Cementation of Cyanidation Tailings
– Effects on The Release of As, Cu, Ni and Zn

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Picture: Open pit at Svartliden gold mine, Sweden
Abstract

Knowledge about mineralogy and chemical composition in sulfidic tailings is essential to predict how tailings management may affect the future leachate quality. At a gold mine in the north of Sweden, gold was extracted from inclusions in arsenopyrite and pyrrhotite by the use of cyanide. Sulfides in the ore dissolved to a large extent during the cyanide leaching process causing sulfide-related elements such as As, Cu, Ni, and Zn to be mobilized to a various extent. In a subsequent water treatment process, a significant proportion of As and Cu was captured in secondary formed Fe-precipitates. Large proportions of water-soluble Ni- and Zn-species in tailings suggested that this treatment was insufficient to reduce the mobility of Ni and Zn. Maintaining oxidized, neutral conditions is of major importance for the immobility of As, Cu, Ni and Zn during further management of the cyanidation tailings (CT).

Part of the CT were planned to be managed in underground cavities by the use of a cemented paste backfill (CPB) -application. In CPB, a monolithic mass is formed as tailings are mixed with small proportions (4-7 weight %) of pozzolanic materials and backfilled into underground excavated areas. Using a CPB-application may decrease the sulphide oxidation rate, reducing exposure of mineral surfaces to oxygen and increasing water saturation levels within the material. In this study, CT was mixed with binders (1-3 wt. %) for the formation of a low-strength (0.2 Mpa) CT-CPB-mass. These mixtures were stored at moisturized conditions and subsequently subjected to oxidized and flooded conditions in a laboratory-based study. During short-term storing, high water saturation levels were preserved in the CT-CPB-mixtures, but, sulphide oxidation still progressed, and the release of Zn, Cu, and Ni was still lower compared to that in CT. The opposite was true for As, probably due to a desorption from Fe-precipitates. The desorbed As was subsequently incorporated into less acid-tolerant species (i.e. Ca-arsenates and As bonded to cementitious phases) in the CT-CPB:s, that readily dissolved and released more As compared to that in CT.

A complete flooding of CPB-filled workings may take a long time to be reached. During this transition period, zones with low levels of water saturation forms in the CPB-monoliths, which could increase the sulphide oxidation rate, lower pH and dissolve the cementitious binders. In this study, strength decreased along with the water saturation levels in the CPB-mixtures, due to a more extensive pyrrhotite oxidation. A minimal proportion (1 wt. %) of binders did not suppress Cu and As leaching during flooding, but Ni and Zn-leaching were still lower than from CT. In the CT-CPB:s, proportions of As, Cu, Ni and Zn associated with cementitious phases increased in tandem with the fraction of binders. Using higher binder proportions in the CPB, as water saturation levels were lowered, substantially increased the Zn-release while there was an insignificant change in the As-release, and substantially lower Cu- and Ni-release. Pyrrhotite oxidation proceeded in the CT-CPB-mixtures independent of water saturation level. So, increasing binder proportion in a CPB does not necessary mean that trace metals are more stabilized, due to the formation of acid-intolerant fractions. Results from this study, pinpoints the importance of having knowledge about trace element distribution and mineral assemblage in tailings before management methods are chosen and implemented.
List of articles


Additional related papers not included in the thesis:

Hamberg, R., Maurice C., Characterization of green liquor dredges for the remediation of mine waste. (2013), Project report, Cooperation, Luleå University of Technology and Processum, Ornsköldsvik (Only available in Swedish).


Hamberg, R., Alakangas, L., Maurice, C., Use of cemented paste backfill based on As-rich cyanidation tailings. Proceedings of the 10th on Acid rock drainage and IMWA annual conference. Santiago, Chile, April 21–24, 2015, 10pp.


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**Appended Papers**

**Paper I**  
The use of low binder proportions in cemented paste backfill:  
Effects on As-leaching

**Paper II**  
Release of arsenic from cyanidation tailings

**Paper III**  
Lowering the water saturation level in cemented paste backfill mixtures  
– effect on the release of arsenic.

**Paper IV**  
The formation of unsaturated zones within cemented paste backfill mixtures  
– Effects on the release of copper, nickel, and zinc
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1. Introduction and background

Mines can be located in settings of relatively unspoiled nature, which may contain ecologically sensitive areas and many important habitats. Mining operations can generate enormous amounts of waste (i.e. waste rock and tailings) that have to be managed and handled in a way that avoids negative environmental impact. Waste rock is a heterogeneous material that has to be removed to reach the ore. The ore is then removed, crushed and refined using various enrichment methods that extract the desired metal and/or mineral. Tailings is the residual material from the enrichment process and consist of a fine grained, silty slurry with a high water content.

Environmental concerns regarding base metal extraction in sulphidic mine ores

Base metals such as Copper (Cu), Nickel (Ni) and Zinc (Zn) are natural constituents of the bedrock and is can occur in sulfides such as chalcopyrite (CuFeS_2), pentlandite (Ni, Fe)_xS_y and Sphalerite (ZnS). It is common that Cu, Ni and Zn also occur as impurities in other sulfides such as pyrite and/or pyrrhotite (Janzen et al., 2000). A major environmental concern associated with the mining of sulfide ores is where these metals are associated with sulfide minerals that can oxidize and form acid mine drainage (AMD). AMD is formed when the sulfide mineral oxidizes in contact with air and water (reaction 1). The formation of AMD can pose a severe pollution problem, especially due to acidic conditions, high concentrations of potentially toxic dissolved metal(loid)s, and sulfates. The extent of sulfide oxidation is dependent on the abundance and type of the sulfide mineral but also on the surface area of the exposed mineral, which increases with smaller grain size. Under reducing alkaline conditions, these minerals are relatively stable and their natural dissolution is quite slow. However, once the ores have been ground, processed, and deposited in tailings facilities where they are exposed to air and water, their dissolution is significantly enhanced. Pyrite (FeS_2) is a common sulfide mineral that generates acid (H^+) upon oxidation (net reaction 1):

$$\text{FeS}_2 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (1)$$

Pyrrhotite oxidizes 20-100 times more rapidly than pyrite (Janzen et al., 2000) when it comes into contact with atmospheric oxygen and water (net reaction 2):

$$\text{Fe}(0.9)\text{S} + 2.175\text{O}_2 + 2.35\text{H}_2\text{O} \rightarrow 0.9\text{Fe(OH)}_3 + \text{SO}_4^{2-} + 2\text{H}^+ \quad (2)$$

In alkaline oxidizing conditions, oxidation of these sulfides is obstructed by the formation of a surface coating that usually contains different forms of iron oxides (hydroxides, oxyhydroxides) and sulfates (Asta et al., 2010; Pérez-López et al., 2007; Yin et al., 2000; Buckley and Woods, 1989; Malysia et al., 2004; Belzile et al., 2004). In these cases, the oxygen supply is restricted but not blocked, resulting in a reduction of the sulfide oxidation rate. Sulfide oxidation can continue despite this. Under oxidizing conditions of pH > 5,
oxidation of chalcopyrite and sphalerite occurs according to net reactions 3 and 4:

\[
\begin{align*}
\text{CuFeS}_2 + 4\text{O}_2 + 3\text{H}_2\text{O} & \rightarrow \text{Cu}^{2+} + \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (3) \\
\text{ZnS} + 2\text{O}_2 & \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \quad (4)
\end{align*}
\]

Under acidic (pH <4) conditions, the dominant oxidant is Fe$^{3+}$ rather than molecular oxygen. In such cases, sulfide oxidation produces more acidity (Blowes et al., 1998).

**Environmental concerns regarding gold extraction in sulphidic mine ores**

Gold can occur in its native form or as inclusions in sulphide minerals such as arsenopyrite, pyrrhotite and pyrite. Cyanide-leaching is a method used to extract gold occurring as inclusions in sulphide minerals that also might contain arsenic, copper, nickel and zinc. Cyanide is used exclusively to dissolve gold, but to increase the extraction efficiency; an oxidation step is often used to dissolve the gold-enclosing sulphide minerals. At this stage, gold is liberated from the sulphide minerals in order to be dissolved in a cyanide solution. A cyanide detoxification step is added to remove toxic cyanide species, before the tailings slurry is to be deposited. The most commonly used cyanide detoxification process is the INCO-process whereas cyanide is oxidized to less toxic cyanate (OCN$^-$) species as shown in reaction (5). The INCO-process utilizes SO$_2$ and O$_2$ in the presence of a soluble copper catalyst to oxidize cyanide to the less toxic compound cyanate (OCN$^-$).

\[
\text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} + \text{CN}^- \rightarrow \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+ \quad (\text{Cu}^{2+}, \text{added as a catalyst}) \quad (5)
\]

The INCO process may leave some small quantities of toxic cyanide in the treated material. It is therefore, sometimes followed up with copper-catalyzed hydrogen peroxide treatment to destroy these remaining cyanides oxidatively, as shown in reaction (6):

\[
\text{H}_2\text{O}_2 + \text{CN}^- \rightarrow \text{OCN}^- + \text{H}_2\text{O} \quad (\text{Cu}^{2+}, \text{added as a catalyst}) \quad (6)
\]

However, the oxidation step and the addition of hydrogen peroxide (H$_2$O$_2$) may also increase the oxidation rate of copper-, nickel- and zinc-sulfides. The slurries produced must therefore be treated before being discharged into tailings facilities. This is commonly addressed with a supplementary water treatment process where lime (Ca(OH)$_2$) and iron hydroxides (in the form of Fe$_3$(SO$_4$)$_2$) are added to the cyanide leaching slurries to raise pH and form stable metal hydroxides (reaction 7 and 12) and metal-bearing Fe-precipitates. In these cases, metals could adsorb onto the Fe-precipitate-(Fe(OH)$_3$)-surfaces or exchange for Fe in the Fe(OH)$_3$ structure (reaction 8).

\[
\begin{align*}
\text{Cu, Ni, Zn}^{2+} + \text{Ca(OH)}_2 & \rightarrow \text{Cu, Ni, Zn (OH)}_2 + \text{Ca}^{2+} \quad 7) \\
\text{Cu, Ni, Zn}^{2+} + \text{Fe}_3(\text{SO}_4)_2 & \rightarrow \text{Cu, Ni, Zn} \equiv \text{Fe(OH)}_3 \quad \text{(adsorption)} \\
\text{and/or Fe(Cu, Ni, Zn)(OH)}_3 & \quad \text{(co-precipitation)} \quad (8)
\end{align*}
\]
The oxidation of arsenopyrite in the ore generates As (III) and As(V) species. As (III) species less attached onto mineral surfaces. Oxidation of As(III) to As(V) is therefore a prerequisite for enhanced stability of As and must precede the co-precipitation step (net reaction 12).

