Delaying flooding of cemented paste backfill mixtures – Effect on the mobility of trace metals

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Abstract Flooding of cemented paste backfill (CPB) filled mine workings is, commonly, a slow process and its rate is important as a rapid flooding could limit sulphide oxidation and subsequent trace metal leaching. CPB-mixtures containing pyrrhotitic tailings with elevated concentrations of trace metals were flooded with different time delays. Delaying the flooding event increased trace metal leaching from CPB-mixtures, but except for copper, it was still lower compared to that in unmodified tailings. Regardless of time for flooding, sulphide oxidation in CPB-mixtures occurred, which poses an environmental risk, whereas a substantial proportion of trace metals was associated with acid-intolerant phases.

Key Words Cemented paste backfill, trace metals, flooding rate

Introduction

One way of managing tailings is by the use of a method called “cemented paste backfill” (CPB). In CPB, low proportions (3-7 wt %) of cementitious binders are mixed with tailings and backfilled into underground workings. Using CPB primarily aims to form a monolith that could act as a geotechnical support to underground mine cavities increasing operational benefits for the mining industry. But using CPB could also prevent air intrusion into tailings and thereby lower sulphide oxidation rate.

The immobilization of trace metals in CPB has been assigned to a combination of a physical encapsulation and chemical stabilisation. A physical encapsulation is largely dependent on the inherent strength of the CPB, which in turn is primarily due to the abundance of Calcium-Silicate-Hydrates (C-S-H) (Peyronnard and Benzaazoua, 2012). C-S-H is formed by the addition of calcium-rich binders that hydrate in solution. Factors governing the stability of C-S-H in a CPB are sulphide and sulphate content, curing time, and the type and proportion of binder material (Benzaazoua et al. 2004). Sulphide oxidation generates sulphates that dissolves the C-S-H (called a sulphate attack) forming expansive phases (i.e. gypsum and ettringite) that could reduce the inherent strength of the CPB. In sulphide-rich CPB-materials, dissolution of C-S-H contributes to neutralization of the acid formed by the oxidation of sulphides. The hydroxyl anions from this process could react with trace metals forming hydroxides that could adsorb onto C-S-H (i.e. Pb and Zn) or be encapsulated within the C-S-H-structure (i.e. Ni and Cr) (Chen et al. 2009). However, introducing highly alkaline conditions (by the release of OH^-) could also increase the mobility of some trace metals (i.e. Cr, Zn and Cu) (Kumpiene et al. 2008). Maintaining the stability of C-S-H is therefore of major importance concerning mobility of trace metals in the CPB.

Curing times of 28 to90 days have been considered to be sufficient to reach the mechanical strength needed in a CPB-application (Benzaazoua et al. 2004, Kesimal et al. 2005). In these studies, the CPBs are to be flooded directly upon curing. In CPB, maintaining a high grade of water saturation will prevent sulphide oxidation and subsequent sulphate attack on the C-S-H. In field conditions, a CPB is typically flooded when mine operations are closed and the groundwater level recovers. Flooding of CPB could take a long time, and unsaturated zones could form within the monolith (Ouellet et al. 2006). This in turn will increase the risk for more extensive sulphide oxidation to occur within the CPB. Studies have shown that the strength in a CPB-material can be reduced by more than 50 % when curing times are prolonged to > 1 year (Kesimal et al. 2005), especially in a sulphide-rich CPB. Cruz and Bertrand (2001) have shown that low proportions of binders could be insufficient to suppress the generation of acid mine drainage. Information on the mobility of trace metals and iron sulphide minerals in CPB is essential for prediction/management of the contaminant release over a extended period of time. It is therefore important to investigate the chemical stability of trace metals in CPB-materials where iron sulphides are occurring. The objectives of this study were to:

- Evaluate the leaching behavior of trace metals in CPB-mixtures
- Delaying a flooding event of CPB-mixtures for > 1 year and evaluate the effects on trace metal leaching

Results from this study may add knowledge about the preparation of CPB-mixtures for use in excavated areas where the recovery of groundwater levels is slow.

