# Alkali activation as new option for gold mine tailings inertization

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## A R T I C L E   I N F O

## A B S T R A C T

The mining industry produces a huge quantity of sulphidic mine tailings, which cause several short- and long-term environmental problems when disposed by landfilling in impounding lakes. The possibility of immobilizing several heavy metals from gold mine tailings by reactive geopolymerization technique has been investigated in the present study. The chemical stability of geopolymers synthetized by the alkali activation of metakaolin and blast furnace slag and the addition of 40—50 wt% gold mine tailings is demonstrated. The geopolymers were cured at room temperature, and the effects of different Si/Al and Na/Al molar ratios and curing times were investigated. The inertization effectiveness was evaluated by means of leaching tests carried out according to standard EN 12457 after 7 and 28 days and after 18 months. The samples were immersed into the water for 1 day, and the leachable metals in the test solution were determined by ICP-OES. The results show that various elements (Cr, Cu, Ni, Zn and Mn) from gold mine tailings are able to immobilize almost completely by alkali activation with proper co-binder material. The immobilization efficiency were highly improved with longer curing period also for the problematic elements As, V, Sb and B.

## 1. Introduction

The mining industry produces a huge amount of solid waste materials during mining's lifetime. Solid mine tailings typically contain many sulfide minerals and heavy metals. These fine-grained residues are usually deposited in impounding lakes near mining sites. Sulphides are oxidized in contact with water, which decreases the surrounding pH, and metal oxides are leached into the environment. This leachability causes short- and long-term environmental problems, such as contamination of surface and ground water (Ahmari and Zhang, 2013a, 2013b). There is increasing interest in discovering new methods to manage mine tailings more effectively in the future. This interest is mainly focused on developing low-cost treatment or confinement processes.

Alkali activation of mine tailing can represent one of these low cost treatments for the capability to generate matrices for the encapsulation of hazardous elements (Ivan Diaz-Loya et al., 2012; Lancellotti et al., 2010; Zheng et al., 2016). Of particular interest in this contest is the alkali activation of aluminosilicate raw materials, which generate inorganic polymers, also known as geopolymers. The alkaline solution dissolves the reactive portion of aluminosilicate powdered material and release aluminum $[AlO4]^{5-}$ and silicon $[SiO4]^{4-}$ tetrahedral units into the solution. In the following few hours the reticulation reactions take place: the neighboring ions are linked together by sharing the oxygen atoms and forming new three-dimensional amorphous Si—O—Si or Si—O—Al bonds and loss of water (Komnitsas and Zaharaki, 2007). The presence of $Al^{3+}$ ions in this structure causes a negative charge, which must be balanced by sufficient alkali cations from an alkaline solution or other cations coming, for example, from wastes (Van Jaarsveld et al., 1997). Geopolymers can be produced at room or slightly highly temperatures; They can have excellent physical and chemical properties, such as high early strength, low density, and micro- and nano-porosity (Davidovits, 1991). According to Davidovits (1994), geopolymers also experience low shrinkage and have high chemical and fire resistance, and they are suitable for long-term hazardous waste disposal techniques thank to their sulphate, freeze-thaw, and

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corrosion resistance.

Due to above mentioned properties, geopolymerization is a potential method of stabilizing various kinds of solid waste materials. According to literature (Stronach et al., 1997.; Van Jaarsveld et al., 1999, 1997) heavy metals can be immobilized by physical encapsulation or chemical interaction. In physical encapsulation, a heavy metal particle is trapped inside the matrix or adsorbed on the geopolymer surface. In chemical interaction, a heavy metal cation is bonded to the geopolymer structure with a charge-balancing role as above described. The immobilization efficiency depends on the reaction conditions and the properties of the starting materials, such as the Si/Al and Al/Na molar ratio and especially the reactivity of the crystalline phases or the amorphous fraction of the aluminosilicate precursor.

Mine tailings are industrial wastes worldwide diffused. There are many kind of tailings such as iron, gold, copper, phosphate, vanadium and bauxite tailings (da Silva et al., 2014; Das et al., 2000; He et al., 2014; Shao et al., 2005; Thomas et al., 2013; Wang and Liu, 2009; Wei et al., 2017; Yang et al., 2009; Zhou et al., 2010). The stabilization of heavy metals from different mine tailings (MT) was performed by means of hot techniques, such as realization of glass-ceramic (Marabini et al., 1998; Ye et al., 2015) or by cold technique such as paste backfilling (Khaldoun et al., 2016).

Another option for mine tailings stabilization by cold technique is by means geopolymerization. There are several studies about geopolymerisation of mine tailings (Van Jaarsveld et al., 2000; Pacheco-Torgal et al., 2007, 2008; Ahmari and Zhang, 2012, 2013a, 2013b; Barrie et al., 2015) but only few of these have focused on leaching of heavy metals from mine tailings. Ahmari and Zhang (2013b) studied immobilization of copper mine tailings and found effective stabilization of Mn, Cu, Zn and Mo. Barrie et al. (2015) are among few authors working on tailings from gold extraction. They prepared geopolymers using as matrix volcanic glass and calcined halloysite-rich clay. In their case, Pb and Zn were effectively immobilized while the leached concentrations of As and Cu remained high after geopolymerization. High leaching of As was explained by high pH during geopolymerization.

