

Steel slag as precursor material in geopolymerization

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RESUMO: Materiais geopoliméricos são cada vez mais estudados devido às suas boas propriedades, que podem até ser comparadas às do concreto de cimento Portland. Para a geopolimerização, é necessário um material precursor que seja rico em alumina (Al_2O_3) e sílica (SiO_2). A escória de forno panela é um rejeito industrial que se adequa às necessidades da síntese de geopolímeros. Este estudo avalia a geopolimerização empregando a escória de forno panela através das análises de difração de raios X (XRD), espectroscopia de infravermelho por transformada de Fourier (FTIR) e microscopia eletrônica de varredura (SEM). Com a análise de XRD foi possível identificar fases cristalinas e alguns picos característicos da geopolimerização; na espectroscopia de FTIR, o deslocamento de algumas bandas pela incorporação de Al; nas imagens de SEM a diferença de morfologia entre a escória pura e o geopolímero, confirmando a ocorrência da geopolimerização.

PALAVRAS-CHAVE: Geopolímero. Geopolimerização. Escória de forno panela.

ABSTRACT: Geopolymer materials are progressively studied due to their good properties that can even be compared to Portland cement concrete. For geopolymerization, a precursor material is required, which is rich in alumina (Al_2O_3) and silica (SiO_2). Ladle furnace slag is an industrial waste that suits the needs of geopolymer synthesis. This study analyzes the geopolymerization performed with ladle furnace slag through X-ray diffraction (XRD); Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analyses. With the XRD analysis, it was possible to identify crystalline phases and some peaks characteristic of geopolymerization; in the FTIR spectroscopy, the displacement of some bands by the incorporation of aluminum and in SEM images, the difference in morphology between pure slag and geopolymer, confirming the occurrence of geopolymerization

KEYWORDS: Geopolymer. Geopolymerization. Ladle furnace slag.

1. Introduction

Ecological system pollution is a global problem and industrial effluents contribute considerably to this problem due to their undeniable effect on public health and the environment [1]. The reduction of waste in mining and industrial activities has become one of the main environmental issues in search of improvements and solutions. Converting waste into value-added products is a key issue for the development of new technologies [2].

During the manufacture of steel, there are by-products that are discarded, such as slag, because they have a high metallic content and because they have an expansion behavior [3]. With this, studies began to emerge with uses for steel slag that were incorporated

in paving, landfills, building masonry, cement production, road construction and fertilizer production [4]. Steel slag qualifies for geopolymer synthesis because it is a material rich in silica and alumina minerals [5].

Geopolymers are semicrystalline inorganic materials formed by alkaline activation of aluminosilicate. Its properties can be compared to common Portland cement concrete, having comparable or even superior mechanical strength and good physical properties such as lower shrinkage, low density-strength ratio and durability characteristics. Thus, there are several applications as a binder for concrete and bricks, embankments, roads and tiles [6]. Geopolymers can also be used in composites having a wide range of applications, such as suitability for transport infrastructure, pavements, underwater applications, repair and rehabili-

tation of structures, as well as recent developments in 3D printing [7]. In recent years, there has been an intense development of studies focused on the use of traditional precursors, such as precursors derived from residues such as slag [8]. Among the slag generated in steel production, there is ladle furnace slag and some studies have shown that it has cementitious properties with the potential to increase the resistance properties of geopolymers [9].

Geopolymerization is a process with the following stages: dissolution, diffusion, oligomerization, further polymerization and hardening by dehydration of aluminum-silicon sources in an alkaline solution [10]. For geopolymerization to occur, there must be a precursor material that can be in natural form or as a by-product. It needs to be rich in alumina (Al_2O_3) and silica (SiO_2). This aluminosilicate precursor material requires an alkaline activating solution such as sodium or potassium hydroxide (NaOH , KOH), potassium or sodium silicate (K_2SiO_3 , Na_2SiO_3), among others. A síntese de geopolímero se inicia pela dissolução das espécies de Al e Si dos materiais precursores sob a ação da solução ativadora alcalina. Ionic interaction then occurs between the species in an alkaline medium, followed by the breaking of the covalent bond between silicon, aluminum and oxygen atoms. Negatively charged ions associated with tetrahedral Al are balanced by alkaline and alkaline earth cations (Na^+ , Ca^{2+} , K^+ , Li^+). After this process, the transport, orientation and condensation of precursor ions into monomers occurs, followed by coagulation and gelation processes. Thus, rigid 3D networks of silica aluminates are formed by polycondensation of monomers [11].