Materials and Methods

Tailings from a cyanide leaching process (CT) were collected from a tailings pond at a gold mine in the north of Sweden. In the cyanide leaching process, lime and $Fe(SO_4)_3$ were added for the immobilization of trace metals by co-precipitation, cyanide destruction and increasing pH in outlet water. The cementitious binders tested for the preparation of various CPB-mixtures were: Portland cement (CE) and biofuel fly ash (FA). The ash was provided from a biofuel incineration plant located nearby the mine site. Elemental compositions of tailings, CE and FA are presented in table 1. Pyrrhotite was the main Fe-sulphide in CT (1 wt. %).

Preparation of CT-CPB-mixtures

CPB-Mixtures were selected to have a minimum strength of 200 kPa with a minimal proportion of binders (Table 2 for proportions). CPB-mixtures (CE and CE-FA) are based on cyanidation tailings (CT); the compositions are presented in table 2. CPB-mixtures of CE and CE-FA were cured for 31days or 446 days, hereafter named CE31, CE446, CE-FA31 and CE-FA446. CE31 and CE-FA31 were kept in humid conditions (70 % humidity), at room temperature, in dark conditions until the 31th day of curing. CE446 and CE-FA446 were kept in dark, room temperature conditions during a period of 446 days.

Table 1 *Total element content of tailings, Fly ash, Cement (a selection of elements are presented) (average content, n=3)*

		CT	Fly ash	Cement
TS	%	89.0	95.2	99.4
SiO_2	% TS	55.0	34.6	20.6
Al_2O_3	% TS	4.69	10.7	5.61
CaO	% TS	4.83	14.1	50.3
Fe_2O_3	% TS	16.7	13.9	2.81
K_2O	% TS	0.92	2.89	0.83
MgO	% TS	3.24	2.54	4.00
Cu	mg/kg	147	136	86.2
Ni	mg/kg	63.8	114	63.8
Cr	mg/kg	166	132	98
S	mg/kg	20933	13700	9960
Zn	mg/kg	25.0	374	149

Table 2 *Composition of cemented paste backfill mixtures containing Cyanidation tailings (CT), Cement (CE) and/or Fly ash (FA)(values reported in weight %)*

Mixture	FA	CE	H_2O	CT
CE		1	26	73
CE – FA	1	2	26	71
CT			11	89

Mixing CE and FA with CT increased of the proportion of Ni and Zn in the CPB-mixtures (CE31, CE-FA 31, CE-FA446 and CE446) compared to that in the CT. The increase (in weight (wt.) %) is presented in table 3.

Table 3 *Additional proportion (%) of Ni and Zn from cement and biofuel fly ash in CPB-mixtures (CE, CE-FA)*

Mixture		CE	CE-FA
Zn	%	5.7	21.7
Ni	%	1.8	3.0

Sequential extraction test

Fractionation of Ca, S, Ni Zn, Cr and Cu was assessed using the modified sequential extraction scheme described by Dold (2003). In each extraction sequence, 2 g of tailings 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)

TLTs were conducted according to the Dutch standard EA NEN 7375:2004 on CT, CE-FA31, CE-FA446, CE31 and CE446. Duplicate samples were removed from the bottles after 31 or 446 days and shaped into regular cylinders. The overall experimental set-up is described in Hamberg et al. (2015). CE 446 were disintegrated and placed in paper filter bags with 0.45 µm pores inside nylon sample holders. Filter bags containing the disintegrated CE446 were changed on a weekly basis and were fully immersed in the water. Water was exchanged and analyzed after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. The mass transfer of Cu, Fe, S, Ca, Zn, Ni and Cr from CT and CT and CPB materials was calculated using equation (1), as specified in the EA NEN 7375:2004 standard:

$$M_{ti} = (Ci \times Vi) / A \qquad (1)$$

M_{ti} (in mg/m^2) is the mass of element released during leaching period i, Ci (mg/l) is the element concentration for period i, Vi (L) is the leachate volume for period i, and A is the specimen surface area exposed to the leachate (m^2).

Modelling – PHREEQC

Speciation-solubility calculations were performed with the geochemical code PHREEQC using the ThermoDem database (including the degradation of cement by a sulphate attack added by Soive et al. (2016)). Element concentrations, redox-potential (E_h) and pH in leachates from the TLT were used for this purpose.

