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Alkali activation as new option for gold mine tailings inertization

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ABSTRACT

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