$$\text{FeAsS}(s) + 4\text{H}_2\text{O} + 3\text{O}_2(\text{aq}) \rightarrow \text{Fe(OH)}_3(s) + \text{H}_3\text{AsO}_3(\text{aq}) + \text{SO}_4^{2-} + 2\text{H}^+ \quad (9)$$

The unloaded arsenite specie formed in reaction (9) can be oxidized as shown in reactions 10 and 11:

$$\text{H}_3\text{AsO}_3(\text{aq}) + 0.5\text{O}_2 \rightarrow \text{HAsO}_4^{2-} + 2\text{H}^+ \quad (10)$$

$$\text{H}_3\text{AsO}_3(\text{aq}) + 0.5\text{O}_2 \rightarrow \text{H}_2\text{AsO}_4^- + \text{H}^+ \quad (11)$$

$$2\text{H}_3\text{AsO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{FeAsO}_4(s) + 3\text{CaSO}_4(s) + 6\text{H}_2\text{O} \quad (12)$$

To be able to form a stable Fe-arsenate, As (V) must be the dominant As-specie; molar ratio Fe/As in the slurry must be more than 4/1 if pH is 4-7. If pH of the slurry is close to 10, more Fe must be added to get a stable Fe-arsenate; a Fe/As-molar ratio of 8/1 is then preferred (Riveros et al., 2001). If insufficient amounts of Fe are available, As could remain in solution and/or precipitate as a Ca-arsenate, which are more soluble than the Fe-arsenate. In a study of Paktunc et al., (2015), arsenosiderite and yukonite were suggested as probable As-minerals in CT. Yukonite is a highly soluble As-mineral while the pH-stability field of arsenosiderite overlaps that of As-bearing Fe precipitates (4-8) (Pactunc et al., 2015; Riveros et al., 2001). Metal(loid)-precipitates formed this way are generally stable in an oxidizing environment at a pH of 4-8. Therefore, reducing environments and acidic or alkaline conditions must be avoided to ensure the stability of Cu, As, Zn and Ni.

**Methods for containment of Cu, Ni, As and Zn in tailings from a cyanide leaching process**

In the remediation of mine waste there are generally three strategies that can be applied: (1) limiting the source for AMD (sulfide oxidation), (2) the collection and treatment of generated effluents or (3) reducing the amount of sulfides present in the tailings by mechanical removal (i.e. flotation). If AMD is generated in the mining process, treatment of the effluents is usually conducted with lime or CaCO$_3$. Most metals can be precipitated as hydroxides during neutralization (pH adjustment), commonly with addition of lime (Ca(OH)$_2$). Upon neutralization, aeration could transform reduced metals to oxidized forms to improve the recovery of metals as stable hydroxides. This process is often combined with the precipitation of Fe-precipitates that have a high affinity for metals in semi-neutral pH conditions. A most frequently-used method for metal immobilization is the oxidation of iron in conjunction with pH adjustment and metal precipitation (Bowell and Craw, 2014).
To reduce the amount of sulfides in the tailings, a method called desulphurization is often used, in which sulfides are removed by froth flotation (Benzaazoua et al., 2017). One way to limit the source of AMD in surficial tailings impoundments is by the use of a water or soil cover (dry or wet cover). The satisfactory function of these methods is based on the fact that the solubility and diffusion of oxygen is much lower in water than in air. A soil coverage, therefore, often contains a liner with low hydraulic conductivity reaching high waterlogging (Lottermoser, 2007). However, using these methods is not appropriate if the tailings are containing secondary metal-bearing Fe-precipitates. In that case, severe water logging can generate a reducing environment where these Fe-precipitates become unstable and releasing large amounts of metals. Consequently, other remediation options must be considered.

**Cemented paste backfill**

If tailings are to be managed and stored in underground workings, the use of a method called cemented paste backfill (CPB) is sometimes suggested. A paste is defined as dewatered tailings whereas no water could migrate from the material. In surficial tailings management facilities (TMF), the paste method is commonly used to reduce the hydraulic pressure in dam constructions, but also to reduce water consumption in mining processes. A CPB-application generally includes dewatered mine tailings mixed with a binder material. A common binder material used in CPB is cement. Typical water content of 20-25%; is used within a CPB-application, this water is required for paste transportation through a pipe networking. A CPB-material could be pumped if it contains more than 20wt. % solids with a particle size less than 20 μm (Landriault et al. 1998). In CPB-applications, a monolithic mass is formed as tailings are thickened (water content reduced), mixed with low proportions (3–7 weight %) of cement or other pozzolanic materials and backfilled into an underground excavated area (Fig. 1). A CPB is primarily used to enhance the geotechnical properties/mechanical strength of surrounding rock, increasing the amount of ore that could be excavated.

The C-S-H phase is considered to be a main contributor of the mechanical strength in a CPB-material (Peyronnard and Benzaazoua, 2012). C-S-H is formed as Ca-silicates are dissolved, and leads to the formation of Ca²⁺, H₂SiO₄²⁻ and OH⁻ (reaction 13). A C-S-H-phase is formed as Ca-silicates dissolved, and leads to the formation of Ca³⁺, H₂SiO₄²⁻ and OH⁻ (reaction 13). In the second stage, Ca, Si is reacts with water and hydroxide ions to form a C-S-H-phase (reaction 14):

\[
2\text{Ca}_3\text{SiO}_5 + 6\text{H}_2\text{O} \rightarrow 6\text{Ca}^{2+} + 8\text{OH}^- + 2\text{H}_2\text{SiO}_4^{2-} \quad (13)
\]

\[
3\text{Ca}^{2+} + 2\text{H}_2\text{SiO}_4^{2-} + 2\text{OH}^- + 2\text{H}_2\text{O} \Rightarrow \text{Ca}_3\text{H}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot32\text{H}_2\text{O} \quad (14)
\]

The environmental benefit of using a CPB application has been of little concern for the mining industry. However, in this case, such a method could prevent air intrusion into the tailings and thus lower the sulfide oxidation rate. The prevention of air intrusion is governed by the water saturation levels within the CPB-mixture and, at levels of
>85 %, oxygen migration is largely prevented (Yanful, 1993). In a CPB, trace metals such as Cu, Ni, As and Zn can be immobilized due to physical encapsulation and chemical stabilization (Chen et al., 2009; Paria and Yuet, 2006; Benzaazoua et al., 2004). A physical encapsulation is largely dependent on the amount and durability of the C-S-H that determines the inherent strength of the monolith. A chemical stabilization may occur as the hydroxyl anions from this process react with trace metals, causing the formation of metal-hydroxides. The stability of C-S-H in a CPB is governed by the sulfide and sulfate content, the curing time as well as the type and proportion of binder material (Ercikdi et al., 2009; Kesimal et al., 2005; Benzaazoua et al., 2004). The efficiency of a CPB to limit sulfide oxidation is therefore largely dependent on the C-S-Hs. The dissolution of portlandite contributes to the hardening of the CPB by the formation of C-S-H as Ca(OH)$_2$ reacts with silicic acid (H$_2$SiO$_4$) (CH + SH $\rightarrow$ C-S-H). But portlandite are also sensitive to a sulfate attack where Ca(OH)$_2$ reacts with sulfates, forming expansive phases such as gypsum and ettringite (reaction 15).

\[
\text{Ca(OH)}_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- \quad (15)
\]

This may cause cracks to form within the CPB material that increase oxygen migration into the monolith. Sulfates in a CPB may originate from sulfide oxidation, gypsum dissolution, the cyanide leaching process, and/or the binders. The effects of a sulfate attack can be reduced by the addition of fly ash replacing a part of the cement. An addition of fly ash can decrease the amount of Ca(OH)$_2$ formed in the CPB-material. Fly ash contains lower proportions of tri-calcium silicates, compared to that in cement, but higher amounts of di-calcium silicates (C$_2$S) phases. This exchange leads to the generation of less
amounts of calcium-hydrate that is sensitive to a sulfate attack (Ercikdi et al., 2009). In CPB materials, dissolution of C-S-H contributes to neutralization of the acid formed by the oxidation of sulfides (reactions 1 and 2). Alkaline cementitious phases neutralize the acidity from sulfide oxidation until exhaustion, at a pH < 9, all cementitious phases are consumed and the matrix consists solely of gypsum, ettringite, Fe or Al oxides (Coussy et al., 2011).

As large mines may produce millions of tonnes of tailings, the cost of the cement needed for CPB can be substantial, and many studies have therefore explored the scope for using alternative binders or otherwise minimizing the amount of cement used in CPB formation. Granulated blast furnace slag (GBFS) and biofuel fly ash (BFA) have successfully been used to partially replace cement in CPB due to their pozzolanic properties (Peyronnard and Benzaazoua, 2012). For a CPB to function as a remediation method, the water saturation level within the monolith must be maintained at high levels (more than 85 %) to obstruct oxygen ingress and thereby reduce the sulfide oxidation rate. This is conducted by a reaction rind containing gypsum and oxide-precipitates that are filling the pores within the CPB-monolith. The reaction rind is formed as the binders dissolve and functions as a diffusion barrier that maintains high water saturation levels within the CPB-monolith (Bowell and Craw, 2014). This decreases the sulfide oxidation rate, and prolongs the mechanical stability of the C-S-H.

**Background**

In Svartliden, gold is extracted from inclusions in arsenopyrite and pyrrhotite using a cyanide leaching process. Occasionally, in outlet process water, levels of As, Ni and Zn have exceeded threshold values. In the gold extraction process, prior to cyanide leaching, an oxidation step is added to liberate the gold occurring as inclusions in arsenopyrite/pyrrhotite. In the oxidation process, pH is raised to 10-11 while oxygen is added. In the subsequent cyanide leaching process, pH is kept at 10-11, to avoid the formation of hydrogen cyanide that easily volatilizes (Mosher and Figueroa, 1996). This in turn, could cause a loss of free cyanide ions (CN-) from the leaching solution and decreases the gold extraction efficiency (reaction 16).

$$4Au + 8CN^- + O_2 + 2 H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \quad (16)$$

After the gold has been dissolved and removed, the tailings slurries were treated with H$_2$O$_2$, CuSO$_4$ and lime (CaO) in order to immobilize heavy metals and detoxify residual cyanides. At this point, pH of the tailings slurry was set to 10-11. To immobilize the metal(oid)s, Fe$_2$(SO$_4$)$_3$ is then added (reaction 12 and 17) until the pH of the tailings slurries has been reduced to 7-8.5 (reaction 17) before deposition in the tailings dams, in accordance with legal guidelines (personal communication, Mattias Koot).

