

# Potentiality of coal mining waste to obtain geopolymers

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## Abstract

Geopolymers are chemically bonded ceramics formed at room temperature and obtained using aluminosilicates and alkali activators. Geopolymers have found applications beyond construction, such as in wastewater treatment and ceramics. This research aims to develop geopolymers using coal mining waste (CMW) for various purposes. The waste used in this study was obtained from the Barro Branco layer in companies located in southern Santa Catarina/Brazil. The waste was thermally treated at 900 °C for 160 min, followed by grinding and characterization using X-ray fluorescence spectroscopy, X-ray diffraction, and particle size analysis. Geopolymeric samples were produced using 60 wt% waste, 25 wt% sodium silicate, and 15 wt% 10 M NaOH. The specimens were divided into three groups and cured using different methods. The results showed that thermal curing enhanced waste reactivity, reduced curing time, and improved compressive strength. However, long-term submersion curing decreased compressive strength due to sodium leaching, reducing reactivity.

**Keywords:** coal, tailings, mining, sustainability.

## INTRODUCTION

Geopolymerization results from an exothermic chemical reaction that requires alkaline activation to start. Some of the essential elements that comprise the  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -alkali geopolymeric binder system are reactive aluminosilicates (metakaolin, ash) and alkaline activators (NaOH, sodium silicate) [1-3]. The kaolinite mineral (kaolin) is thermally processed at temperatures ranging from 700 to 900 °C in industrial operations to create a metastable and reactive phase for application in various production processes, such as geopolymers. Other raw materials, such as chemically linked ceramics and alkali-activated materials, can be employed in these materials and assigned different names [4]. The development of waste valorization practices is becoming more common worldwide, and obtaining geopolymers from waste is widely discussed in the literature [5-7], making the geopolymerization process more sustainable and increasing the advantages of its use over Portland cement. These efforts address present environmental concerns by minimizing the environmental impacts induced by global economic expansion.

Coal is the most abundant and widely used fossil fuel and the world's second most crucial energy source, accounting

for 40% of total primary energy production. Santa Catarina State is a major coal producer in Brazil. The quality of coal varies depending on where it is extracted, and in Brazil, the run of mine (ROM) has a low carbon/energy fraction, and much of it is wasted. When coal mining waste is discarded, it likely enters the acidic soil and has a significant environmental impact [8]. In 2022, there was a production of 11,528,892 tons of ROM coal (raw coal before processing) in southern Brazil, with Santa Catarina producing most of this total (6,152,365 tons), followed by Rio Grande do Sul (5,092,738 tons) and Paraná (283,789 ton) States [9]. The percentage of waste generated in this sector is high, reaching up to 63% of ROM in Santa Catarina and having high concentrations of clay fractions and sedimentary rocks. This waste fraction has high compositional potential for use in cementitious materials, such as geopolymer cement. The waste generated in coal processing is usually sent to landfills, which entails the company's daily environmental monitoring and transportation, disposal, and control costs. New solutions for the valorization of these materials are essential for the southern region of Brazil and become one of the transition strategies for a circular economy in the coal sector.

The performance of geopolymers based on tailings and mining waste depends on several factors, such as their chemical and mineralogical composition and the synergistic effects of these characteristics during geopolymerisation [10]. Some of these aspects still need to be discovered in the

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literature, and there is a need for further studies to better understand the intrinsic characteristics of these materials and their interactions during alkaline reactions [11]. These materials still need to be studied in the literature, which shows an opportunity for scientific advancement to fill knowledge gaps in this theme. Li et al. [12] studied geopolymers made with coal mining waste and blast furnace slag by varying the heat treatment temperature and particle size. The results show that the ideal particle size for the geopolymers obtained is 200 mesh, and the optimal activation temperature is 700 °C [12]. One of the novelties of this work is to use only coal mining waste as a geopolymeric precursor, avoiding commercial materials such as metakaolin or other ordinary wastes used in this process, such as ash and blast furnace slag. From this perspective, this work aims to develop geopolymeric cement from coal mining waste as alternative materials for use in civil construction. The analysis and characterization of the obtained results indicate the optimal use, considering the needs of the studied region and the transition strategies for the coal sector's circular economy.

