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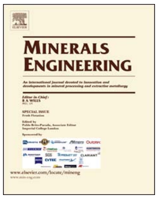

Lowering the water saturation level in cemented paste backfill mixtures – Effect on the release of arsenic

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ABSTRACT

The Cemented Paste Backfill (CPB) method allows the mixing of dewatered tailings slurries with cementitious binders to backfill excavated underground workings. After mine closure, CPB workings are permanently flooded by rising groundwater. This flooding is considered beneficial for reducing the risk of acid generation associated with CPB containing sulphide minerals. In general, CPB workings are slowly flooded and the process may lead to regions with a low degree of water saturation to form within the CPB. This in turn, may increase oxygen ingress in the CPB, thereby prolonging oxidation of the minerals. To investigate the environmental impact of this oxidation, tailings containing elevated concentrations of arsenic (As) and pyrrhotite were handled via CPB. In this study, CPB mixtures containing 1–3 wt.% of cementitious binders and tailings was studied. The water saturation level in the CPB-mixtures was lowered as curing time extended. In mimicked flooded conditions, the mobility of As in the CPB mixtures was correlated with As-bearing cementitious phases that are sensitive to a reduction in the pH. In CPB-mixtures with lower proportions of binders, cementitious As-phases dissolved while the water saturation level decreased to form more stable As-phases. Increasing binder fractions, most of the cementitious As-phases persisted in the CPB while water saturation levels were lowered and release of As increased. Regardless of curing conditions, managing these tailings via the CPB method yielded increased mobility of As compared with that in the unmodified tailings; this resulted possibly from the formation of less acid-tolerant As species.

1. Introduction

Arsenic (As) minerals (i.e. arsenopyrite and loellingite) are typical gold-bearing constituents in gold ore deposits. These minerals often co-occur with other sulphide minerals, such as pyrite and pyrrhotite. Gold encapsulated in these minerals is typically extracted by using cyanide. To increase the gold-extraction efficiency, an aeration step (addition of H_2O_2 and O_2) is added with the aim of oxidizing sulphide minerals to facilitate cyanide dissolution of gold (Mesa Espitia and Lapidus, 2015). The tailings slurry produced in this process must be treated to immobilize As before discharge at the storage facility (Kyle et al., 2012; Deschênes et al., 1998; Paktunc et al., 2004). The As in these slurries is usually immobilized by adding an iron sulphate salt that promotes the formation of iron arsenates (reaction (1)).

$$2H_3AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2FeAsO_4(s) + 3CaSO_4\cdot 2H_2O(s) + 6H_2O \quad (1)$$

However, As-species such as arseniosiderite and yukonite (Ca-Fe-Arsenates) could also form during the cyanide leaching process, due to the interaction of Ca-rich, alkaline solutions (by the addition of $Ca(OH)_2$) containing amorphous ferric arsenates (Paktunc et al., 2015). The stability of As in these precipitates varies with the pH. For example, under acidic conditions, the Fe-oxides dissolve and As is released, whereas As adsorbed on the surfaces of the oxides can be desorbed under alkaline conditions (Riveros et al., 2001).

Tailings are typically managed by using a cemented paste backfill (CPB). In CPB, tailings are dewatered, converted into a monolithic mass through the addition of low fractions (3–7%) of cementitious binders (i.e. cement and biofuel fly ash), and backfilled into underground mine cavities (Coussy et al., 2011; Benzaazoua et al., 1999, 2002). The resulting monoliths can enhance the geotechnical properties/mechanical strength of the surrounding rock, thereby increasing the amount of ore that can be excavated (Kesimal et al., 2005; Fall et al., 2007). In a CPB material, the physical strength of the monolith stems mainly from the formation of Calcium-Silicate-Hydrates (C-S-H) (Peyronnard and Benzaazoua, 2012). The strength of CPB materials is governed by the sulphide and sulphate content, curing time, as well as the type and

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fraction of binder material (Ercikdi et al., 2009; Kesimal et al., 2005; Benzaazoua et al., 2004a). Using CPB results in increased saturation levels in the material, and reduced availability of oxygen (Ouellet et al., 2006) and may therefore lead to a decrease in acid mine drainage (AMD).

