Mine Tailings Geopolymers as a Waste Management Solution for A More Sustainable Habitat

Helena Paiva [1], Juho Yliniemi [2], Mirja Illikainen [2], Fernando Rocha [3] and Victor M. Ferreira [1,4,*]

[1] Civil Engineering Department/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal; hpaiva@ua.pt
[2] Fibre and Particle Engineering Research Unit, Oulu University, PO Box 4300, 90014 Oulu, Finland; Juho.Yliniemi@oulu.fi (J.Y.); Mirja.Illikainen@oulu.fi (M.I.)
[3] Centre GeoBioTec (Georesources, Geotechnics, Geomaterials Research Group), University of Aveiro, 3810-193 Aveiro, Portugal; tavares.rocha@ua.pt
[4] Civil Engineering Department/RISCO, University of Aveiro, 3810-193 Aveiro, Portugal
* Correspondence: victorf@ua.pt; Tel.: +351-937-205-010

Abstract: The demand for low environmental impact of materials in our habitat is one of the current societal challenges. Along with other solutions of waste valorisation, alkali activation as geopolymers can be one possible solution of waste valorisation because they may allow, for instance, an alternative solution for cement-based materials in some applications and it is one contribution for circular economy. This work has focused on the development and processing of geopolymers that incorporates as a fine aggregate a high-sulfidic mining waste (mine tailing), a difficult waste to process. Rheology analysis was applied as an important step to understand not only the geopolymers behaviour but also its transition from the fresh to the hardened state. The effect of precursor binder type (metakaolin or blast furnace slag), of mine tailing content and also the effect of temperature and curing conditions of different formulations were studied in this solution. It was possible to conclude that although this particular mine tailing is not a geopolymer binder precursor, it may be incorporated as an alternative fine aggregate in construction products. Furthermore, rheology could be used to follow up the geopolymer alkali-activation process and even to setup proper curing conditions and components contents in order to optimize the final mechanical strength of this material as a waste management solution. The final properties of these geopolymers compositions were adequate and after 28 days of curing, these geopolymers exhibit significant chemical resistance under severe test conditions.

Keywords: rheology; geopolymers; mine tailing; waste

1. Introduction

Mining activities produce millions of tons of mine tailing waste after extraction and separation of the ore at world level [1]. Mine tailings are usually placed in environmentally controlled landfills, because these materials contain sulphates and some heavy metals. This implies the need for large areas of land for the construction of landfills and the need for skilled labor for environmental monitoring. Furthermore, they strongly condition the duration of the mine exploration activity and have a strong impact in our habitat that needs to be addressed.

Alkali-activated materials (AAM) production may constitute a waste management solution and its derived products a replacement for cementitious materials in particular applications, since the production of cement involve huge energy needs and high CO_2 emissions (1 ton of cement may generate around 0.6 up to 1 ton of CO_2 emissions, depending on the processing technology) [2]. Hence, alkali-activated materials, also called geopolymers, have an extensive range of applications as

substitutes for ordinary Portland Cement (PC) in certain applications due to their properties, such as chemical durability. These materials can improve mechanical properties and have the ability to withstand high temperatures and chemical attack by acids and salts [3].

Geopolymers are soluble alkali metal compounds in conjunction with aluminosilicates systems either with (i) Low calcium content, such as volcanic ash, coal fly ash, metakaolin (MK) and others. They are materials rich in SiO_2 and Al_2O_3 (Na_2O-Al_2O_3-SiO_2-H_2O system) or with (ii) Calcium-rich compounds such as lime, Portland cement, aluminous cement, blast furnace slag (BFS), involving alkaline-earth materials with significant calcium content (Na_2O-CaO-Al_2O_3-SiO_2-H_2O system). Both systems can be subjected to an alkali-activation reaction that will cause fundamental change in the structure of materials components [4,5].

Feng Rao and Qi Liu [6] made a review on the potential application of geopolymerization on the consolidation of mine tailings. They revealed that geopolymerization reactions are effective in the consolidation and strengthening of mine tailings if these materials contain aluminosilicates required for the polymerization reaction. There are some conflicting results regarding the proper Si/Al ratio, the function of metal cations such as sodium and potassium and the effect of calcination [5]. High activator concentration results in better mechanical properties of the geopolymers but, lower alkali activator content also presents good results in long time reaction. This review showed that geopolymerization reactions are effective on consolidation and strengthening of mine tailings only if they contain enough aluminosilicates required for the geopolymer reaction [5].

Several studies have been conducted using metakaolin as the geopolymer binder precursor [7–9]. These studies agree that metakaolin is a good precursor as a binder in the geopolymer reactions. Mechanical strength of blended pastes was enhanced with the increase in metakaolin content and also when increasing the SiO_2/Al_2O_3 ratio. These studies have also found that the metakaolin physical and chemical characteristics influenced the geopolymerization reaction.

The alkali activator binder based on calcium-rich precursors has been used for a long time [10], for instance, blast-furnace slag (BFS) where its particle size was found to be a very important factor on geopolymer reaction, namely on setting, mechanical strength and microstructure [11].

A study on geopolymer mortars with blast furnace slag (BFS) and coarse fly ash (FA) found that longer curing times reduces the water absorption and porosity of geopolymers [12]. Density increased with the increase of fine materials (BFS) and that has promoted an increase in compressive strength. In this particular study [12], the cure conditions were 48 h at 60 °C. Longer curing times at 60 °C has decreased compressive strength. Introduction of BFS in metakaolin (MK) activated mortars has shown advantages such as reduction of alkaline activation solution to maintain workability and also improvement in mechanical strength [13].

Rheology concerns with the flow and deformation of materials, studying the relationship between stress, strain, and time [14]. Some rheometers have been designed for particular applications or materials such as the Viskomat NT, which was specifically designed to evaluate rheological behavior of materials such as mortars, which behaves usually as a Bingham fluid. They are described by a Bingham relation ($\tau = \tau_0 + \eta\gamma$), which shows a linear relationship between stress and strain and is characterized by a particular value of initial shear stress (called Bingham or yield stress, τ_0). These materials resist without flow to shear stresses below the yield stress, but above this value they present a linear relationship between shear stress and strain rate, characterized by a plastic viscosity (η). The Viskomat NT rheometer operates by measuring torque as a function of rotation speed for different speed-time profiles that can be set up initially. The Bingham behavior is then expressed through the equivalent relation of torque (T) with rotation speed (N), $T = g + hN$, where g (N.mm) and h (N.mm.min) are coefficients related to yield stress and plastic viscosity, respectively [15,16]. Few works [17] exist that uses this kind of rheometer to evaluate the rheological behaviour of geopolymers and its correlation with product final properties.

Most of papers found use low sulfidic mine tailing or don't give importance to high SO_3 levels [6,18]. This work aims to analyze the use of high sulfuric mine tailing in geopolymer-based

construction material, namely, the effect of precursor type, of mine tailing content and also the effect of temperature and curing conditions of different geopolymers formulations using rheology and other final relevant properties evaluation. This waste valorisation solution could be an interesting one from the point of view of elimination of a potential environmental and economic problem and so contributing for a more sustainable habitat.

2. Materials and Methods

2.1. Materials and Formulations

The raw materials for geopolymer formulations include a blast furnace slag (BFS), two different metakaolins (MKP and MKF) and a copper and zinc mine tailing (MT). They were chemically and physically evaluated by X-ray diffraction (Rigaku, Geigerflex model) and X-ray fluorescence (Panatylical, Axicos model). Specific surface area (Micromeritics, Gemini 2380 model) on these finer raw materials were also performed. Bulk density was measured according to EN 1097-3 standard.