## EXPERIMENTAL

**Materials:** a waste originating from the hydraulic separation of jigging and extracted from the Barro Branco stratum of the Catarinense coal mine (Santa Catarina, Brazil) was used in this study (Fig. 1a). The waste was previously thermally treated (900 °C) in a rotary oven (FRO 1700, Fortelab;  $\phi 80 \times 1500$  mm) with a 5° inclination for 160 min. Following heat treatment, the material was comminuted in a gyro-jar mill (CT-12248, Servitech; 5 L) for 8 h and sieved through a 0.075 mm sieve. Sodium silicate (28.5% SiO<sub>2</sub>, 8.8% Na<sub>2</sub>O) and 10 M sodium hydroxide solution (NaOH, 97%) were utilized as activators.

**Geopolymer processing:** 10 M sodium hydroxide solution (60 g) and sodium silicate solution (100 g) were first mixed on a magnetic stir plate for 10 min. Subsequently, a batch of 400 g of paste was made using only coal mining waste (CMW) as the aluminosilicate source. In a planetary mixer (Artisan KEA30CPPNA, KitchenAid; 4.83 L, Fig. 1b), the alkali activators (160 g) and CMW (240 g) were mixed for 10 min at 225 rpm and 5 min at 322 rpm. The formulation originated molar ratios SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=4.16, H<sub>2</sub>O/Na<sub>2</sub>O=15.24, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>=0.60, and Na<sub>2</sub>O/SiO<sub>2</sub>=0.14. After mixing and molding the samples, the specimens were divided into three curing processes. The first group was cured at room temperature for 60 days (RC); the second group was cured for 24 h in an oven at 40 °C and the rest of the days (up to 60 days) at room temperature (UC); and the third group was cured at room temperature until hardening and then until completing the 60 days in water (SC).

**Characterization of materials and products:** the raw materials were chemically characterized by X-ray fluorescence spectroscopy (XRF) and mineralogically by X-ray diffraction (XRD). The loss on ignition (LOI) test was performed following the ASTM D7348 standard

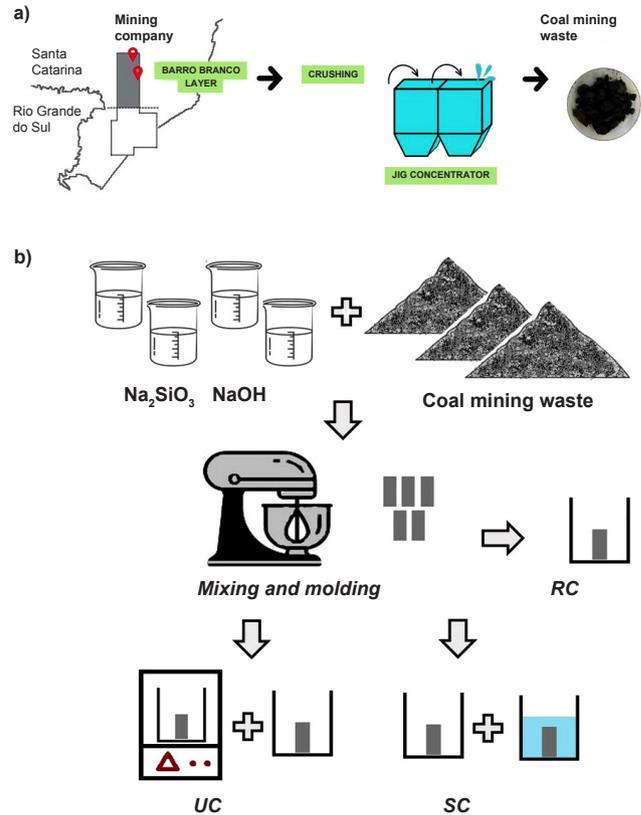


Figure 1: Schematics of: a) coal mining waste generation; and b) method used for preparing and curing geopolymers. RC: room condition; UC: usual condition; SC: submerged condition.