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \quad (17)$$
Overall, the cyanide leaching process and the supplementary water treatment process could have a large impact on the mobility of arsenic, copper, nickel and zinc. Alkaline and/or acidic conditions may cause desorption from the metal(loid)-bearing Fe precipitates or their dissolution (Moon and Peacock, 2012; Cornell and Schwertmann, 2003). Therefore, it is advantageous if the sulphide minerals are dissolved or otherwise removed during the cyanide-leaching process. However, a complete removal of sulfide minerals seldom happens, because it is a common fact that mining processes are never 100% effective and remnants of gold and sulfide minerals are always present in the end product (tailings). Where acid-generating sulfide minerals still exist after cyanide leaching, the effects of the sulphide oxidation or the oxidation itself must be prevented to ensure the stability of metal-bearing phases formed during the water treatment process. Before managing CT by the use of a CPB-application, it is critical to understand how the cyanide leaching process and a supplementary water treatment process could affect the mobility of Cu, Ni, As and Zn.

Previous studies by Ercikdi et al. (2009) and Peyronnard et al. (2010) have shown that using a CPB application could reduce AMD generation and contaminants release in sulfide-rich tailings. However, in these studies, binder proportions of < 3 wt.% were used in the CPB-applications. Highly alkaline conditions (resulting from C–S–H-dissolution and the subsequent release of OH−) could also increase the mobility of some trace metal(oids) (i.e., As) (Kumpiene et al., 2008). As the cementitious phases hydrates, pores within the CPBs are filled, high water saturation levels can be maintained, decreasing the oxygen ingress and the sulfide oxidation rate. Maintaining the C–S–H-structures intact is therefore of major importance for the immobility of trace metals in a CPB application. Before a CPB-application is chosen as a management method for sulfide rich tailings, it is vital to know how this could affect the mobility of trace metals.

As remediation methods are expected to withhold a good function for a long time, it is important to address the potential long-term performance of a CPB application. Underground mines become flooded by groundwater after mining processes have ceased, which is seen as a positive thing in respect of sulfide oxidation as the solubility of oxygen (which is the primary oxidation agent of sulphide minerals in a pH of > 4) is much lower in water than in air. However, in field conditions, the groundwater raising is a slow process and a complete flooding of the CPB-materials takes long time to be reached. During this transition period, zones with low levels of water saturation may form in

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**Fig. 2. Process schedule, Svartliden**

- **Preoxidation step:** O₂ and H₂O₂
- **Cyanide leaching step:** O₂ addition, pH 10-11
- **Detoxification step:** Fe₂(SO₄)₃, pH: 7-8.5
- **Co-precipitation step:** CuSO₄, pH: 10-11
- **Deposition in tailings dam**
the CPB monoliths, which in turn can increase the sulfide oxidation rate, lower the pH and destabilize the metal-bearing phases. A previous study by Kesimal et al. (2005) has shown that the strength within a sulfide-rich CPB material could decrease by more than 50% during prolonged (>1 year) periods of curing. The stability of the C-S-Hs must be guaranteed over a long time. It is, therefore, important to determine the effect of unsaturated conditions in CT-CPB mixtures on the leaching behavior of As, Ni, Zn, and Cu.

2. Scope and aims

The overall aim for this study was to gain knowledge about the mobility of As, Cu, Ni and Zn in tailings from a cyanide leaching process, and then address the following questions:

Could a low strength CPB (0.2 Mpa) be an environmentally acceptable option for managing tailings with elevated concentrations of Cu, As, Ni and Zn from a cyanide leaching process? These specific questions provide the focus of the thesis:

- How could a cyanide leaching process and the associated water treatment affect the mobility of Cu, As, Ni and Zn in tailings?

- How does the use of a low-strength CPB application affect leaching of As, Cu, Ni and Zn?

- How does the establishment of unsaturated zones within low-strength CPB mixtures affect leaching of As, Cu, Ni and Zn?

The results may contribute to knowledge about the preparation/management of CPB mixtures for use in underground mine workings.

3. Materials and methods

Tailings from a cyanide leaching process (CT) and grinded ore originating from the Svartliden Gold mine, Sweden were provided by the mining company Dragon Mining AB.

Materials

The ore was considered to be refractory because the gold occurred as inclusion in sulfide minerals. Fresh tailings were sampled at depths of 0-30 cm from ten different locations on the tailings dam and mixed to form a bulk sample of 15 kg. The weight of the crushed ore samples were approximately 3kg. The materials used for the CT-CPB mixtures were biofuel fly ash (FA) and ordinary cement (CE). CE was provided by Allmix AB in Trollhättan, Sweden. FA (ash from wood products), was provided by a fluidized bed combustion plant in Lycksele, Sweden. The ash was dry, having been collected directly after incineration.
Fig. 3. Svartliden mine in Sweden

Fig. 4. Tailings dam, Svartliden, Sweden
Preparation of CT-CPB mixtures

CT was managed by the use of a laboratory-based CPB application, where the required strength was set to 0.2 MPa by the mine operator. CT-CPB mixtures were designed with minimal additions of binders and involved 1-3 wt % of binders (CE and FA) (Paper II). The preparation of the CT-CPB mixtures is described in detail in Paper (II and III). A slump test was not conducted while only 15 kg of CT was available for analyses and experiments. Water contents in the CT-CPB mixtures were set to ~25 wt. % in order to make them pumpable in a pipe system. CT-CPB mixtures of CE and CE-FA were cured for 31 days or 446 days (named CE31, CE446, CE-FA31, and CE-FA446 hereafter). In this study, CT-CPB mixtures were stored at ~80% humidity until the 31st day (concerning CE31 and CE-FA31) and subsequently at ~60% humidity until the 446th day (concerning CE446 and CE-FA446). Until the 31st of curing, CT-CPB mixtures were stored in a container (with a perforated lid) containing water that maintained the humidity at high levels. During day 31 to 446, the container storing the CT-CPB mixtures was uncovered and drained. A curing period of 31 days was chosen based on the study of (Ercikdi et al., 2009) which suggested that the mechanical strength in CPBs with small proportions of binders develops along with the hydration of cement, which is nearly complete after approximately 30 days. Ouellet et al., (2006), showed that unsaturated zones could appear on CPB surfaces during underground storage. The reduction of the humidity levels and increase in the curing period in CE446 and CE-FA446 were carried out to enhance the formation of unsaturated zones. The curing period was terminated on the 446th day when brighter areas on the CPB surfaces indicated the formation of unsaturated zones. Mixtures of CE31, CE446, CE-FA31 and CE-FA446 underwent a tank leaching test (TLT) to evaluate the effects of a slow recovery of natural groundwater levels on the mobility of Cu, Ni, Zn and As.

Methods

Most of the methods used in this study are standardized, well-established and are described in detail in Papers I–IV. However, evaluating the release of As, Cu, Ni and Zn from a granular material (CT and CE446) using a tank leaching test (TLT) is not a standardized procedure. CT and CE446 were placed in paper filter bags (1μm) recessed in nylon filters before the TLT was carried out (Papers II–IV). The filter bags were replaced upon each leachate renewal. A TLT using granular CT was carried out to evaluate the effects of cementation on the mobility of Cu, Ni, Zn and As and to examine their behavior under simulated flooded conditions. The sequential leaching test was modified to include 2 grams of material instead of 1 gram. The purposes of these methods are briefly described in Table 1. The weathering cell test (WCT) was carried out over a period of 32 cycles (217 days). During cycles 13–18, acid was added to consume the buffering minerals within the CT-CPB materials and stimulate the formation of acid mine drainage (AMD). This was done to assess element leaching in response to the dissolution of the binders (Table 1).
4. Results

Results from an Acid-Base-Accounting (ABA) test and analyses of the particle size distribution of CT previously conducted in Hamberg (2014) are shown in table 2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) were carried out on ore, CT, fly ash and cement. CT and ore had low contents of sulphide-associated elements such as Cu, Ni, Pb and Zn. The As-content in the tailings was considerably higher in ore compared to that in the CT (Table 2). The opposite concerned for Cu and Zn. According to previous analysis (personal communication, Lars-Åke Lindahl, Dragon Mining AB), the As-content in the ore is highly variable (100–10 000 mg/kg). Results from the ABA-test suggested that CT could be considered acid-generating (~60.8 kg CaCO3/t). Compared with CT,
cement and fly ash contained higher total concentrations of Ni and Zn. An addition of CE increased the fraction of Ni by 1.8 %, in CE-mixtures compared to that in CT. The corresponding increase in CE-FA was 21.7 (Zn) and 3.0 % (Ni). CT could be pumped while the particle size distribution showed that close to 20wt. % solids had a particle size less than 20 μm. The fly ash can be classified as a class C fly ash according to (ASTM C618-05) (Table 2).

**Table 2. Results from ICP-AES-, ICP-MS-analyses of Ore, CT, Fly ash and Cement (n = 3, ± SD). Results from the ABA test, particle size distribution, (n = 3, ± SD) of CT**

<table>
<thead>
<tr>
<th>Unit</th>
<th>Ore</th>
<th>CT</th>
<th>Fly ash</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids (TS)</td>
<td>%</td>
<td>99.97 ± 0.06</td>
<td>89.0 ± 0.4</td>
<td>95.2 ± 0.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>% TS</td>
<td>30.3 ± 0.9</td>
<td>55.0 ± 4.9</td>
<td>34.6 ± 1.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&quot; &quot;</td>
<td>1.74 ± 0.07</td>
<td>4.69 ± 0.04</td>
<td>10.7 ± 0.6</td>
</tr>
<tr>
<td>CaO</td>
<td>&quot; &quot;</td>
<td>4.26 ± 0.09</td>
<td>4.83 ± 0.25</td>
<td>14.1 ± 1.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&quot; &quot;</td>
<td>12.6 ± 0.5</td>
<td>16.7 ± 0.6</td>
<td>13.9 ± 1.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>&quot; &quot;</td>
<td>0.32 ± 0.00</td>
<td>0.92 ± 0.03</td>
<td>2.89 ± 0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>&quot; &quot;</td>
<td>2.38 ± 0.07</td>
<td>3.24 ± 0.01</td>
<td>2.54 ± 0.08</td>
</tr>
<tr>
<td>As</td>
<td>mg/kgTS</td>
<td>4703 ± 781</td>
<td>1070 ± 30</td>
<td>124 ± 5</td>
</tr>
<tr>
<td>Cu</td>
<td>&quot; &quot;</td>
<td>82.0 ± 12.1</td>
<td>147 ± 7</td>
<td>136 ± 10</td>
</tr>
<tr>
<td>Ni</td>
<td>&quot; &quot;</td>
<td>126 ± 12</td>
<td>63.8 ± 2.1</td>
<td>114 ± 9</td>
</tr>
<tr>
<td>S</td>
<td>&quot; &quot;</td>
<td>25367 ± 2363</td>
<td>20933 ± 493</td>
<td>13700 ± 200</td>
</tr>
<tr>
<td>Zn</td>
<td>&quot; &quot;</td>
<td>10.6 ± 1.5</td>
<td>25.0 ± 0.42</td>
<td>374 ± 10</td>
</tr>
<tr>
<td>AP</td>
<td>N.D</td>
<td>65.3</td>
<td>N.D</td>
<td>N.D</td>
</tr>
<tr>
<td>NP</td>
<td>kg CaCO₃/t</td>
<td>&quot; &quot;</td>
<td>4.48 ± 1.31</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>NNP</td>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>-60.8 ± 1.32</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>D₂₀</td>
<td>μm</td>
<td>&quot; &quot;</td>
<td>20.0 ± 0.3</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>D₅₀</td>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>91.0 ± 2.7</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>D₉₀</td>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>195 ± 8</td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>