Geopolymer formulations involved two metakaolins (MKP or MKF) or a blast furnace slag (BFS) as well as the mine tailing (MT), in both cases replacing the MK or BFS, with contents of 0%, 50% and 62%. The alkaline activator aqueous solution in the MK-based geopolymers was a sodium metasilicate (a mixture of sodium silicate and sodium hydroxide, named here as AD solution). In the BFS-based formulations, only a 10M NaOH aqueous solution was used as the alkaline activator. The amount of activator was set in order to keep the following molar ratios in the geopolymer compositions: Si/Al ≥ 2 and Na/Al = 1 [19]. A small amount of excess water (100 mL for the composition with 38% BSF and 200mL for the composition with 50% BSF) was also added in the mixing procedure to improve workability of the BFS-based formulations. No extra water was needed in the MK-based formulations for this purpose. The mixture condition for all formulations was 40 min at 120 rpm.

Metakaolin and blast furnace slag were used as binders in the geopolymer process using mine tailings in the composition. A set of different formulations was set to evaluate the effects on rheology and final properties of the precursor binder type, of mine tailing content and also of temperature and curing conditions.

2.2. Characterization Methods

The rheological behaviour was studied with a specific rheometer (Viskomat NT, Schleibinger Gerate), normally used for mortars with particles up to 3 mm in size. All formulations were also mixed during 40 min at 120 rpm for the rheological measurements performed after mixing.

Viskomat NT consists of a cylindrical container, where the same sample amount is placed ready to rotate according to the speed–time profile set up for the measurement. A fixed blade is automatically inserted in the center of the container and measures continuously the torque during the test (Figure 1).

The rotation speed can be programmed in a profile and torque values are registered. The speed profile, used at 20 °C and 50 °C, is set at a constant value (0 rpm) for a long period of time (160 min). The rheological measurements at 50 °C were performed with the same speed profile with the material kept at that temperature. Every 20 min the speed is brought to 100 rpm and then back to 0 rpm during 2.5 min (Figures 2 and 3) to enable flow curves (torque vs. speed) to be built and rheological parameters (g and h) to be assessed from the Bingham relation [20].

Measurements of pH were also performed in geopolymers batches with a multi-parameter analyzer (Consort C860) and all samples had pH values around 13 and 13.5 at 20 °C. Bulk density was measured according to EN 1097-3:1999 standard. Mechanical strength characterization was made according to EN 1015-11:1999, where three samples of each composition with dimensions of $160 \times 40 \times 40 \text{mm}^3$ were measured. For these measurements, samples were subjected to a curing process until 28 days (including the time in the mold) in a conditioned room with temperature and relative humidity controlled at 20 ± 5 °C and 65 ± 5% RH (relative humidity), respectively. Some

samples, appointed further below, were also cured at 50 °C or in sealed conditions (involved in a plastic foil) at 50 °C.
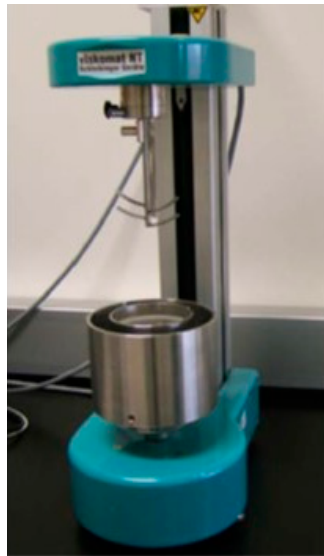
Figure 1. Viskomat NT rheometer.
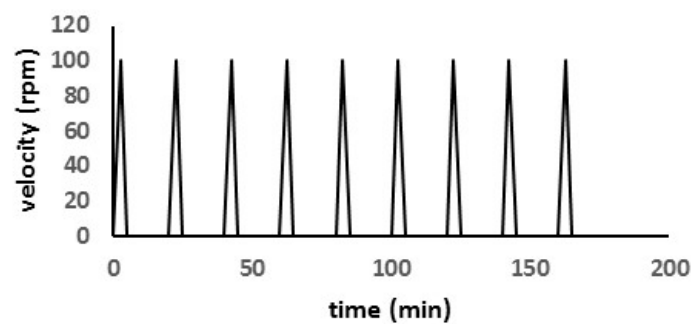
Figure 2. Speed profile for rheometer measurements.
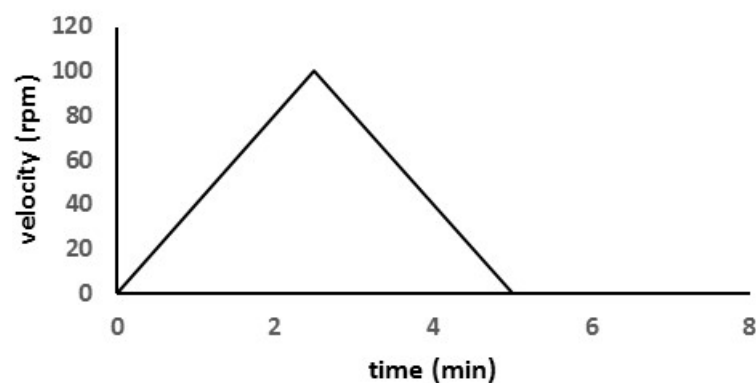
Figure 3. Example of upward and downward curves in the speed profile for rheometer measurements.

3. Results and Discussion

3.1. Mine Tailing Characterization

This particular mine tailing (MT) comes from a copper and zinc mine. The material had a bulk density (powder) of 1.28 g/cm^3 and around 30% humidity. Because of this, it needed to be dried to process it in the geopolymer formulations.

Figure 4 show the mine tailing X-ray diffraction. It is possible to observe that there are no aluminosilicates in this mine tailing and, for that reason, makes it impossible to be used as a binder precursor but it can be used as a fine aggregate. This is corroborated by the results of X-ray fluorescence (Tables 1 and 2). The analysis of Table 1 shows, among other elements, a low content of Al_2O_3 in the mine tailing.
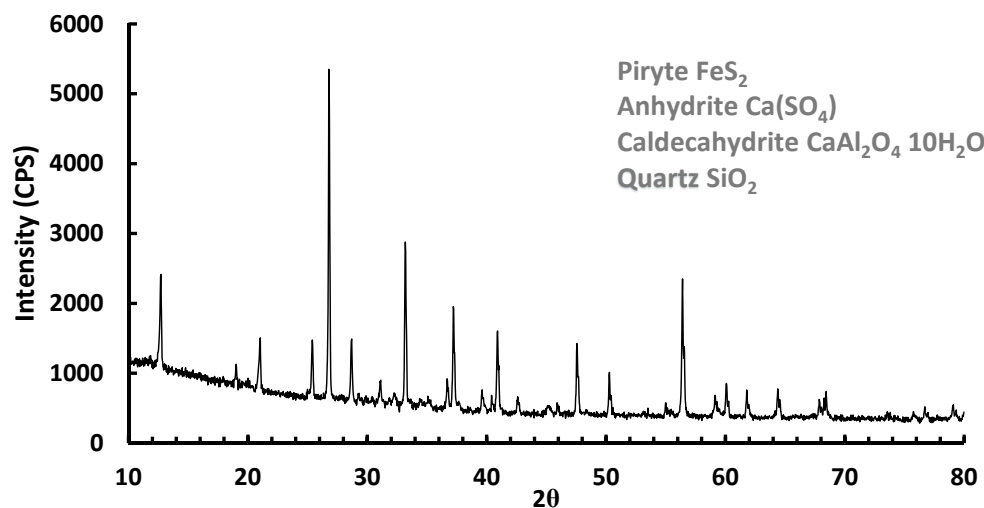
Figure 4. Mine tailing X-ray diffraction.

Table 1. Mine tailing X-ray fluorescence: Major elements (%).

