

## Article

# Methodologies for the Possible Integral Generation of Geopolymers Based on Copper Tailings

Hengels Castillo <sup>1,2,\*</sup>, Humberto Collado <sup>1,2</sup>, Thomas Droguett <sup>3,4</sup>, Sebastián Sánchez <sup>3,5</sup>, Mario Vesely <sup>1</sup>, Pamela Garrido <sup>3</sup> and Sergio Palma <sup>2</sup>

- <sup>1</sup> JRI Ingeniería, Santiago 7770445, Chile; hcollado@jri.cl (H.C.); mvesely@jri.cl (M.V.)  
<sup>2</sup> Department of Metallurgical Engineering and Materials, Complex Fluids Laboratory, Universidad Técnica Federico Santa María, Santiago 8940572, Chile; sergio.palma@usm.cl  
<sup>3</sup> CIMS-JRI, Santiago 7850000, Chile; thomas.droguett@cimsjri.cl (T.D.); sebastian.sanchez@jri.cl (S.S.); pgarrido@cimsjri.cl (P.G.)  
<sup>4</sup> Department of Metallurgical Engineering, Universidad de Santiago de Chile, Santiago 9170022, Chile  
<sup>5</sup> Escuela de Ingeniería Química, Pontificia Universidad Católica de Valparaíso, Valparaíso 2340025, Chile  
\* Correspondence: hcastillo@jri.cl

**Abstract:** It is of interest to study the use of copper tailings as a raw material to generate geopolymers due to the exorbitant amounts of existing tailings deposits, which also produce different risks to nearby communities. Therefore, using this industrial waste as construction material would result in several environmental and economic benefits. Due to the above, it is necessary to perform laboratory tests that account for the relevant variables to obtain fresh geopolymer pastes with good consistency, and to obtain hardened geopolymers with good mechanical strength. This report gives an account of the experimental work carried out in the laboratory of the CIMS Sustainable Mining Research Center of the Engineering Consulting Company JRI, exposing the preliminary results observed in the generation of geopolymers by means of seven different methods using copper tailings and NaOH. Of the seven methods evaluated in the laboratory, it was observed that two of them deliver better results from a qualitative point of view, where the influence of the curing stage stands out, reflecting that temperature is one of the critical variables for the formation of geopolymers based on copper tailings and NaOH. The best means to work the mixtures should be studied to optimize the solubility of the NaOH and, therefore, the dissolution of the aluminosilicates in the tailings.

**Keywords:** copper tailings geopolymers; geopolymer generation; mechanical strength; curing temperature



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## 1. Introduction

The mining industry is the foundation for the manufacture of electronic communication equipment, machinery, aerospace materials, etc. In the process of refining valuable minerals, large amounts of mine tailings are produced. In China, approximately 10 billion tons of tailings were stored until 2009, with 1.5 billion tons of tailings being produced in 2011 alone [1]. Therefore, it is critical to develop procedures to address potential tailing-induced environmental pollution. Thus, there is great interest in the utilization of mine tailings, for which much energy is consumed during the comminution process, as construction materials using geopolymerization, a novel alkali-activation technique [2–5].

Geopolymerization is a process for obtaining a polymeric structure from aluminosilicate by dissolving aluminosilicate sources in a strong alkali (most commonly used is NaOH) solution [6,7]. In addition to mine tailings, there are a variety of sources of aluminosilicates that can be used to produce geopolymers. The most common sources of aluminosilicates used for geopolymer production are metakaolin and by-products from other industries, such as fly ash, red muds, and slags. The geopolymer precursor materials must be rich in alumina (Al<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>), preferably in amorphous reactive form [8], because these compounds are essential for the formation of the geopolymer gel, which is responsible for providing the geopolymer with rigidity and resistance.

In addition to the aluminosilicate reagent, an alkaline activator is needed to produce the geopolymer. The alkaline activator causes the dissolution of the raw materials [9], and it must be carefully selected because its composition has different impacts on the properties of fresh geopolymer paste and development of the mechanical strength in the hardened geopolymers [10]. The process in which the aluminum and silicon present interact to form an amorphous solid structure is called polymerization, and this polymerization is favored by the application of moderate temperatures [2]. In the activation of the aluminosilicate source with NaOH (the most used alkaline reagent), the reaction starts with the dissolution of Al and Si, which are precursor particles in the alkaline solution, and is then followed by polymerization in the aluminum-rich first gel phase, which will be transformed into silicon-rich final geopolymer gel [11]. The product resulting from the reaction between the aluminosilicate source and the alkaline activator is an amorphous substance composed of solid phases of aluminosilicates armed based on connections of  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  as tetrahedra forming a 3D structure.

The process of hardening the geopolymer is called curing, and this can be accomplished by the application of heat, or by simply leaving the geopolymer at ambient temperature if the composition of the geopolymer permits [12–14]. After curing for a specific time, the geopolymerization product shows greatly increased compressive strength. Therefore, the product can be used as construction materials such as bricks or road pavement material [15].

Geopolymers have been studied to a great extent as materials for construction [4,16], being considered more environmentally friendly compared to the use of traditional Portland cement [17]. Geopolymeric blends use industrial waste to develop materials with properties similar to those of concrete [18]. The best known example of this reuse is the fly ash from coal-based power plants [19].

It is of interest to the CIMS Sustainable Mining Research Center of the Engineering Consulting Company JRI to study the use of copper tailings as raw material for the generation of geopolymers, in order to be able to use this technology as filling of underground stopes [20–23]. To achieve this purpose, the research team made a set of seven geopolymer mixtures to be made in the CIMS's labs to capture the predominant variables in the generation of geopolymer mixtures.

This report gives an account of the experimental work that was carried out and the preliminary results that were observed in its execution, focusing on the influence of the methodologies used in the laboratory.