N.D: Not determined

**Mineralogical studies**

According to the X-ray diffraction (XRD) analyses (Paper I), the tailings mineral composition in Svartliden consisted of quartz (80 wt. %), tremolite (<5 wt.%), albite (<5 wt.%), microcline (<5 wt.%) and jarosite (KFe₃(SO₄)₂(OH)₆) (<5 wt.%). Analyses of scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (SEM-EDS) revealed that pyrrhotite (< 1 wt %) and arsenopyrite (< 0.1 wt.%) were the main Fe- and As-sulfide minerals in the CT (Paper I). No Cu-, Ni- or Zn-carrying minerals were found (Paper IV). Rims of hydrous ferric oxides (HFO) that could sequester arsenates were detected on arsenopyrite grains (Paper I).
Sequential extractions were carried out on tailings and ore samples in triplicate (Paper I). The fractionation of Ca, Fe, As, S, Ni, Zn and Cu in CT was compared to that in the ore. The results are summarized as relative abundances of Ca, Fe, As, S, Ni, Zn and Cu in the fractions:

- **Water-soluble fraction**: Ni > S > Zn > Cu > Ca > Fe = As. In comparison to those in the ore, large proportions of Ni (80 wt.%), S (35), Zn (20), Cu (10) and Ca (8) were evident. No change in As (0 wt.%) and Fe (0 wt.%) fractionation.

- **Acid exchangeable (AEC) fraction**: S > Zn > Ni > Cu = Fe = As = Ca. In comparison to the ore, minor/no changes (< 5 wt.%) of Zn, Ni, Cu, As, Fe and Ca. A small change in S (10) was evident.

- **Fe(III) oxyhydroxide fraction**: As > Fe = Cu > Zn > Ni = S > Ca. In comparison to the ore, there were large proportions of As (95), Fe (30) and Cu (30), a small proportion of S (10) and no changes in Zn, Ni and Ca.

- **Fe(III)oxide-fraction**: Zn = S = Fe > As > Ni > Cu = Ni. In comparison to the ore, overall small changes in fractionation.

- **Sulfide/residual fraction**: Ca > Fe > Cu > Zn > S > Ni > As. In comparison to the ore, minor proportions of As (3), Ni (10), S (40), Zn (55), Cu (60), Fe (65) were evident. Proportions of Ca were higher in CT compared to that in ore (95).

The most significant difference in fractionation is the higher proportion of water-soluble S, Ni and Zn in the CT compared to that in ore. The sulfide/residual fractions of these elements in the ore have been redistributed to less recalcitrant phases. Major proportions of sulfide-associated As and Cu have been redistributed to the Fe(III) oxyhydroxide phases (Fig. 5).
Sequential leaching test of CE446 and CE-FA446

Sequential extractions were conducted on CE446 and CE-FA446 samples in triplicate (Paper III and IV). Results are summarized as relative abundances of Ca, Fe, As, S, Ni, Zn and Cu in the fractions:

- **Water-soluble fraction:** In CE446, S > Ca > Zn > Ni > As = Fe = Cu. In CE-FA446, S > Ca > Zn > Ni = As = Fe = Cu.

- **Acid exchangeable (AEC) fraction:** In CE446, Zn > Ni > S > Ni > As > Ca = Fe = Cu. In CE-FA446, Ca = Zn > Cu = Ni > S > As > Fe.

- **Fe (III) oxyhydroxide fraction:** In CE446: As > Ni = Zn > Cu > Fe > S > Ca. In CE-FA446, As > Ni = Zn > Cu > Fe > S > Ca.

- **Fe(III)oxide-fraction:** In CE446: S > Zn > As > Ni = Fe > Cu = Ca. In CE-FA446: Zn = S > Fe > As = Ni > Cu = Ca.

- **Sulfide/Residual fraction:** In CE446: Ca > Fe > Cu > S > Ni > Zn > As. In CE-FA446: Fe > Ca > Cu = S > Ni > Zn > As

**Fig. 5.** Distributions of elements across different phases in tailings and unprocessed ore based on the results of sequential extraction tests (n = 3, averaged results shown)

**Sequential leaching test of CE446 and CE-FA446**

Sequential extractions were conducted on CE446 and CE-FA446 samples in triplicate (Paper III and IV). Results are summarized as relative abundances of Ca, Fe, As, S, Ni, Zn and Cu in the fractions:

- **Water-soluble fraction:** In CE446, S > Ca > Zn > Ni > As = Fe = Cu. In CE-FA446, S > Ca > Zn > Ni = As = Fe = Cu.

- **Acid exchangeable (AEC) fraction:** In CE446, Zn > Ni > S > Ni > As > Ca = Fe = Cu. In CE-FA446, Ca = Zn > Cu = Ni > S > As > Fe.

- **Fe (III) oxyhydroxide fraction:** In CE446: As > Ni = Zn > Cu > Fe > S > Ca. In CE-FA446, As > Ni = Zn > Cu > Fe > S > Ca.

- **Fe(III)oxide-fraction:** In CE446: S > Zn > As > Ni = Fe > Cu = Ca. In CE-FA446: Zn = S > Fe > As = Ni > Cu = Ca.

- **Sulfide/Residual fraction:** In CE446: Ca > Fe > Cu > S > Ni > Zn > As. In CE-FA446: Fe > Ca > Cu = S > Ni > Zn > As
The proportions of Ca, Fe, As, S, Ni, Zn and Cu in CE446 and CE-FA446 were compared to those in CT (Table 3). Overall, the most significant changes in the fractionation of the studied elements in the CT-CPB mixtures were the proportions of Ni, Cu and Zn associated with the water-soluble phase, being lower in the CT-CPBs compared to those in CT. These water-soluble elements were redistributed into less mobile phases, and most frequently to the AEC and Fe(III) oxyhydroxide phase. A small amount of As in CE-FA446 was redistributed from the Fe(III) oxyhydroxide phase to the AEC and Fe(III) oxide phase (Table 3).

Table 3. Changes in distribution of elements across different phases in crushed CT-CPB-mixtures (CE446 and CE-FA446) (CE-FA446-valuation within brackets) compared to those in CT based on the results of sequential extraction tests.

<table>
<thead>
<tr>
<th>Element</th>
<th>Water-soluble</th>
<th>Acid Exchangeable (AEC)</th>
<th>Fe(III) oxyhydroxides</th>
<th>Fe(III)-oxides</th>
<th>Sulfide/Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>+ (-)</td>
<td>sim (+ +)</td>
<td>sim (sim)</td>
<td>sim (sim)</td>
<td>- (-)</td>
</tr>
<tr>
<td>Fe</td>
<td>sim (sim)</td>
<td>sim (+)</td>
<td>- (-)</td>
<td>sim (sim)</td>
<td>+ (+)</td>
</tr>
<tr>
<td>As</td>
<td>sim (sim)</td>
<td>sim (+)</td>
<td>- (-)</td>
<td>+ (+) sim (sim)</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>sim (- -)</td>
<td>+ (+ +)</td>
<td>+ (+ +) sim (sim)</td>
<td>+ (+ +)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>- - (- - -)</td>
<td>+ (+ + +)</td>
<td>+ (+ +) sim (sim)</td>
<td>- - (- -)</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>- (- -)</td>
<td>+ + (+ + +)</td>
<td>+ + (+ +) sim (sim)</td>
<td>- (- -)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>- (-)</td>
<td>+ (+ + +)</td>
<td>- (-) sim (sim)</td>
<td>+ (sim)</td>
<td></td>
</tr>
</tbody>
</table>

sim: similar; +: < 100 % increase and/or < 5 % in total; + +: 100-500 % increase; + + +: > 500% increase; - : < 100 % decrease and/or < 5 % in total; - -: 100-500 % decrease; - - -: > 500% decrease

Weathering Cell Test (WCT)

The WCT on CT, CE31 and CE-FA31 exhibited good reproducibility with only small differences between runs; average values are therefore given. The cumulative release of Fe, As, Cu, Ni and Zn from CT was 1393, 1.5, 23.3 and 8.7 mg/kg, respectively (Fig. 6). The endpoint pH for CT was approx. 3.5. The Cu and As releases evolved in a similar way in CT and increased most extensively towards the end of the WCT, as the Fe/S molar ratio increased to 0.8 and the pH decreased below 4. The release of Ni and Zn in CT were less pH-dependent. Ni release was most abundant during the first few cycles but was almost zero thereafter whilst Zn release increased progressively throughout the WCT. In CT, the release of As, Cu, Fe and S increased alongside a pH decrease and a higher solubility of ferrihydrite. The release of Ni from CT showed water-soluble behavior while the Zn release increased gradually throughout the WCT (Fig. 6).

Initially in the WCT, the release of S, Fe, Ni, Cu and Zn from CE31 and CE-FA31 showed a pH-dependent behaviour and increased as pH decreased steeply during the first days of leaching. The As and Si release evolved in similar ways during this period. The cumulative release of Fe, Cu, Ni, S and Zn from the CT-CPB samples was lower compared to that from CT. Arsenic leaching from CE31 and CE-FA31 was more abundant compared
to that from CT in alkaline conditions. In alkaline conditions, the release of Ni, Zn, Si, Cu and Fe from the CT-CPBs was pH-dependent, but overall much lower compared to that from CT. The As release was more abundant than that from CT and increased gradually in alkaline conditions.

![Graphs showing the evolution of pH and cumulative release of Cu, Ni, Zn, Fe, S, Si, and As from CE31, CE-FA31 and CT over time during the WCT.](image)

**Fig. 6.** Evolution of pH and the cumulative release of Cu, Ni, Zn, Fe, S, Si and As from CE31, CE-FA31 and CT over time during the WCT (Average values shown, n = 2). Acid added on day 70–147.

