

## Research Article

# An Assessment of Reuse of Light Ash from Bayer Process Fluidized Bed Boilers in Geopolymer Synthesis at Ambient Temperature

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Sustainable civil construction in the future, besides having low energy consumption and greenhouse gas emissions, must also adopt the principle of reusing wastes generated in the production chain that impact the environment. The aluminum production chain includes refining using the Bayer process. One of the main wastes produced by the Bayer process that has an impact on the environment is fly ash. Geopolymers are cementitious materials with a three-dimensional structure formed by the chemical activation of aluminosilicates. According to studies, some are proving to be appropriate sources of Al and Si in the geopolymerization reaction. The research reported here sought to assess the possibility of reusing fly ash characteristic of the operational temperature and pressure conditions of Bayer process boilers in geopolymer synthesis. Geopolymerization reaction was conducted at an ambient temperature of 30°C, and the activator used was sodium hydroxide (NaOH) 15 molar and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) alkaline 10 molar. Fly ash and metakaolin were used as sources of Al and Si. XRD, XRF, and SEM Techniques were used for characterizing the raw materials and geopolymers. As a study parameter, the mole ratios utilized followed data from the literature described by Davidovits (year), so that the best results of the geopolymer samples were obtained in the 2.5 to 3.23 range. Resistance to mechanical compression reached 25 MPa in 24 hours of curing and 44 MPa after 28 days of curing at ambient temperature.

## 1. Introduction

The chain for producing aluminum from bauxite to primary aluminum includes refining using the Bayer process. One of the main waste products of the Bayer process is the fly ash collected from the cyclone overflow of the fluidized bed boilers at operational conditions of 900°C of temperature and 120 kPa of pressure. The pressure and temperature conditions influence the specification and morphology of the ash waste generated [1].

In the Bayer process, the circulating-type fluidized bed boilers operate at specific conditions of 900°C and 120 kPa as a means of guaranteeing maintenance of the bed and generate

a specific fly ash characteristic of that process. Fly ashes are classified into two types. These are C type class with a higher amount of calcium oxide and F type class with a lower amount of calcium oxide [2].

When the sum of the levels of silica, alumina, and iron oxide is greater than 70%, the fly ash is classified as class F [3].

Geopolymers are synthesized at a different temperature by the alkaline activation of aluminosilicates derived from natural minerals, calcined clay or industrial by-products 2008. This activation is generally done with metakaolin silicates of sodium or potassium. Geopolymers are inorganic ligands with good resistance to high temperatures and degradation by acid, as well as good mechanical properties. They

are thus an attractive alternative to Portland-type cement, and their use makes it possible to recycle large quantities of industrial wastes. The mechanical properties of geopolymeric materials depend upon the alkaline cation ( $\text{Na}^+$ ), the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar relation as used by Davidovits and the conditions under which the reaction occurs [4, 5].

The term “geopolymer” describes the chemical properties of aluminosilicate-based inorganic polymers. Geopolymers present properties of cement and therefore have great potential for use in the civil construction industry [6].

The water trapped in a network of geopolymers generates porosity, which results in a reduction of mechanical properties. Their three-dimensional structure is made up of  $\text{SiO}_2$  and  $\text{MAIO}_4$  tetrahedrons, where M is a monovalent cation, typically  $\text{Na}^+$ . This network is comparable to some zeolites but differs in its amorphous character. The polymeric character of those materials increases with the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  relation, as the aluminum atoms cross the  $\text{SiO}_2$  tetrahedron chains [7].

Changing the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  relation in geopolymers thus enables the synthesis of materials with different structures. The geopolymerization mechanism is particularly difficult due to the kinetics of the reaction. However, the majority of authors agree that the mechanism involves dissolution, followed by gel polycondensation [8, 9].

Studies show that the mechanical forces of geopolymers increase with elevation of the temperature of kaolin calcination in order to generate metakaolin; however, the ideal temperature for calcination of kaolin is around  $700^\circ\text{C}$  for 2 hours [10, 11].