## 2. Materials and Methods

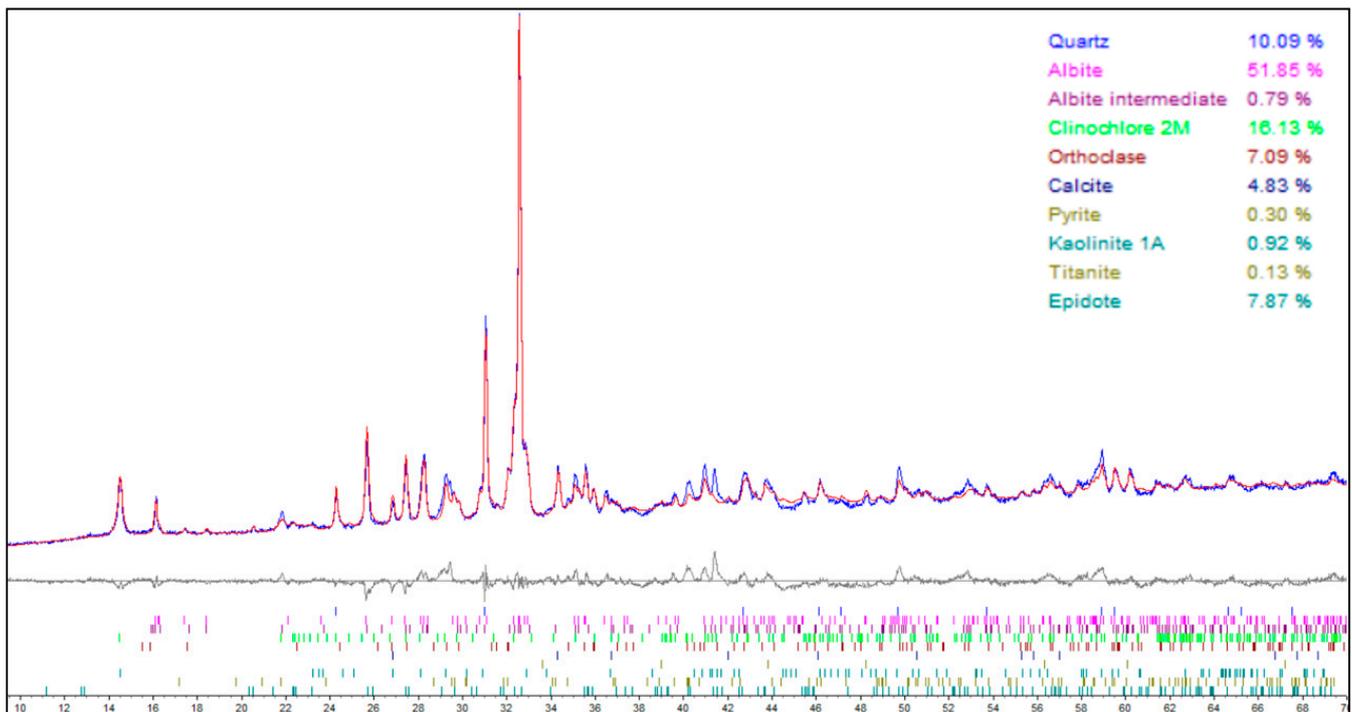
### 2.1. Materials

The copper tailings used in this research come from the San Pedro mining company, located in the commune of Til Til, Chile, which, by means of a subway operation, obtains polymetallic copper and silver concentrates. The type of deposit from which these concentrates are extracted corresponds to a copper porphyry, where the main element of interest extracted is copper. The tailings obtained from this mine were filtered, obtaining a solids content of  $C_p = 85.85\%$  (Figure 1). Process water samples were taken to be used in the formation of geopolymers.



**Figure 1.** Filtered copper tailings in a mining company in Chile.

The XRD pattern of the copper tailings powder is shown in Figure 2. The copper tailings used in this research is mainly a crystalline material which is composed mostly of albite ( $\text{NaAlSi}_3\text{O}_8$ ), and to a lesser extent, clinocllore ( $\text{Mg}_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$ ), quartz ( $\text{SiO}_2$ ), epidote ( $\text{Ca}_2(\text{Al}_2, \text{Fe})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ ), and orthoclase ( $\text{KAlSi}_3\text{O}_8$ ). The XRD analysis was carried out in the Geomaq Chile laboratory and all XRD data were collected using a D8 diffractometer of EE.UU. Data for the Rietveld refinement were collected on the Endeavor-Bruker geometry of  $3^\circ$  to  $70^\circ$   $2\theta$  with an increase of  $0.02^\circ/\text{s}$  and a step time of 0.2 s.



**Figure 2.** XRD pattern of un-reacted copper tailings.

The tailings samples were homogenized by adding industrial water until reaching a  $C_p$  solids content of 70%. After this, the tailings were filtered until they had a  $C_p$  of 83%.

The characterization of the copper tailings used in this research was undertaken by means of the Inductive Coupling Plasma (ICP) test, where the results obtained correspond to the average values obtained in the analysis of several samples. The chemical composition of the tailings is presented in Table 1. The ICP analysis was performed under the ISO 17025:Of.2005 Accredited Method INN, LE1386, using an analytical balance with a minimum precision of 1 mg to weigh the sample and prepare it for leaching at a temperature of  $23 \pm 2$  °C, for  $18 \pm 2$  h at  $30 \pm 2$  rpm. Then the precipitation test is carried out for which a 20 mL extract is taken and 2 mL of  $HNO_3$  is added; if precipitation is observed, the rest of the extract is not acidified, and the measurement is obtained. If the extract does not present precipitation, it is acidified with  $HNO_3$  acid to pH = 2 and stored at 4 °C, for later measurement. After this, 2.5 mL of the 20 mL extract is diluted and emptied into a 50 mL volumetric flask containing 12.5 mL of quenched aqua regia, to enable measurement by ICP-MS with an ICP-MS AURORA BRUKER, EE.UU., in the Andes Analytical Assay Laboratory: 3AAA in Chile.

**Table 1.** Tailings chemical characterization test (ICP).

Element	Concentration [mg/L]	Element	Concentration [mg/L]
Si	26.95	K	1.19
Al	9.50	Ti	0.60
Fe	8.05	Mn	0.25
Ca	3.28	S	0.12
Na	2.67	Cr	<0.01
Mg	2.10		

Due to the procedures for obtaining results by means of an ICP test, which consist of dehydrating the sample, atomizing it, exciting the atoms present, and finally ionizing them, which is achieved due to the high temperatures reached by the plasma, the samples may be affected by such procedures. This may have an effect on the results obtained. Because of this, caution should be exercised when using these data.