Acid was added on days 70–147 to consume the buffering minerals in the crushed CT-CPB mixtures. Different amounts of acid were added to each CPB material (CE: 0.47 M H+/kg TS and CE-FA: 0.69 M H+/kg TS). The addition of acid lowered the pH to 4.5 in leachates from CE31 and CE-FA31. At this stage, leaching of Cu, As, Fe, Si and Zn from CE31 increased in conjunction with the Fe/S-molar ratio, the solubility of Ferrihydrite and a pH decrease (Figs. 6 and 7).
In CE-FA31, this pattern was only evident for the release of Zn and Si, as it was for the Ni release in CE31. The S-release in the CT-CPB:s was unaffected by the acid addition. During the acid addition, the Cu release was more extensive from CE-FA31 compared to that CE31, while the opposite was true for Fe. Overall, following the acid addition, the leaching of Cu, Ni, S, Si and Zn were lower in the CT-CPB:s compared to that in CT. This was especially evident for Ni that leached more than a 10-fold less from CE-FA31, compared to CT. Arsenic leaching from CE31 was more abundant compared to that in CT, during acidic conditions. The opposite was true for the As release from CE-FA31 (Fig. 6). During the acid addition, the release of As, Cu, Ni, Si, Fe and Zn increased while the S release was not significantly affected (Fig. 6).

**pH-dependent leaching test**

The pH-dependent leaching test of CE446 and CE-FA446 exhibited good reproducibility with only small differences between runs; average values are therefore given. The release of Ni and Zn increased in conjunction with a decrease in pH. Cu release reduced as pH decreased from 8 to 6, especially from CE446, as did the release of As from CE-FA446 (Fig. 8). The release of Ni and Zn increased along with a decrease in pH. This was not evident for the release of As and Cu, which was greater in semi-alkaline conditions compared to a pH of 6 (Fig. 8).
Tank leaching test

The As release was greatest from CE31 and increased along with Si due to diffusion-like behavior throughout the TLT. In CE-FA31 and CE-FA446, the As release was less but evolved in a similar way. The As release in CE446 and CT was lower compared to that from the other CT-CPBs and occurred through a surface wash-off effect. The initial release of As from CT and CE446 occurred along with the dissolution of ferrihydrite. Towards the end of the TLT, As release was almost zero in CT, but increased slightly in CE446. As release increased along with Si as pH increased in CE446 leachates towards the end of the TLT (Fig. 9). Molar ratios of Fe/S were higher in CT compared to those in CE-FA31, CE31, CE-FA446 and CE446 (Table 4). In CT, the molar ratio of Fe/S was highest initially during the TLT, reaching a value of ~0.1.

Table 4: Molar ratios of Fe/S and cumulative amounts of As, Cu, Ni and Zn (in mg/m²) released from CT, CE31, CE-FA31, 46 and CE-FA446 through the dominant leaching mechanism during TLT (Averaged values shown, n=2).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
<th>As</th>
<th>Molar ratio Fe/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT</td>
<td>8.0 DF</td>
<td>162 SW</td>
<td>199 SW</td>
<td>5.5 SW</td>
<td>0.01 – 0.1</td>
</tr>
<tr>
<td>CE 446</td>
<td>35 SW</td>
<td>8.6 SW</td>
<td>8.9 SW</td>
<td>12 SW</td>
<td>0.002 – 0.03</td>
</tr>
<tr>
<td>CE 31</td>
<td>2.7 DF</td>
<td>3.3 DF</td>
<td>31 DF</td>
<td>98 DF</td>
<td>0.001 – 0.003</td>
</tr>
<tr>
<td>CE-FA 446</td>
<td>7.7 DF</td>
<td>1.0 DF</td>
<td>124DS</td>
<td>62 DF</td>
<td>9E-5 – 0.003</td>
</tr>
<tr>
<td>CE-FA 31</td>
<td>2.5 DF</td>
<td>1.5 DF</td>
<td>68 DF</td>
<td>53 DF</td>
<td>5E-5 – 0.0001</td>
</tr>
</tbody>
</table>

SW: Surface wash-off, DF: Diffusion, DS: Dissolution
Cu release from CT occurred initially through a surface wash-off effect where surface-attached Cu was rinsed off the surface. The Cu release decreased steeply during the first days of extraction. However, it increased towards the end of the TLT in CT leachates, from which the dissolution of ferrihydrite increased as pH dropped below 4. The Cu release from CE31, CE-FA31 and CE-FA446, was stable throughout the TLT, not pH-dependent and lower compared to that from CT. The Cu release from CE446 was significantly higher compared to that from CT. The Cu release from CE446 was greatest initially during the TLT, and occurred along with the dissolution of ferrihydrite, when pH was ~4.5 (Fig. 9).

Fig. 9. Evolution of pH, Saturation Index (SI) of Ferrihydrite and release of As, Cu, Ni, Zn, and Si (in mg/m²) during the TLT. Averaged values shown, n = 2.
From CT, the Ni release occurred solely as a result of a surface wash-off effect, with the majority of Ni being rinsed off the surface of CT. The Ni release decreased steeply during the first days of extraction. From CE-FA31, CE31 and CE446, Ni-release was stable throughout the TLT, not pH-dependent and significantly lower compared to that from CT. The cumulative Zn release was higher from CT compared to that from the CT-CPB mixtures. The Zn release was more extensive from the CE-FA mixtures compared to that from the CE mixtures (Table 4). The release of Zn from CE-FA446 increased steeply between days 16 and 32, along with Si but decreased during the last extraction (Fig. 9).

The release of Ni and Cu evolved in a similar way in the CT-CPB mixtures (Fig. 9). The amounts of Ni and Cu released from CE-FA446 and CE-FA31 were similar, while there was a small increase in the Ni released from CE446 compared to that from CE31. In CE446 and CT, the release of Ni, Cu, and As was greatest initially at pH < 4.5, with a negative SI of Ferrihydrite suggesting dissolution. This pattern was not seen for CE-FA446, where the release of Ni, Cu and As increased initially and then stabilized. The Zn release from CE-FA31, CE31 and CE446 showed a similar pattern, that is, it increased initially and then stabilized. Again, this pattern was not seen in CE-FA446, where the Zn release increased steeply as pH exceeded 8 (Fig. 9).

5. Discussion

The cyanide leaching process and the associated water treatment - effects on the mobility of As, Cu, Ni and Zn in CT

According to Sciuba (2013), the major sulfide minerals in Svartliden consists of pyrrhotite (Fe\textsubscript{7}S\textsubscript{8}), arsenopyrite (FeAs\textsubscript{S}), traces of chalcopyrite (CuFeS\textsubscript{2}), pyrite (FeS\textsubscript{2}), and sphalerite (ZnS). In the detox-, pre-oxidation- and cyanide leaching process these sulfides are likely to have been oxidized, releasing various amounts of As, Cu, Ni and Zn into solution. Whether the stability of As, Cu, Ni and Zn have increased or not after the cyanidation process, and the associated water treatment process, is depending on the environment at the final storage. If a neutral pH and oxidized conditions could be maintained in the tailings storage; As-, Cu-, Ni- and Zn-bearing Ca (and/or Fe) precipitates are stabilized more efficiently compared to the sulphide species. If reducing conditions prevails, the opposite is true.

For As-removal, and Fe-arsenate-precipitation, Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} was added to the slurry before discharge onto the tailings dam. A highly variable As-content in the ore suggest that As-species with differed molar Fe/As-ratios could have formed during the water treatment process. Results from the sequential leaching tests suggested that a majority of the As-sulphides in the ore has been oxidized during the cyanide leaching process. Dissolved As in cyanide leaching process was then resented as Arseniosiderite or in As-bearing Fe-precipitates in the water treatment process. These phases could be associated with the Fe(III)-oxy-hydroxide-fraction (Parviainen et al., 2012). In Paper I, arsenates within HFO-rims onto arsenopyrite grains and was found in the tailings. The solubility of these phases increases at acidic, oxidized conditions. In reducing conditions, As in arsenopyrite is largely immobilized while the opposite prevails for As in As-bearing Fe-precipitates. However, a
majority (95 wt. %) of the total As in CT was associated with the Fe(III)-oxy-hydroxide-fraction (Fig. 5). So, the stability of As in tailings could therefore be controlled by the solubility of As-bearing Fe-precipitates and arseniosiderite. This suggests that reducing, acidic conditions should be avoided in the further management of CT, otherwise, large amounts of As could be released.

Results from sequential leaching tests suggested that a large proportion of Cu associated with the sulfide/residual fraction in the ore has been redirected to the water soluble- and Fe(III)-oxy-hydroxide-fraction. However, the water-soluble fraction of Cu could also originate from the addition of CuSO₄ in the cyanide detoxification process (reactions 5 and 6). Similar to As, Cu-sulphides in the ore have probably been oxidized during the cyanide leaching process and dissolved Cu was incorporated in newly-formed Fe precipitates in the tailings (Paper IV). This is likely since it has been known for a long time that Cu²⁺ bonds strongly to iron (hydr)oxides, such as ferrihydrite, at pH 4–8 (Benjamin and Leckie, 1981; Karapinar, 2016). Under conditions prevailing in the cyanide leaching process and the associated water treatment, Ni and Zn can also be incorporated into the structure of Fe(III) oxyhydroxide minerals (Gunsinger et al., 2006). Of Cu, Zn and Ni, Cu is most extensively removed from solution by adsorption onto ferrihydrite under pH-neutral, oxidizing conditions (Karapinar, 2016; Smith and Macalady, 1991). In CT, this would explain why a larger proportion of Cu, compared to Zn and Ni, is associated with the Fe(III) oxyhydroxide fraction (Fig. 5). The mobility of Cu has increased because of the cyanidation process and the associated water treatment process, in tandem with the proportion of Cu associated with the water-soluble phase. Maintaining neutral, oxidized conditions, in the further management of CT is therefore of major importance considering the immobility of Cu. In these conditions, the oxidation rate of chalcopyrite and solubility of Cu-bearing Fe-precipitates is low (Kimball et al., 2010).