Even if the previous research about immobilization of As rich tailings shows discouraging results, there is need for further studies with different precursors and longer curing time. In this study, the immobilization efficiency of the various elements in gold-mine-tailing-based geopolymers were studied using as aluminosilicate precursors a mixture of metakaolin and ground granulated blast furnace slag (GBFS) without the use of coal fly ash. The gold mine tailings (MT) used in the present study include elements such as Mn, As, Cr, Cu, Ni, Zn, Sb, V, and Ba. Particular attention was payed to As and Sb, which can hardly be inertized via most techniques, including geopolymerization, because in an alkaline environment, their anionic forms can occurs (Fawcett et al., 2015). Metakaolin (MK), which is highly reactive aluminosilicate raw material, was used as a co-binder, together with amorphous, ground granulated blast furnace slag (GBFS), to optimize the chemical composition of the samples. A mixture of the above mentioned solid materials, also called MT_GBFS_MK precursor, was alkali activated with sodium hydroxide solution, together with sodium silicate solution. The geopolymer samples were cured 7 and 28 days, and after 18 months before they were characterized. The aim was to analyze the leaching of heavy metals from MT-based geopolymers with various proportions of MT_GBFS_MK after different curing times. The leaching test was performed according to European standard EN 12457. The results were compared with the leaching rate before geopolymerization and in terms of total MT powder concentration. Potential breakdown of each geopolymer containing metal contaminants due to the leaching of the matrix constituent elements, such as Na, K, Si, Al and Ca, were analyzed after geopolymerization

to better understand the properties of the solid matrices produced.

## 2. Materials and methods

### 2.1. Raw materials

Mine tailings (MT) were received as a slurry from a gold mining site in Northern Finland. The slurry was dried at 105 °C before using it in powder form. Commercial ground granulated blast furnace slag containing a large glassy fraction (GBFS, KJ 400; Finnsementti, Finland) and commercial metakaolin (MK, Argical 1000, Imerys Minerals Ltd., UK), were used as aluminosilicate precursors in these tests.

### 2.2. Geopolymer preparation

The geopolymer formulations are presented in Table 1. The total amounts were 40–50% MT, 20–30% GBFS, and 30% MK. Due to the fact that the Si/Al molar ratio affects the physical properties of the geopolymer matrix and its inertization capacity, all the formulation were designed according to Davidovits (1999) who reports that the Si/Al molar ratio should be < 3 in order to produce a rigid 3D geopolymer network suitable for waste encapsulation. Rowles and O'Connor (2003) has shown highest strength for the geopolymer matrix with a Si/Al ratio of 1.5–2.5 and a Na/Al ratio of 1.0–1.29. The same kinds of observations were made by Duxson et al. (2007), who reported the highest compressive strength with a Si/Al ratio of 1.15–1.90. Aly et al. (2008) has shown that the proper Si/Al ratio should be near 2 and that the Na/Al should be near 1 for nuclear waste immobilization. Some authors have already shown that a Si/Al ratio close to 3 is good for immobilizing heavy metals cations dispersed in water in soluble form (Ponzoni et al., 2015); thus, in the prepared geopolymers, the theoretical Si/Al molar ratios were between 1.8 and 2.6, while the sample without metakaolin (50_50_0) had a Si/Al ratio of 3.5. For all samples, the Na/Al molar ratios were near 1 (except for the 50_50_0 sample, which is 1.5) (Table 1), a value that guarantee the proper dissolution of $Si^{4+}$ and $Al^{3+}$ from the starting material (Murayama et al., 2002). Rao and Liu (2015) also observed that the type of alkali activator used affects the properties of the geopolymer matrix. In this paper the Si/Ai and Na/Al ratios are calculated taking into account the overall chemical composition and not the reactive amorphous fraction. In this way these ratios are only indicative, yet comparable to literature studies. In future the ratios can be modified taking into account the reactive fraction of the raw materials. NaOH-solution (8M and 9M) and sodium silicate solution ($SiO_2/Na_2O$ molar ratio of 3) were used as the alkali activators in these tests.

The preparation of the samples produced was carried out according to the following steps:

- The sodium hydroxide solution (50 wt% -) was diluted with distilled water to obtain the desired concentrations: 8M and 9 M.
- The NaOH solution was mixed with the sodium silicate solution.

**Table 1**
Geopolymer formulations from a mixture of mine tailings (MT), blast furnace slag (GBFS), and metakaolin (MK).

| MT_GBFS_MK | NaOH (ml) | Na silicate (ml) | Si/Al | Na/Al |
|---|---|---|---|---|
| 50_50_0 | 30 (8M) | 0 | 3.5 | 1.5 |
| 50_20_30_(8MNaOH) | 20 (8 M) | 25 | 2.6 | 0.9 |
| 40_30_30_(8MNaOH) | 20 (8M) | 25 | 2.5 | 0.8 |
| 50_20_30_(9MNaOH) | 20 (9M) | 25 | 2.6 | 0.9 |
| 40_30_30_(9MNaOH) | 20 (9M) | 25 | 2.5 | 0.9 |

- Dry powders containing various proportions of MT, GBFS, and MK were mixed together carefully, and the mixture was slowly added to the alkaline solution, with intensive stirring.
- The mixture was mixed intensively to create a homogeneous paste.
- The produced paste was inserted into plastic molds, and these molds were placed inside a plastic bag to cure for 24 h at room temperature.
- After 24 h, the molds were removed from the plastic bags and allowed to cure at room temperature and at an approximate moisture level of 50–60% for 7 and 28 days.

## 2.3. Geopolymer and raw materials characterization

### 2.3.1. Raw materials characterization

The mine tailings were characterized by analyzing the chemical and phase composition, particle size distribution, specific surface area, and loss of ignition. The chemical composition was analyzed by X-ray fluorescence (XRF) spectrometer (Axios Omnian, PAN-alytics B.V., Eindhoven, the Netherlands) and the crystal phases of the powdered samples and materials produced were identified using a X-ray diffractometer (XRD, D5000, Siemens A.G., Munich, Germany). The step interval, integration time, and angle interval used were $0.04°$/step, 4 s/step, and $10–50°$ 2Θ, respectively. The ICDD-database (PDF-2, 2006) was used to identify the crystal phases of the material. The content of trace elements was analyzed by microwave-assisted wet digestion using a 3:1 mixture of $HNO_3$ and HCl for mine tailings and determinations were made using an inductively coupled plasma-optical emission spectrometer (ICP-OES, IRIS Intrepid II XDL Duo, Thermo Fischer Scientific, Waltham, MA, USA). Particle size distribution was measured using a laser diffraction particle size analyzer (LS 13320, Beckman Coulter, Inc., Brea, CA, USA). Specific surface area measurement was based on the physical adsorption of gas molecules on a solid surface using a physisorption analyzer (ASAP, 2020, Micromeritics Instrument Corp., Norcross, GA, U.S.A.), and the results were reported in a form of a B.E.T.- isotherm. Loss of ignition (LOI) at 525 and 950 °C was determined using thermo-gravimetric analysis equipment (Pre-pAsh, Precisa Gravimetrics A.G., Dietikon, Switzerland).