From the characterization of the tailings presented in Table 1, it is observed that the main element in the sample is silicon and, to a lesser extent, aluminum, and iron, being the first two fundamentals for geopolymer's synthesis [23–26].

The characterization of the industrial water used for the homogenization of the tailings was undertaken also by means of the Inductive Coupling Plasma (ICP) test, where, as in the case of the tailings, the results obtained correspond to the average values obtained from the analysis of several samples. These results are described in Table 2.

**Table 2.** ICP test for characterization of industrial water.

Element	Concentration [mg/L]	Element	Concentration [mg/L]
S	215	Ta	<1.00
K	210	Th	<1.00
Na	158	Tl	<1.00
K	28	W	<1.00
Mg	23	As	<0.50
Al	<5	La	<0.50
Fe	<5	Li	<0.50
Ti	<5	P	<0.50
Sr	1.7	Sb	<0.50
Ga	<1.00	Sc	<0.50
Nb	<1.00	Te	<0.50
Sn	<1.00	Ag	<0.25
-	-	Bi	<0.25

It is observed in Table 2 that the highest concentration corresponds to sulfur ions. These can react with sodium hydroxide or some component of the tailings causing impurities or unwanted components that alter the results.

The granulometry of the tailings obtained in the laboratory by means of the Ro-Tap test and laser technology is shown in Figure 3.

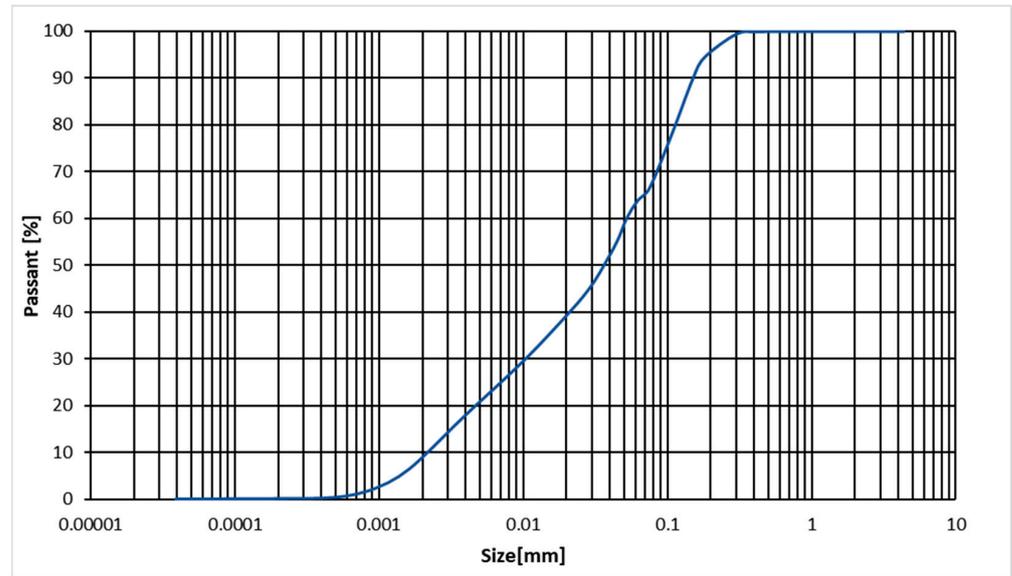


Figure 3. Tailings granulometric curve.

Based on Unified Soil Classification System (USCS) classification tests of tailings and their Atterberg limits, the tailings are classified as a low plasticity silt type soil (ML) according to Figure 4, which is an inorganic silt with low compressibility.

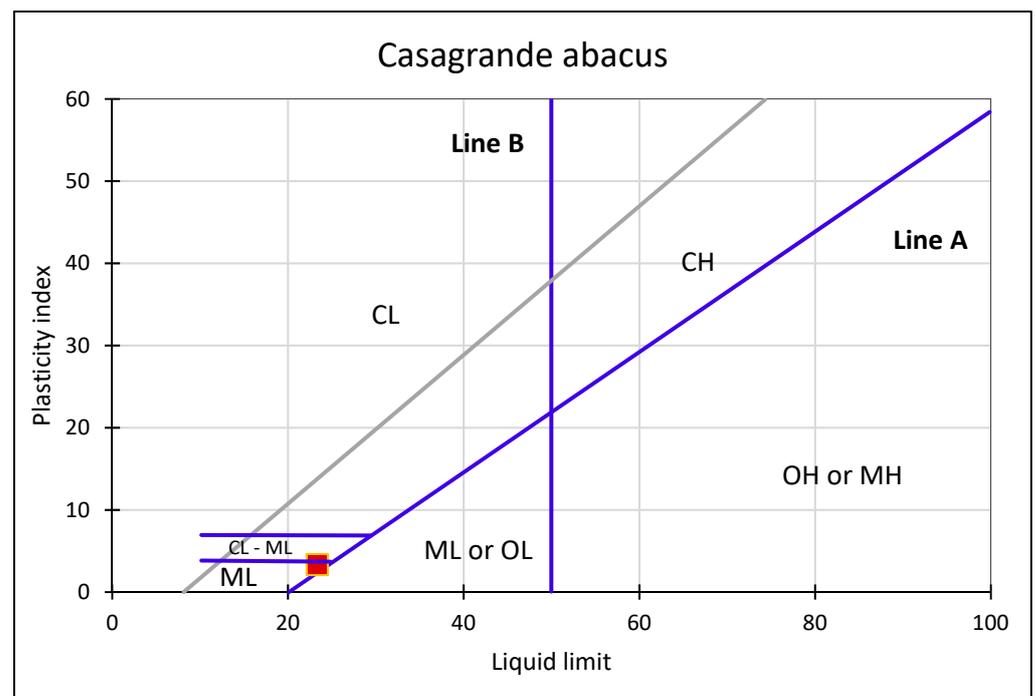


Figure 4. Tailings plasticity chart.

The Atterberg limits, that is, the water contents in which the behavior of the soil is modified, of the tailings are included in the Table 3.