This study refers to the production of geopolymer using ladle furnace slag as precursor material. In the geopolymerization process, two different mass/volume proportions of solid/liquid are tested, using an alkaline solution of sodium metasilicate. Analyzes of the materials were performed using Fourier transform infrared spectroscopy (FTIR),

X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Materials And Methods

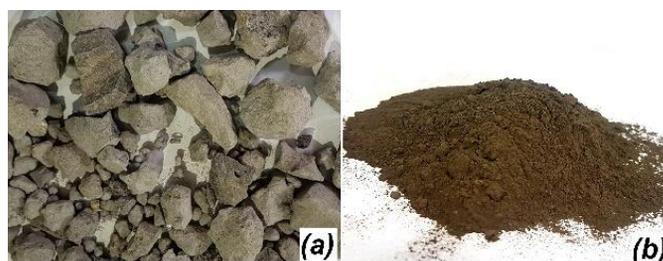
In the present work, the geopolymerization with precursor material being the ladle furnace slag was studied. The ladle steel slag was supplied by USIMINAS and has a chemical composition according to **Fig. 1**.

Fig. 1 – Composition (%) of ladle steel slag.

FeT	Fe ⁰	FeO	CaO	SiO ₂	MgO
53,58	32,03	26,42	17,30	7,11	5,35
MnO	Al ₂ O ₃	S	ZnO	K ₂ O	Na ₂ O
2,09	3,97	0,68	< 0,005	0,26	0,08

In order to reduce the granulometry, the ladle slag was placed in a planetary mill for a period of one hour and thirty minutes, at a speed of 300 rpm. **figure 2** shows the condition of the ladle steel slag before and after grinding.

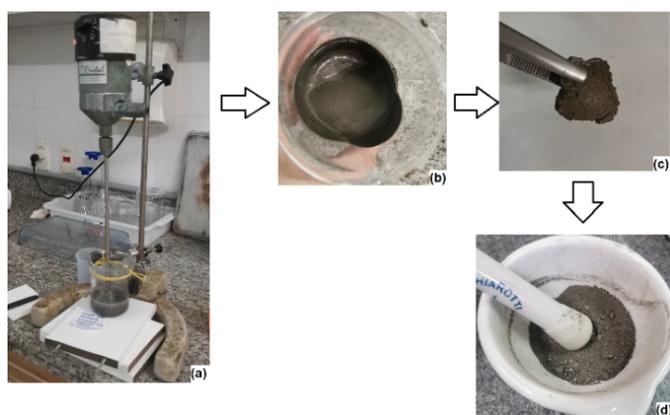
Fig. 2 – Slag before (a) and after grinding (b).



In the geopolymerization, sodium metasilicate was used to produce the alkaline solution. Two different solid/liquid ratios were tested, based on the ratio between the mass of particulate slag and the volume of solution: 1,4 and 1,6 g/ml. At a concentration of 1,4 g/ml, 27,90 g of sodium metasilicate were added to 60 ml of deionized water. This mixture was stirred for 2h initially so that complete dissolution occurred. Then the steel slag was added little by little, totaling 56,10 g and the mixture continued in the mechanical stirrer for another 20 h. For the concentration of 1.6 g/ml, the same procedures were performed, but with 31,80g of sodium metasilicate and 63,99g of slag. After the stirring time, the mixture

gained viscosity and was placed in an oven at 70 °C for solidification. With the solidified material, some samples were taken for characterization. The geopolymers were named geopolymer 1.4 and 1.6. The rest of the material was macerated for pulverizing. **Figure 3** presents the steps carried out in the geopolymerization process, starting with the mixing of the materials using the mechanical stirrer (a), followed by the geopolymer after 20 h of stirring (b), the solidified geopolymer (c) and finally the macerated geopolymer (d).

Fig. 3 – Mixing of materials using a mechanical stirrer (a), geopolymer after 20 h of stirring (b), solidified geopolymer (c) and macerated geopolymer (d).



2.1 X-Ray Diffraction (XRD)

In order to investigate the present phases, an XRD analysis was performed at the X-ray Diffraction Laboratory at IME. The analysis was carried out in a PANalytical diffractometer, model X'Pert MRD, operated with CuK α copper radiation ($\lambda=1,54060\text{\AA}$), current of 40mA, voltage of 45 kV, 2θ range from 10° to 90°, scan with a step of 0.050° and a collection time of 180 seconds.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Samples in powder form were submitted to *Fourier Transform Infrared Spectroscopy* (FTIR) analysis in order to identify functional groups and band shifts. The test was carried out at the Centro Brasileiro de Pesquisas Físicas (CBPF), with an IR Prestige-21 equip-

ment, being used in the average IR range of 4000 to 400 cm^{-1} with 128 scans and a resolution of 4 cm^{-1} .