Arsenopyrite and loellingite often co-occur with other sulphide minerals, such as pyrite and pyrrhotite. Pyrrhotite is a highly reactive sulphide mineral which generates acid upon contact with water and air (Belzile et al., 2004). If pyrrhotite is left in cyanidation tailings, further actions are needed to avoid acidic conditions and thereby preserve the stability of the iron arsenates. The oxidation of pyrrhotite in the CPB mixtures may contribute to the excessive release of sulphates in the leachates (reaction (2)) (Benzaazoua et al., 1999). In CPB mixtures based on tailings from a cyanide leaching process (CT), sulphates could also origin from the destruction of cyanide (INCO SO_2-air process) but also from the binder themselves. These sulphates react with the binders, thereby forming gypsum and ettringite (a sulphate attack; reactions (3) and (4)) that may generate cracks and increase the availability of oxygen in the CPB material (Ercikdi et al., 2009). This phenomenon is referred to as a sulphate attack (Benzaazoua et al., 1999; Kesimal et al., 2005), where the formation of expansive phases (such as gypsum and ettringite) may lead to decreased strength of the CPB material. In sulphidic CPB materials, the dissolution of these cementitious binders contributes to neutralization of the acidity generated from the oxidation of sulphides (reactions (2) and (3)).

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{2}$$

$$Ca(OH)_2 + 2SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^- \tag{3}$$

$$Ca_4Al_2(SO)_4 \cdot 12H_2O + 2SO_4^{2-} + 2Ca^{2+} + 20H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O \tag{4}$$

Previous studies have shown that CPB can immobilize As (Benzaazoua et al., 2004a; Coussy et al., 2011, 2012) in tailings. In these studies, cement based CPB:s were used, whereas As occurred as a primary mineral or as spiked As. In addition, 4–7 wt.% of binders yielded strengths of 0.5–1 MPa for CPB mixtures cured for 28–90 days. These times are considered sufficient for achieving the mechanical resistance needed in the mining operations (Benzaazoua et al., 2004a). Kesimal et al. (2005) showed that sulphate attack may lead to a > 50% decrease in the strength of a CPB material (binder fraction: 5 wt.%), subjected to curing times of > 1 year.

Hamberg et al. (2015) determined the effect of binder fraction (1–3 wt.%) on the mobility of As in cyanidation tailings containing As mainly as associated with Fe(III)-oxy-hydroxides. These tailings contained 2 wt.% of pyrrhotite, 1000 ppm of As and was mixed with binders (cement and biofuel fly ash) for the formation of a monolithic CPB mass. The CPB-mixtures were then exposed to a tank leaching test (TLT). In a TLT, the mixtures are submerged in a solution of deionized water to simulate an initial underground storage of a monolithic mass. Results from the TLT showed that more As is leached from the CPB materials than from the unmodified tailings. A decrease in the pH during TLT indicates that the sulphides in the CPB monoliths are oxidized. TLT results also indicated that As-release from the CPB materials can increase over time (Hamberg et al., 2015). However, in that study, As-behaviour of the materials was evaluated during flooding (by groundwater) after 31 days of curing under water-saturated conditions. Under complete water-saturated conditions, sulphide oxidation in these materials is obstructed and sulphates affecting the mechanical strength originate mainly from the initial tailings (pre-oxidized products) (Benzaazoua et al., 2004b). Under field conditions, groundwater rises very slowly and complete flooding of the CPB materials is achieved after long time (INAP, 2009). During the transition period, zones with low levels of water saturation could form at the CPB monoliths surfaces which in turn may increase the sulphide oxidation rate (Ouellet et al., 2006, 2003). An investigation of the geochemical stability of As in CPB materials cured under conditions of low water saturation is therefore essential. In this regard, the objectives of this study were to:

- Lower the water saturation level in CPB mixtures, and assess the mobility of As
- Evaluate the mobility of As in such CPB mixtures during an event of flooding

The aim of this investigation was to predict the post-mining water quality, to prevent acid generation and the occurrence of high As concentrations in mine drainage.