**Table 3.** The Atterberg limits of the tailings used.

Parameter	Value
Liquid limit	23.3%
Plastic limit	19.7%
Shrinkage limit	20.5%
Plasticity index	3.5%

Sodium hydroxide (in pellet form) was purchased from Winkler Ltd.a., Chile, having a purity of 99%. For the dissolution of NaOH, different methods were used, including the previous dissolution of this reagent in process water to create an activating solution of different concentrations depending on the method to be used and the addition of NaOH directly to the tailing, where it is dissolved in the water included in the tailing.

The steel molds used for the experimentation were 12.5 cm in height and 6 cm in diameter. These are the interior measures of the cylindrical mold having a height of 10 cm and a diameter of 5 cm, which are in order with the standards, where it is recommended, for cylindrical molds, to use a diameter “d” and a height “2d”. The molds were also greased on their base plate and on the inner cylinder, and finally, a plastic film was put on their base. It is important to check for any leaks on the molds; Figure 5.



**Figure 5.** Prepared steel molds.

## 2.2. Mix Variables

For the realization of geopolymer mixtures, the quantities of raw material must be chosen; therefore, the researchers focused mainly on the following variables.

### 2.2.1. Alkaline Concentration

Corresponds to the molar concentration (M) of the alkaline solution used, which may correspond to a sodium hydroxide solution. Multiple previous studies [9,27–29] show that the higher the NaOH concentration, the higher the compressive strength obtained, while deteriorating the rheological properties of the mixture. It was decided to evaluate

three levels of molar concentration: 12, 14, and 16 M, in order to cover a range that various authors already have investigated.

### 2.2.2. Water/Solids Ratio

The state of the art of geopolymers shows that the higher the water/solids ratio, the lower the resistance, but in turn the better workability of the geopolymer, and vice versa [13,30,31]. Due to the above, it was decided to work with water/solid ratio values of 30%, 35%, and 40%, which would correspond to  $C_p$  values (concentration of solids with respect to pulp) close to 77%, 74%, and 71%, respectively. These chosen water/solids ratio values are similar to those used in most previous studies on geopolymers [30,32–35].

The molar concentrations of the alkaline activator and the water/solids ratios to be used in the different mixtures to be created in this research are presented in Table 4.

**Table 4.** Proportions of the mixtures to be made.

N°	Concentration [M]	Water/Solids [%]	Mixture
1	12	30	M1-C1
2	14	30	M1-C2
3	16	30	M1-C3
4	12	35	M1-C4
5	14	35	M1-C5
6	16	35	M1-C6
7	12	40	M1-C7
8	14	40	M1-C8
9	16	40	M1-C9

### 2.3. Methodologies

The following is a description of the 7 different methods developed in this research for the production of geopolymers based on copper tailings and sodium hydroxide.

#### 2.3.1. Method I

This consisted of taking a sample of homogenized tailings pulp with a solids concentration  $C_p = 83\%$ , and the remaining water was added to meet the water/solid ratio defined in Table 4. The corresponding quantity to obtain the molar concentration of NaOH defined in Table 4 was added. The raw materials were mixed for 15 min with a mechanical stirrer and deposited in the molds shown in Figure 5. The mixes were set for 7 days at room temperature to observe if their consistency was sufficient to be removed from the mold. This method applied to the nine mixtures presented in Table 4. After being set for 7 days at room temperature, they were placed in an oven at a curing temperature of 60 °C for a period of 7 more days.

#### 2.3.2. Method II

This consisted of taking the mixture M1-C3 according to Table 4 and dissolving the NaOH only in the amount of missing water to complete the  $C_p = 83\%$  in the total mixture. The NaOH was diluted for 15 min in water at room temperature with a mechanical stirrer. The mixture was maintained at room temperature while waiting for the temperature to drop. The solution was added to the tailings pulp, and mixed for 15 min with a mechanical stirrer to later be deposited in the molds shown in Figure 5. Its consistency was observed after 24 h of setting at room temperature to enable comparison with Method I.

#### 2.3.3. Method III

This method took the characteristics of the M1-C3 mixture according to Table 4, and dissolved the NaOH in the 100% of water necessary to bring the tailings pulp to a solid concentration  $C_p = 83\%$ . Subsequently, this solution was incorporated into the tailings that already had a solids concentration  $C_p = 83\%$ . The total mixture ( $H_2O + NaOH +$  tailings

pulp  $C_p = 83\%$ ) had a water/solids ratio of approximately 50%, which was mixed for 15 min with a mechanical stirrer. Its consistency was observed after 24 h of setting at room temperature to enable comparison with the other methods.

#### 2.3.4. Method IV

This method was similar to Method II, in which the mixture M1-C3 was used according to Table 4, but, in this case, the  $H_2O + NaOH$  solution was added to the tailings pulp in less than a minute, making the exothermic reaction occur together with the tailings. Its consistency was observed after 24 h of setting at room temperature to enable comparison with the other methods.

#### 2.3.5. Method V

This method consisted of the same procedure indicated for Method IV, with the difference that, after mixing for 15 min, the mixture was subject to a thermal bath at a controlled temperature of 23 °C for a setting time of 24 h. Its consistency was observed after 24 h of setting at room temperature to enable comparison with the other methods.

#### 2.3.6. Method VI

For this method, the tailings were dried to work as close as possible to the methodology presented in previous investigations [3,18,36,37]. When the tailings were dry, the alkaline solution was prepared with the corresponding amounts of water and NaOH in order to comply with the parameters of the M1-C3 mixture. The mixture of  $H_2O + NaOH +$  dry tailings was mixed for 15 min with a mechanical stirrer and then placed in the molds (Figure 5). Its consistency after 24 h of setting at room temperature was observed to enable comparison with the other methods. Simultaneously, this method was replicated using a water/solids ratio of 20% for a curing process at 60 °C for 24 h and another for 7 days. Additionally, a duplicate was cured in an oven at a temperature of 90 °C for 24 h and another for 7 days. Due to the composition of the tailings used and its low reactivity when in contact with the alkaline solution, it is necessary to cure the mixtures with the application of external heat, i.e., they must be cured in an oven. The choice of temperatures and curing times were based on studies previously carried out in the creation of geopolymers based on copper tailings.