to eliminate organic components and constitutive water present in the material. After completing the LOI, the sample was ground and pressed into a tablet for further chemical analysis by energy-dispersive XRF (EDX 7000, Shimadzu, Japan). Mineralogical analysis was conducted in an X-ray diffractometer (LabX XRD 6100, Shimadzu, Japan), with Cu radiation,  $2\theta$  ranging from 4° to 70°, and a speed of 0.02 °/s. Laser diffraction was used to determine the particle size distribution (mod. 1064, Cilas). A polished sample of each curing process (SC, RC, and UC) was analyzed using a scanning electron microscope (SEM, EVO MA10, Zeiss, England). The products were characterized by XRD, water absorption, and compressive strength. The compressive strength of the samples was evaluated after 60 days of curing using a universal testing machine (DL10000, Emic) with a displacement rate of 0.5 mm/min. Five samples of each composition were tested. Water absorption was made following ASTM C 373-88 standard [13]. Previous works [5, 6, 14] using stone-cutting waste (SW) and biomass ashes (BA) did not naturally indicate the presence of efflorescence in the short term. To assess potential efflorescence, samples were partially submerged in 50 mL of water and left until their total evaporation [6, 15].

**Quantity and viability of recycling:** besides technical tests, some coal mining waste generation projections and the feasibility of using these materials in geopolymers are discussed.

## RESULTS AND DISCUSSION

The XRF results showed the predominance of  $\text{SiO}_2$  (55.66 wt%),  $\text{Al}_2\text{O}_3$  (27.57 wt%),  $\text{Fe}_2\text{O}_3$  (6.53 wt%), and  $\text{K}_2\text{O}$  (2.88 wt%) in the waste after heat treatment (Table I). XRF tests were also performed for the waste without thermal treatment, showing the same oxides in smaller proportions and with a loss on ignition of  $\sim 17.66$  wt% (Table I). Mineralogical characterization by XRD (Fig. 2) of the waste identified silica (quartz), kaolinite, mica, and pyrite peaks. These minerals align with the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{K}_2\text{O}$  found by XRF (Table I). The XRD patterns of the thermal-treated waste showed peaks of the minerals present in the waste without thermal treatment. The typical amorphous band of commercial metakaolin was not evident, and other more crystalline phases were current (quartz). The run of mine (ROM) processing is related to the particle size of the residual fractions. The residual fractions studied in this work had coarse particles 90% larger than 2.0 mm (Fig. 3a). This characteristic of the material justified milling after thermal treatment for geopolymerization. Fig. 3b shows the particle size distribution curve after thermal treatment and milling. The D10, D50, and D90 values were  $\sim 2.14$ , 16.42, and 56.99  $\mu\text{m}$ , respectively. These values were compatible with other materials usually used for geopolymerization [6].

Table I - XRF results of the studied raw materials (wt%).

Oxide	CMW	Thermally activated CMW
$\text{SiO}_2$	47.00	55.66
$\text{Al}_2\text{O}_3$	23.77	27.57
$\text{Fe}_2\text{O}_3$	5.96	6.53
$\text{K}_2\text{O}$	3.18	2.89
$\text{TiO}_2$	1.58	1.50
$\text{MgO}$	0.00	0.47
$\text{SO}_3$	0.14	0.17
$\text{ZrO}_2$	0.04	0.05
$\text{ZnO}$	0.07	0.04
$\text{CaO}$	0.43	-
$\text{MnO}$	0.02	0.02
$\text{SrO}$	0.02	0.02
LOI	17.66	5.05

CMW: coal mining waste; LOI: loss on ignition.