Results and discussion

Evolution of the cementitious binders in CPB – effects of a delayed flooding

Ideally, cementation will reduce the open porosity and obstruct water percolation through the CPB-mixtures. Trace metal leaching would then dominantly occur by rinsing surfaces of the monoliths. This will lead to a release that is most abundant initially but diminishes towards the end of the TLT. However, if the cementitious phases dissolved, the permeability and release of trace metals may increase in the CPB-mixtures.

In this study, pyrrhotite oxidation occurred in all CPB-mixtures during the TLT, regardless of curing conditions, but most extensively in CE446 and CE-FA 446 whereas acidic conditions initially prevailed (Fig. 2). Cementitious phases are stable at pH > 9 (Benzaazoua et al. 2004). At the end of TLT, pH in each of the CPB-leachates was below 9. A dissolution of cementitious binders that reduces mechanical strength is therefore evident in all CPB-mixtures during the TLT (Fig. 2).CE446 was disintegrated during the curing period. According to Dold (2003), gypsum is readily dissolved, releasing Ca and S that is associated with the water soluble phase (Fig. 1). The low strength in CE446 is also reflected by a more abundant proportion of gypsum, represented by a higher proportion of water-soluble Ca and S, compared to that in CE-FA446 (Fig. 1).

Leaching behavior of Cu, Cr, Ni and Zn in CPB– effects of a delayed flooding

The addition of cementitious binders to CT has increased the proportion of Ni, Zn, Cu associated with the AEC- and amorphous Fe-oxide-fraction (FeO) (Fig. 1). Elements associated with the AEC- and FeO-fraction are bound to carbonate phases or Fe-oxides that are sensitive to pH-fluctuations. Fractionation of Cr was not different in CPB-mixtures compared to that in unmodified tailings. Cr-release was low and not significantly different in CPB-mixtures compared to that in CT (Fig. 1).

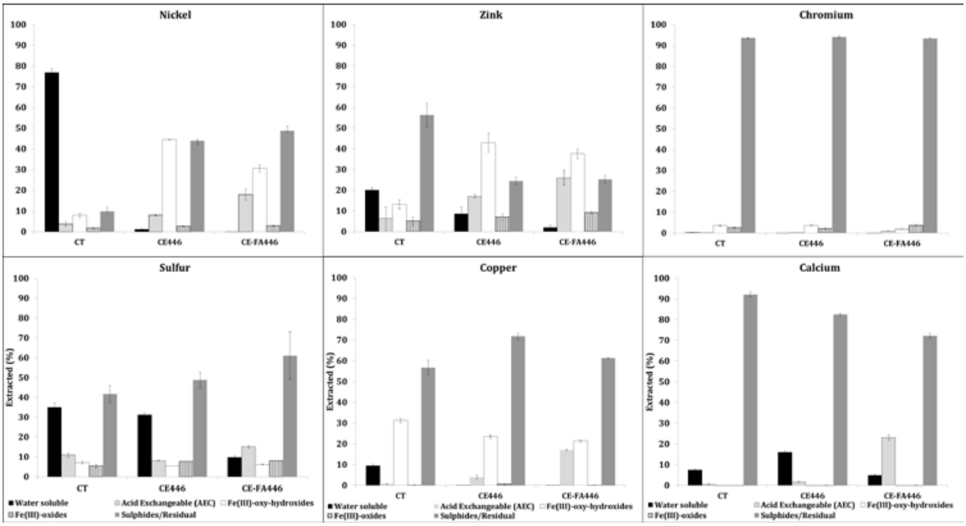

Figure 1 *Fractionation of Ni, Zn, Cr, Cu, S and Ca in CT, CE446 and CE-FA446, (n = 3, ± SD)*

