Cementation of cyanidation tailings – Effects on the release of As, Cu, Ni and Zn

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Abstract

Maintaining saturated conditions in two cemented paste backfill (CPB)-mixtures (1-3 wt.% of binders) based on cyanidation tailings was vital for reducing the pyrrhotite oxidation rate and the release of Cu, Ni and Zn. The opposite was true for As, that desorbed from Fe-precipitates and formed soluble Ca-arsenates. Flooding of CPB-fillings could be a long-term process, where unsaturated zones can form within CPB-masses. At this stage, leachates from CPBs (1 wt. %), became acidic, causing As-release to decrease but the opposite for Cu. In CPBs (3wt. %), As-release was unaltered but the Zn-release increased as binder-related Zn-phases dissolved in alkaline conditions.

Keywords: Tailings management, cement, trace metal leaching

Introduction

Cyanide-leaching is used when gold occurs as inclusions in sulfide minerals that might contain As, Cu, Ni and Zn. However, it is a common fact that mining processes are never 100 % effective and remnants of gold and sulfide minerals are always present in the cyanidation tailings (CT). So, effects of the sulfide oxidation or the oxidation itself must be obstructed to ensure the stability of As, Cu, Ni and Zn. Therefore, before further managing CT, it is critical to understand how the cyanide leaching process could affect the mobility of Cu, Ni, As and Zn. One way of managing CT is the use of a method called Cemented paste backfill (CPB). In CPB, low proportions (3-7 wt. %) of cementitious binders are mixed with CT to form a saturated, monolithic mass. CPB aims to reduce oxygen availability and the sulfide oxidation rate. Belie et al. (1996) suggested that a strength loss within a cement-stabilized material could cause the leachability of metals to increase. In a CPB-material, the formation of Calcium-Silicate-Hydrates (C-S-H) is the main contributor to the mechanical strength. Sulphates from the sulfide oxidation may react with the C-S-H, forming ettringite and gypsum (a sulphate attack), and cause a strength loss within the CPB. In some underground workings, strength of the CT-CPB-material is of less concern, but aims to enhance trace metals stability still exist. At completely saturated conditions in the CPB-materials, sulfide oxidation is obstructed and sulfates mainly supposed to be pre-oxidized products (Benzaazoua et al. 2004). In field conditions, extended time periods are expected for the groundwater table to rise and flood the CPB-materials. During that period of time, local desaturation in the CPB-monoliths is possible and this could increase the sulphide oxidation rate (Ouellet et al. 2006). It is therefore important to investigate the geochemical stability of As, Cu, Ni and Zn in CPB materials where unsaturated areas are present. For this reason, it is important to study: (1) how the cyanide leaching process and an associated water treatment affect the mobility of Cu, As, Ni and Zn in tailings, (2) how the use of a low-strength CPB affect leaching of As, Cu, Ni and Zn, (3) how does the establishment of unsaturated zones within low-strength CPB mixtures affect leaching of As, Cu, Ni and Zn?

Materials and Methods

Prior to cyanide leaching, an oxidation step is added to liberate the gold occurring as inclusions in arsenopyrite/pyrrhotite. In the oxidation step and the cyanide leaching process, pH is raised to 10-11 while oxygen is added. In an subsequent water treatment process, H_2O_2, $CuSO_4$ and lime (pH of 10) was added in order to detoxify residual cyanides. To immobilize the metal(oid)s, $Fe_2(SO_4)_3$ is then added until the pH of the cyanidation tailings (CT) slurries was reduced to 7-8.5 before deposition in the tailings dams, in accordance with legal guidelines. Binders used in CPBs were: Portland cement (CE) and biofuel fly ash (FA). Elemental compositions of ore, CT, CE and FA are presented in table 1. FA is classified as a class C fly ash according to (ASTM C618-05) as the content of SiO_2+Al_2O_3+Fe_2O_3 is approx. 60 wt. %. XRD and SEM-EDS revealed that pyrrhotite (1 wt. %) and arsenopyrite (0.1 wt. %) are the main Fe- and As-sulphide minerals. Arsenopyrite grains have iron-oxide-rims that could sequester arsenates. CT was considered to be acid-generating with a NNP of -60.8 kg $CaCO_3$/tonne, 20 % of CT have a particle size of less than 19.5 μm.

Speciation-solubility calculations were performed with the geochemical code PHREEQC. Element concentrations, redox-potential (Eh), and pH in leachates from the TLT and WCT were used.