#### 2.3.7. Method VII

The objective of this method was to use the water contained in the tailings without the addition of extra liquid. Therefore, we worked with the wet tailings ( $C_p = 83\%$ ) and based on the water already in the tailings, the amount of NaOH was added until a NaOH molar concentration of 19 M was reached. From this mixture, a water/solids ratio = 20.5% was obtained. After the addition of NaOH, the geopolymeric mixture was stirred manually with a paddle until it had the necessary consistency to be stirred mechanically. The total stirring time was 30 min, alternating between manual and mechanical stirring. After stirring, the mixture was placed in metal molds (Figure 5) and placed in the oven to cure at 60 °C for 1 and 7 days, and at 90 °C for a period of 7 days.

This method is more relevant than the previous ones because one of the objectives of this study is to generate a geopolymer made from copper tailings to be used as the filling of stopes in underground mining. As a result, it would be favorable to use the filtered tailings without the need to dry it prior to use.

### 2.4. Testing Procedure

To analyze the alkalinity of the system, pH measurements were performed on the fresh geopolymer pastes using a DFRobot digital pH meter previously calibrated between pH 7 and 13, at a controlled temperature of 20 °C.

At the same time as the pH measurements were made, temperature measurements were taken on the fresh geopolymer pastes, using a digital thermometer, in order to obtain the temperature of the mixtures at all times during agitation.

Rheological measurements of some geopolymer pastes were carried out using a HAAKE RheoStress 6000 rheometer with a FL100 paddle probe at different times after stirring (0 to 4 h post-stirring), using a shear rate of 0.1 1/s for 60 s.

Finally, a visual analysis of the geopolymers was carried out, based on their consistency after curing.

### 3. Results

#### 3.1. Method I

Figure 6 shows the sample made with Method I, which presented a low consistency. After 24 h of setting at room temperature, the mixtures failed to harden. It was observed that on its face exposed to the air, the mixture formed a layer of a whitish product, which is attributed to carbonation produced by excess NaOH in contact with the CO<sub>2</sub> present in the air, and indicates a possible decrease in alkalinity during the process, as indicated by several authors [38–40], thus damaging the mechanical properties of the geopolymer.



**Figure 6.** Carbonation observed in the geopolymer created by Method 1 with 24 h at room temperature.

According to the phase diagram of the NaOH–H<sub>2</sub>O system presented in the study of Provis [41], it is observed that NaOH has a dissolution of more than 70–80% in water, at a temperature between 70 and 80 °C. Hence, due to the temperature of the pulp, adding the NaOH directly to the tailings pulp does not ensure the defined concentration is obtained.

The mixtures made for this method according to Table 4, after 7 days set at room temperature, were entered into an oven at a curing temperature of 60 °C for 7 days to observe their behavior, which did not vary, resulting in greater carbonation and no hardening, as shown in Figure 7.



**Figure 7.** Carbonation observed in the geopolymer created by Method 1, cured for 7 days at 60 °C.

### 3.2. Method II

Figure 8 shows the consistency of the mixture made with Method II, where a better consistency was observed compared to Method I; however, the mixture did not present hardening after 24 h of setting at room temperature.



**Figure 8.** Consistency of Method II, 1 day set at room temperature.

The loss of solubility of NaOH at low temperatures, as mentioned in Method I, is only about 45% at a temperature of 23 °C, and crystallization was observed in the NaOH dissolution, as seen in Figure 9.



**Figure 9.** Crystallized sodium hydroxide from the alkaline solution of Method II.

### 3.3. Method III

Figure 10 shows a mixture made with Method III, where the ratio of water/solids was increased and the concentration of NaOH was simultaneously decreased. Dissolving the NaOH in a greater amount of water allowed for better workability and dissolution; however, given the temperature of the water, it was estimated that the solubility of NaOH was low.



**Figure 10.** Consistency of Method III, 1 day set at room temperature.

This mixture presented a very low consistency and obtained a completely liquid produce; thus, after 24 h of setting at room temperature, no hardening was obtained.

The effect of increasing the water/solids ratio and decreasing the NaOH concentration, in which adding the water content to the tailings pulp was not considered, generated a mixture with a liquid and non-moldable consistency.

### 3.4. Method IV

The consistencies obtained with this method were better than those of the previous methods, according to the observation in Figure 11; however, after 24 h of setting at room temperature, this mixture failed to harden. It was observed that during the stirring process, this mixture showed a greater consistency than that of the previous methods, and achieved greater stability.



**Figure 11.** Consistency of Method IV, 1 day set at room temperature.

The immediate addition of the supersaturated NaOH solution to the tailings was beneficial for the mixture because it was possible to work with the necessary amount of alkali. In addition, the kinetics of NaOH [42] and its exothermic reaction were fully exploited.

### 3.5. Method V

Figure 12 shows the consistency of a mixture made with Method V, where it was observed that its consistency was more liquid compared to the previous method. The condition of introducing the mold to a thermal bath did not favor the consistency of the sample; on the contrary, it was harmed by becoming more liquid and losing shape.



**Figure 12.** Consistency of Method V, 1 day of thermal bath at 23 °C.

### 3.6. Method VI

Figure 13 shows the consistency of a mixture made with Method VI, where a better consistency was observed. With 24 h of setting at room temperature, it was observed that it did not achieve hardening.



**Figure 13.** Consistency of Method VI, 1 day set at room temperature.

For the same mixture but cured at 60 °C for 1 and 7 days, consistencies similar to a clay-silty were obtained (Figures 14 and 15).



**Figure 14.** Consistency of Method VI with water/solids ratio of 20%, 1 day at 60 °C.



**Figure 15.** Consistency of Method VI with water/solids ratio of 20%, 7 days at 60 °C.

For the mixture cured at 90 °C for 1 and 7 days, consistencies with higher hardening were obtained, and it managed to maintain its shape with a remarkable hardness (Figure 16). This result demonstrates that the curing temperature plays an important role in the generation of the N-A-S-H gel, as indicated by previous authors [2,8,22,43]. Moreover, this result is similar to those obtained previously by several authors [2,3,5,22,25,43–45], who worked by separately varying the curing temperature of geopolymers based on fly ash and mine tailings. In most cases, the optimum curing temperature was in the range between 80 and 90 °C because at these temperatures the highest compressive strengths were obtained (see Figure 17).