### 2.3.2. Chemical stability

The structural integrity and chemical stability of the specimens were checked after only 4 days of curing in order to determine whether the matrices were stable and therefore geopolymerization had occurred. The weighted specimens were immersed into bidistilled water with solid/liquid ratio of 1/100 at room temperature for 24 h. After immersion, the samples were cured at 100 °C for 24 h, and the dry specimens were weighed. The weight loss of the specimens was calculated.

### 2.3.3. Leaching test

The leachability of the heavy metals from the starting materials and samples produced were carried out according to the European standard EN 12457 "Characterization of waste-Leaching-Compliance test for leaching of granular waste materials and sludge." After being crushed and sieved to a particle size under 2 mm, the samples were placed in bidistilled water with a liquid/solid weight ratio of 10 l/kg and maintained for 24 h. After the extraction and filtration of the leachates, the concentrations of heavy metal ions were determined with ICP-OES. Before ICP-OES analysis, the samples were acidified with $HNO_3$ to pH = 2. During the leaching test, the pH and conductivity of the solution were measured after 1, 30, 60, 90, 210, and 1440 min to evaluate the chemical stability of the samples produced. The leaching procedure was repeated after 7 and 28 days of curing and on 40-40-30 composition after 18 months to evaluate long-term stability.

### 2.3.4. Microstructural analysis

The microstructure of the specimens produced was conducted by Environmental Scanning Electron Microscope (ESEM, Quanta200, FEI Company from Thermo Fischer Scientific, Waltham, MA, USA) equipped with Energy Dispersion Spectroscopy (EDS) (INCA-350, Oxford Instruments Plc, Tubney Woods Abingdon, UK) for the chemical analysis. The aim was to evaluate the formation of geopolymer gel after 28 days of curing at room temperature and humidity.

## 3. Results and discussion

### 3.1. Characterization of raw materials

Table 2 presents the main elements of the raw materials and the physical properties of the mine tailings used. Mine tailings are fine-grained materials with a mean particle size of around 49 μm and consist mainly of $SiO_2$, $Al_2O_3$, and CaO. In addition, a significant amount of iron, around 10%, and a high level of sulphur content were detected (Table 3), confirming the presence of the crystalline pyrite residues identified with XRD and reported in a previous paper (Kiventerä et al., 2016). Iron and sulphur originate from arsenopyrite and pyrite minerals, which are the main minerals in

**Table 2**
Main elements and physical properties of mine tailings (MT), ground granulated blast furnace slag (GGBFS) and metakaolin (MK).

| Component | MT | GGBFS | MK |
|---|---|---|---|
| $SiO_2$ (%) | 49.9 | 32.3 | 58.9 |
| $Al_2O_3$(%) | 10.4 | 9.6 | 34.7 |
| $Fe_2O_3$(%) | 9.7 | 1.2 | 1.4 |
| CaO (%) | 11.1 | 38.5 | 0.1 |
| MgO (%) | 5.9 | 10.2 | 0.1 |
| $Na_2O$ (%) | 3.0 | 0.5 | 0.1 |
| $K_2O$ (%) | 1.3 | 0.5 | 0.7 |
| $TiO_2$(%) | 1.3 | 2.2 | 1.3 |
| BET surface area ($m^2$/g) | 7.2 | | |
| pH | 9.6 | | |
| LOI 525 °C | 0.7 | | |
| LOI 950 °C | 12.9 | | |
| Particle size d50 (μm) | 45 | 10.8 | |

**Table 3**
Minor elements in mine tailings (MT).

| Component | MT (mg/kg) |
|---|---|
| S | 18900 |
| As | 1520.0 |
| Cd | <0.3 |
| Cr | 74.0 |
| Cu | 120.0 |
| Ni | 100.0 |
| Mn | 1500 |
| Pb | 4.3 |
| Zn | 71.0 |
| B | 9.6 |
| Be | <1 |
| Co | 22.0 |
| Mo | 1.5 |
| Sb | 32.0 |
| Se | <3 |
| Sn | <3 |
| V | 59.0 |
| Ba | 29 |

this particular gold mine. Indeed, ICP-OES analysis confirmed the presence of a significant amount of arsenic (1520 mg/kg). Ground granulated blast furnace slag (GBFS) has a mean particle size of around 10.8 μm, and the main components are $SiO_2$, $Al_2O_3$, and CaO (~80%). Metakaolin with a Si/Al mass ratio of 1.7 was used to adjust the Al content, Al being scarce in the other two precursors.

### 3.2. Chemical stability and microstructure of the geopolymer

The samples, produced with the formulation reported in Table 1, were demolded without damage and without any cracks after only 4 days of curing at room temperature. After contact with water for



**Fig. 1.** The samples (from left to right: MT_GBFS_MK: 50_50_0, 50_30_20 and 40_30_30 activated by 8M of NaOH and sodium silicate solution; 50_30_20 and 40_30_30 activated by 9M of NaOH and sodium silicate solution) after immersion in bidistilled water for 24 h.

24h, all samples were stable and were investigated further (Fig. 1).

