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Research paper

Potential of inorganic polymers (geopolymers) made of halloysite and volcanic glass for the immobilisation of tailings from gold extraction in Ecuador

E. Barrie [a], V. Cappuyns [b], E. Vassilieva [a], R. Adriaens [a], S. Hollanders [a], D. Garcés [c], C. Paredes [d], Y. Pontikes [e], J. Elsen [a], L. Machiels [e,*]

[a] *KU Leuven, Department of Earth and Environmental Sciences, Applied Geology and Mineralogy Research Group, Celestijnenlaan 200E, 3001 Leuven, Belgium*
[b] *KU Leuven, Faculty of Economics and Business, Campus Brussel, Warmoesberg 26, B-1000 Brussels, Belgium*
[c] *Escuela Superior Politécnica del Litoral (ESPOL), Facultad de Ingeniería en Ciencias de la Tierra (FICT-ESPOL), Campus Gustavo Galindo Velasco, Km 30.5 vía perimetral, Guayaquil, Ecuador*
[d] *Escuela Superior Politécnica del Litoral (ESPOL), Laboratorio de Ensayos de Materiales (LEMAT), Área de Materiales y Procesos de Transformación, Facultad de Ingeniería Mecánica y Ciencias de la Producción, Campus Gustavo Galindo Velasco, Km 30.5 vía perimetral, Guayaquil, Ecuador*
[e] *KU Leuven, Department of Materials Engineering, High Temperature Processes and Industrial Ecology Research Group, Kasteelpark Arenberg 44, 3001 Leuven, Belgium*

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ABSTRACT

In the present study, inorganic polymers (geopolymers) were synthesised using volcanic glass, calcined halloysite-rich clay and mine tailings, all from Ecuador. In addition to the possibility of making a geopolymer binder from these materials, the influence of geopolymerisation on the immobilisation of the mine tailings was investigated. The research focused on the effect of synthesis conditions on the strength, microstructure and composition of the geopolymer binder and on the leaching behaviour of heavy metals and Arsenic (As). A water insoluble material with a compressive strength of 30 MPa was synthesised using a Na-silicate activator (composition in wt.%, Na_2O: 15; SiO_2: 13; H_2O: 72) and using 110 kg of activating solution per tonne of raw material. It was shown that incorporation of mine tailings in the geopolymers did not have an effect on the mechanical properties. The production of geopolymer based tailing pastes thus shows potential for use on the mining site, for example as a capping material of tailing ponds. Geopolymerisation influences pH-dependent heavy metal leaching but does not cause a complete immobilisation of heavy metals and As. In general, the leaching of heavy metals is limited, below the regulatory concentrations for using the geopolymers in building materials. An exception on this are Cu and As, which show increased mobility due to the higher pH obtained in the geopolymerisation.

1. Introduction

Considerable volumes of residue resulting from the extraction and processing of minerals in mining and metallurgical operations are stock-piled at the site or stored in tailing ponds, where they remain typically for long periods of time after mining operations are closed down (Harrison et al., 2002). The very fine grain size of these tailings often results in particulate matter emissions. Commonly high concentrations of heavy metals and metalloids are present, which could possibly be mobilised and infiltrate in surface or ground water, which may lead to environmental problems. As the construction and monitoring of such tailing ponds represent a large investment during the mining process and during the post-closure phase of a mining operation, alternative treatment methods of tailings should be considered. In certain mining operations, tailings are blended with a binder such as ordinary Portland cement (OPC) in order to create a cemented paste backfill (CPB), alternatively named "tailing paste". Tailing pastes can be used to stabilise the tailings in the tailing basin or for ground stabilisation on the mining site (Kesimal et al., 2005). They can also be used as a back-fill in the open mine pit or in closed underground mine corridors to provide stability allowing further development of the mining site. The practice of using tailings in CPB is especially interesting in dry areas, as the fine tailings are affected by wind erosion. When toxic constituents or elements with higher levels of naturally occurring radioactivity are present in the tailings, it is also a common practice to stabilise the tailings in a solid form, by mixing with cement, rather than storing them in traditional water filled open tailing basins. It is expected that physical encapsulation of tailings by cement enhances the immobilisation of toxic constituents, as cement stabilisation limits water permeability and leaching. However, the suitability of using OPC in a mining site can be questioned, as OPC has a very low resistance to the acidic conditions

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* Corresponding author. Tel.: +32 494 91 86 49.
E-mail addresses: lieven.machiels@gmail.com, lieven.machiels@mtm.kuleuven.be (L. Machiels).