Na$_2$O (%)	MgO (%)	Al$_3$O$_2$ (%)	SiO$_2$ (%)	P$_2$O$_5$ (%)	SO$_3$ (%)	Cl (%)	K$_2$O (%)	CaO (%)
0.229	1.689	6.409	25.157	0.036	26.177	0.041	0.405	0.837
TiO$_2$ (%)	**Cr (%)**	**MnO (%)**	**Fe$_2$O$_3$ (%)**	**Cu (%)**	**Zn (%)**	**Rb (%)**	**Sr (%)**	**Zr (%)**
0.094	0.015	0.068	19.237	0.192	0.310	0.001	minor	0.003
Sb (%)	**Ba (%)**	**Pb (%)**	**As (%)**	**Ce (%)**	**Co (%)**	**Sn (%)**	**V (%)**	**LOI* (%)**
0.003	0.008	0.140	0.196	minor	0.037	0.022	minor	18.680

(*LOI—Loss on Ignition).

Table 2. Mine tailing X-ray fluorescence: Minor elements (ppm).

Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	Ge (ppm)
4.3	50.9	major	major	18.1	major	major	19.4	ND*
As (ppm)	**Se (ppm)**	**Br (ppm)**	**Rb (ppm)**	**Sr (ppm)**	**Y (ppm)**	**Nb (ppm)**	**Mo (ppm)**	**Ag (ppm)**
major	56.8	11.1	24.2	21.4	18.8	4.4	5.8	21.3
Cd (ppm)	**Sn (ppm)**	**Sb (ppm)**	**Te (ppm)**	**I (ppm)**	**Cs (ppm)**	**La (ppm)**	**Ce (ppm)**	**Nd (ppm)**
19.2	major	major	ND*	27.1	ND*	17.8	44.6	16.6
Sm (ppm)	**Yb (ppm)**	**Hf (ppm)**	**Ta (ppm)**	**W (ppm)**	**Ti (ppm)**	**Pb (ppm)**	**Bi (ppm)**	**Th (ppm)**
ND*	ND*	ND*	ND*	ND*	7.9	major	51.4	3.7

(*ND: not detectable).

Geopolymers are composed of a negatively charged aluminosilicates framework where, as it happens in zeolites, some cations (Na^+, K^+ or Ca^{2+}) may be exchanged with cations in the solution [18]. Metakaolin geopolymers have been also studied for the removal of Pb^{2+}, $Cu2^+$, Cr^{3+}, Cd^{2+} and Cs^+ [21–23]. These studies have shown that geopolymerization significantly improves the sorption capacity of the raw material.

3.2. Metakaolin and Mine Tailing-Based Geopolymers

3.2.1. Metakaolin Characterization

This study has used two metakaolins (named MKP and MKF) with different chemical and physical properties. Figure 5 shows the X-ray diffraction pattern for both metakaolins. Both of them are low calcium content precursors. MKF (Figure 5a) is completely amorphous presenting only a small peak of TiO_2. MKP metakaolin show some crystalline compounds such as quartz and muscovite (Figure 5b). It is also possible to observe in Table 3 that both metakaolin shows very similar oxide compositions.

(**a**)

(**b**)
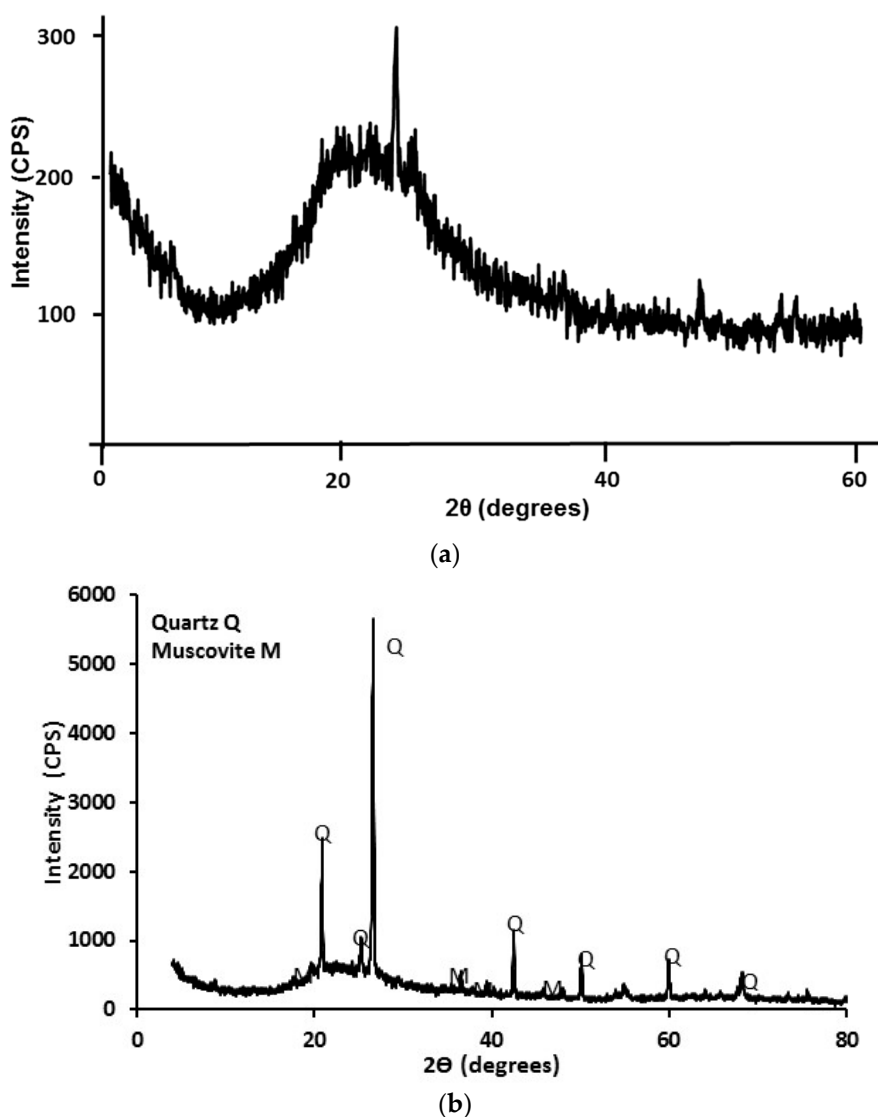
Figure 5. Metakaolin X-ray diffraction: MKF (**a**) and MKP (**b**).

Table 3. Metakaolins X-ray fluorescence.

(%)	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	P$_2$O$_5$	LOI
MKP	52.17	44.50	0.45	ND*	ND*	0.01	ND*	0.15	1.42	0.12	1.42
MKF	52.50	43.50	1.10	ND*	ND*	0.20	0.30	0.20	1.80	0.10	1.30

(*ND: not detectable).

On the other hand, the analysis of Table 4 shows that MKF metakaolin is finer than the MKP metakaolin since the last one presents a lower surface area and a higher bulk density. Taking into account these features, one could expect that MKF is more reactive than MKP as a binder in the alkali-activation process.

Table 4. Surface area and apparent density for both metakaolin.

	Specific Surface Area (m^2/g)	Apparent Density (g/cm^3)
MKP	16.19	0.25
MKF	18.13	0.20

3.2.2. Metakaolin and Mine Tailing-Based Geopolymer Behaviour

Table 5 presents compositions based on both metakaolins and mine tailing. This allowed the study of the effect of the metakaolin type, the effect of mine tailing addition and also the effect of temperature and curing conditions of different geopolymers formulations on rheology and final hardened product characteristics.

Table 5. Geopolymer compositions with metakaolin as precursor.