SEM micrographs (Fig. 2) of the obtained samples show that the addition of metakaolin as aluminum-rich precursor to mine tailings favors the geopolymerization process with respect to the formulation containing only mine tailings and slag. This may be related to the optimization of the Si/Al and Na/Al ratios, which reach values near 2.5 and 1.0, due to the Al content of the MK. Fig. 2 shows that the addition of MK to the starting material produces a homogenous matrix after alkali activation and curing at room temperature for 28 days. Further, the decrease of MT content from 50 wt% to 40 wt% and the corresponding increase of GBFS leads to the formation of larger amount of geopolymeric gel and a structure more homogeneous and dense. This behavior confirms the importance of a good balance of aluminosilicate precursor to obtain a stable matrix. The Si/Al ratio of the geopolymer gel in the sample without metakaolin (50_50_0), as calculated by EDS analysis, was 3.9 (compared to a theoretical Si/Al molar ratio of 3.5). In that gel, the percentages of Si, Al, Ca, and Na were 11.8%, 3%, 15%, and 10.2%, respectively. When comparing these results with those obtained for the sample with MK addition (50_20_30), the Si/Al ratio of the gel was 2.3 (theoretical value of 2.6), with Si, Al, Ca, and Na percentages of 19.3%, 9%, 6%, and 8%, respectively. The other sample (40_30_30), containing lower amount of mine tailings, shows an average Si/Al value of 2.6 and higher amount of Ca, 11 wt%, in the gel than the 50_20_30
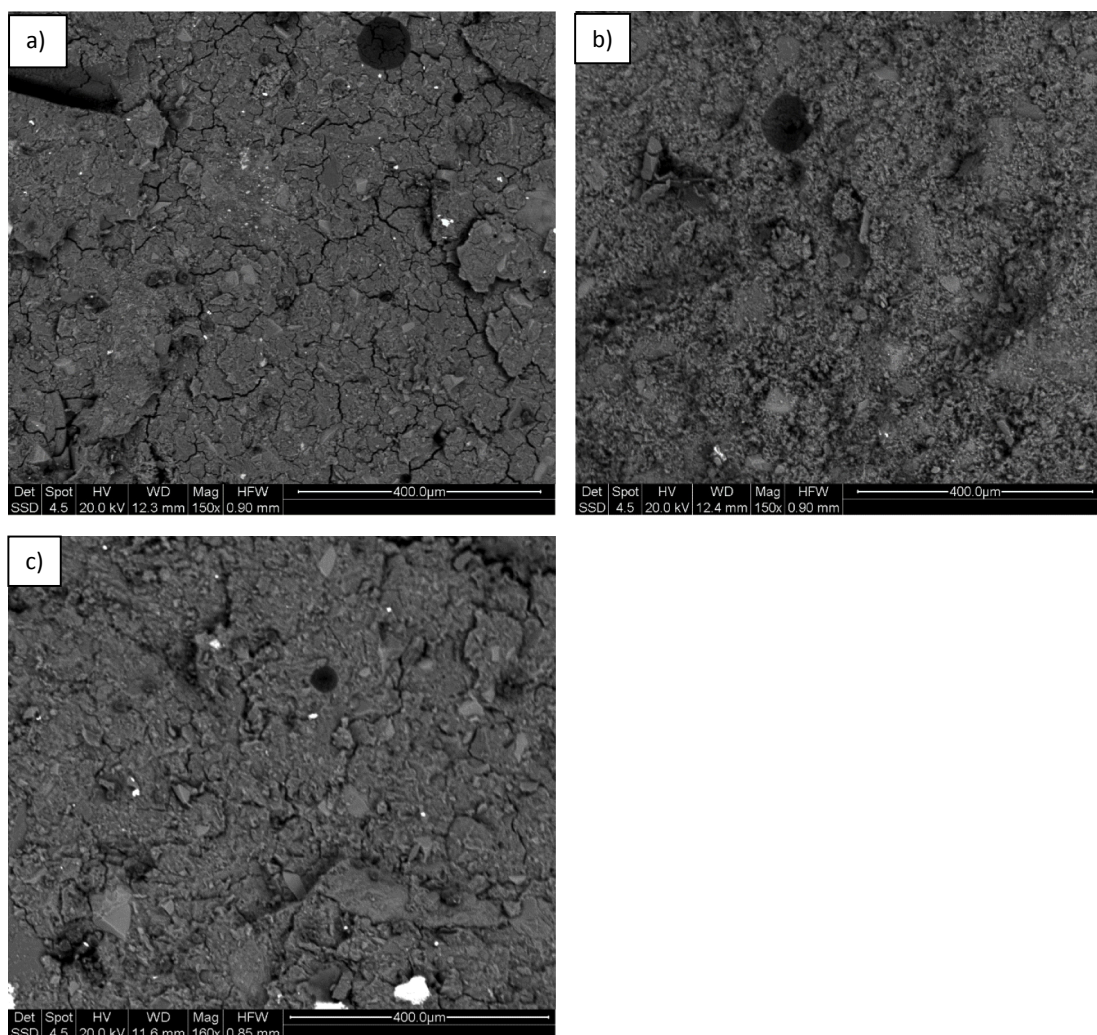


**Fig. 2.** The SEM images of the MT_GBFS_MK samples: 50_50_0 (a), 50_20_30 (b), and 40_30_30 (c) activated by 8M NaOH and sodium silicate solution after 28 days of curing.
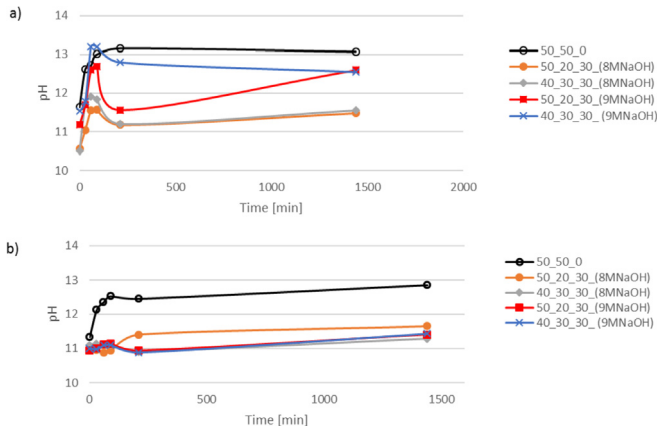
Fig. 3. pH values of the leaching test solutions after a) 7d and b) 28d of curing.

sample, demonstrating that the slag and mine tailing are reacting in the alkaline environment. It is worth noting that in all the samples, the Si/Al ratios measured by EDS analysis are very similar to the theoretical values. The results of the EDS analyses reported above imply that with the addition of metakaolin to the powder mix, more Si and Al ions had contributed to form the geopolymer gel. Without metakaolin (50_50_0), there were more Ca ions in the geopolymer gel, as would be expected based on the higher GBFS content in the matrix.