The development of ash-based geopolymer derived from burning coal shows promise as a means of reusing that waste. The worldwide demand for coal will continue to grow up to 2030, achieving a duplication in relation to current demand. With the increasing consumption of coal for generating energy, there will be an increased production of ashes as a byproduct of burning coal [12].

The cements produced by alkaline activation of aluminosilicates were studied in a search for materials with bonding properties more resistant than those of current Portland cements, as well as materials that can be produced with low cost raw materials, little expenditure of energy, and especially with low levels of toxic gas emissions into the atmosphere [13].

Those studies point to excellent possibilities for being implanted around the world and such materials can be produced on a large scale, suppressing the demand for cement in a market that is growing every year. In that context, this study was performed with the objective of assessing the microstructural properties and resistance to compression of geopolymeric materials produced using the light ash characteristic of the Bayer process.

## 2. Materials and Methods

Fly ash waste was collected from the cyclone overflow of the fluidized bed circulating-type boilers of the Bayer process at conditions of  $900^\circ\text{C}$  of temperature and 120 kPa of pressure. That waste was utilized as a source of Si and Al in

TABLE 1: Compositions formulated using fly ashes and metakaolin for obtaining geopolymers.

Geopolymers	Fly ash (mass %)	Metakaolin (mass %)	$\text{SiO}_2/\text{Al}_2\text{O}_3$
1	100	0	4.4
2	94.24	5.76	4.11
3	90.39	9.61	3.94
4	84.62	15.38	3.72
5	75	25	3.4
6	69.2	30.8	3.23
7	61.54	38.46	3.041
8	53.85	46.15	2.87
9	42.31	57.69	2.65
10	34.62	65.38	2.52

TABLE 2: Molar concentration and proportions of the activating solution.

Activator	NaOH	$\text{Na}_2\text{SiO}_3$
Molar concentration	15	10
Proportion ( $\text{NaOH}:\text{Na}_2\text{SiO}_3$ )	1 : 3 in mass of solution	

geopolymer synthesis. Besides the fly ash, another source of Si and Al was metakaolin produced by the calcination of kaolin at a temperature of  $800^\circ\text{C}$  for two hours.

To analyze the crystalline structure of ash, kaolin, and metakaolin, X-ray diffractometry (XRD—Bruker LyuxEye) was utilized. For chemical analyses, X-ray fluorescence was employed using equipment from AxiosMinerals (PAN-alytical), with a ceramic X-ray tube and rhodium anode. For the morphology study, we made use of the scanning electron microscopy (SEM) technique using Zeiss MEO 1430 equipment. Ash and metakaolin were submitted to granulometric analysis of their particles, in a Fritsch Analysette 22 Micro tec plus laser granulometer.

The mole ratios utilized by Davidovits ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) are an important parameter for orienting the best compositions for geopolymer synthesis [14]. Ten compositions of geopolymers were formulated using fly ash and metakaolin as a base, with different mole ratios among  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Table 1 presents the geopolymers studied with their respective  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios.

The alkaline activator used for synthesizing the geopolymer was composed of a solution of sodium hydroxide (NaOH) micro pearl (neon, 97% purity). A solution of alkaline sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (Manchester Química do Brasil S.A.,  $\text{SiO}_2/\text{Na}_2\text{O} = 3.2$ ) was also used. Table 2 shows the composition of the activator.

The compositions were prepared in a mechanical mixer and placed in cylindrical molds with 100 mm height and diameter of 50 mm. After molding, the molds were submitted to curing at an ambient temperature of  $30^\circ\text{C}$ . Geopolymers at 24 hours and 7 and 28 days of curing were submitted to compression resistance testing in an Emic SSII300 press. Geopolymers before and after synthesis were submitted to XRD analysis in order to assess their degree of polymerization. SEM tests were performed after the geopolymer synthesis.

TABLE 3: Chemical composition in % of ash and of metakaolin.