Sample	Composition	Temperature (°C)	Time in Mould
G_MKP	300 g MKP 580 g AD 80 g NaOH (10 M)	20 °C	7 days
G_MKF	300 g MKF 580 g AD 80 g NaOH (10 M)	20 °C	7 days
G_50% MKP	300 g MKP 300 g MT 580 g AD 80 g NaOH (10 M)	20 °C	7 days
G_38%MKP	300g MKP 500g MT 580g AD 80g NaOH (10 M)	20 °C 50 °C 50 °C (Sealed in plastic film)	7 days 24 h 24 h

Looking at the effect of metakaolin type, Figure 6 shows the variation of torque values with test time for both metakaolins (MKP and MKF) formulations. The metakaolin is the precursor in the geopolymer formation reaction and both compositions have the same amount of activator (AD plus NaOH) since the contents of Al$_2$O$_3$ and SiO$_2$ are almost the same in both metakaolins. MKF metakaolin shows higher values of torque due to its smaller particle size, offering a higher resistance to flow (Figure 6). Smaller particles adsorbed more water in its surface promoting a system thickening noticeable by the torque increase.
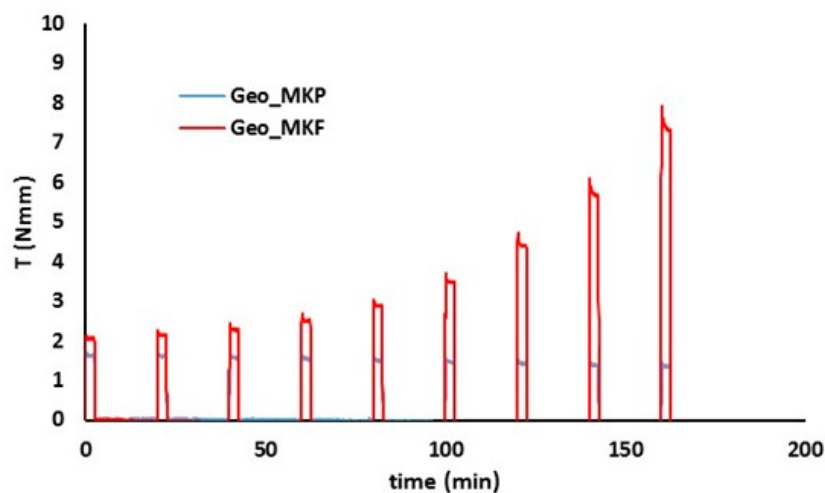
Figure 6. Variation of torque values with test time for MKP and MKF metakaolin.

Figure 7 shows a typical Bingham flow curve during the upward and downward variation of speed, taken at 20 min of test of MKF-based geopolymer. The flow curves (torque vs. rotation speed) allows to extract from the Bingham relationship (T = g + hN) the rheological parameters g and h, which are coefficients related to yield stress and plastic viscosity, respectively.
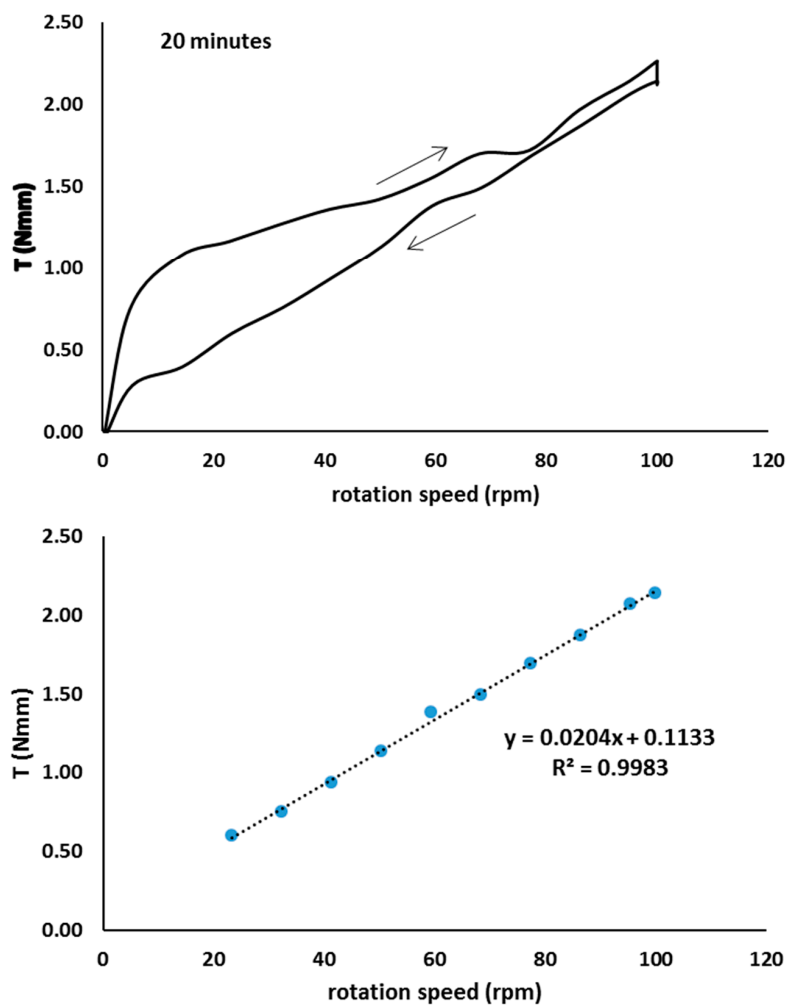
Figure 7. Flow curve (**above**) and rheological parameter h and g determination (**below**).

Figure 8 show that metakaolin MKP and metakaolin MKF show the same viscosity values (h) up to one hour of test and, after that MKF h value begins to increase while MKP h value remains constant.
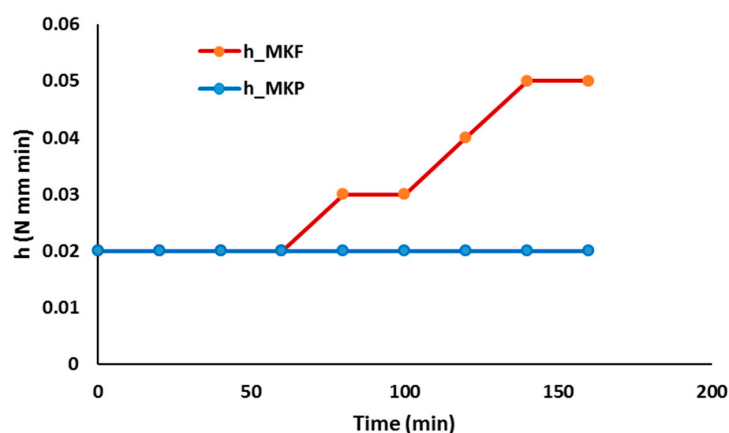
Figure 8. Variation of h parameter with test time for MKP and MKF metakaolin.

Figure 9 clearly shows the difference between the two metakaolins. As a matter of fact, MKF metakaolin have smaller particles, reflected on the higher surface area (Table 4) and, due to the water adsorption, it gets less free water for system lubrication promoting a thickening of the mixture. On the other hand, the fact that MKF metakaolin is completely amorphous makes it more reactive, hence, promoting a faster formation of geopolymer connections causing a marked increase in yield stress (g value) sooner.
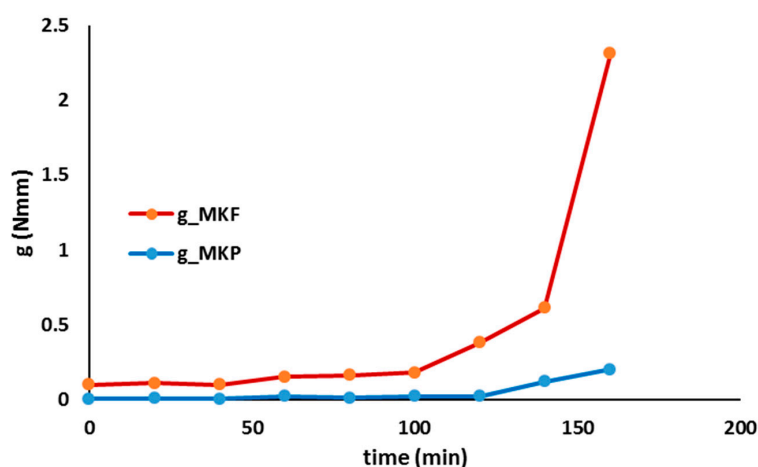
Figure 9. Variation of g parameter with test time for MKP and MKF metakaolin.

Table 6 presents the compressive strength and bulk density results for both metakaolin-based geopolymers. MKF physical and chemical characteristics lead to a higher compaction and compressive strength compared to MKP geopolymer samples.