Preparation of CT-CPB-mixtures

CPB-Mixtures were selected to have a strength of 200 kPa with a minimal proportion of binders. CPB-mixtures (CE and CE-FA) are based on CT; and consist of CE (1 wt.% of cement) and CE-FA (2 wt. % of cement, 1 wt. % of FA). CPB-mixtures of CE and CE-FA were cured for 31 days or 446 days, hereafter named CE31, CE446, CE-FA31 and CE-FA446. CE31 and CE-FA31 were kept in humid (85 % humidity), room tempered, dark conditions until the 31th day. CE446 and CE-FA446 were kept in dark, room temperatured conditions (approx. 50 % humidity) until the 446th day to facilitate the formation of unsaturated zones within the monoliths.

Sequential extraction test

Fractionation of Ca, S, Ni Zn, Cr and Cu was assessed using the modified sequential extraction scheme described by Dold (2003). CT, CE446 and CE-FA446 was used and extracted with five different solutions in succession. Overall details about the extraction procedure are presented in Hamberg et al., (2016).

Flooded monoliths – Tank leaching test (TLT)

TLT were conducted with CT, CE-FA31, CE-FA446, CE31 and CE446. Duplicate CPB-samples were removed from the bottles after 31 or 446 days. Granular CT and CE 446 (disintegrated) were placed in paper filter bags with 0.45 μm pores inside nylon sample holders. Water was exchanged and analyzed after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. Results were expressed in mg/m^2.

Weathering cell test

CT, CE31 and CE-FA31 (crushed) and approximately 70 g of the resulting material was placed on a paper filter in a Büchner-type funnel. Duplicate samples were then subjected to weekly cycles involving one day of leaching, three days of ambient air exposure, another day of leaching and finally two days of air exposure. The test was conducted over a period of 32 cycles (217 days). During cycles 13 - 18, 1M HCl was added to simulate the degeneration of cementitious phases within the CPB-materials.

Table 1. *Elemental composition and Paste-pH of Ore, CT, Fly ash and Cement*

	Unit	Ore	CT	Fly ash	Cement
As	mg/kg TS	4703 ± 781	1070 ± 30	124 ± 5	10.2 ± 0.2
Cu	" "	82.0 ± 12.1	147 ± 7	136 ± 10	86.2 ± 2.9
Ni	" "	126 ± 12	63.8 ± 2.1	114 ± 9	63.8 ± 1.3
Zn	" "	10.6 ± 1.5	25.0 ± 0.42	374 ± 10	149 ± 3
Paste-pH	-	N.D	5.03 ± 0.25	13.2 ± 0.6	12.7 ± 0.3

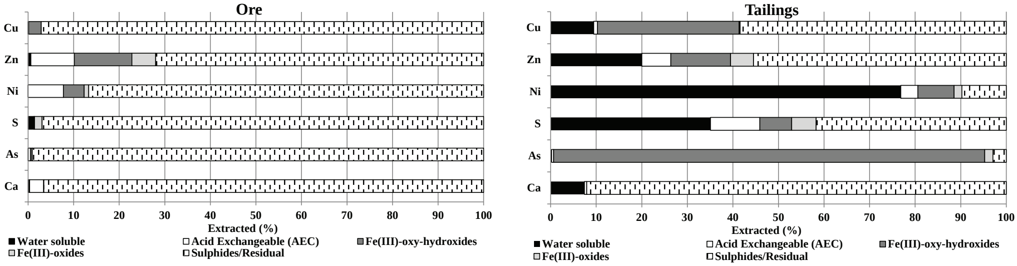

Fig. 1. Fractionation of Cu, Zn, Ni, S, As and Ca in CT and Ore.

pH-dependent leaching test

Duplicate samples from the outermost areas of CE-FA446 and CE446 were crushed into a pulverized material that was exposed to three HNO_3 concentrations. The pH ranged from 8 to ≈2.7 corresponding to the normal pH of CE446, CE-FA446 and CT, respectively.

Results and Discussion

A significant difference in fractionation is the higher proportion of water-soluble Cu, S, Ni and Zn in the CT compared to that in ore. Sulfides in the ore oxidized during the cyanidation process. Major proportions of sulfide-associated As and Cu was then re-sented as Arseniosiderite or in Cu- and As-bearing Fe-precipitates, mainly associated with amorphous Fe-precipitates in the water treatment process. These phases are stable at oxidizing environment at a pH of 4-8. Of Cu, Zn and Ni, Cu is most extensively removed from solution by adsorption onto ferrihydrite (Dzombak and Morell, 1990). In CT, this would explain why a larger proportion of Cu, compared to Zn and Ni, is associated with the Fe(III) oxy-hydroxide-fraction (Fig. 1). To ensure immobility of As, Cu, Ni and Zn in the further management of CT, maintaining neutral, oxidized conditions, is therefore of major importance.