2. Material and methodology

Tailings were collected from a gold mine in the north of Sweden. Effluents from the cyanidation process are treated with the INCO SO_2-air process, H_2O_2, $Fe_2(SO_4)_3$ and lime to immobilize As and destroy toxic cyanides. Hydrogen peroxide (H_2O_2) and Oxygen gas (O_2) is added aiming to oxidize arsenopyrite and pyrrhotite to facilitate the cyanide dissolution of gold. The pH of the outlet water is restricted to 8–8.5. $Fe_2(SO_4)_3$ is added to the effluent in order to form iron arsenates. The content of fine material (< 20 µm in size) in tailings from Svartliden is about 19 wt.%. In the ore, gold occurred as inclusions in arsenopyrite. Portland cement (CE) and biofuel fly ash (FA) were used as cementitious binders in the preparation of various cemented paste mixtures. FA was obtained from a biofuel incineration plant located near the mine. The main elements and the corresponding content of the tailings, CE, and FA are shown in Tables 1 and 2. The content of $SiO_2 + Al_2O_3 + Fe_2O_3$ in FA is approx. 60 wt.%. In comparison with ashes from coal combustion, FA could be classified as a class C fly ash according to (ASTM C618-05). SEM-analyses suggested that arsenopyrite grains have iron-oxide-rims that could sequester arsenates (Hamberg et al., 2016). Hamberg et al. (2016) assessed the speciation of As in cyanidation tailings, using the modified sequential extraction scheme described by Dold (2003). The results suggested that most (~95%) of the As in the tailings is associated with Fe-(III)oxy-hydroxides (Hamberg et al., 2016). A small fraction (< 3%) of As is associated with the primary sulphide fraction corresponding to remnants of arsenopyrite.

XRD, sequential extractions, and SEM-EDS revealed that pyrrhotite and arsenopyrite are the main Fe- and As-sulphide minerals in tailings (Hamberg et al., 2016). Quartz is the main mineral in the studied tailings (approx. 80 wt.%). Other important minerals are Tremolite, Albite and Microcline that comprises for less than 5 wt.% each. Total element contents were determined by high resolution inductively coupled plasma–mass spectrometry (HR-ICP-MS).

Table 1

Oxide composition and total Sulfur-content (S_{tot}) weight (wt.)% in Tailings, Portland Cement (CE), and Biofuel fly ash (FA) (n = 3, ± SD) (DS = Dry solids).

Element	Unit	Tailings	FA	CE
Total solids (TS)	%	89.0 ± 0.4	95.2 ± 0.7	99.4 ± 0.0
SiO_2	wt.% of DS	55.0 ± 4.9	34.6 ± 1.3	20.6 ± 0.8
Al_2O_3	”	4.69 ± 0.04	10.7 ± 0.6	5.61 ± 0.45
CaO	”	4.83 ± 0.25	14.1 ± 1.0	50.3 ± 1.8
Fe_2O_3	”	16.7 ± 0.6	13.9 ± 1.0	2.81 ± 0.05
K_2O	”	0.92 ± 0.03	2.89 ± 0.08	0.83 ± 0.05
MgO	”	3.24 ± 0.01	2.54 ± 0.08	4.00 ± 0.17
MnO	”	0.14 ± 0.01	0.92 ± 0.03	0.10 ± 0.01
Na_2O	”	0.82 ± 0.03	1.24 ± 0.08	0.65 ± 0.07
P_2O_5	”	0.24 ± 0.01	2.25 ± 0.05	0.06 ± 0.00
TiO_2	”	0.18 ± 0.00	0.34 ± 0.01	0.42 ± 0.02
S_{tot}	”	2.10 ± 0.50	1.37 ± 0.02	1.00 ± 0.02