The proportion of Ni and Zn associated with the water-soluble fraction was ~80 and ~20 wt.%, respectively (Fig. 5) and probably originated from the oxidation of sulfides during the cyanide leaching process (Paper IV). At best, the water-soluble fraction of these elements is small, otherwise large amounts of Cu, Ni and Zn would be released. In the water treatment process, there must be sufficient amounts of Fe precipitates for the adsorption of Ni, Cu and Zn (Lee et al., 2002). While Cu has a higher affinity for Fe-precipitate-surfaces, a large proportion of Ni and Zn could have remained in solution or precipitated as hydroxides (when lime (Ca(OH)₂) is added) during the water treatment phase (reaction 7). These species are probably represented by Ni and Zn hydroxides associated with the water-soluble phase and are soluble when pH<7 (Karapinar, 2016). As for Cu, the mobility of Ni and Zn increased because of the cyanidation process and the associated water treatment process. Large proportions of water soluble species must be detained in neutral, oxidized conditions, in the further management of CT.
Managing CT by the use of a CPB-method with low proportions of binders - effects on the leaching behavior of Cu, As, Ni and Zn

Leaching behavior - Flooded conditions

In CT, the Zn, Ni and Cu release was mostly due to water-soluble species that were rinsed off the surface in a wash-off process. The mobility of Cu, Zn and Ni is strongly related to pH and decreases in alkaline conditions, but could increase in extreme alkaline conditions due to the formation of negatively charged complexes that have a low affinity for Fe (oxy)hydroxides (Kumpiene et al., 2008). In CT, the pH of the leachates was in the range 3.5–5, and the release of Cu was less than that of Ni and Zn because Cu binds more strongly to Fe precipitates, compared to Ni and Zn. Low (~0.1, Table 4) Fe/S ratios in the CT leachates could be an indicator of a low Cu and As sulfide oxidation rate, which prevents the oxidation-produced As and Cu sulfides becoming the main contributors for Cu and As release. Instead, modelling has suggested that the majority of the As release could be due to leaching of unloaded As(III) species (Table 5) that are less attached to mineral surfaces (Jain et al., 1999). The unloaded arsenite (As(III)) species form during arsenopyrite oxidation in reaction (9) and may be oxidized over days or months to As(V) (Paper I). Ferrihydrite (a Cu and As bearing Fe (oxy)hydroxide) 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. Such iron crusts are common in mine waste dumps cementing the pores and reducing metal release (Valente et al., 2012). This suggested that sulfide oxidation is not to be considered as a source for the As, Cu, Ni and Zn 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.

Maintaining high water saturation levels is of major importance to reduce the sulfide oxidation rate within CT-CPB-mixtures. But the evolution of pH and Si in the leachates from CE31 and CE-FA31, suggested that a sulfide oxidation has occurred to some extent, dissolving the cementitious phases. Trace metal immobilization in CPB has been attributed to a combination of physical encapsulation and chemical stabilization (Chen et al., 2009; Paria and Yuet, 2006; Cornelis et al., 2008). In that way, there is a apparent connection between the stability of C-S-H and the release of metals. In a CPB, porosity decreases by the formation of gypsum and a hydration of cementitious phases filling the pores (Belem et al., 2001). This in turn, reduces permeability and could lead to the formation of a diffusion barrier. If the CPB remains intact, maintaining high water saturation levels, a metal release would then be controlled by a wash-off effect whereas metals are rinsed from the surface (Bowell, 2014) followed by a diminished metal-release. Otherwise, metal release could be governed by diffusion and dissolution processes, increase with time or even continue until depletion. In CE31 and CE-FA31, a C-S-H formation (reactions 13 and 14) increased the pore water pH to alkaline levels where water-soluble species of Cu and Ni to precipitated as hydroxides, and/or adsorbed onto Fe precipitates and C-S-H surfaces (Li et al., 2001). These phases were stable throughout the TLT when very small amounts of Ni and Cu were released. In CE31 and CE-FA31, the release of Cu and Ni evolved in a similar way and was largely immobilized compared to CT (Fig. 9).
A Zn release from CE31 and CE-FA31 was greatest when pH<10 and about ten-fold higher compared to the release of Ni and Cu (but still lower than from CT). During the TLT, the pH in leachates from CE31 and CE-FA31 was 8–11, and Zn\(^{2+}\) and HZnO\(^{-}\) were the dominant species, as predicted by modeling (Table 5). A Zn release from CE31 and CE-FA31 could therefore have an amphoteric leaching pattern (Kumpiene et al., 2008), governed by dissolution of Zn hydroxides and/or desorption of HZnO\(^{-}\). A release of Zn could also originate from the binders themselves, as they are more abundant in Zn compared to CT (Table 2). According to Lou et al., (2011) the Zn release from a class C fly ash (as in CE-FA31) could be governed by the dissolution of calcium aluminosilicate glass that is more soluble under alkaline conditions than acidic. In that case, desorption is not expected to govern the release of Zn from CE-FA31. In cement, Zincate (Zn(OH)\(_4\))\(^{2-}\) ions are the dominant Zn species, according to Tsuyumoto and Uchikawa (2004). These ions could be incorporated in the C-S-H-structure, and released due to desorption and the dissolution of the cementitious phases. Another reason for the evolution of the release of Zn could be water migration through the CT-CPB mixtures. At the beginning of the TLT, a Zn release from CE-FA31 and CE31 occurred due to a wash-off effect but, as a reaction rind formed, water migration was obstructed and Zn release decreased. This reaction rind within the CE31 and CE-FA31 probably did not hinder water migration through the mixtures efficiently, as indicated by an increasing Si release towards the end of the TLT. This caused the Zn release to remain the same or even increase towards the end of the TLT (as in CE31) (Fig. 7). The Zn release from CE-FA31 was more than ten-fold higher than from CE31 (Table 5), but still lower compared to CT. So, in CE31 and CE-FA31, the Zn release could be governed by desorption of negatively charged Zn ions and an abundance of calcium aluminosilicate glass, respectively.

The release of As was up to 18 times higher (Fig. 9) from CE31 and CE-FA31 compared to CT and greatest as the pH decreased from 10 to 8. The oxidation rate of arsenopyrite is higher in alkaline conditions than in neutral ones (Yu et al., 2007) but, as Benzaazoua et al. (2004) stipulated, arsenopyrite quickly becomes passivated in a cementitious environment. Instead, 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 (Roddick-Lanzilotta et al., 2002). As(V) released in alkaline conditions could then adsorb onto C-S-H-surfaces or form Ca arsenates, as previously suggested by Cornelis et al. (2008) and Benzaazoua et al. (2004). However, these phases are sensitive to a drop in pH, when the surfaces of C-S-H become negatively charged (Cornelis et al., 2008) and Ca arsenates dissolve readily as the pH drops below 10 (Benzaazoua et al., 2004). From the evolution of As release from the CT-CPB, it seems that these phases could govern the mobility of As. In the CT-CPB mixtures, almost twice as much As was released from CE31 compared to CE-FA31. These As-phases are probably associated with the AEC-fraction (Pantuzzo and Ciminelli, 2010). Coursy et al., (2012) suggested a relation Si-As-release from CPB-mixtures, meaning that As are released from being trapped in the cementitious matrix. This is also seen in Paper (II) whereas the evolution of As- and Si-release was similar from CE-FA31 and CE31 during the TLT. Fly ash-based (Class C) CPB is not suitable for the stabilization of As, but increasing amounts of lime could have a stabilizing effect on As in CPB mixtures. Another reason for this to happen could be that, in cement-stabilized materials, leachability is reduced along with permeability and porosity, both
of which are connected with mechanical strength (Belie et al., 1996). It is well known that fly ash increases the sulfate resistance and hence the strength-durability of a CPB (Chindaprasirt et al., 2004). The CE mixtures only contain low (1 wt.%) proportions of cement, and therefore have a small sulfate resistance compared to CE-FA mixtures. The mechanical strength can be reduced at a higher grade in CE31, and hence, the As release can be greater. Results from the TLT suggested that the function of the CT-CPBs was not satisfactory when the As release was governed by diffusion and seemed to increase, even after 64 days (Fig. 9 and Table 4). The As release from CE31 and CE-FA31 increased, compared to that from CT, due to the dissolution of less acid-tolerant As species and instability of the cementitious matrix.

Table 5. Dominating species of As, Cu, Ni, Zn and Fe in leachates from CT, CE31, CE446, CE-FA31 and CE-FA446 during the TLT.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT</td>
<td>u, u, u, u, u, u</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
</tr>
<tr>
<td>CE31</td>
<td>- overall</td>
<td>- overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>- overall</td>
</tr>
<tr>
<td>CE446</td>
<td>u, u, u, u, u, u</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
</tr>
<tr>
<td>CE-FA31</td>
<td>- overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>- overall</td>
</tr>
<tr>
<td>CE-FA446</td>
<td>- overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>+ overall</td>
<td>- overall</td>
</tr>
</tbody>
</table>

*: anionic species; +: cationic species, u: unloaded As(III) species, overall: during all extractions

In CE31 and CE-FA31, the release of As and Zn were governed by a diffusion-like behavior. High saturation levels within the CT-CPBs did not block pyrrhotite oxidation to occur and this caused a strength loss as the C-S-H-phases dissolved. As the cementitious phases dissolves during the TLT, As (V)-species, FA-related Zn, Zn-hydroxides surface-attached or encapsulated onto C-S-H could migrate into solution (Malviya and Chaudhary, 2006).

Leaching behaviour – reactivity of CT and CT-CPB in oxidized conditions

During the WCT, wetting and drying cycles accelerated the sulfide oxidation rate in the CT. A Ni-release in the WCT exhibited a typical water-soluble-behaviour while most abundant initially and thereafter steeply decreased and diminished towards the end (Fig. 6). Towards the end of the WCT, the molar ratios of Fe/S in CT leachates increased to \(
\sim 0.8\), indicative of pyrrhotite oxidation occurring at a higher rate (Fig. 7). Small amounts of As were released from CT in the WCT as the pH was higher than 4. Arseniosiderite and As-bearing Fe precipitates are stable in gypsum-saturated solutions at a pH of 3.5–7.5 (Paktunc et al., 2015). Therefore, these phases and remnants of arsenopyrite are probably the main As-controlling media in the CT. At a pH less than 4, the oxidation rate of arsenopyrite and chalcopyrite increases while both the adsorption capacity and the stability of ferrihydrite decrease (Dzombak and Morel, 1990; Riveros et al., 2001). This is also evident at the end of the WCT where the release of Cu and As increased along with the solubility of ferrihydrite, while the pH decreased to < 4, due to more extensive pyrrhotite
oxidation (Fig. 6), as suggested in Papers I and IV. At this stage, Zn release in the WCT was not related to pH, Fe release or the dissolution of ferrhydrite (Fig. 5). Instead, Zn release probably originated either from the oxidation of Fe-poor sphalerite, which liberate small amounts of Fe over Zn, or Zn impurities in pyrrhotite (Moncur et al., 2005, Janzen et al., 2001). From CT, the Ni release was largely governed by water-soluble phases. With respect to Zn, As and Cu, acidic conditions can liberate large proportions of these elements due to desorption from Fe precipitates and oxidation of Zn, As, and Cu-bearing sulfides.