### 3.3. Leaching test results

#### 3.3.1. pH and conductivity

During the leaching test, chemical stability was investigated by analyzing the pH and conductivity after various lengths of time in contact with water. For all specimens, there was a significant increase in pH after a few minutes (Fig. 3a and b), and after a few hours, the pH stabilized. The lowest pH values were achieved by adding metakaolin to the matrix (samples 50_20_30 and 40_30_30). This behavior may be related to geopolymerization process, which occurs in a more complete way in the presence of metakaolin which adjusts the aluminum content and Si/Al ratio. From Fig. 3a appears evident that for short curing time (7 days), the activation solution 8M is more efficient with respect to solution 9M, while for longer time (28 days) both the solutions behaves in the same way. Also, the conductivity values increased after a few minutes in contact with water and then stabilized after a few hours (Fig. 4a and b). The only exception was the sample without metakaolin (50_50_0), for which the conductivity did not stabilize even after 24 h in contact with water. After longer curing period, the conductivity of the samples decreased, already after few minutes in contact with water. This could be related to the fact that the geopolymer reaction continues and the chemical stability of the samples improves with longer curing. The addition of metakaolin into the matrix decreased the conductivity values after various curing times confirming the formation of a stable geopolymeric gel able to immobilize ions.

According to Aly et al. (2008) this kind of behavior is typical for geopolymers. They have shown that the most leachable ions from geopolymers in deionized water are alkali ions and that the pH value of the geopolymer is high. They also observed that the leachable amount of $Na^+$ ions decreased at lower Si/Al molar ratios, which could be the reason why the lower pH and conductivity have been recorded for the samples with metakaolin in the matrix. In order to better understand the matrix produced and its degree of consolidation, the leaching quantities of various elements were evaluated and are reported below.
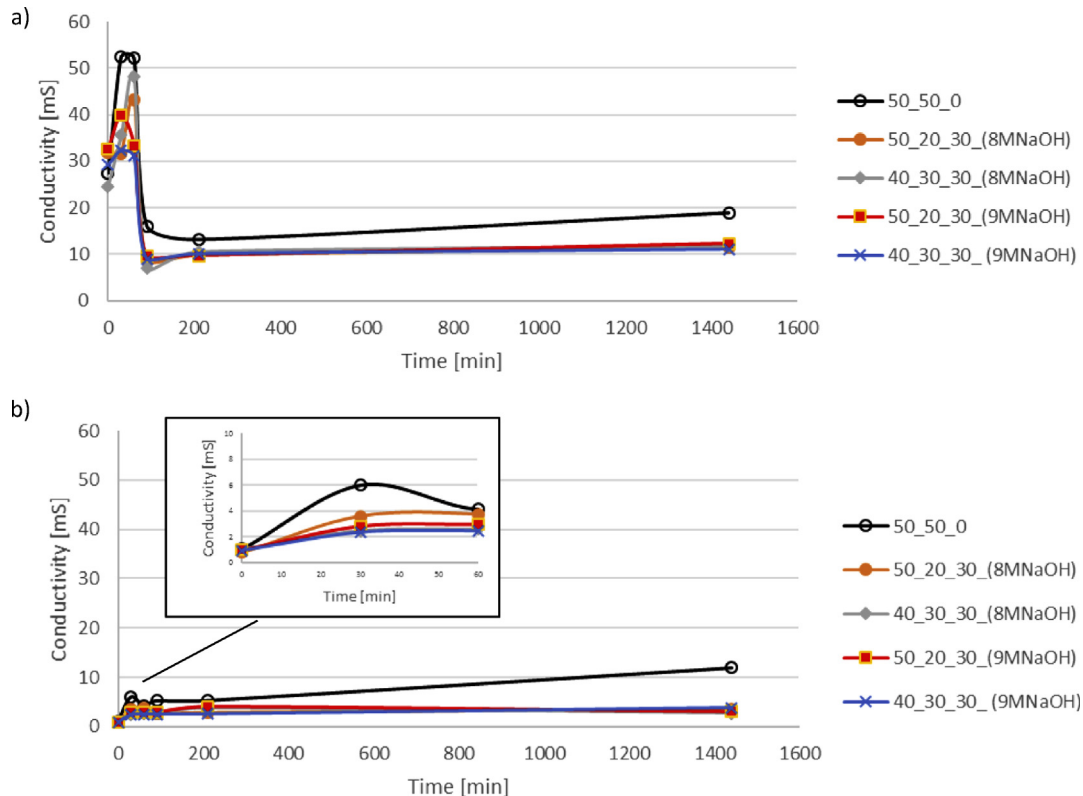


Fig. 4. Conductivity values of the leaching test solutions after a) 7d and b) 28d of curing.

### 3.3.2. Leaching test results for the main elements

The most leachable components from geopolymers are alkali ions (Aly et al., 2008). In this study, the release of $Na^+$ ions was high after 7 days of curing, and the amount decreased significantly (by two orders of magnitude) after a longer curing period (Fig. 5a). The leachable amount of K increased significantly after 28 days of curing, mainly for the sample containing only mine tailings and slag, characterized by low degree of geopolymerization, and this amount was higher than the amount of Na ions released (Fig. 5b). Previous researchers have observed that the size and valence of an ion are important properties when considering the incorporation of a particle into a geopolymer matrix (Rao and Liu, 2015; Van Jaarsveld et al., 1998). In this case, the $Na^+$ ion is smaller than the $K^+$ ion and could be more strongly bonded to the matrix based on its larger ionic radii.