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which are common in certain mining environments. Many tailing deposits contain considerable amounts of residual sulphides that upon oxidation produce sulphuric acid, resulting in an acidification of pore water. This process is commonly referred to as acid mine drainage (Johnson and Hallberg, 2005) and can lead to pore waters with very low pH (pH ≅ 1), resulting in the dissolution of OPC and the possible leaching of heavy metals.

As an alternative to OPC, other binders could be used for the immobilisation and stabilisation of mine tailings. Different authors have proposed the use of inorganic polymers, often found in literature under the name "geopolymers", for the stabilisation of tailings. Geopolymers are synthetic alumino-silicate binders, which can be applied in a way similar to that of traditional OPC. Due to some particular advantages, such as high acid and sulphate resistance, high strength development and low permeability compared to OPC, geopolymers are of major interest for use on a mining site. The possibility of incorporating heavy metals in the geopolymer framework is also beneficial (Van Jaarsveld et al., 1999, 2000; Panias and Giannopoulo, 2007). Geopolymers are synthesised from reactive alumina- and silica-rich source materials and an alkaline activating solution (Davidovidts, 2011). This results in a series of chemical reactions (dissolution, speciation equilibrium, gelation, reorganisation and polymerisation) leading to the formation of an alkali-aluminosilicate gel (N-A-S-H gel) (Duxson et al., 2007; Li et al., 2010). This gel consists of an X-ray amorphous, three-dimensional network. In general, any reactive Al- and Si-rich material can be used for geopolymerisation, but the most commonly used source materials are kaolinite-rich clays, ground granulated blast furnace slag (GGBFS, a residue from steel production) and fly ash, a residue from coal combustion for electricity production (Majidi, 2009). By calcining kaolinite to metakaolin, an amorphous material is formed which is a highly reactive geopolymer precursor. Sodium hydroxide (NaOH), most commonly in combination with sodium silicate, is frequently used as the alkaline activating solution (Provis, 2009). This solution not only provides a high alkalinity, which improves dissolution of constituents for the polymerisation process, but the presence of cations such as K^+ and Na^+ is also necessary to compensate for the negative charge created by Al^{3+} in a four coordinated position (Van Jaarsveld et al., 1997; Pacheco-Torgal et al., 2007). An important advantage of developing geopolymer based tailing pastes compared to OPC based tailing pastes is the possibility of using waste materials or locally available raw materials such as calcined kaolinitic clays and volcanic ashes as the reactive source for silica or alumina. Dependent on their reactivity, metallurgical tailings can be used as an active component that contributes to the geopolymerisation reaction or as an inactive component (filler) in the geopolymer paste. Several authors previously reported the successful synthesis of geopolymers from calcined clay rich mine tailings (Van Jaarsveld et al., 1997; Panias and Giannopoulo, 2007; Ahmari and Zhang, 2013).

In the present study, tailings were sampled in the mining area of Zaruma, Provincia del Oro, in the Southern Andes of Ecuador. The Zaruma-Portovelo gold deposit is an epithermal vein deposit associated with Early Miocene continental volcanic arc magmatism (Vikentyev et al., 2005). The deposit is polymetallic, meaning that next to gold and silver substantial amounts of Pb, Cu and Zn as well as other elements are present. In 1999, the Portovelo-Zaruma mining district consisted of approximately 400 mines, 66 plants for crushing, grinding and amalgamation, and 80 cyanidation plants (SGAB-Prodeminca, 2000 in Tarras-Wahlberg et al., 2001). Metallurgical plants in this area are in general small scale operations and gold recovery occurs either artisanal through amalgamation or in small scale plants through lixiviation using cyanide. In most operations, only Au and Ag are recovered from the ore, while Pb, Cu and Zn and other constituents, such as Cd and As, are discarded with the residue. Fluvial contamination of Cd, As and Hg associated with artisanal and small-scale gold mining has been indicated in the area by various authors (e.g. Appleton et al., 2001; Tarras-Wahlberg et al., 2001).