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Loi
Ash	42.531	16.399	19.005	7.081	0.941	0.264	0.897	0	12.882
Metakaolin	53.36	43.58	0	0.6	0.33	0	1.51	0.13	0.49

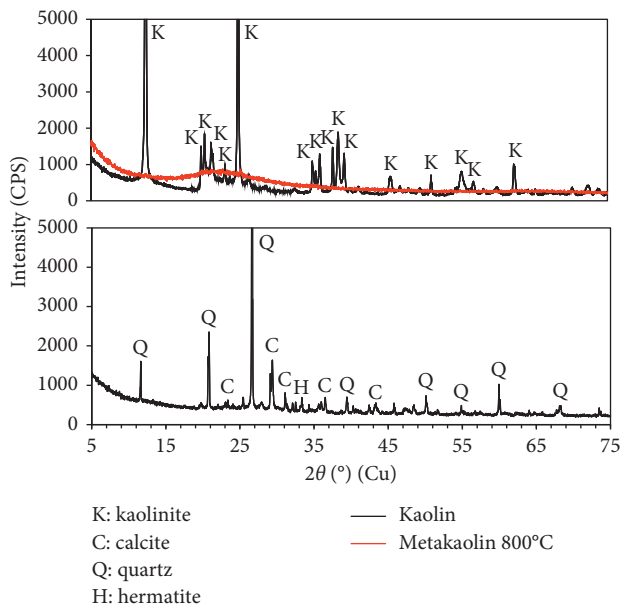


FIGURE 1: XRD of kaolin, of metakaolin, and of fly ash.

### 3. Results

Table 3 presents the results of the XRF analyses of the materials used in geopolymer synthesis. One may observe (Table 3) the 42.531% level of SiO<sub>2</sub> and 16.399% level of Al<sub>2</sub>O<sub>3</sub> in the fly ash used, which indicates that ash is a rich source of Al and Si. Metakaolin (Table 3) is composed of 43.58% Al<sub>2</sub>O<sub>3</sub> and 63.36% SiO<sub>2</sub> which characterizes it as a predominant source of aluminum in proportion [15–18].

The use of fly ash waste from burning charcoal as a source of Si and Al favors the geopolymerization reaction and guarantees good durability for the geopolymer [19–23].

According to the result from XRF, the fly ash generated in the Bayer process under the operational temperature and pressure conditions may be classified as C class type fly ash, due to the sum of the levels of silica, alumina, and iron oxide being lower than 70%.

Figure 1 presents the result of the XRD test of fly ash, of kaolin, and of metakaolin calcined at 800°C for 2 hours.

As shown in Figure 1, the calcination of kaolin at 800°C for two hours was satisfactory because it generated a change in the crystalline phase, transforming into an amorphous phase, which characterizes metakaolin.

The change occurring in the material after thermal treatment frees Al and Si for the geopolymerization reaction. Kaolin calcined at a range from 600°C to 800°C for a time interval from 2 to 4 hours, shows itself to be adequate for obtaining metakaolin applied to the development of geopolymer [24–26].

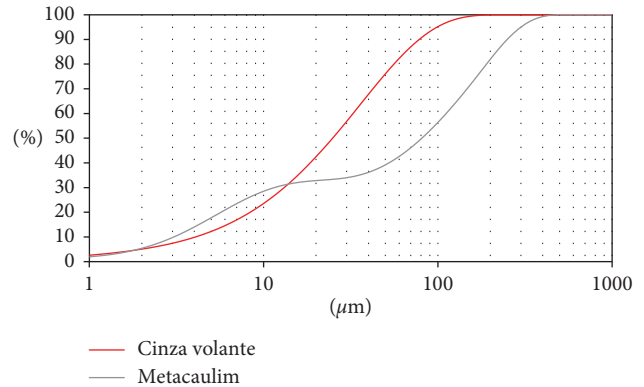


FIGURE 2: Distribution of the size particles for fly ash and metakaolin.