After alkaline activation, the samples were processed differently to evaluate the obtained properties. The conditions were room condition (RC, without oven), usual condition (UC, with oven), and submerged condition (SC, in water). All samples reacted and formed geopolymers (Fig. 4) but with different hardening times. The air curing (room condition) took 6 days to harden and be able to be removed from the cylindrical molds, while the oven-cured samples had their curing time reduced to 24 h. This characteristic showed that the coal mining waste had less reactivity when compared to commercial metakaolin. When

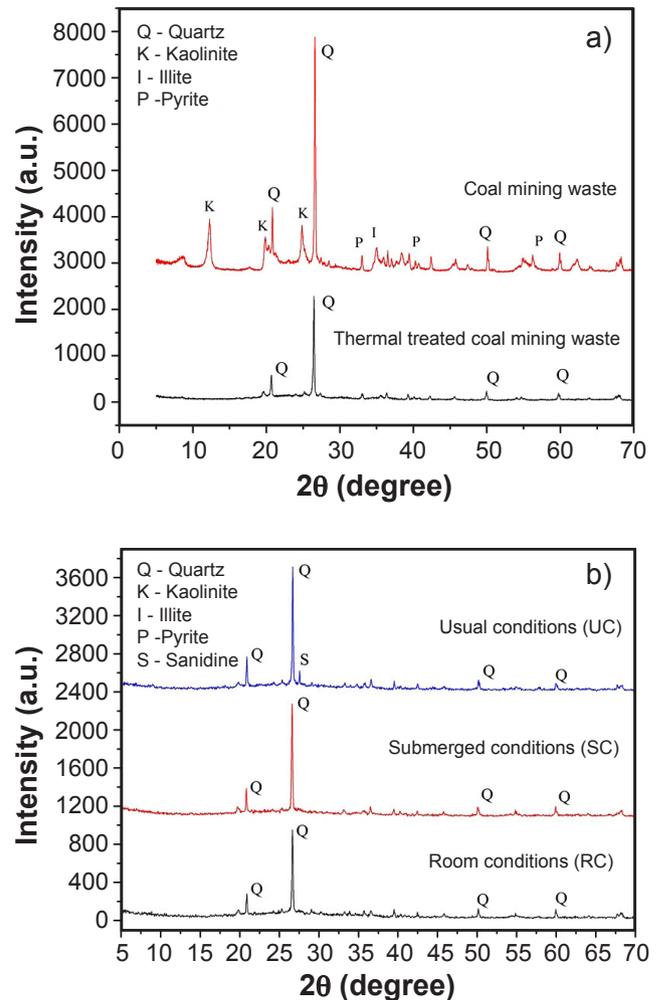


Figure 2: XRD patterns of raw materials (a) and prepared geopolymers (b).

metakaolin-based geopolymer is cured at room temperature, the setting time is less than one day [16]. In the first weeks after geopolymerization, the samples cured in air and oven had efflorescence, mainly those cured outside the oven. This efflorescence was due to sodium not being consumed in the early ages of the material obtained. The cured samples immersed in water did not show short-term efflorescence, as excess sodium was leached into the water. This strategy was used in previous works using biomass ash and stone-cutting waste [5, 6, 14]. Regarding the sustainability of the process, this curing water could be used again to produce new geopolymers. In the long term ( $>6$  months of curing), the efflorescence test demonstrated no efflorescence formation in the room condition and submerged condition samples. In the usual condition sample, there was a small formation of whitish crystals (Fig. 4).

The X-ray diffractograms of the obtained products showed no significant change among the raw material (coal mining waste after thermal treatment) and SC and RC samples. The quartz crystalline phase was the only one present in all the processes used (Fig. 2b). A small peak was identified at the UC sample related to the sanidine  $[\text{K}(\text{Si}_3\text{Al})\text{O}_8]$  crystalline phase.