In order to stabilise the tailings, we attempted to synthesise a geopolymer from Ecuadorian raw materials. Ecuador is situated on the active continental margin created by the subduction of the Farallon/Nazca plate underneath the South American Continental Plate and therefore nearly the whole Ecuadorian Andes is formed by volcanic rocks. Kaolinitic clays are commonly associated with hydrothermal alteration in porphyry-type gold deposits and are thus also commonly encountered close to areas where gold is mined. To conclude, a high amount of raw material is present to produce geopolymer cement. Limestone, the main raw material required to produce Portland cement, is unfortunately scarce in Ecuador (Longo and Baldock, 1982). Although official data is not available (Robalino-López et al., 2014), it is clear that this supply shortage, in combination with an increasing demand for cement, makes Ecuador largely dependent on import of cement (OPC) from other countries. The choice for using local raw materials to prepare geopolymers rather than using OPC thus becomes even more beneficial. The aim of this study was to synthesise a geopolymer using Ecuadorian raw materials and to contribute to a more effective tailing treatment. Local Ecuadorian raw materials, such as volcanic glass and calcined kaolinitic clay, were used to prepare tailing pastes aiming at an improved immobilisation of heavy metals present in the tailings. The research was focused on the effect of raw material and activating solution composition on strength, microstructure and geopolymer composition and leaching behaviour of heavy metals.

2. Materials and methods

2.1. Materials

Two natural raw materials, i.e. a volcanic glass and kaolinitic clay, as well as mine tailings were sampled in Ecuador. All samples were dried at a maximum temperature of 80 °C and stored in sealed bags after sampling. Mine tailings (MTs) were sampled at the processing plant of a gold mine in Zaruma (El Oro province, Ecuador) named SODIREC S.A. (from the BIRA S.A. Company) (Fig. 1). A fresh sample (approximately 5 kg), resulting from the gold lixiviation process was taken before the material was stored in the tailing pond. The sample was washed thoroughly to remove remaining cyanide from the gold extraction process. No further grain size reduction was performed (d_{50}: 22 μm).

To ensure that proper raw materials were used to prepare the geopolymer samples and as no existing quarries of volcanic glass and kaolinitic clay were identified in the area of Zaruma it was chosen to sample these raw materials at a larger distance. Volcanic glass (VG) was sampled in Latacunga (0° 56′ 53.16" S and 78° 37′ 31.05" W) and represents pyroclastic material of the Cotopaxi volcano. For geopolymer synthesis, the grain size of VG was reduced using a disk mill (Fritsch) followed by a centrifugal grinding mill (Retsch ZM 100, sieve size 500 μm and 80 μm) until a grain size d_{50}-value of 10 μm was obtained. A second type of raw material sampled was halloysite, a 1:1 layer lattice aluminosilicate clay mineral similar to kaolinite but characterised by an extra layer of water molecules (Grim, 1968). This sample was taken at the quarry 'Nudo de Tinajillas' on the road Cuenca-Loja, close to km 33. The sample was milled in a Retsch disk mill and sieved through a sieve with opening of 100 μm, resulting in a d_{50} − value of 23 μm. The particle size distribution curves of the milled and/or pretreated VG (volcanic glass), CL (calcined clay) and MT (mine tailing) as used to prepare the geopolymer samples are shown in Fig. 2. CEN standard sand (EN 196-1 conforming to ISO 679) was used as aggregates in the preparation of geopolymer mortar samples. For the activating solution a combination of sodium hydroxide (NaOH) and a sodium silicate solution was used in a 50:50 proportion (by weight). The NaOH (10 mol/l) solution was prepared by dissolving NaOH pellets overnight in distilled water in sealed plastic containers. For the sodium silicate solution, a commercial solution was used (SiO_2 25.5–28.5%, Na_2O 7.5–8.5%, density 1.345–1.382 g/ml). The resulting mixture of Na-silicate and NaOH had a