Ferrihydrite in CT dissolved throughout the whole TLT, but Cu and As release was still low, even though pH decreased below 3.5 at the end of the TLT (Fig. 9). Diffusion in CT could have been hindered by the appearance of a Fe crust that are common in mine waste dumps cementing the pores and reducing metal release. Instead, a release of Cu, Ni, and Zn in CT was mainly governed by water soluble phases while an As-release was less abundant and governed by As(III)-species. In CE31 and CE-FA31, high water saturation levels were maintained to reduce the sulfide oxidation rate. But the evolution of pH (10-8) and Si, suggested that a sulfide oxidation has occurred to some extent, dissolving the cementitious phases. During the curing period, water-soluble species of Cu and Ni precipitated as hydroxides, and/or adsorbed onto Fe precipitates and C-S-H surfaces that were stable throughout the TLT releasing very small amounts of Ni and Cu. A Zn release from CE31 and CE-FA31 was amphoteric while greatest when pH > 8 and <10 and about tenfold higher than the release of Ni and Cu (but still lower than from CT). A release of Zn can also originate from the binders themselves. According to Lou et al. (2011) the Zn release from a class C fly ash (as in CE-FA31) is due to the dissolution of calcium aluminosilicate glass more soluble under alkaline conditions than acidic. The release of As was up to 18 times higher from CE31 and CE-FA31 compared to CT and greatest as the pH decreased from 10 (11) to 8 (Fig. 2). Alkaline conditions in CT-CPB leachates caused desorption of As(V) from the As-bearing Fe precipitates, while adsorption of As(V) is largely ineffective at pH≈10. As(V) released could then re-adsorb onto C-S-H-surfaces or form Ca arsenates, which dissolves readily as the pH drops below 10 (Benzaazoua et al. 2004).

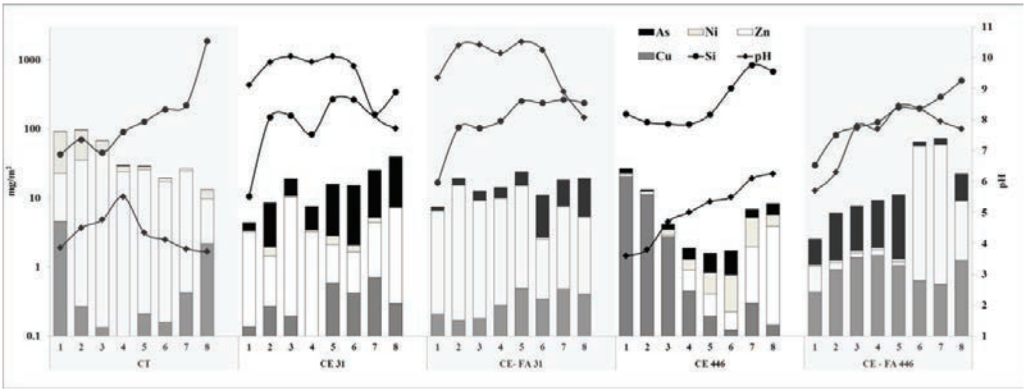

Fig. 2. Evolution of pH, Ferrihydrite, As, Cu, Ni, Si and Zn (in mg/m2) in CT, CE31, CE-FA31, CE446 and CE-FA446 during the TLT.

The establishment of unsaturated zones within the CT-CPB mixtures promoted sulfide oxidation and acidic conditions in the TLT leachates. During the formation of the CT-CPBs, the water-soluble fractions of Cu, Ni and Zn in the CT seemed to have been redistributed to less recalcitrant phases (AEC-fraction) (Fig. 3). The evolution of pH in the CT-CPB leachates during TLT suggested that a strength-loss has occurred, as the cementitious phases are highly soluble at pHs lower than 9. In CE446, a majority of the Cu release occurred as the Cu-bearing Fe precipitates dissolved and was greater than from CT, even though the water-soluble fraction of Cu was less for CE446 (Figs. 1, 3).