**Figure 16.** Consistency of Method VI with water/solids ratio of 20%, 7 days at 90 °C.

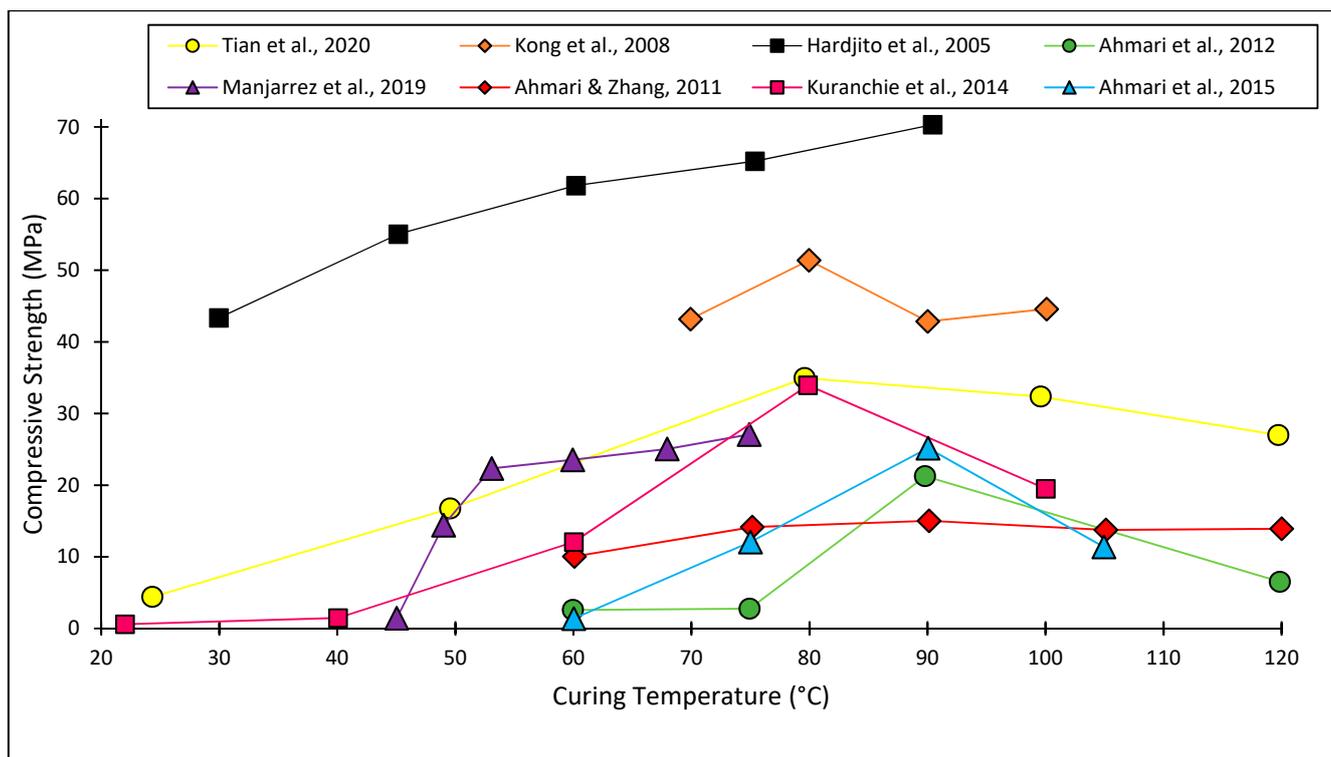


Figure 17. Compressive strength as a function of curing temperature; data obtained from previous investigations [2,3,5,22,25,43–45].

### 3.7. Method VII

The operation and preparation of these mixtures in the laboratory was difficult because the sodium hydroxide added in its pure state to the tailings pulp made it more consistent and thicker, thus making it difficult to mix with the mechanical stirrer. Therefore, stirring was performed manually for 15 min to integrate the NaOH into the tailings pulp, to enable subsequent working with the mechanical agitator for an additional 15 min.

The mixtures that were cured for 1 day at a temperature of 60 °C showed a consistency similar to a clay soil or a consistent mud; however, as time passed, the samples lost their shape, as shown in Figure 18.



Figure 18. Consistency of Method VII, cured at 60 °C for 24 h.

The mixtures that remained for 7 days at a curing temperature of 60 °C (Figure 19) achieved a better consistency, compared to the mixture cured for 24 h at 60 °C (Figure 18). It follows that the formation of N-A-S-H gel is a slow process, and that the main variables to be controlled in order to obtain hardened geopolymers are temperature and curing time.



**Figure 19.** Consistency of Method VII, 7 days at 60 °C.

The mixtures that remained for 7 days at a curing temperature of 90 °C managed to maintain their shape with remarkable hardness, similar to a concrete grout specimen (Figure 20). This confirms that increasing the curing temperature from 60 to 90 °C produces a significant increase in the hardening of copper tailings-based geopolymers, as shown in Figures 15, 16, 19 and 20.



**Figure 20.** Consistency of Method VII, 7 days at 90 °C.

Figure 21 shows the interior of a specimen created using Method VII cured at 90 °C for 7 days, following a petrographic study. From this study it was found that the sample corresponds to a pyroclastic rock of vesicular texture, which is mainly composed of plagioclase and quartz, and to a lesser extent calcite. It presents a level of holohyaline crystallinity; that is, the sample is of a high crystallinity, composed of 95% vitroclasts. Furthermore, in the size classification, the sample is classified as an ash (<2 mm).



Figure 21. Sample created using Method VII after petrographic study.

Due to the good consistency of the mixture and subsequent hardness of the geopolymer cured using this method, in addition to being the most feasible mixture for the industrial production of geopolymers, the geopolymeric mixture was repeated, but this time, measurements of both pH and temperature were taken at all times during mixing. The results of these measurements are shown in Figures 22 and 23.