In TLT, small deviations are observed for the duplicate tests of CT, CE 31, CE 446, CE-FA 31 and CE-FA 446; average values are therefore presented. Cu-release during TLT was lower in CE31, CE-FA31 and CE-FA446 compared to that from CT. Cu-release from CE446 was higher than that in CT, although the water soluble proportion of Cu in CT is most abundant in comparison (Fig. 1). In CE446, Cu-release followed Fe and could be caused by the dissolution of amorphous Fe-minerals (Fig. 3) generated by pyrrhotite oxidation in alkaline conditions. The mobility of Cu is strongly related to pH and decreases in alkaline conditions at pH<10, but could increase in extreme alkaline conditions, due to the formation of $Cu(OH)^-$ – complexes that have a low affinity for Fe-oxides (Kumpiene et al. 2008) and C-S-H-surfaces (Phenrat et al. 2005). In CT, Cu-release seemed pH-dependent and most pronounced as pH dropped to < 3 during the last extractions (Fig. 2). In CE31 and CE-FA31, Cu-release is probably due to the desorption of $Cu(OH)^-$ – complexes, which is more extensive in alkaline conditions (pH>10) but is lowered as pH drops to 8 (Fig. 2). Cu-release from CE-FA446 increases along with pH and stabilizes at a pH of 8.

Ni-release was most extensive from CT followed by that from CE446. The release of Ni and Cu had a similar pattern in all CPB-mixtures. In the case of CE31 and CE-FA31, Ni-release is related to desorption from Fe-oxides or C-S-H-surfaces. In CE-FA446 and CE446, Ni-release seemed related to the dissolution of amorphous Fe-minerals (Fig. 3) or pH-fluctuations. Ni-release could also originate from CE and FA, which is more abundant in Ni than CT (Table 3).

Zn-release is most abundant from CT, followed by CE-FA446, CE-FA31, CE31 and CE446 (Fig. 2). In CE31 and CE-FA31, Zn-release is most extensive as pH<8 or higher than 10. The mobility of Zn is probably governed by zinc hydroxides ($Zn(OH)_2$) that are amphoteric and released in both alkaline and acidic conditions but are generally stable at pH 8-10. The presence of anionic Zn-complexes in more alkaline conditions precludes their adsorption onto Fe-oxide-surfaces (Li et al. 2001). Concerning CE446 and CE-FA446, Zn-release increases along with pH as the cementitious phases are dissolving. Zn-release could also originate from CE and FA, which have higher Zn content than CT (Table 3). The results show that Zn-release in CT- and CPB-leachates was generally governed by the stability of $Zn(OH)_2$ and/or cementitious phases.

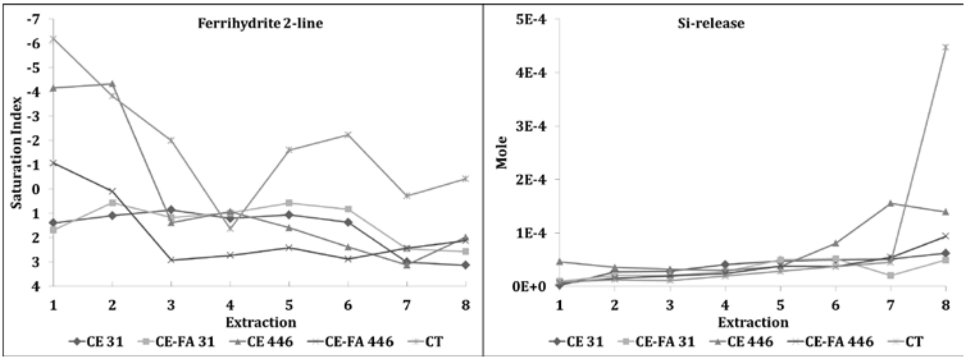

***Figure 2**: Si-release and saturation indexes of 2-L Ferrihydrite during TLT*

Cu- and Ni-release from the CPB-mixtures increased while the curing period was extended and water saturation levels decreased. That was not evident for the Zn-release, which is probably due to the dissolution of the binders (CE and FA), suggested by a release of Si (Fig. 2). The release of Zn was most abundant from CE-FA-mixtures which have a higher content of Zn compared to that in CE-mixtures.