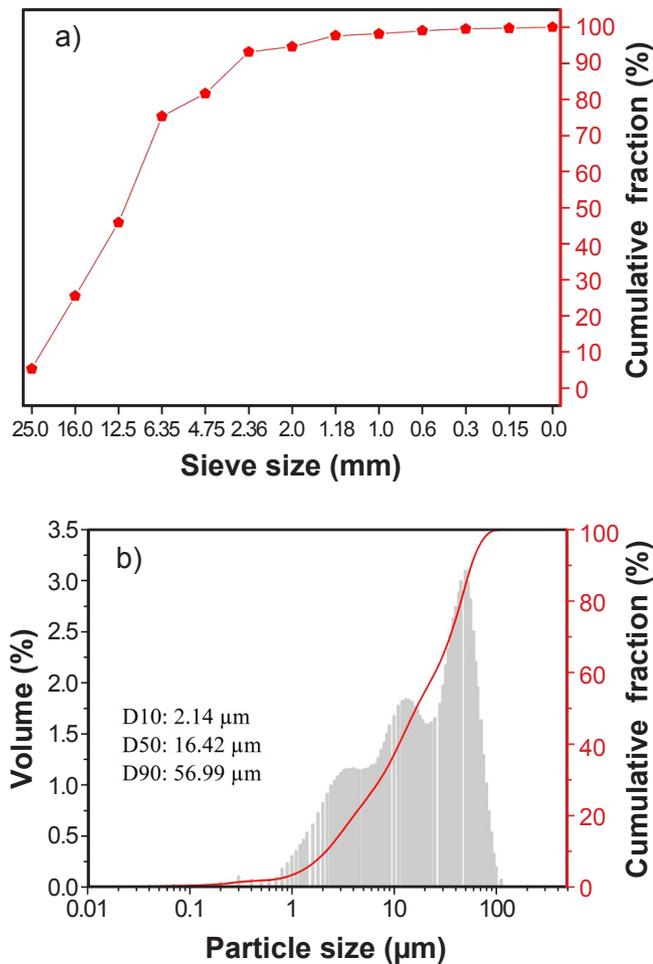


Figure 3: Particle size distribution curves of the studied materials: a) as received; and b) after thermal treatment and milling.

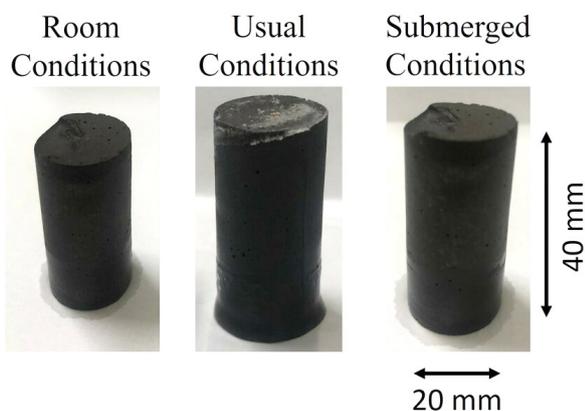


Figure 4: Photographs of the samples after the efflorescence test.

This phase is a potassium aluminum silicate also identified in other works that use heating during the geopolymer curing process [17, 18]. When potassium cations are used as activators, kalsilite ( $KAlSiO_4$ ), leucite ( $KAlSi_2O_6$ ), and sanidine phases could be formed, whereas sodium cations could produce nepheline ( $NaAlSi_3O_8$ ), jadeite ( $NaAlSi_2O_6$ ), and albite ( $NaAlSi_3O_8$ ) phases [1, 17]. In this work, the cure

temperature and the potassium present in CMW may explain the residual phase obtained.