The Cu-fraction released under neutral conditions is higher compared to Zn and Ni (Fig. 4). As pH is lowered, this fraction can re-adsorb onto Fe-precipitates. These newly-formed Cu-Fe precipitates are, however, less stable in acidic conditions than those originally formed (Munk et al., 2002). This, in turn, probably resulted in a more abundant release of Cu from CE446 during the TLT than from CT. The amount of Zn released from CE-FA446 was twice that from CE-FA31, but more than a 10-fold higher compared to that in CE446 (Fig. 2). The evolution of pH and Zn could be explained with the variance of Zn species, and the water migration in the CT-CPB mixtures. However, less Zn was released from CE-FA31 compared to CE-FA446, despite the higher pH (in which Zn-bearing calcium aluminosilicate glass is more soluble) in the CE-FA31 leachates (Fig. 2). This might be due to increased water transport through the unsaturated CE-FA446 mixture. Ni release was low, irrespective of the water saturation level in the CT-CPBs. As the water saturation levels decreased, As release from CE-FA mixtures increased while the opposite was true for CE mixtures. Cementitious As-phases still existed for CE-FA446, releasing more As, while in CE446, the As release seems to have been governed mostly by As(III) species that are less attached to oxide surfaces.

During the WCT, the Ni-release exhibited a typical water-soluble-behaviour while most abundant initially and thereafter steeply decreased and diminished towards the end (Fig. 5). Towards the end, the molar ratios of Fe/S in CT leachates increased to ≈0.8, indicative of pyrrhotite oxidation occurring at a higher rate (Fig. 5). As pH was lowered to < 4, As- and Cu-release increased due to the destabilization of ferrihydrite and a more extensive sulfide oxidation. At this stage, Zn release was not pH-related, Fe release or the dissolution of ferrihydrite (Fig. 5). Instead, Zn release probably originated from Zn impurities in pyrrhotite. WCT:s was carried out using crushed CT-CPB-mixtures in an oxidized environment. Therefore, cementitious phases dissolved at a higher rate in the WCT compared to that in TLT (Fig. 5), followed by a rapid decrease in pH (from pH 11 or 10 to pH 8). In the CT-CPB-mixtures, the Ni-, Cu- and Zn-release were substantially lowered compared to that in CT. The opposite was true for the As-release (2-4 times greater) (Fig. 5). In the TLT-leachates, pH was main-

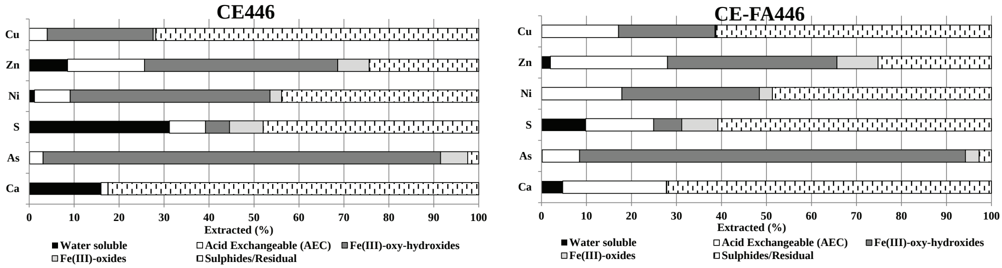

Fig. 3. *Fractionation of Cu, Zn, Ni, S, As and Ca in CE446 and CE-FA446.*

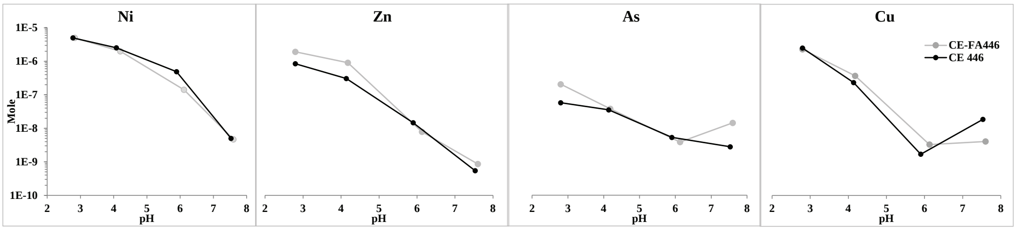

Fig. 4. *Evolution of As, Cu, Ni and Zn in CE446 and CE-FA446, during the pH-dependent leaching test*

tained at alkaline levels for a prolonged period compared to that in WCT due to a lower reactivity at water saturated conditions. This probably caused more As, Cu, Ni and Zn to desorb from Fe precipitates in the CT-CPB:s during the TLT compared to that in WCT. As acid was added to stimulate dissolution of the cementitious phases, the release of As, Ni, Cu and Zn increased in conjunction with Fe, and was more abundant from CE31 compared to CE-FA31 (Fig. 5). Large proportions of these elements were associated with amorphous Fe precipitates (Fig. 3).

This might explain a greater, Fe-related release of As, Cu, Ni and Zn from CE31 compared to CE-FA31, while the pH was slightly lower in CE31 leachates (Fig. 5). In the CT-CPB mixtures, Cu release seemed less affected by accelerated weathering, compared to Ni and Zn. That is because Cu being readily adsorbed to Fe precipitates at a pH of 4, whereas Ni and Zn remains in solution (Dzombak and Morel 1990).