The WCT was carried out using crushed CT-CPB-mixtures in an oxidized environment. Therefore, cementitious phases dissolved at a higher rate (a higher Si-release) in the WCT compared to that in TLT (Fig. 10), followed by a rapid decrease in pH (pH of 11 or 10 to a pH of 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, which was greater (2-4 times) compared to that from CT (Fig. 7). Initially, the release of As, Cu, Ni and Zn from CE31 and CE-FA31 increased alongside with a pH-decrease from alkaline conditions to semi-neutral. At this stage, a lower As-release at semi-neutral conditions could be due to a less comprehensive desorption from Fe-precipitates (Roddick-Lanzilotta et al., 2002). In the CT-CPB-leachates from the TLT, pH could be maintained 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 (Fig. 10).

As acid was added to stimulate dissolution of the buffering capacity in CT-CPB mixtures, the release of As, Ni, Cu and Zn increased in conjunction with Fe, and was more abundant from CE31 compared to CE-FA31 (Fig. 6). Large proportions of these elements were associated with amorphous Fe precipitates (Fig. 7) phases that are more soluble in acidic conditions (Dzombak and Morel, 1990; Riveros et al., 2001). This might explain a greater release of Ni, Zn, As and Cu from CE31 compared to CE-FA31, while the pH was slightly lower in CE31 leachates, leading to greater leaching of Fe (Fig. 6). In the CT-CPB

![Graph showing the release of elements in CT-CPB mixtures during TLT, WCT and Accelerated weathering (acid addition) compared to CT.](image)
mixtures, Cu release seemed less affected by accelerated weathering, compared to Ni and Zn. This might be explained by Cu being readily adsorbed onto Fe precipitates at a pH of 4, whereas other metals (i.e. Ni and Zn) remained in solution (Dzombak and Morel, 1990). In CE-FA, less Zn was released under acidic conditions compared to alkaline ones (Fig. 10). This might due to the presence of Zn-bearing calcium aluminosilicate glass in FA, which is more soluble in alkaline conditions (Luo et al., 2011).

How does the establishment of unsaturated zones within CT-CPB-mixtures affect the leaching behavior of As, Cu, Ni and Zn?

An establishment of unsaturated zones within the CT-CPB mixtures promoted sulfide oxidation and hence, acidic conditions in the TLT leachates. This facilitated oxygen migration through the CT-CPB-mixtures, while the solubility of oxygen is hampered in water (Yanful, 1993). In the outer areas of the CT-CPB mixtures, unsaturated zones occurred and these can have a lower permeability than the bulk CPB (Ouellet et al., 2006). In CE446 and CE-FA446, this will initially promote wash-off behaviour where water rinses highly soluble oxidation products from the surface, causing acidic conditions in the leachate (Fig. 9). In leachates from CE446 and CE-FA446, the pH increased throughout the TLT. As the oxidation products were rinsed off from the surfaces of CE446 and CE-FA446, permeability increased, and water gradually penetrated deeper into the unoxidized CPB mass, dissolving the cementitious phases and causing a pH increase. This scenario has a negative effect on the strength within the CT-CPB mixtures, something demonstrated by CE446 which fell apart into a granular material during the test period. As the cementitious phases dissolve, gypsum becomes more abundant in the CT-CPBs, suggesting a loss of strength. Low strength within CE446 is also indicated by a larger amount of gypsum, suggested by the higher fraction of water-soluble Ca and S (Dold, 2003) compared to that of CE-FA446 (Table 3).

The evolution of pH in the CT-CPB leachates during TLT suggested that a loss of strength has occurred, as the cementitious phases are highly soluble at pHs lower than 9 (Benazzoua et al., 1999). Belie et al. (1996) suggested that a loss of strength within a cement-stabilized material could cause the leachability of metals to increase. In this study, this was most significant for the Zn release from CE-FA446 and the Cu release from CE446. A majority of the Cu increase occurred initially in the TLT, when the pH was <4, and as Cu-bearing Fe precipitates dissolved (Fig. 7). Cu release was greater from CE446 than from CT, even though the proportion of Cu associated with the water-soluble fraction was less for CE446 (Table 3 and Fig. 9). This might be because Cu has a sorption edge onto Ferrihydrite at a lower pH compared to that of Ni and Zn (Munk et al., 2002). The fraction of Cu released under neutral conditions could therefore be higher. This is also seen in the pH-dependent test, where a higher fraction of Cu compared to Zn and Ni was released under neutral conditions (Fig. 8). As pH is lowered, this fraction will 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 Fe-associated Cu from CE446 during the TLT than from CT. In the CT-CPB mixtures, a large proportion of Cu is associated with the AEC fraction. Based on these results, Cu release seemed to be pH-dependent as more
Cu was released as the pH decreased. Therefore, a key issue in reducing the release of Cu is maintaining the strength within the CT-CPB mixtures. Otherwise, water migration increases along with pyrrhotite oxidation, promoting more acidic conditions.

The establishment of unsaturated conditions in CE-FA446 increased Zn leaching but, in CE446, the effect was the opposite. The amount of Zn released from CE-FA446 was twice that from CE-FA31, but more than 10-fold higher compared to CE446 (Fig. 9). The majority of the Zn release from CE-FA446 occurred during the final extractions of the TLT (Fig. 9), and was greatest as pH increased above 8. The evolution of pH and Zn could be explained with the variance of Zn species, and the water migration in the CT-CPB mixtures. Water migration is largely governed by the water saturation level within the CT-CPBs. At high water saturation levels, oxygen and water migration through the CT-CPBs is largely obstructed. Increasing the binder proportion by adding FA (such as in CE-FA mixtures) may thicken the microstructure and thus decrease the oxygen and water migration through the CT-CPBs (Aldhafeeri and Fall, 2017). The extent of pyrrhotite oxidation was therefore lower in CE-FA mixtures, causing the start and end-points of pH to be higher (6–8) in CE-FA446 compared to CE446 (4–6). The evolution of Zn release is somewhat similar for all the CT-CPBs, being greatest at the highest pH. However, less Zn was released from CE-FA31 compared to CE-FA446, despite the higher pH of CE-FA31 leachates (Fig. 9). This might be due to increased water transport through the unsaturated CE-FA446 mixture. At this stage, Zn release is not only due to desorption from Fe precipitate surfaces, but also to the dissolution of a Zn-bearing calcium aluminosilicate glass in FA, which is more soluble in alkaline conditions than acidic ones (Luo et al., 2011). This could have caused lower Zn release from CE446 compared to CE-FA446. Ni release was low, irrespective of the water saturation level in the CT-CPBs.

As the water saturation levels decreased within the CT-CPB mixtures, pyrrhotite oxidation could proceed more extensively, and this seems to have increased As release from CE-FA mixtures while the opposite was true for CE mixtures. An As-Si relationship still exists for CE-FA446 as shown in Paper III, while in CE446, the As release seems to have been governed mostly by the occurrence of As(III) species that are less well attached to oxide surfaces (Table 5). This could mean that a larger proportion of cementitious As phases still persisted in CE-FA446, while more acidic conditions, as in CE446, dissolved these phases to a greater extent. The As release is less from CE446, regardless of the fact that more Si is released, compared to that from CE-FA446. This could be explained by the binding process of As(V) onto positively charged C-S-H surfaces. As C-S-Hs dissolve buffering acidity from pyrrhotite oxidation, Ca is released before Si (Coussy et al., 2012). The release of positively charged Ca$^{2+}$-ions causes the C-S-Hs to have a net negative surface charge, while negative SiO moieties dominate (Phenrat et al., 2005). At this stage, negatively-loaded As species, that dominate in the leachates of CE446 and CE-FA446 (Table 3), will desorb from the C-S-Hs. In a pH of 4–7, As anions can then quickly re-adsorb onto Fe-precipitate surfaces. With pH above 7, the ability for Fe –precipitates to adsorb decreases (Roddick-Lanzilotta et al., 2002), and more As is maintained in solution. However, as stated in Paper II, upon re-adsorption of As, a release of Ca$^{2+}$ (due to binder dissolution) may function as a multi-absorbent for As, increasing the adsorption ability for Fe (oxy)hydroxides, especially at pH values of 4–9 (Jia and Demopoulos, 2005; Wilkie and Hering, 1996). Considering the stability of As, it seems that As is stable under acidic
conditions (as in CT), releasing small amounts of As into solution. Adding binders to the CT is therefore unnecessary to maintain the stability of As, at least as long as a cementing oxide surface within the CT is present.

Overall – could a low strength CPB (0.2 Mpa) be an environmentally accepted option for managing tailings from a cyanide leaching process?

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, as water saturation levels decreased, Cu release increased and became greater compared to CT, probably due to the formation of a substantial proportion of acid-intolerant phases that are susceptible to remobilization in acidic conditions. Arsenic leaching increased compared to that from CT, regardless of binder proportion and water saturation level. In water-saturated, alkaline conditions, pyrrhotite oxidation is retarded. The pH is maintained at alkaline levels for prolonged periods, as As has a higher mobility. This causes more As to be released from the CT-CPBs. The results from this study indicated that using a low strength CPB is not an environmentally-friendly option for underground storage of CT. If used, larger amounts of Cu and As compared to that from unmodified tailings (CT) might be released.

6. Conclusions

In this study, CT used in the CPBs originates from an oxidizing cyanide leaching process used to extract gold from inclusions in arsenopyrite and loellingite. In a subsequent water treatment process, Fe-oxides were added to form metal(loid)-bearing Fe-precipitates that could ensure the immobility of Cu, Ni, Zn and As. In the ore, pyrrhotite and arsenopyrite were the main sulfide minerals, but remnants of Cu- and Zn-sulfides were also present. A significant proportion of sulfides oxidized during cyanidation, an addition of Fe-oxides seemed to have been insufficient to adsorb all the dissolved 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. Pyrrhotite and arsenopyrite still occurred in the tailings to a small extent, governing the acid generation and some of the As release. Overall, the cyanide leaching process increased the mobility of Cu, Ni and Zn due to the formation of water soluble species. A major proportion of As were associated with amorphous Fe-precipitates. Consequently, the management of CT should focus on avoiding the establishment of, acidic and reducing conditions.

Managing the CT by using a laboratory-based low strength CT-CPB-application decreased leaching of Cu, Ni and Zn. In water saturated conditions, the release of As was low from granular CT, due to the stability of As in acidic conditions and to the formation of a enclosing Fe-oxide crust that hindered metal(loid)-diffusion. In CT-CPB-mixtures stored to maintain high levels of water saturation, low amounts of Cu, Ni and Zn were released, due to desorption and dissolution of secondary formed cementitious species. At this stage, alkaline conditions caused As-desorption and the dissolved As to be attached onto cementitious phases. These As-phases were highly acid-intolerant and their dissolution caused the As-release to be a 10-18-fold higher in CT-CPBs compared to
that from CT. In oxidized conditions, the cementitious phases dissolved at a higher rate in the CT-CPBs. This occurred alongside with a lower As-, Ni-, Cu- and Zn-release. The As-release was still higher compared to that in CT, especially in alkaline conditions. This was not true regarding Cu, Ni and Zn, which showed an enhanced stability in acidic and alkaline conditions, compared to that in CT.