Table 6. Hardened state features of MKP and MKF-based geopolymers.

Composition	Compressive Strength (MPa)	Bulk Density (g/cm^3)
MKP	32 ± 0.02	1.67 ± 0.05
MKF	45 ± 0.02	1.95 ± 0.04

The effect of mine tailing (MT) content is presented in Figures 10–12 and Table 7. All formulations have the same MKP amount (300 g) and because the mine tailing does not react the amount of liquid

activator is also the same (580 g AD plus 80 g NaOH). In addition to the reference compositions with 100% metakaolin, two other compositions were analyzed. A composition with 50% mine tailing plus 50% MKP and another one with 62% mine tailing and 38% MKP (Table 5).
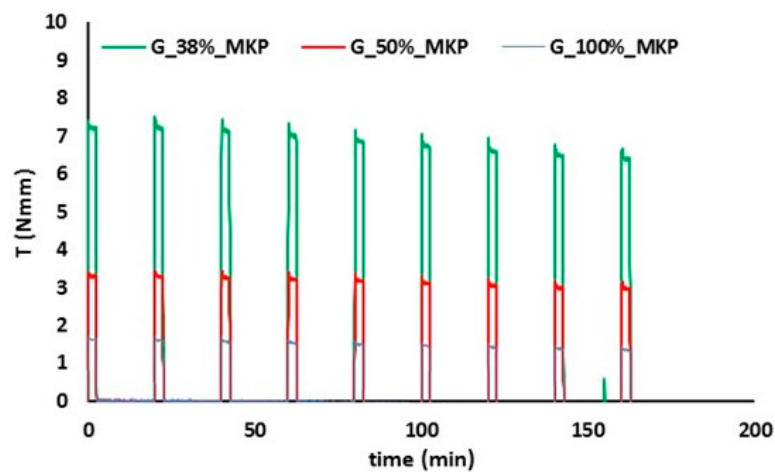
Figure 10. Variation of torque values with test time for 100, 62 and 50% of mine tailing.
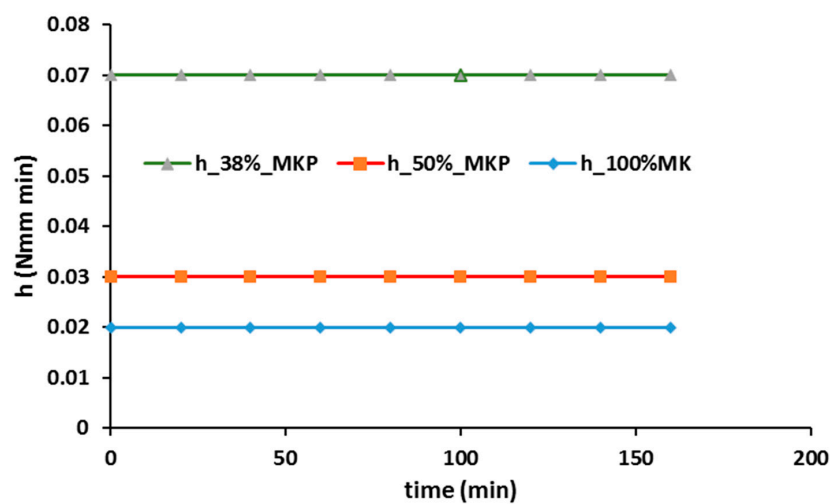
Figure 11. Variation of h parameter values with MKP content.
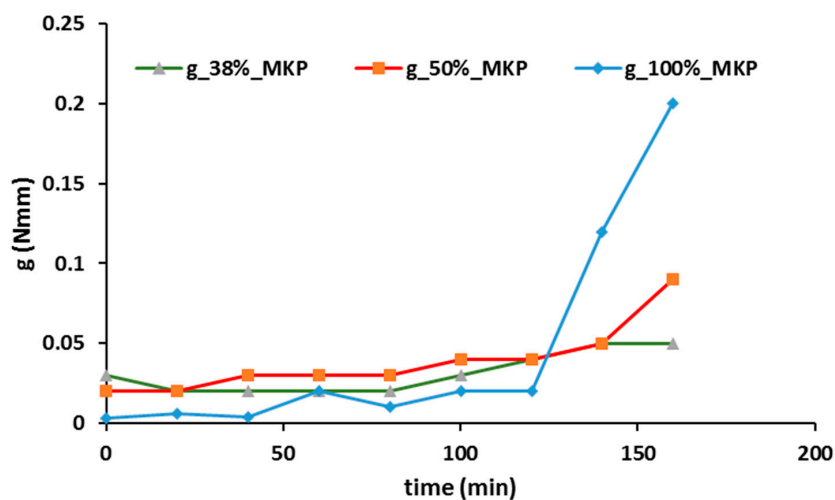
Figure 12. Variation of g parameter values with MKP content.

Table 7. Hardened state features of MK-based geopolymers with different contents of mine tailing.

Composition	Compressive Strength (MPa)	Bulk Density (g/cm^3)
100% MKP + 0%MT	32 ± 002	1.70 ± 0.10
50% MKP + 50%MT	22 ± 0.02	2.16 ± 0.02
38% MKP + 62%MT	14 ± 0.03	1.94 ± 0.04

Figure 10 shows the evolution of torque values with the increase in mine tailing amount. This is due to the increase in the solids amounts in these formulations, while keeping the liquid content constant (activator was AD plus NaOH). With the increase in solids content and the water adsorption on its surface, there is a decrease in the free water content to the system lubrication need. The behavior of h and g parameters (Figures 11 and 12) shows the same tendency as observed in Figure 10. Viscosity and yield stress increases with the increase in mine tailing content.

Table 7 presents the compressive strength values of the different compositions. The system thickening with increased mine tailing content may induce a greater compaction and lower system porosity due to the lower content of free water but, Table 8 shows that an increasing of mine tailing content promotes a decrease in compressive strength. The mine tailing cannot be considered a binder precursor as it is not reactive and so compressive strength decreases because the reactive part, the MK binder is being reduced by substitution. Table 7 also shows that bulk density increases with the increase of mine tailing content but this fact, also due to the mine tailing bulk density (1.28g/cm^3) being higher than the metakaolin bulk density (0.53/cm^3), does not imposes over the compressive strength effect caused by the MK content.

Table 8. Hardened state features of 38% MKP or MKF compositions at 20 °C and 50 °C.

Samples	Compressive Strength (MPa)	Bulk Density (g/m^3)
38%MKP_20 °C	14 ± 0.06	1.9 ± 0.04
38%MKP_50 °C_24 h	4 ± 0.04	1.8 ± 0.05
38%MKF_20 °C	22 ± 0.02	1.9 ± 0.01
38%MKF_50 °C_24 h	8 ± 0.01	1.6 ± 0.02

Regarding the effect of temperature and curing conditions, Figures 13 and 14 show the behavior of the composition with 38% MKP and 62% MT, cured at 20 °C and at 50 °C. It is possible to observe that h and g parameters values, on composition cured at 20 °C, stay the same during all test time. For the composition cured at 50 °C, parameter h shows at the beginning a decrease due to a decrease of viscosity with temperature but, after 240 min of test, it shows a fast increase. Regarding the g parameter variation, it shows a steady increase from the beginning of the test that gets higher near the end of test. This fact indicates an increase in the system reactivity with temperature. This result clearly shows how these rheometer measurements are quite interesting to follow up the startup process of geopolymer formation reaction (hardening process).