2.3 Scanning electron microscopy (SEM)

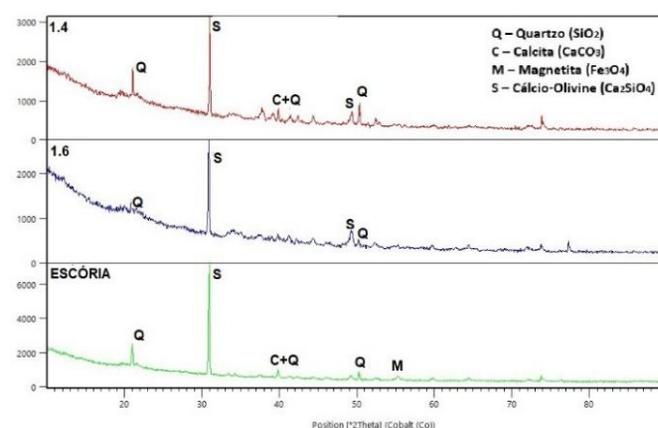
In order to analyze the microstructure and particle dimensions, samples of steel slag and all stages of geopolymerization were analyzed by a scanning electron microscope (SEM). The equipment brand FEG-SEM, manufactured by FEI, model Quanta 250, belongs to IME and a voltage of 15 kV was used. The surfaces of the samples were covered with gold, which was deposited in the coating apparatus, manufactured by Leica, model Ace 600, for 180 seconds, with an estimated layer of 16 nm.

3. Results And Discussions

3.1 X-Ray Diffraction (XRD)

Through X-ray diffraction analysis (XRD) it was possible to obtain the diffractograms of the samples of geopolymers 1.4 and 1.6 and of the ladle slag, which were indexed by the HighScore software, shown in **figure 4**.

Fig. 4 – Diffractograms of geopolymers 1.4 and 1.6 and ladle slag.



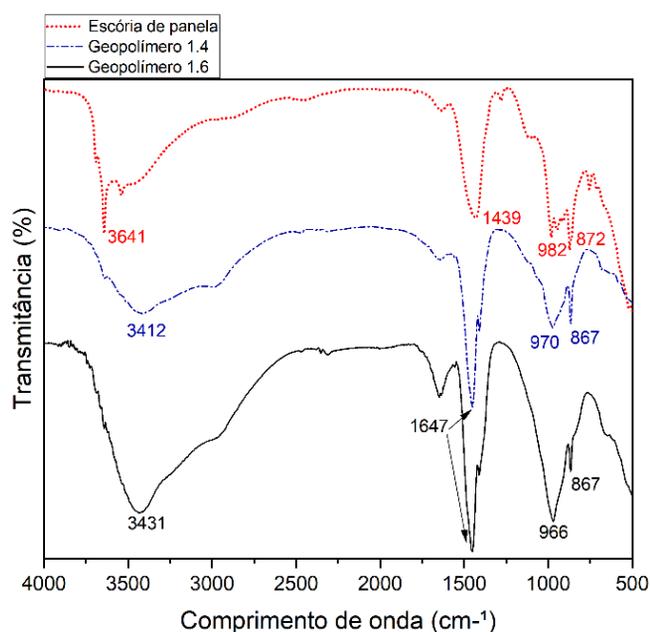
The diffractograms show crystalline phases that include quartz (Q), calcite (C), magnetite (M) and calcium-olivine (S), identifying the composition of the ladle slag [10]. By comparing the diffractograms shown in **figure 4**, it is possible to observe the diffractograms of geopolymers 1.4 and

1.6, where new diffraction peaks of the S phase appeared near $49^\circ(2\theta)$, in addition to new peaks of phases not yet indexed, which suggests the confirmation of geopolymerization. Furthermore, the peak near 50° that contains the Q phase in geopolymer 1.4 became more intense related to the high content of crystalline silica. As for geopolymer 1.6, there was reduction and broadening of the peak, which may be associated with the crystallite size or a different reorganization [13, 14].

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The spectra for ladle slag and geopolymers 1.4 and 1.6 are shown in **figure 5**.

Fig. 5 – Fourier transform infrared (FTIR) spectrum of ladle slag and geopolymers 1.4 and 1.6.



