cm^{-1}, 800 cm^{-1} e 460 cm^{-1} of the S-AS 900 °C curve are similar to those in metakaolin, Figure 3, indicating the similarity between the materials and its potential for the production of geopolymer.

Figure 4 details the spectra of aluminosilicates and the geopolymer produced from the powder heat treated at 900 °C. The geopolymer FTIR spectrum shows that bands related to hydroxyl group at 3475 cm^{-1} and 1648 cm^{-1}. The bands at 1420 cm^{-1} and 1380 cm^{-1} in the geopolymer spectrum indicate the presence of sodium carbonate (Na_2CO_3) due to the presence of free NaOH and water in the geopolymer preparation. The Na migrates to the surface and reacts with atmospheric CO_2. The kneading water initially participates in the synthesis of the geopolymer by dissolving the solid aluminosilicate by alkaline hydrolysis (consuming the water) then the aluminates and silicates condense to produce the geopolymer network and water as a by-product. In this way the bands referring to the OH group reappear intense in the geopolymer.

It is also possible to notice in the geopolymer spectrum the intense band at 1018 cm^{-1} which corresponds to the Si-O-Al bond, replacing the Si-O-Si bond of S-AS 900 °C (band 1080 cm^{-1}). The region between 800 cm^{-1} and 500 cm^{-1}, reveal several weak bands attributed to the flexion of the Al-O-Si bond, that replaced the 808 cm^{-1} band in the S-AS 900°C curve (due to the polyhedrons AlO_x). The 439 cm^{-1} peak in the geopolymer relative to Si-O bond while in powders this bond manifest at approximately 456 cm^{-1}.

3.4 NMR spectra

The results of the ^{27}Al isotopes analysis of the heat treated powders at 105 °C, 300 °C, 900 °C e 1000 °C are displayed in Figure 5. The resonance at approximately 0 ppm, 25 - 30 ppm and 55 - 60 ppm indicate, respectively, the presence of aluminum at coordination VI, V and IV. It can be observed that the samples heat treated at 105 °C do not indicate the presence of Al (V) which is responsible for making the aluminosilicate capable of being activated in the geopolymerization reactions [2].

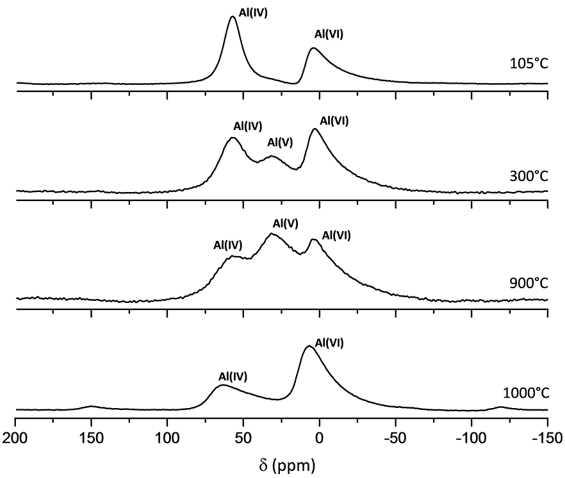

Figure 5. ^{27}Al NMR spectra of the synthetic aluminosilicate heat treated at 100 °C, 300 °C, 900 °C and 1000 °C.

By means of this technique it is possible to quantify the relative coordination of Al, as noticed in Figure 6. The peak areas of the ^{27}Al spectrum after deconvolution represent the ratio of each binding [30]. Then, in Figure 6, the deconvolution of the three peaks present in the heat treated powders at 900 °C. From the deconvolution it is possible to calculate the area of each peak and infer the proportion of each link, note the presence of 36% of Al (V), 34% of Al (VI) and 30% of Al (IV).

From the spectra of ^{29}Si, Figure 7, broad peaks are observed in calcined aluminosilicates heat treated at 105 °C to 900 °C. It is suggested that there is overlapping of the peaks and that Al present on the aluminosilicate network causes the displacement of the ^{29} Si spectra. Results previously reported

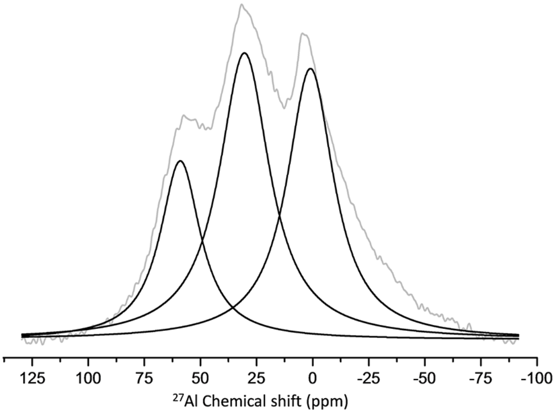

Figure 6. ^{27}Al NMR spectrum deconvolution of the synthetic aluminosilicate heat treated at 900 °C, with coefficient of determination (r^2) = 0.992.