Table 8 show that the composition cured at 50 °C during 24 h show a high decrease of strength compared to the same composition kept at 20 °C. It is important to remember that the sample was kept at 50 °C during 24 h. According to Kürklü [12] excessive curing time causes dramatic decrease in the strength values. They refer that the main reason for this was the evaporation of the liquid content in the mixture before the completion of the reaction during this time and an increase in the silica coagulation. The same behavior was observed with the MKF metakaolin-based geopolymer (Table 8).
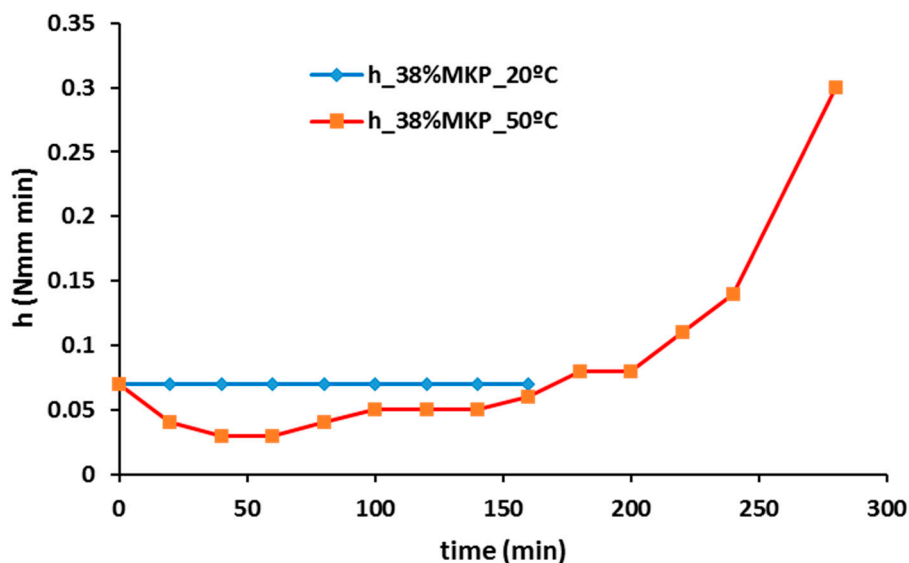
Figure 13. Variation of h values with test time to the 38%MKP composition at 20 and 50 °C.
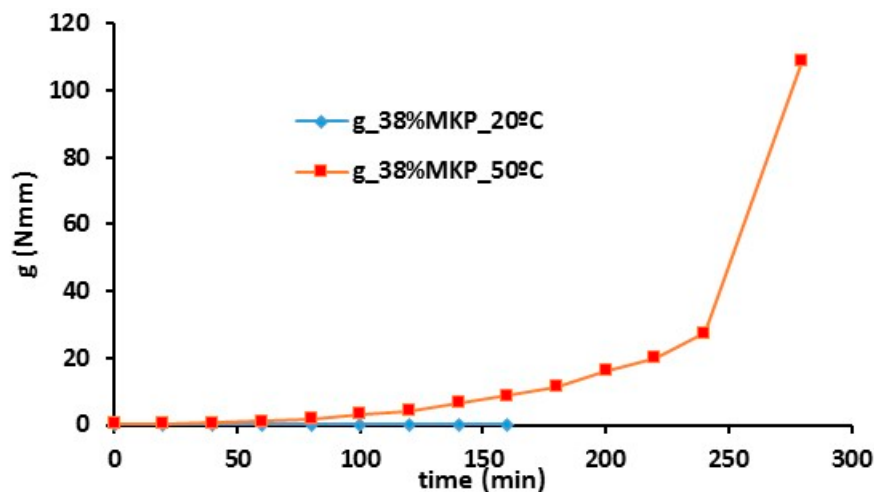
Figure 14. Variation of g values, with test time to the 38%MKP composition at 20 and 50 °C.

However, returning to Figures 13 and 14 it can be seen that after 240 min of test, workability presents a great decrease. According to this information, the sample with 38% MKP must be at 50 °C only during 240 min (4 h). This shows the importance of correlating rheology and final properties measurements (i.e., fresh and hardened state features).

Table 9 shows that if samples are kept initially at 50 °C only during 4 h, a higher increase in the geopolymer compressive strength is promoted due to the fact that hardening is started without the loss of activator liquid, which is essential for that process.

Table 9. Hardened state features for 38% MKP geopolymer cured at 50 °C during 4 and 24 h.

Samples	Compressive Strength (MPa)	Bulk Density (g/m^3)
38%MKP_20 °C	14 ± 0.06	1.9 ± 0.04
38%MKP_50 °C _24 h	4 ± 0.04	1.8 ± 0.05
38%MKP_50 °C _4 h	23 ± 0.02	2.0 ± 0.03
38%MKP_50 °C _24 h sealed	22 ± 0.02	2.1 ± 0.01

Finally, another possibility for curing conditions was considered. Composition with 38% of MKP was sealed and placed at 50 °C for 24 h (Table 9). After 24 h, sealing was removed. Compressive strength is much better with the sealed samples compared with the same samples placed also at 50 °C for the same time (24 h) without sealing. Notice that the value for this 24 h sealed sample is similar to the samples placed for 4 h at 50 °C, due to excessive evaporation being prevented in both cases.

3.3. Blast Furnace Slag and Mine Tailing Based Geopolymers

3.3.1. Blast Furnace Slag Characterization

Figure 15 shows the X-ray diffraction pattern of blast furnace slag (BFS). It is possible to conclude that is a completely amorphous material. Table 10 presents the BFS X-ray fluorescence results. BFS it is a high calcium content precursor (38.5%), different from the MK also in the SiO_2 and Al_2O_3 contents.
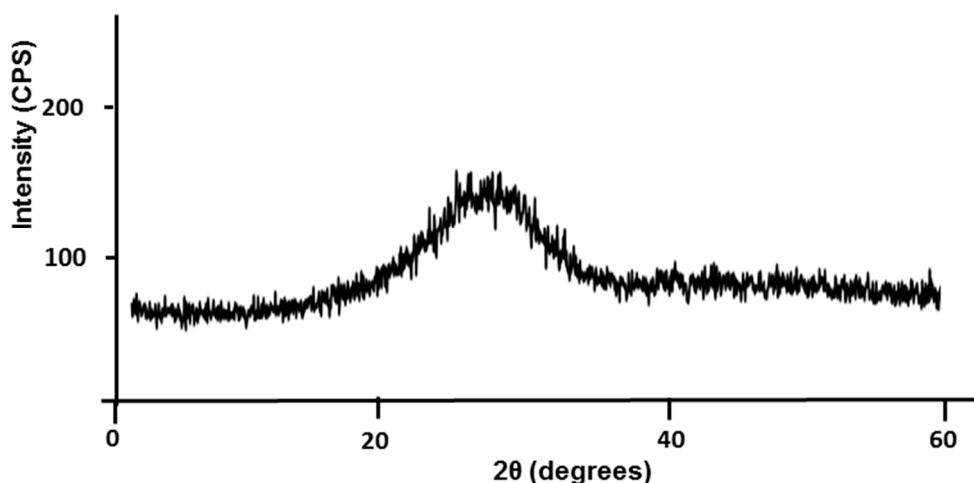
Figure 15. Blast furnace slag (BFS) X-ray diffraction.

Table 10. X-ray fluorescence of blast furnace slag (BFS).

(%)	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Cl
BFS	32.3	9.6	1.2	4.0	10.2	38.5	0.5	0.5	2.2	0.0	0.0

BFS is rich in calcium, hence, calcium silicate hydrate (CSH) gels are the main reaction products. Normally, the binder or precursor materials for the conventional geopolymers are low in calcium and rich in silicate and aluminum (as in the metakaolin) [5].

3.3.2. Blast Furnace Slag and Mine Tailing Based Geopolymer Behaviour

Table 11 present the BFS and MT geopolymer studied compositions. BFS compositions did not need the AD activator solution because BFS already presents a Si/Al > 2 ratio. For the BFS compositions only the 10 M NaOH solution as liquid activator were used.

Opposite to the MK formulations, excess water need to be used to control workability. BFS compositions did not have the same liquid amounts. Composition with 50% BFS presents less water in its composition in order to keep similar workability (Figure 16).

Table 11. Compositions with blast furnace slag and mine tailing.