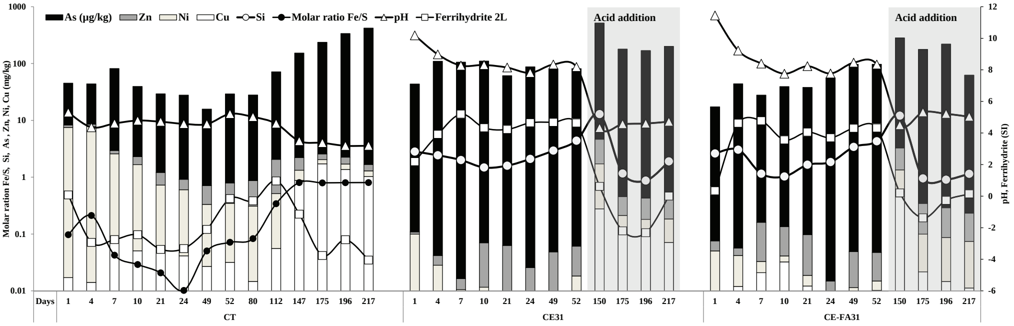

Fig. 5. *Evolution of pH, Fe/S-molar ratio, Ferrihydrite, As, Cu, Ni, Si and Zn in CT, CE31 and CE-FA31 (acid addition on days 70-150) during the WCT.*

Conclusions

In this study, CT used in the CPBs originates from a cyanide leaching process used to extract gold from inclusions in arsenopyrite and pyrrhotite. A significant proportion of sulfides oxidized during cyanidation, an addition of Fe-oxides seemed to have been insufficient to adsorb all the dissolved sulfide-related Cu, Zn and Ni. A significant proportion of Cu, Zn and Ni in the tailings were, therefore, water-soluble and could dissolve in mildly acidic conditions. A major proportion of As were associated with amorphous Fe-precipitates. Pyrrhotite and arsenopyrite still occurred in the tailings to a small extent, governing the acid generation and some of the As release. Managing the CT by a low strength CT-CPB-application decreased leaching of Ni and Zn. In water saturated conditions, the release of As was low from granular CT, in despite of acidic conditions, due to the formation of a enclosing Fe-oxide crust. In CT-CPB-mixtures, low amounts of Cu, Ni and Zn were released, due to desorption and dissolution of cementitious species. The dissolution of cementitious As-phases or Ca-arsenates caused the As-release to be a 10-18-fold higher in CT-CPB:s compared to that from CT. As the water saturation levels decreased within the CT-CPB mixtures, sulfide oxidation progressed more extensively and the release of Cu, Ni, and Zn increased from all of the CT-CPB mixtures. However, the Zn and Ni release was still lower compared to CT. In CE mixtures, Cu release increased and became greater compared to CT, due to a substantial proportion of acid-intolerant phases susceptible to remobilization in acidic conditions. Arsenic leaching increased compared to that from CT, regardless of binder proportion and water saturation level.

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References

Belie ND, Verselder HJ, Blaere BD, Nieuwenburg DK, Verschoore R, (1996). Influence of the cement-type on the resistance of concrete to feed acids. Cem Concr Res., 26 (1996), pp. 1717-1725).

Benzaazoua M, Fall M, Belem T, (2004). A contribution to understanding the hardening process of cemented pastefill. Miner Eng 17 (2), 141–152. doi:10.1016/j.mineng.2003.10.022.

Dold B, (2003). Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. J Geochem Explor 80 (1), 55–68.

Dzombak DA, Morel FMM, (1990). Surface Complexation Modelling: Hydrous Ferric Oxide. John Wiley and Sons, Toronto, Canada.

Li XD, Poon CS, Sun H, Lo IMC, Kirk, D, (2001). Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. J. Hazard Mater. 82 (3), 215–230. doi:10.1016/S0304-3894(00)00360-5.

Luo Y, Giammar DE, Huhmann BL, Catalano JG, (2011). Speciation of selenium, arsenic, and zinc in class C fly ash. Energ Fuel. 25(7), 2980-2987. 10.1021/ef2005496

Munk L, Faure G, Pride DE, Bigham JM, (2002). Sorption of trace metals to an aluminum precipitate in a stream receiving acid rock-drainage, Snake River, Summit County, Colorado. Appl Geochem 17, 421–430.

Ouellet S, Bussière B, Mbonimpa M, Benzaazoua M, Aubertin M, (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. Miner Eng. 19(5), 407–419. doi:10.1016/j.mineng.2005.10.006.