In order to understand the properties of the geopolymer matrix produced, the amount of Si and Al ions released must be investigated (Hajimohammadi and van Deventer, 2016). During geopolymer formation, a condensation reaction can occur between $AlO_4^{5-}$ aluminate units and $SiO_4^{4-}$ monomers or only between silicates; this depending on the concentration of Si ions in the system. In our case, the leaching of Si increased and the leaching rate of Al decreased from day 7 to day 28 of curing (Fig. 6). According to Hajimohammadi et al. (2011, 2010), this kind of behavior of the Si and Al could be related to the speed and solubility of the silica and aluminum obtained from the aluminosilicate raw material. The rapid dissolution of aluminum during the early stage may decrease the solubility of the Si ions by sorption of Al ions onto the Si particles. This could be one reason why the Si solubility was initially low. When the solubility of Si increases with time, there are more sites in the geopolymer gel where Al ions can be placed, and the solubility of Al decreases. Apart from the geopolymer matrix, the high level of Si in the leachate could also be because of the unreacted silicate solution.

The addition of the metakaolin slightly increased the solubility of the Si and Al ions after 7 days of curing (Fig. 6). Using a higher amount of metakaolin, more dissolution of silicon ions at the beginning of the reaction was recorded (Rao and Liu, 2015; Van Jaarsveld et al., 1998). It is important to keep in mind that, even though the leachable amounts of Si and Al are high, these are not directly related to immobilization efficiency or properties of the matrix produced.

The amounts of Ca leached increased after longer curing periods (Fig. 6c). Calcium is known to react with silicon and aluminum to form calcium silicate or calcium aluminate hydrate phases. The amount and form of the calcium affect the properties of the final matrix. The lowest level of calcium release was seen in the 50_50_0 sample (without any metakaolin), and the leaching rate increased after metakaolin addition. After the addition of metakaolin, the geopolymer matrix probably produced between silicon and aluminum ions to a greater degree, and the excess calcium is leached from the structure. The reactivity of the formulations increases with the addition of metakaolin, which favors geopolymerization. Therefore, when mine tailing and slag particles dissolve, part of the Ca enters the geopolymeric gel, while the other part remains free and leachable. In the formulation without metakaolin, the reactivity of particles is lower, so the amount of Ca in the samples is fixed.
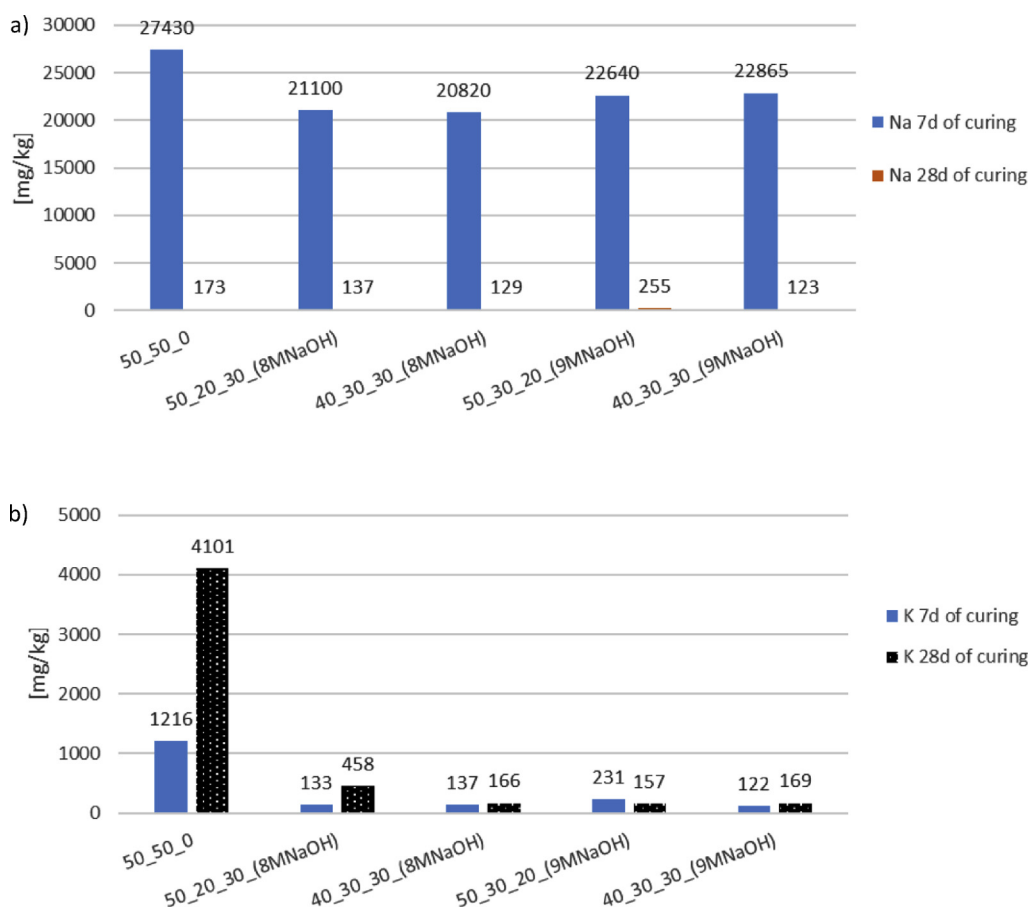