Sample	Composition	Temperature (°C)	Time in Mould
G_50% BFS	300 g BFS 300 g MT 198 g NaOH (10 M) 200 g H_2O	20 °C	24 h
G_38% BFS	300 g BFS 500 g MT 198 g NaOH (10 M) 100 g H_2O	20 °C 50 °C (for 40, 60 or, 90 min)	24 h 24 h
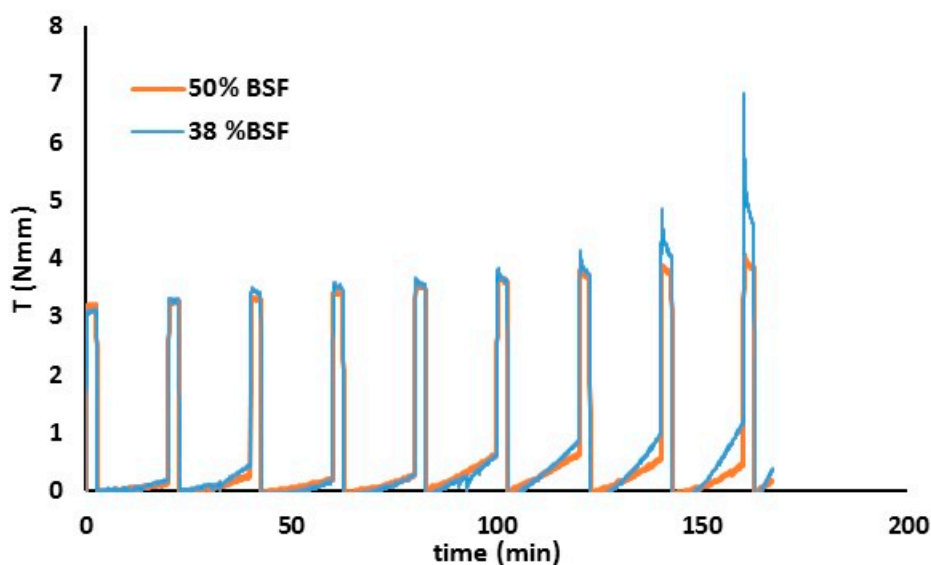
Figure 16. Torque values for 38% and 50% BFS geopolymers with time of test.

Regarding the MT content effect on BFS + MT geopolymers, Figures 17 and 18 show clearly that the two compositions have a very similar rheological behavior. Indeed, quite constant g and h values during test time were obtained. This is an indication that BFS reacts slower in the geopolymer formation process, when compared with MK as a precursor.
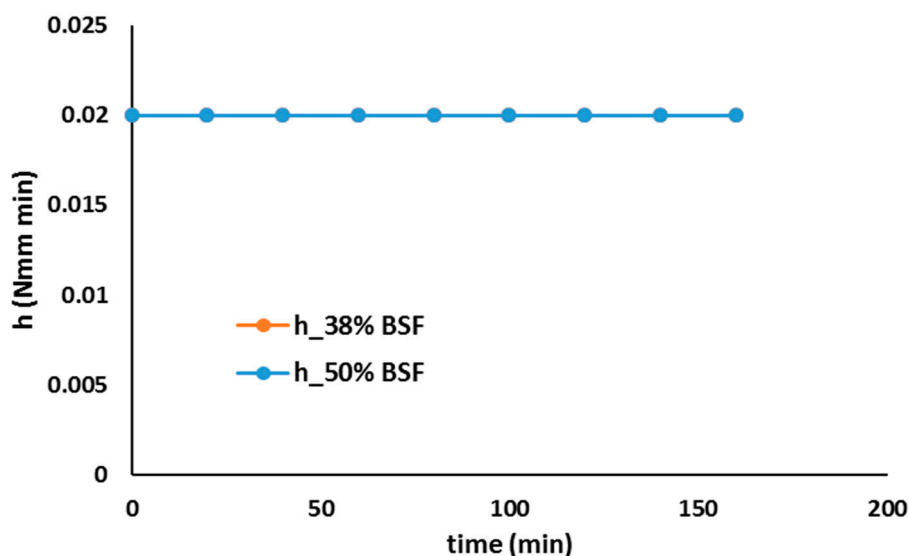
Figure 17. Variation of h values with test time for the 38% and 50% BFS compositions.
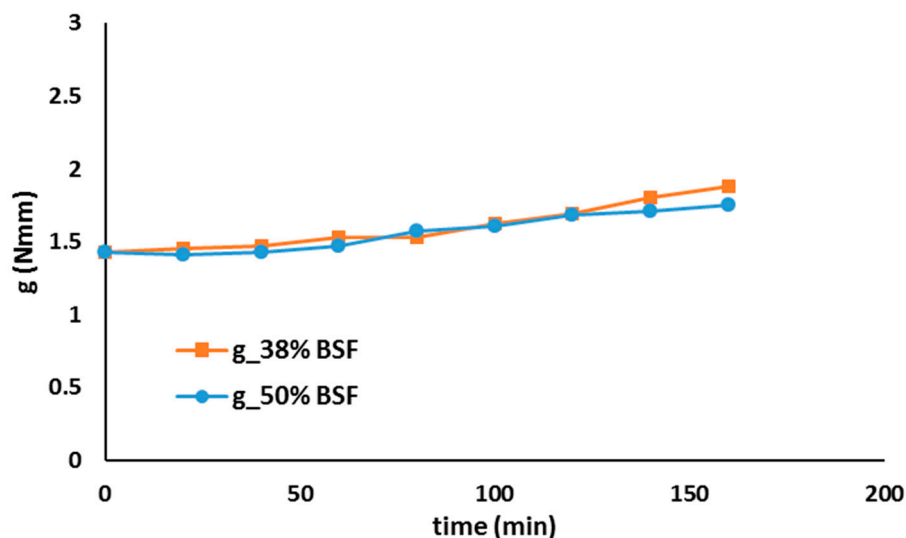
Figure 18. Variation of g values with test time for the 38% and 50% BFS compositions.

The increase in mine tailing content did not change the compressive strength at these curing times (28 days) as it is possible observe in Table 12. This fact was already expected because the workability was kept similar and that means that the properties in hardened state only depend of compositions components and, in all formulations, the reactive material content (300 g BFS) is the same. The mine tailing is not a reactive component from the geopolymer formation point of view as already seen.

Table 12. Hardened state features for BFS and MT-based compositions.

Composition	Compressive Strength (MPa)	Bulk Density (g/cm^3)
38% BFS + 62% MT	14.5 ± 0.02	1.9 ± 0.01
50% BSF + 50% MT	15.4 ± 0.01	2.1 ± 0.01