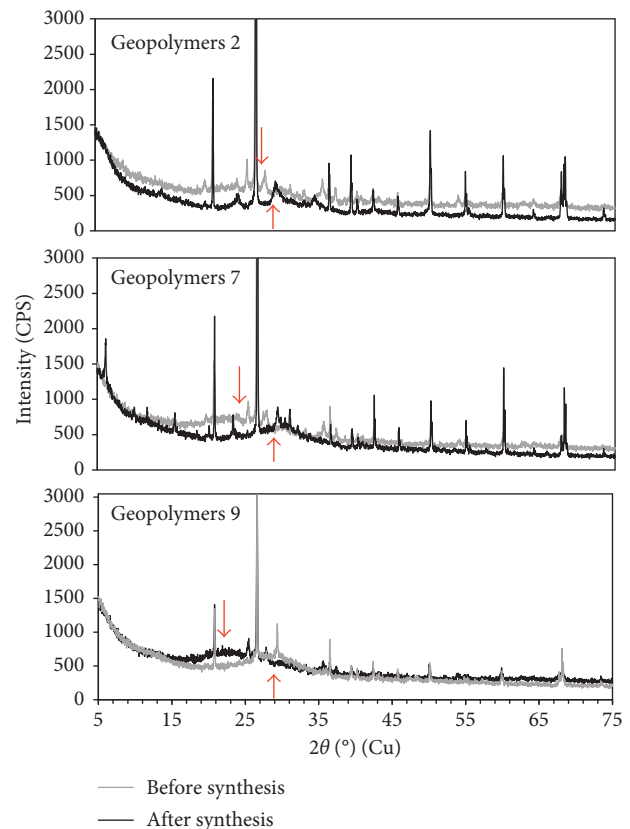


FIGURE 3: XRD of geopolymers 2, 7, and 9 before and after synthesis.

The fly ash generated in aluminum refineries presents quartz and calcite in its composition as shown in the diffractogram for ash in Figure 1.

The distribution of the particle size for the raw materials used in synthesizing the geopolymer resulted in an average

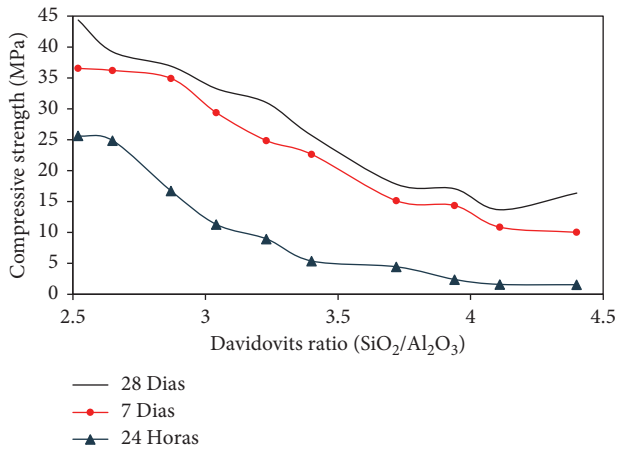


FIGURE 4: Compressive Strength (MPa) of the geopolymers.

diameter ( $d_{50}$ ) of  $24\mu\text{m}$  for the fly ash and  $88\mu\text{m}$  for the metakaolin. Figure 2 presents the results of the laser granulometric analysis for fly ash and metakaolin.

Nath et al. [27] worked on a synthesized geopolymer with fly ash at a granulometry of  $4.7\mu\text{m}$  and studied the geopolymerization reaction using metakaolin with an average diameter of  $18\mu\text{m}$ .

Figure 3 presents the result of the XRD analysis for geopolymers 2, 7, and 9 with the arrow showing the halo before and after synthesis. According to Salih et al. [5] the geopolymer with the best formed and defined halo indicates larger amorphous zones and thus greater regions of reaction occurrence. In his studies, Salih et al. [5] showed that the greater displacement of the halo after synthesis indicates geopolymers with a greater degree of geopolymerization and thus greater mechanical resistance.