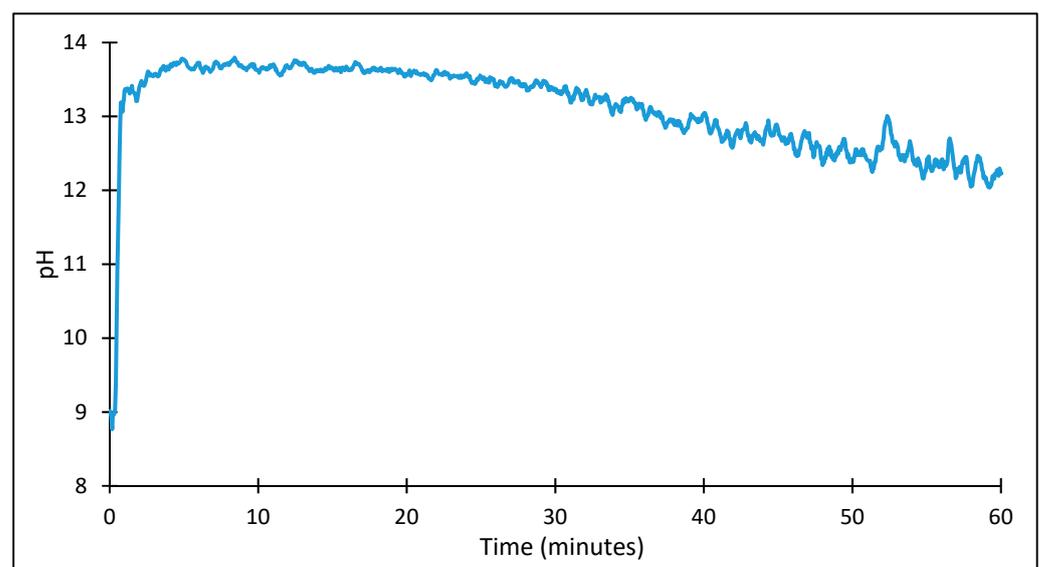
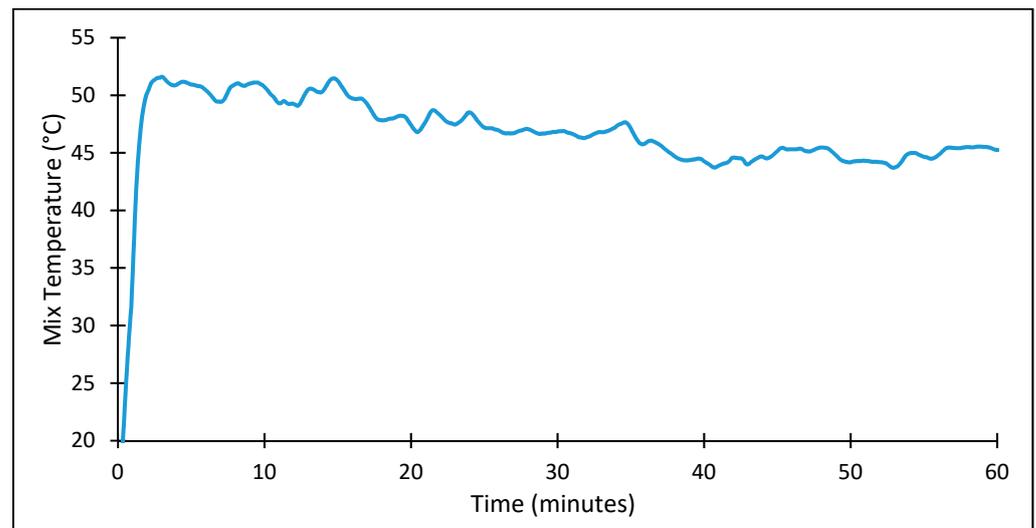


Figure 22. pH values of fresh geopolymer paste using Method VII.



**Figure 23.** Temperature of fresh geopolymer paste using Method VII.

From the pH measurements obtained (Figure 22) it can be observed that the mixture increases its pH rapidly to a value of 13.8 due to the dissolution of the NaOH in contact with the water coming from the tailings. This indicates that the alkalinity of the system is in the correct range, because most authors recommend working in a pH range between 13 and 14 [46–49], in order to obtain a good dissolution of the aluminosilicates coming from the source, which later contribute to the formation of the NASH gel. In addition, it can be observed that the pH of the mixture remained relatively constant during the first 20 min of the test, after which the pH began to decay, and reached a pH value close to 12 after 1 h of the test. This may be associated with the fact that the hydroxide ions decrease in concentration as they generate complexes with the other elements present in the mixture (such as silicon and aluminum) to subsequently generate the geopolymer. Figure 23 shows that the temperature of the geopolymeric mixture rose rapidly in the first minutes of the test. This is due to the dissolution of NaOH in the water coming from the tailing, where this dissolution, being an exothermic reaction, generates heat. The maximum temperature reached by the mixture was 51.6 °C. At this temperature, the solubility of NaOH in water is approximately 60%, which means that not all of the NaOH added to the mixture was dissolved, and an undissolved amount remained.

After the pH and temperature tests, rheology tests were carried out on the mixture at different times after agitation, in which five measurements were made with 1 h difference between them (Figure 24). From these results it is observed that the longer the time after mixing, the higher the yield strength of the fresh geopolymer paste, which increased from 1140 Pa at time 0 to 1370 Pa at 4 h after mixing.

From the results of the compressive strength test performed on the geopolymer created using Method VII, cured for 7 days at 90 °C (Figure 25), a maximum compressive strength of 19 MPa was obtained, which is a high value of compressive strength and is similar to those obtained in previous studies of geopolymers based on copper tailings. Therefore, this geopolymer could be used for industrial applications that demand materials with good compressive strength. However, this maximum compressive strength was obtained with a 2% deformation, which is a high value compared to the typical deformation of concrete.