Regarding the effect of temperature and curing conditions, comparing the behavior of rheological parameters h and g during the test time at 20 °C and 50 °C (Figures 19 and 20), a drastic loss of workability after 40 min test is observed. This fact implies that this formulation should be cured at 50 °C only up to 40 min.
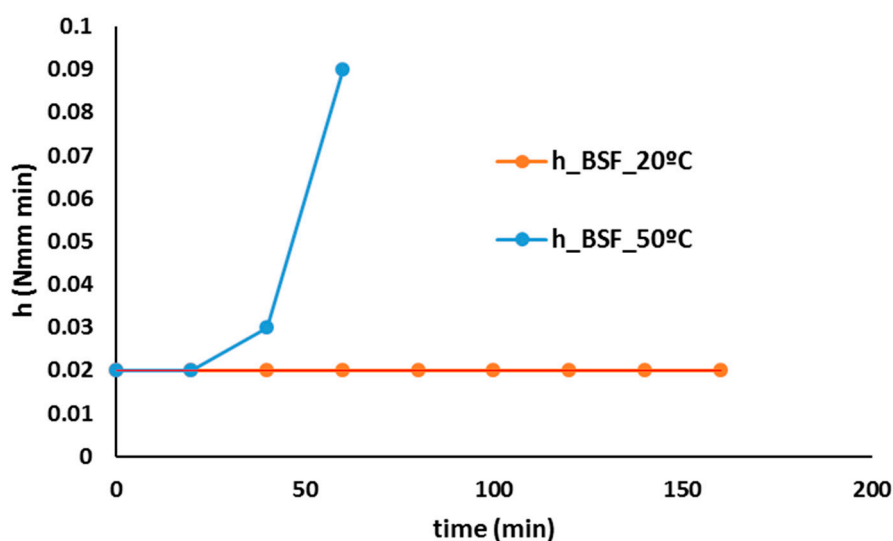
Figure 19. Variation of h values, with test time for the 38% MKP cured at 20 and 50 °C.
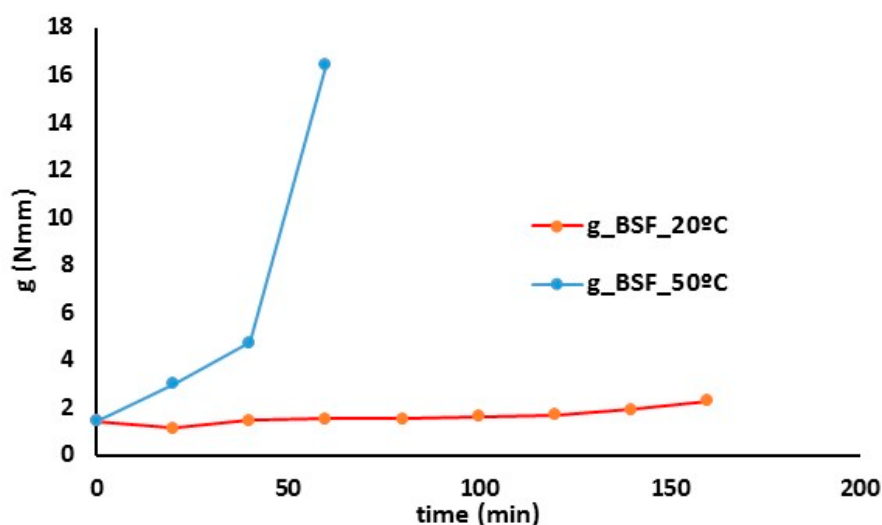
Figure 20. Variation of g values, with test time for the 38% MKP cured at 20 and 50 °C.

Table 13 shows a compressive strength increase for 40 min curing at 50 °C compared with 20 °C cured sample (effect of curing temperature). A decrease of compressive strength result when curing time is increased beyond 40 min at 50 °C. Just like the samples with MK, excessive curing time at high temperatures stops geopolymer reactions due to excessive drying.

Table 13. Hardened state features for 38% BFS compositions curing at 50 °C for different times.

Samples	Compressive Strength (MPa)	Bulk Density (g/m^3)
38%BFS_20 °C	15.4 ± 0.01	1.9 ± 0.01
38%BFS_50 °C _40 min	18.0 ± 0.01	2.2 ± 0.02
38%BFS_50 °C _60 min	10.0 ± 0.01	1.8 ± 0.01
38%BFS_50 °C _90 min	9.4 ± 0.02	1.8 ± 0.01

In conclusion, each geopolymer composition for each temperature has a correct time to remain at that temperature.

3.4. Geopolymer Chemical Durability

Looking at the results previously presented, it is found that the compressive strength presents suitable results for a mortar, especially when cured at 50 °C. Bulk density values may also be considered adequate specifically for compositions with 50% of precursor (MK or BFS).

According to company data, mine refilling does not require a compressive strength greater than 5 MPa. On the other hand, decreasing more the MKP content may prevent the immobilization of harmful metals (MTP composition).

Geopolymer durability was performed using a severe static leaching test [24]. Static leaching test was performed by soaking the geopolymer samples in two different solutions (solution volume 14 times higher than sample volume), one at pH 4 and the other at pH 7, to study the effectiveness of geopolymerization. This was adjusted by adding nitric acid to the solution to keep the pH constant on the predefined value. The choice of nitric acid was motivated by the necessity of compensating the pH raise due to the release of unreacted NaOH from the geopolymer specimen, without altering the leachability of heavy metals through complexation reactions. A liquid/solid mass ratio of 14 was used for all the specimens throughout the experiment. Samples with 14 and 28 days of cure were placed in solutions of pH 4 and pH 7 for 40 days. When the samples were removed from the solutions to determine weight loss, a solution sample was taken and analyzed by IC and ICP-MS

techniques. The pH4 and pH7 solutions with samples with 28 days of cure after 40 days were evaluated. The solutions with samples with only 14 days of curing became turbid after 24 h, being impossible to perform the analysis. Curing time is a very important factor to ensure that all the geopolymerization reactions take place. For these compositions it was observed that their properties at 60 days showed no significant improvements.

Tables 14 and 15 show the leaching results. It is possible to verify that the values of the solubilized elements are smaller than the reference values (MT powder). One can say that there is a metal immobilization efficiency after 28d of curing even with low quantity of binder.

Table 14. Mass loss after 40 days in pH 4 and pH 7.

pH	Compositions	Mass Loss (%)
4	50% MKP	7.2
	50% BFS	9.4
	38% MKP	9.0
7	50% MKP	4.2
	50% BFS	5.6
	38% MKP	5.3

Table 15. Leaching results for the three compositions at pH 4and pH 7.

	Cr	Cu	Ni	Zn	V	As	Sb	Mn	Be	Co	Hg	Pb	SO$_3$
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MTP power	15	192	18.1	0.310	50.9	200	3	10	ND	30		100	26180
pH 4													
50% MKP	0.05	2.00	0.07	6.49	0.07	110	10.98	3.83	<0.001	0.02		1.74	5819
50% BFS	1.71	4.72	0.2	22.21	0.24	200	21.12	33.6	0.01	0.28		9.98	7793
38% MKP	0.05	4.48	0.07	7.4	0.07	175	31.25	0.58	<0.001	0.05		2.88	5267
pH 7													
50%MKP	0.01	1.97	0.003	<0.20	<0.01	84	0.68	0.04	<0.001	<0.001		<0.05	3679
50% BFS	0.15	3.15	0.14	18.89	0.1	93	1	0.30		0.21		2.77	11343
38% MKP	0.01	2.17	0.03	6.48	0.030	93	0.97	0.19		0.02		2.44	7303

4. Conclusions

This study has evaluated the possibility of a waste management solution using high sulfidic mine tailing as raw material in geopolymer production. Mine tailing was used as a fine aggregate together with metakaolin and blast furnace slag as geopolymer precursors. The evaluation of the effects of the precursor type, the effect of the mine tailing addition and also the effect of temperature and curing conditions of different formulations of geopolymers containing mine tailing allowed the following conclusions:

- This particular mine tailing does not act as a geopolymer precursor (binder) because it is not reactive due to its composition; Nevertheless, it can be incorporated as a fine aggregate;
- Metakaolin plus mine tailing geopolymers generates quite good compressive strength products (>20MPa) showing a faster reactive nature than the blast furnace slag plus mine tailing formulations.
- Rheology proved to be an interesting approach to follow up the geopolymer process and even to control the proper curing conditions and components amount, when optimizing final properties such as mechanical strength:
- The use of curing temperature to accelerate the geopolymer reaction is only effective, for a given temperature, until a certain time limit that depends on each precursor (metakaolin or blast furnace slag) and each composition.
- Regarding chemical resistance, curing time is a very important factor in these formulations with small amount of binder (MK and BFS). These compositions, with high MT content, tested in very severe conditions (pH 4 and 7 during 40 days) show a significant chemical strength. In this way and, under normal weather condition (rain, water infiltrations), these compositions can be used in mines refilling.
- Finally, one can say this waste-based geopolymer solution could be an interesting waste management solution, contributing for the sustainability of our habitat. Indeed, the working period of a mine is directly conditioned by the landfill capacity. Apart from an environmental contribution by preventing more landfill deposition, this waste valorization solution is also impacting in the economic and social aspects of mining activity which has a great local significance.

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