According to the data presented in Figure 3, geopolymer 2 presented a low halo formation, indicating a lower degree of geopolymerization in relation to geopolymer 7. Geopolymer 9 presented a good definition and displacement of the halo before and after the synthesis. That agrees with Figure 4 that presents the results of mechanical compressive strength in MPa, indicating that geopolymer 9 has greater mechanical compressive strength to geopolymers 7 and 2.

Geopolymers with a ratio in the 2.5 to 3.23 range, as indicated by Davidovits, presented mechanical resistance to geopolymers with a greater ratio. Geopolymer 9 with a ratio of 2.65 presented a high compressive strength, reaching values of 25 MPa, 36.22 MPa, and 44 MPa in 24 hours, 7 days, and 28 days of cure, respectively, at ambient temperature. From the results of Figure 4, the geopolymers from samples 8, 9, and 10 in 24 hours achieved the resistance of conventional Portland-type concrete at 28 days of curing, but compressive strength continues to increase in the tested range and is thus higher [28].

Figure 5 presents the result of scanning electron microscopy (SEM) with 500x expansion of geopolymer 9 in (a) and of geopolymer 4 in (b).

In Figure 5, one may observe that geopolymer 9 presented a denser and more homogenous morphology when compared to geopolymer 4. The more uniform morphology

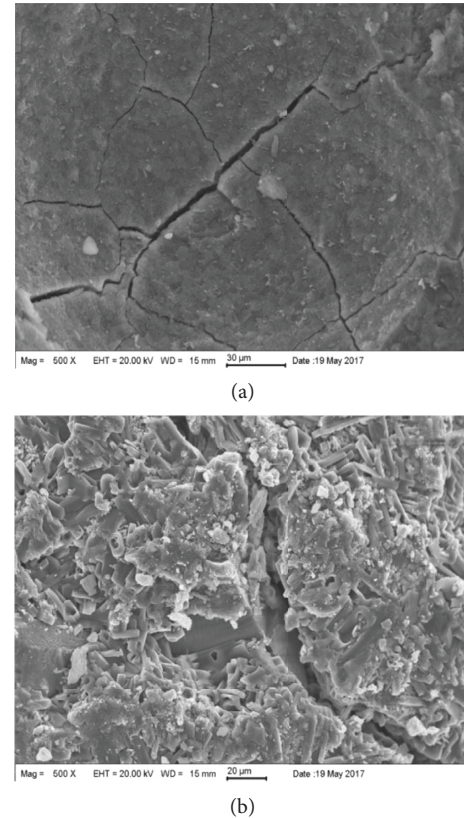


FIGURE 5: Scanning electron microscopy (SEM): (a) Geopolymer 9 increase 500x; (b) Geopolymer 4 increase 500x.

of geopolymer 9 is in accord with the results obtained in the compression resistance tests and also indicated a greater degree of geopolymerization after the reaction. Salehi et al. [29] found in his studies that the denser and more uniform morphological aspects provide greater mechanical performance to the geopolymers and thus greater advance in the geopolymerization reaction.

#### 4. Conclusion

This research made it possible to develop a geopolymer from metakaolin and industrial waste from the Bayer process that contained amorphous aluminosilicates in their composition. The waste utilized was fly ash generated in the operational conditions of the Bayer process. As seen in the procedures, the synthesis of the geopolymer according to the 2.5 to 3.3 mole ratios utilized by the researcher Davidovits was favorable to the process, and geopolymers with greater mechanical compressive strength were obtained. Geopolymers synthesized at ambient temperature with an activator having a composition of 15 molar of sodium hydroxide and 10 molar of alkaline sodium silicate appear to be a viable alternative for supplying demands for cement, achieving resistance superior to that of conventional concretes derived from Portland-type cement. Furthermore, the geopolymers were produced with low emissions of  $\text{CO}_2$ , when compared with conventional cements, which is environmentally favorable. With the characterization of the synthesized



geopolymers, it was concluded that the waste from the Bayer process presents a characteristic favorable to the synthesis of geopolymeric materials, classified by the study as class C ash. Our research concludes that synthesized geopolymers have great potential for production of geopolymeric materials.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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