Regarding mechanical strength, it can be seen that the highest compressive strength was found in the oven-cured sample (UC), reaching a value of  $23.1 \pm 5.5$  MPa. The sample cured in the air (RC) reached 16.0 MPa, lower than that cured in the oven (UC), but higher than the values of other geopolymers [5, 6, 14] obtained with commercial metakaolin and biomass ashes (Fig. 5). The sample cured in water (SC) had a reduction in compressive strength due to the loss of activators by leaching. This curing in water at early ages may have been responsible for the drop in values. In future works, it is suggested to water cure at ages more than seven days, seeking not to lose the activators by leaching and consequently not reducing the geopolymer reaction. However, the mechanical strength obtained for the SC sample is still attractive for several applications in civil construction that do not require high compressive strength values. In addition to civil construction, environmental applications, and other emerging ones in studying these materials can be researched to enhance the properties achieved. Some studies about these applications are available in the literature, taking advantage of the superficial properties, porosity, and similarity between zeolites and geopolymers. In these applications, high compressive strength is not required [19, 20]. The water absorption values were coherent with the mechanical compressive strengths. The highest water absorption value was for the sample submerged in water ( $35.7 \pm 0.5\%$ ) since sodium leaching during the process left voids in the structure. Likewise, the lowest value was for the sample cured in an oven ( $25.7 \pm 0.4\%$ ), better densifying the structure and increasing the compressive strength. The air-cured sample showed water absorption of  $29.5 \pm 0.7\%$  close to UC. The apparent porosity had the same tendency with  $48.1 \pm 0.3\%$  to SC,  $43.0 \pm 0.7\%$  to RC, and  $39.8 \pm 0.5\%$  to UC. The SEM micrographs of the samples cured at different methods are shown in Fig. 6. The micrographs ratify that the microstructures of UC and RT were more densified than SC. SC sample had a more dispersed microstructure and confirmed that the loss of activators by leaching generated more pores.

Some considerations can be reported regarding the quantity and feasibility of using these materials. The waste generated during the extraction and processing of Brazilian coal is approximately 5 million tons per year. The estimated

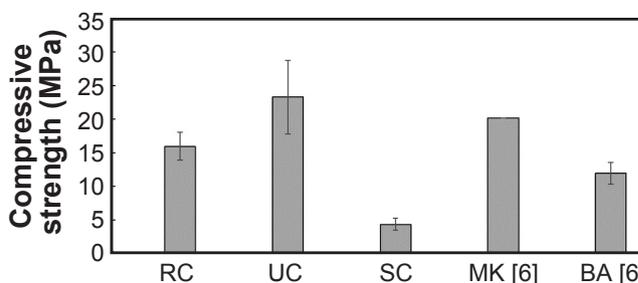


Figure 5: Compressive strength for RC, UC, SC, and literature samples.