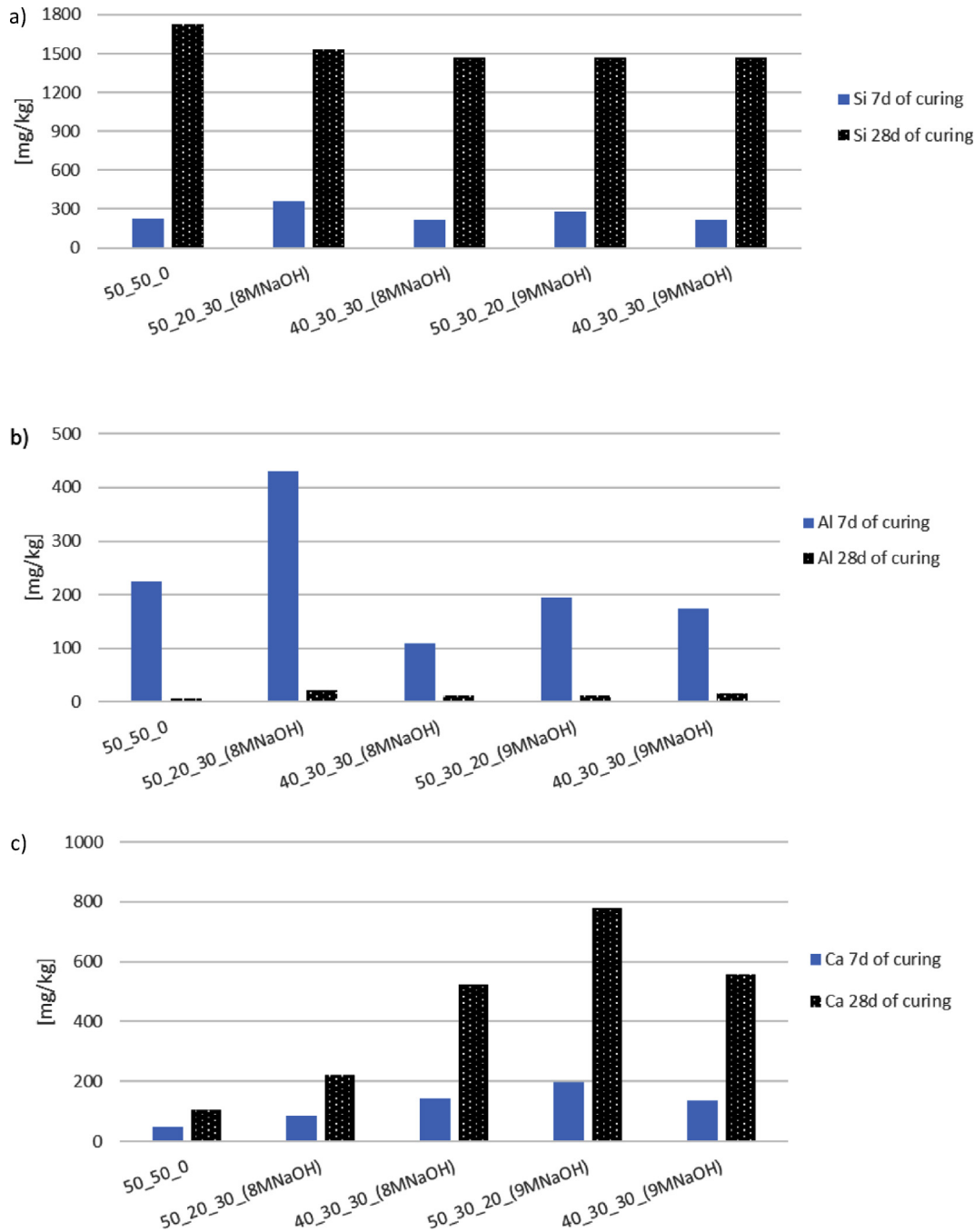**Fig. 5.** The leachable amounts of a) Na and b) K after 7d and 28d of curing.

**Fig. 6.** The leachable amounts of a) Si, b) Al, and c) Ca after 7d and 28d of curing.

### 3.3.3. Immobilization/leaching of heavy metals

In this study, MT powder was found to have high levels of Cr, Cu, Ni, Zn, V, As, and Mn content and minor quantities of B, Be, Co, Hg, Pb, Sb, and Ti. The leaching amounts of various elements before and after the geopolymerization are presented in Table 4, and the immobilization efficiency is shown in Fig 7. The immobilization efficiency compares the theoretical total amount in the geopolymer based on the value of the starting material (MT) and the leachable amount of the element from the geopolymer structure. The leachable amounts of Be, Co, Hg, Pb, and Ti were very low before and after geopolymerization, therefore these element are not a problem for this kind of waste. Even if the immobilization of these elements improved slightly between 7 and 28 days of curing, which

implies that the geopolymer reaction occurred during longer time and a highly consolidated matrix formed with time. Also, the leaching amounts of Cr, Cu, Zn, and Ni were low after geopolymerization notwithstanding the total concentrations of Cr, Cu, Zn, Ni, and Mn were high in the MT powder. The immobilization efficiencies of those elements were higher than 98%. This means that there is a possibility of immobilizing huge amounts of different elements by reactive geopolymerisation.

As, Sb, B, and V were the most problematic elements to stabilize effectively. Arsenic shows high release after 7 days of curing, when geopolymeric matrix is not completed formed, but decreased values with respect to leachable amount in MT after 28 days, confirming that for longer curing time geopolymerizaion occurs. The

**Table 4**
The total concentration, leachable amount from MT powder, and leachable amount from samples of various elements after 7d and 28d of curing.