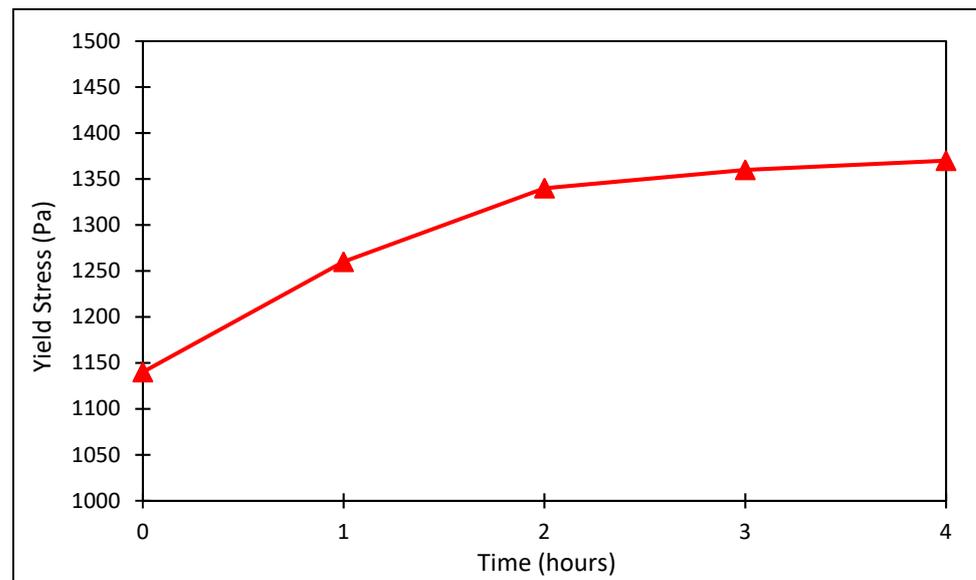


Figure 24. Rheology curves of mixture VII at different times after mixing.

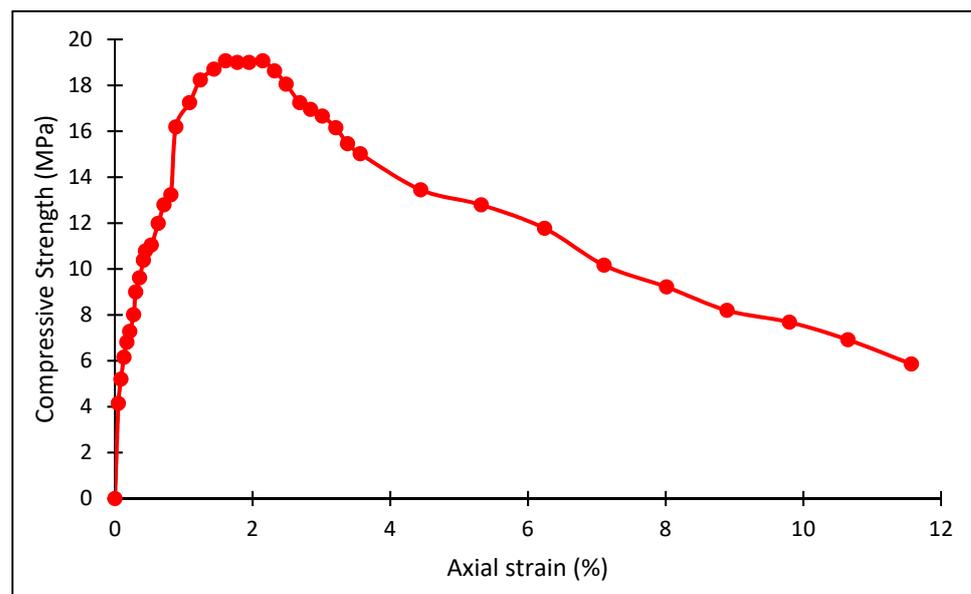


Figure 25. Stress–strain graph for the geopolymer created using Method VII.

#### 4. Conclusions

For all the methods, the most important variable in the result was the NaOH addition procedure, and it was found to be detrimental to first dilute the water with the tailings and then the sodium hydroxide. As observed in the phase diagram of the NaOH–H<sub>2</sub>O system, it is necessary to dissolve the NaOH at a temperature higher than 80 °C to obtain a higher solubility and thus a higher dissolution.

The mineralogical characterization of the tailings is essential to provide an indication of the amount of soluble material that the tailings contain, which is the ultimate source of the aluminosilicate [20,50–53].

From the first methods used for the creation of geopolymers it was concluded that the application of external heat, i.e., the use of an oven during the curing process, is necessary to obtain hardened geopolymers with the copper tailings used with the addition of NaOH. It was also observed that it is necessary to use low quantities of water in the geopolymeric

mixture to obtain a good consistency and subsequent hardening of the geopolymer. The optimum was found with a water/solids ratio of 20%.

From the different results obtained in Methods VI and VII based on the curing time in the oven at different temperatures, it can be inferred that longer curing times and higher curing temperatures are favorable for the hardening of the sample. After spending time in the oven, the test tubes at 90 °C demonstrated remarkable hardness in both methods.

The curing temperature is very important in the process of generation of geopolymers based on copper tailings with the addition of NaOH because copper tailings are known to be less reactive than other sources of aluminosilicates such as fly ash or slag. Thus, when they come into contact with a highly alkaline solution, they dissolve less of the elements important for the occurrence of geopolymerization, such as silicon and aluminum. For this reason it is necessary to apply heat during the curing process, which helps the dissolution of aluminosilicates, and increases the interaction between the source of aluminosilicates and the alkaline solution, thus increasing the reaction speed of geopolymerization, in addition to favoring the hardening of geopolymers [2]. The results shown confirm that working at a temperature of 90 °C is favorable for hardening.

The pH values obtained were in the range for a correct dissolution of the aluminosilicates from the copper tailings, which in turn favored the hardening process of the geopolymer [46–49].

The temperature of the mixture during agitation rose to 51.6 °C due to the dissolution of NaOH in contact with the water included in the tailings pulp. Because this temperature is not sufficient for the complete dissolution of NaOH, it is deduced that a quantity of this reagent remained without going into solution.

The longer the waiting time after mixing, the higher the yield stress of the geopolymer pastes. Thus, if this mixture needs to be molded or pumped for transfer from one point to another, it should be done immediately after mixing to avoid increasing the rheological properties of the paste.

The obtained mixtures with Methods VI and VII showed high resistance, and achieved good consistency and complete hardening of the specimens.

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