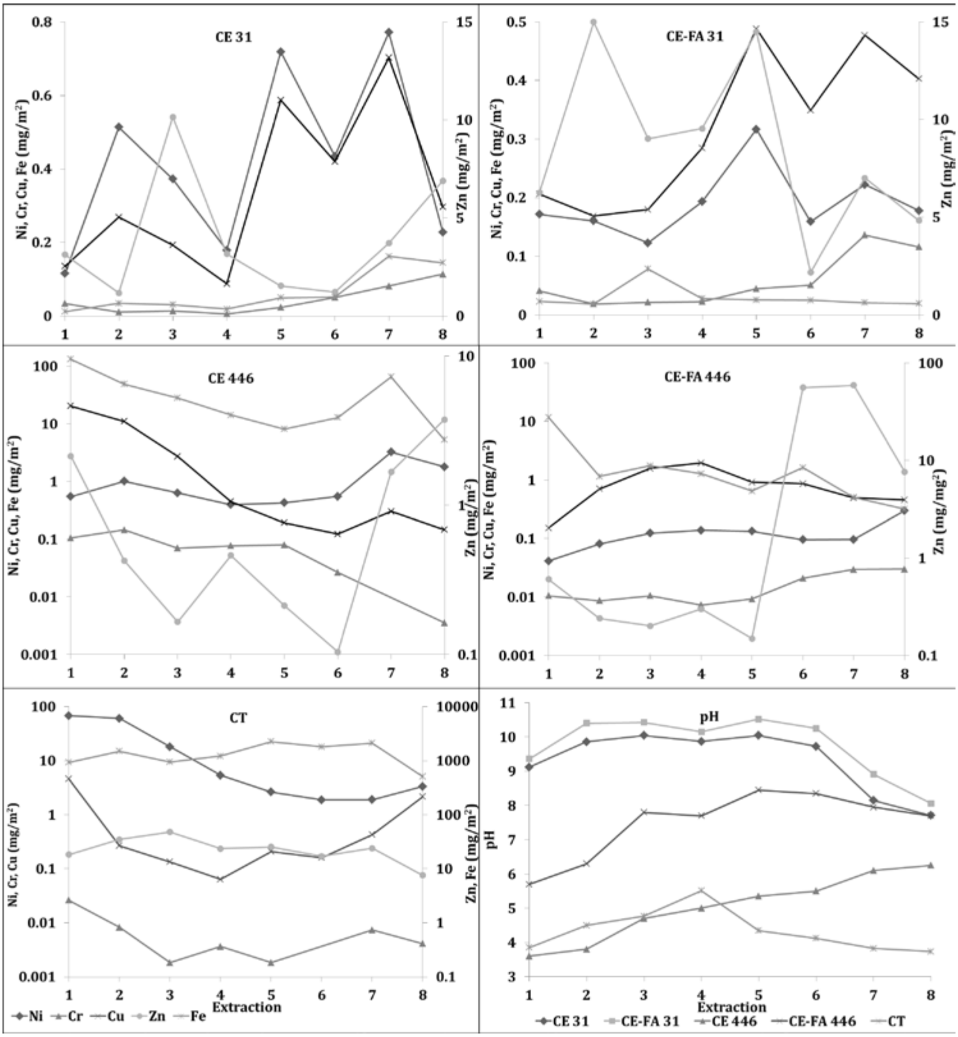

***Figure 2**: Release of Cu, Zn, Cr, Fe and Ni (in mg/m2), evolution of pH in leachates from CT, CE-FA31, CE31, CE-FA446 and CE446 during TLT (averaged values, n = 2).*

Conclusions

Leaching of Ni, Cr and Zn from the CPB-mixtures was lower, regardless of the delay to flooding, compared to that in unmodified tailings. Dealying the flooding event increased trace element leaching from the CPB-mixtures, especially forCu, which was more extensive compared to that in unmodified tailings. Ni, Zn, and Cu in the CPB-mixtures have been redistributed into less soluble phases compared to that in unmodified tailings. A substantial proportion of trace metals in the CPB-mixtures was associated with acid-intolerant phases and is susceptible to remobilization in acidic conditions. This suggests that flooding of CPB should occur rapidly to ensure the prevention of pyrrhotite oxidation and the immobility of trace metals.

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