| | Cr ppm | Cu ppm | Ni ppm | Zn ppm | V ppm | As ppm | Sb ppm | Mn ppm | B ppm | Be ppm | Co ppm | Hg ppm | Pb ppm | Ti ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total concentration in MT powder | 74 | 120 | 100 | 71 | 59 | 1520 | 32 | 1500 | 9.6 | <1 | 22 | | 4.3 | |
| Leachable from MT powder | 0.3 | 0.2 | 0.1 | 0.5 | 1.3 | 68 | 0.1 | 4.2 | 7 | <0.1 | 0.4 | <0.1 | 0.1 | <0.1 |
| 50_50_0 (7d) | 0.2 | 1.7 | 0.1 | 0.4 | 59 | 113 | 0.4 | 0.3 | 10 | 0.1 | 0.3 | 0.1 | 0.4 | 0.1 |
| 50_50_0 (28d) | 0.5 | 0.1 | 0.2 | 0.1 | 5.2 | 52 | 0.1 | 3.3 | 5.5 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| 50_20_30 (8MNaOH) (7d) | 0.6 | 2.3 | 0.3 | 0.9 | 50 | 173 | 0.2 | 3.3 | 5.5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 50_20_30 (8MNaOH) (28d) | 0.6 | 0.1 | 0.2 | 0.1 | 6 | 43 | 1.1 | 3.9 | 8.3 | 0.1 | 0.1 | 0.1 | 0.3 | 0.1 |
| 40_30_30 (8MNaOH) (7d) | 0.7 | 1.7 | 0.3 | 0.6 | 63 | 133 | 0.2 | 1.4 | 8.3 | 0.1 | 0.3 | 0.1 | 0.2 | 0.1 |
| 40_30_30_ (8MNaOH) (28d) | 0.6 | 0.1 | 0.3 | 0.1 | 5 | 24 | 0.7 | 3.5 | 8.7 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| 40_30_30 (8MNaOH) (18months) | 0.11 | 0.05 | < QL | < | 1.3 | 0.12 | < QL | < QL | 7.4 | < QL | < QL | < QL | 0.1 | < QL |
| 50_20_30 (9MNaOH) (7d) | 0.4 | 3.3 | 1.6 | 1 | 59 | 160 | 0.4 | 11.6 | 9.9 | 0.1 | 2.5 | 0.1 | 0.2 | 0.2 |
| 50_20_30_ (9MNaOH) (28d) | 0.3 | 0.1 | 0.3 | 0.1 | 5.9 | 32 | 0.5 | 3.6 | 9.7 | 0.1 | 0.1 | 0.1 | 0.5 | 0.1 |
| 40_30_30 (9MNaOH) (7d) | 0.4 | 1.3 | 0.1 | 0.8 | 52 | 105 | 0.2 | 4.9 | 9.6 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 40_30_30 (9MNaOH) (28d) | 0.5 | 0.1 | 0.2 | 0.1 | 4.2 | 35 | 1 | 3.8 | 9.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| 40_30_30 (9MNaOH) (18months) | < QL | < QL | < QL | < QL | 1.7 | 0.15 | < QL | < QL | 7.3 | < QL | < QL | < QL | < QL | < QL |

*QL = Quantification limit.
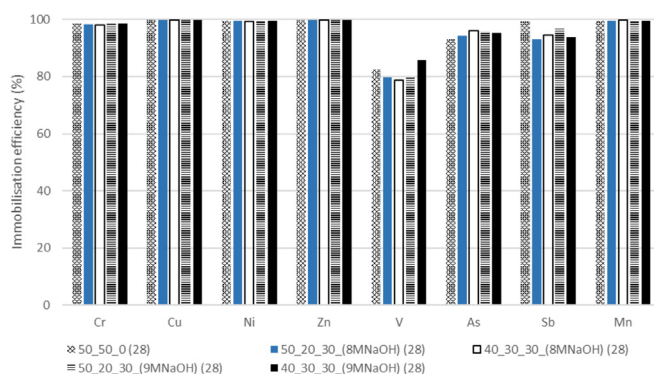


**Fig. 7.** The immobilisation efficiency of Cr, Cu, Ni, Pb, V, As, and Sb after 28d of curing.

leached amounts of Sb, B and V were increased after geopolymerization. The same trend in leaching results have been reported previously (Ahmari and Zhang, 2013b; Álvarez-Ayuso et al., 2008; Izquierdo et al., 2009; Pesonen et al., 2016; Yliniemi et al., 2015). The problematic behavior of Sb, As, B and V is due to the fact that these elements can form oxyanions and the higher leachability of these oxyanions is related to the alkaline conditions of the geopolymer gel. Oxyanions can have a negative oxidation state, and they cannot balance the negative charge of the geopolymer matrix. . In addition, there may occur an alkaline oxidation of arsenopyrite that releases arsenic from MT (Mesa Espitia and Lapidus, 2015), as represented by the equation (1).

$$2FeAsS + 100H^- + 7O_2 \leftrightarrow Fe_2O_3 + 2AsO_4^{3-} + 2SO_4 + 5H_2O \quad (1)$$
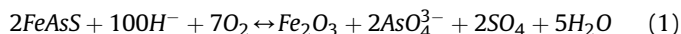
Even though the leaching amounts of As and V are higher after geopolymerization, a huge improvement between 7 and 28 days of curing can be seen. The immobilization efficiency for As after 28 days of curing was more than 93%; for V, it was more than 80%; and for Sb, it was more than 95%. In order to evaluate the long-term stability of geopolymers, the composition 40-30-30 activated with NaOH 8 and 9M was subjected to leaching test after 18 months of curing. Data reported in Table 4 show a very significant decrease of all the investigated elements. In particular also problematic elements such as V, Sb, As and B shows release values very low in line with the limits for a disposal in landfill for no dangerous wastes (0.2 mg/l for As and 0.07 mg/l for Sb from Tab 5 DM 03/08/2005 in Italy). These long-term data demonstrate that the geopolymeric matrix increases the consolidation degree with time. However, further studies are needed to understand the long-term behavior of

arsenic mine tailings in geopolymers in order to enable their practical use e.g. in urban construction or mine backfilling.

## 4. Conclusion

The aim of this study was to evaluate the possibility of inertizing gold mine tailings by reactive geopolymerization method, using different ratios of metakaolin and ground granulated blast furnace slag as a co-binder material. The leaching rates of the heavy metals and the main elements were analyzed after 7 and 28 days and 18 months of curing. According to the results, there is a possibility of stabilizing huge quantities of various elements from gold mine tailings by reactive geopolymerization. The immobilization efficiency was high for the main hazardous elements (Cr, Cu, Ni, Zn, and Mn), and it was improved with a longer curing period (28d). The problematic oxyanions (As, Sb, B, and V), after 18 months of curing show leaching values very low in line with the disposal in landfill for no dangerous wastes. These results are very important because confirm the improvement of the consolidation degree with time for the geopolimeric matrix. The immobilization efficiency after 7 and 28 days was relatively high (for As, > 93%; for V, > 80%; and for Sb, > 95%) when compared to the total concentration of those elements in the starting material.

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