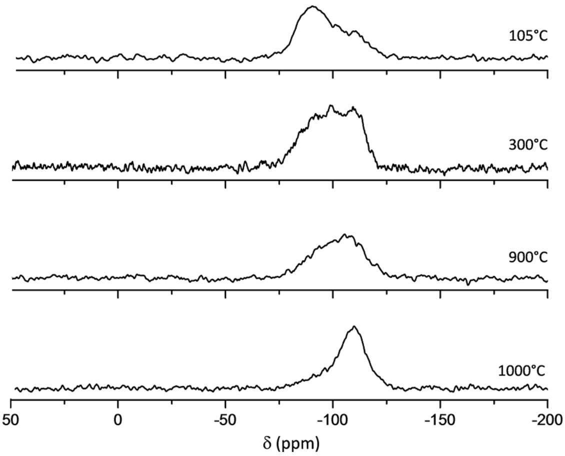

Figure 7. ^{29} Si NMR spectra of the synthetic aluminosilicate heat treated at 105 °C, 300 °C, 900 °C and 1000 °C.

in the literature [2,31] indicate that each AlO_4 unit connected to the SiO_4 group shift the ^{29}Si by 5 ppm in the ^{29}Si spectra. In addition, the average peak value shifts to a smaller value and the peak becomes more acute, indicating the decrease of Al in the Si sphere. Thus, at 1000 °C, increasing intensity with peak thinning and shifting of the chemical shift to a smaller value indicates the formation of crystalline silica, confirmed by XDR analyzes. As observed by other authors [30], the presence of Al in the Si bonds, changes to a value higher than the ^{29} Si chemical shift.

3.5 Compressive strengths

Compressive tests, Table 1, showed that the powers dried at 100 °C and 200 °C do not have polycondensation activity, with very low mechanic resistance, whereas the powders calcined above 300 °C exhibit enough alkaline polycondensation activity. Since the synthetic aluminosilicate of this work is amorphous, as shown in XDR results, this does not make it sufficient amenable to being activated. At 1000 °C the samples also did not present mechanical resistance, indicating that there was no polycondensation. A tendency also is observed to increase the mechanical strength as the heat treatment temperature of the synthetic powders, indicating the gradual increase of the presence of Al (IV) and (V) with increasing temperature.

Table 1. Compressive strength of Na-geopolymers produced from powders heat treated at different temperatures.

Powder treatment temperature (°C)	200	300	400	500	600	700	800	900
Maximum compressive strength (MPa)	0	4.3	4.8	4.4	5.4	5.9	6.1	9.9

The characteristics noted by the NMR technique corroborate the results of the compressive strength tests that only show the mechanical strength for materials heat treated above 300 °C. The highest compressive strength was obtained for sample heat treated at 900 °C and above this temperature there is no mechanical resistance again, indicating the importance of the presence of Al (V) in the geopolymerization reactions.

An increase in mechanical strength is expected with the improvement of the interaction of Al and Si in the sol gel synthesis process, since the presence of unreacted silica was observed in SEM images. Thus, changes in the productive process in order to make the interaction more effective are still being investigated by the authors.

4. Conclusions

The pure synthetic aluminosilicate developed in this study by the sol-gel route was confirmed as a potential alternative for the production of geopolymer, exhibiting characteristics similar to the reference natural aluminosilicate (metakaolin). Geopolymerization of aluminosilicate is possible when the Al with coordination numbers of IV and V are present, which is obtained by heat treatment. By the results of the NMR and FTIR analyses, the presence of Al (IV) and (V) in the synthetic aluminosilicate were confirmed, while is compatible with the results of the tests of resistance to compression.

Highest values of mechanical resistance were obtained for the geopolymer produced from the powder heat treated at 900 °C. For heat treatments below 300 °C and above 900 °C there was no observed polymerization. Since it is a pure synthetic material, it can be used in more noble applications that require higher purity.

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