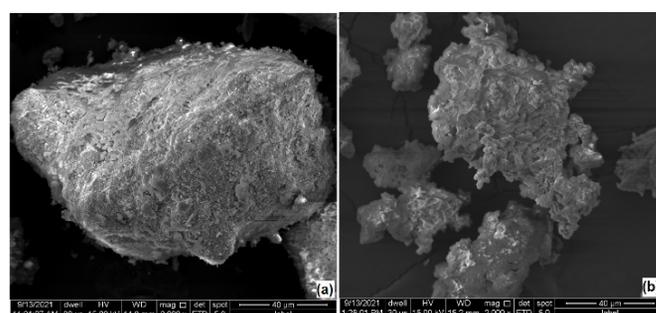
The bands are present in the regions of 3641, 1439, 982 and 872 cm^{-1} in the ladle slag; 3412, 1647, 970 and 867 cm^{-1} in geopolymer 1.4 and 3431, 1647, 966 and 867 cm^{-1} in geopolymer 1.6. In the ladle slag spectrum, the 3641 cm^{-1} band reflects H–O–H groups from crystalline water, which indicates that carbonates were formed with water of crystallization. In bands 1439 and 872 cm^{-1} an asymmetric CO_3 elongation occurs⁻² which can be attributed

to the presence of CaCO_3 . The 982 cm^{-1} band is related to the elongation of the Si–O vibration bands [15, 16]. The bands at 3412 and 343 cm^{-1} present in geopolymers 1.4 and 1.6, respectively, refer to the OH stretching vibration, corresponding to structural water and free water. The 1647 cm^{-1} band found in both geopolymers refers to the bending vibration absorption of H–O–H bonds indicating free water [17]. The bands of 970 and 966 cm^{-1} of the geopolymers were displaced compared to the ladle slag, in addition to a small band close to 1100 existing in the slag having disappeared in the geopolymers. This is due to the formation of the geopolymer matrix indicating the incorporation of Al atoms in the tetrahedral structure. The greater the displacement, the greater the degree of Al penetration of the vitreous parts into the $[\text{SiO}_4]^{-4}$ network and, therefore, the formation of the polymeric gel. The formation of this gel phase suggested the depolymerization and structural reorganization of amorphous phases in the geopolymer. The band at 867 cm^{-1} present in both geopolymers indicates bending vibrations of Ca–O and Si–O [6, 9].

3.3 Scanning electron microscopy (SEM)

Morphology, microstructure, particle dimensions and particulate dispersion of ladle slag and geopolymers 1.4 and 1.6 were analyzed in SEM. It is possible to verify the occurrence of geopolymerization due to the morphological alteration presented in the SEM images with a magnification of 2,000x contained in **figure 6**, which contains the images of the ladle slag (a) and the geopolymer 1.4 (b).

Fig. 6 – Morphological difference between ladle slag (a) and geopolymer 1.4 (b).



It is also possible to observe the morphological alteration in the micrographs with a magnification of 1000x in **figure 7**, allowing the differentiation of ladle slag (a) with geopolymer 1.6 (b), which also confirms the occurrence of geopolymerization.

Fig. 7 – Morphological difference between ladle slag (a) and geopolymer 1.6 (b).

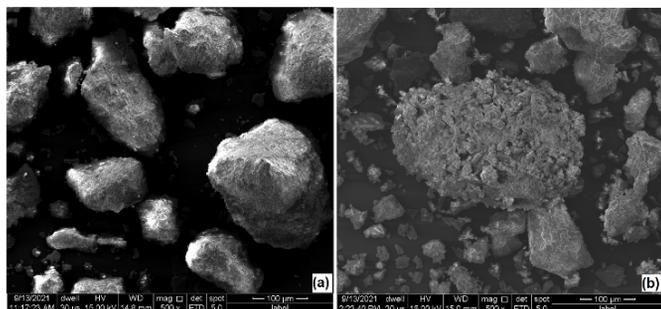


Figure 8 shows the micrograph of geopolymer 1.4 with a magnification of 5000x, where it is possible to observe a structure composed of compacted granules in a homogeneous structure. This cubic crystal structure has a morphology similar to zeolites [18, 19].

4. Conclusions

Through X-ray diffraction performed on ladle furnace slag, it was possible to identify crystalline phases such as quartz, calcite (C), magnetite (M) and calcium-olivine (S). In the diffractogram of the geopolymer 1.4 it was possible to confirm the geopolymerization due to the fact that the peak close to 50° (2θ) is more intense, which is related to the Q phase, due to the increase in the silica content. Furthermore, the diffractograms of both geopolymers showed new crystalline phases that were not indexed.

In the FTIR analysis, it was possible to identify the shift of some bands in the spectra of the geopolymers compared to the slag, in addition to the disappearance of the band at 1100 cm^{-1} . Such factors are related to the formation of the geopolymeric matrix, indicating the incorporation of Al atoms in the tetrahedral structure.

The SEM analysis showed the difference in morphology of the ladle slag micrographs with those of geopolymers 1.4 and 1.6, which reaffirms the occurrence of geopolymerization.

In view of the results of the analyzes carried out on the steelworks slag and on geopolymers 1.4 and 1.6, it is possible to state that ladle furnace slag is an efficient precursor material for carrying out geopolymerization.

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