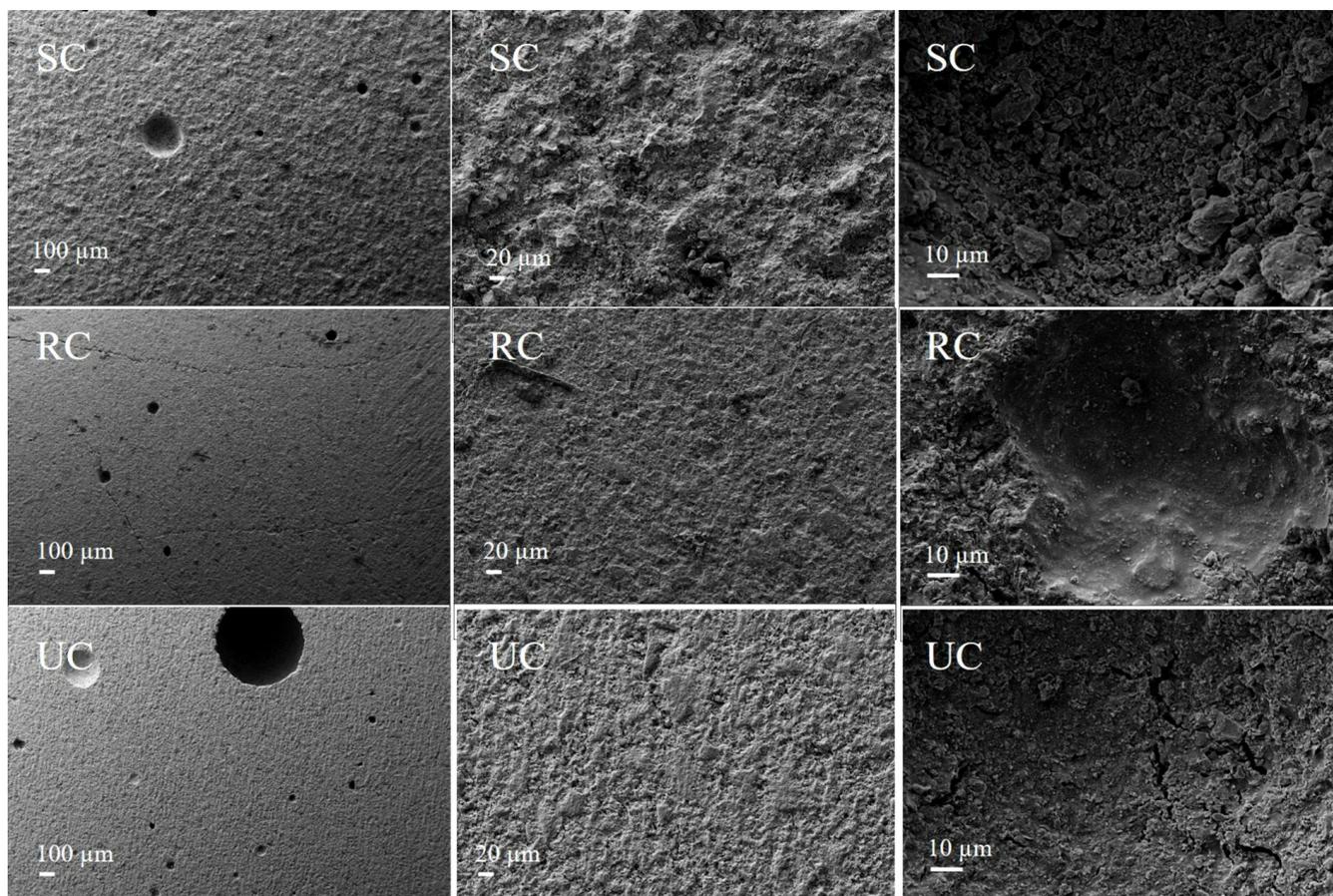


Figure 6: SEM micrographs of SC, RC, and UC samples.

mass of CMW in Brazil is 320 million tons. The mining company under study extracts and processes two geological layers in the studied region: the Barro Branco and Bonito layers. The processing of ROM extracted from the Barro Branco layer results in 32,000 t/month, and from the Bonito layer 50,000 t/month. The waste used in this study resulted from a two-cut jig with an estimated generation of 13,000 t/month. These values ratify the need for mineral valorization to reduce the materials sent to landfills in the studied region. Regarding applications, it can be seen that several companies in the civil construction sector in the studied region could use these materials as alternative minerals in civil construction, as reported by Acordi et al. [21].

## CONCLUSIONS

The results suggested the potential use of coal mining waste (CMW) in geopolymer formulations. Thermal curing proved to be an efficient way to increase the reactivity of the waste. The sample cured in the air (RC) reached compressive strength of  $16.0 \pm 2.1$  MPa, the sample cured in the oven (UC) reached  $23.3 \pm 5.5$  MPa, and the sample cured in water (SC) reached  $4.4 \pm 0.9$  MPa. The submerged curing of the specimens showed that there is a considerable reduction in compressive strength in the long term. The cost-benefit and the use of wastes are what make the geopolymer such an efficient alternative material.

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