To address the long-term performance of a CPB application, it is important to understand that unsaturated zones could form within CPBs, as complete flooding of CPB-filled workings could take several years to happen. The establishment of unsaturated zones in CT-CPB mixtures caused the strength to decrease due to a more extensive pyrrhotite oxidation. Using a small proportion of binders did not suppress Cu and As leaching, but Ni and Zn leaching were still less than from unmodified tailings. Proportions of Zn, Ni, As and Cu associated with acid-soluble phases increased in conjunction with the binder fraction. In CT-CPB mixtures with 3 wt.% of binders, Zn release increased substantially while the opposite was true for Cu, As and Ni. This was due to the occurrence of a binder-related Zn phase soluble in alkaline conditions. Increasing the binder proportion in a CPB, does not necessary mean that trace metals are more stabilized, due to the formation of acid-soluble fractions. This increases the importance of minimizing the effects of a sulfide oxidation in a low-strength CPB application. Overall, the use of a low strength CPB presents no major environmental gains, because of a more abundant release of Cu and As compared to that from unmodified tailings.

7. Future Research

Gold is most often extracted in an oxidized, alkaline cyanide solution. Generally, in the associated water treatment, heavy metals and metal(loid)s originating from gold-bearing sulfide minerals are stabilized through co-precipitation and the formation of metal hydroxides. Metals such as arsenic and copper, nickel and zinc are mobilized in different conditions. Arsenic is mobilized in neutral to alkaline conditions, while the majority of heavy metals are less mobile in these conditions. In the slurries from a cyanide leaching process, it is common that remnants of sulfides and secondary forms of arsenic and heavy metals co-exist. In that case, the water treatment process must be adapted to ensure the stability of these co-occurring constituents. Previous research has often focused on the stability of the end product (the tailings), whilst process-like studies of whether an efficient gold extraction method could work alongside the long-term immobility of the metal(loid)s have had less attention. Focus for future research could therefore be on obtaining knowledge about the mobility of metal(loid)s in common gold extraction processes. This knowledge could be used to adapt the processes for an efficient gold extraction that works with the long-term immobility of metal(loid)s.

In this study, a method called Cemented Paste Backfill (CPB) was used to manage tailings from a cyanide leaching process. In the CT-CPBs large proportions of acid intolerant metal (oid) species could have formed. Little is known about the speciation of arsenic, copper, nickel and zinc within a low-strength CPB-mixture. Using low-strength CPBs could be an option for storing tailings in surficial facilities. It is therefore of interest to investigate the speciation of As, Cu, Ni and Zn in various CPB-mixtures in order to identify compositions suitable for the stabilization and management of CT.
8. References


Paper I

Release of Arsenic from cyanidation tailings

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As (V)-immobilization

ABSTRACT
At a gold mine in northern Sweden, gold occurring as inclusions in pyrrhotite and arsenopyrite is leached by cyanidation of the ore. The main sulphide minerals in the ore are pyrrhotite and arsenopyrite. Effluents from the cyanidation process are treated with Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} to form Fe-precipitates suitable for the co-precipitation of As. The aim of this study was to perform static and kinetic leaching tests on the ore and tailings to define geochemical processes governing As mobility. Sequential leaching tests suggested that the majority of dissolved As deriving from the sulphide fraction in the ore was incorporated in newly formed Fe-precipitates in the tailings. The mobility of As in the tailings was therefore mainly dependent on the stability of these Fe-bearing Fe-precipitates. Weathering cell tests (WCT) involving 31 weekly cycles of wetting and air exposure were conducted to assess the stability of the As in the tailings under accelerated weathering conditions. The first stage of the WCT was characterized by a pH <5 and low As leaching, probably driven by the dissolution of amorphous Fe-As species. In the second stage of the WCT, leaching of Fe, S and As increased and the pH decreased to <3.5. An increase of the leachate’s molar Fe/S-ratio suggested that pyrrhotite oxidation was occurring. The falling pH destabilized As-bearing Fe-precipitates, causing further As release. The total As release during the WCT corresponded to only a small proportion of the tailings’ total As content. The accelerated As-leaching observed towards the end of the WCT could thus indicate that its release could increase progressively over time.

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1. Introduction
Gold can occur in its native form (free gold) or may be encapsulated in other minerals (e.g. pyrite, quartz, arsenopyrite, loellingite, etc.). Gold particles are usually separated by gravity or recovered by leaching the ore using a cyanide solution. During the cyanidation process, the ore is subjected to a cyanide solution under alkaline conditions (pH 9.5–10) for up to 36 h. Many gold ores contain arsenic (As) in the form of arsenopyrite, which usually co-exists with other sulphide minerals, such as pyrrhotite and pyrite. Tailings from sulphide ore mines are often chemically reactive due to their content of Fe-sulphide minerals, such as pyrite and pyrrhotite. The weathering of Fe-sulphide minerals can be a strongly acidifying process and is considered to be the main cause of acid mine drainage (AMD) (INAP, 2009). Arsenic does not form strongly acidifying process and is considered to be the main cause of acid mine drainage (AMD) (INAP, 2009). Arsenic does not form.

management of As-rich tailings generated by gold extraction processes generally focuses on the stability of secondary As-phases because As-sulphides are assumed to be oxidized during gold extraction (Paktunc et al., 2004). The main secondary As minerals present in tailings after cyanide leaching are believed to be arsenates (Craw et al., 2003). Under oxidizing conditions, arsenates form complexes with metals such as Fe, Al and Ca. The stability of these metal arsenates depends on several factors, including the pH, metal/As ratio, redox conditions, availability of O\textsubscript{2} and CO\textsubscript{2} and the presence of anions, such as SO\textsubscript{4}\textsuperscript{2−}, that compete with arsenates for sorption surfaces. Iron and Al-arsenates are dominant phases in acidic environments and are less soluble than Ca-arsenates, which predominate in calcareous tailings (Williams et al., 1996). Arsenate may precipitate as scorodite, Fe\textsubscript{3}Al\textsubscript{2}O\textsubscript{10}(\textsubscript{2}H\textsubscript{2}O) (Paktunc et al., 2009), or poorly-crystalline Fe(III)-arsenates (Le Berre et al., 2007; Parviainen et al., 2012). Alternatively, it may co-precipitate as Ca-Fe-arsenates (Pantuzo et al., 2008), sorb to amorphous Fe\textsubscript{3}O\textsubscript{4} oxy-hydroxide phases (Korte and Fernando, 1991) or substitute for sulphate in jarosite (Paktunc and Dutrizac, 2003).

Gold mine tailings slurries from As-enriched sulphide ores are often treated with lime and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} to promote the formation of stable Fe-As-precipitates and increase the pH to prevent AMD. The tailings slurries are also often pre-treated with H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2}
in order to promote the oxidation of arsenite complexes into less mobile arsenate species. Gaining knowledge about the distribution and speciation of As in such tailings is essential for their future management. For this reason, we studied cyanided tailings from a mine in the north of Sweden where gold has been extracted from inclusions in arsenopyrite. The original ore and tailings (which had been pre-treated with Fe(SO₄)₃) were studied in detail by static and kinetic leaching experiments, analysis of their chemical composition and geochemical modelling. The specific objectives of this investigation were as follows:

- Chemical characterization of the ore and tailings at the mine and speciation of As phases in each case.
- Determine the mobility of As under oxidizing conditions by static and kinetic leaching tests.

It was anticipated that these investigations would yield new insights into the geochemical processes governing As mobility at the studied mine and, in general, allow the development of more effective ways of managing As-bearing tailings that prevent the occurrence of high As concentrations in mine drainage.

2. Site description

The Svartliden gold ore deposit is situated along the so-called Gold Line (Fig. 1), southwest of the Skellefte ore district in northern Sweden. The operational time was 2005–2014 and until 2012, approx. 2.4 Mt of ore at a grade of 4.4 ppm Au was generated (Sciubità et al., 2013). The Svartliden gold deposit is considered to be a structurally controlled epigenetic lode gold deposit (Hart et al., 1999; Bark and Weihed, 2003, 2012) with key features resembling orogenic gold-style mineralization. Gold is the only economic mineral at Svartliden. The mineralization is spatially associated with a banded iron-formation (Schlöglöva et al., 2013; Sciubità, 2013) situated at the contact zone between metasedimentary rocks and amphibolites. The metasedimentary host rocks exhibit interbedded carbonate-silicate shales with up to 30% pyrrhotite (Hart et al., 1999).

The mineralogy of the ore zone (including the banded iron-formation) constitutes mainly quartz, magnetite, diopside, hedenbergite, tremolite, garnetite, fayalite, pyrrhotite, arsenopyrite and löllingite (Sciubità, 2013). Gold occurs as electrum (Au/Ag alloy). The gold grain size ranges between 5 and 100 μm with an average grain size of ca. 45 μm, and the gold occurs as inclusions in arsenopyrite-hosted löllingite, commonly at the grain boundary to arsenopyrite and within arsenopyrite. Gold grains are also found in the silicate matrix, commonly spatially related to arsenopyrite (Bark et al., 2013).

3. Materials and methods

Tailings and crushed ore originating from the Svartliden Gold mine, Sweden were provided by the mining company Dragon Mining AB. Tailings have been deposited in a tailings impoundment at the mine for 8 years (2005–2013) at a rate of approx. 0.3 million tonnes/year. Tailings were sampled at depths of 0–30 cm from approx. ten different locations on the impoundment and mixed to form a bulk sample of approx. 15 kg. The masses of the crushed ore samples were approx. 3 kg. The tailings slurries at the mine are routinely treated by aeration and hydrogen peroxide (H₂O₂) to avoid the formation of AMD and toxic cyanide gas. Hydrogen peroxide is used to increase the oxidation rate of arsenites into arsenates, which is the preferred species when considering the stability of As.

\[
2H_2AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2FeAsO_4(s) + 3CaSO_4 + 2H_2O(s)
\]

The pH of the treated effluent is reduced to 8–8.5 before deposition in the tailings dams, in accordance with legal guidelines.

3.1. Tailings and ore characteristics

The acid potential (AP), neutralization potential (NP) and net neutralization potential (NNP) of the tailings samples were determined in triplicate by the acid-base accounting (ABA) test according to Swedish standard (SS-EN 15875:2011). Tailings were dried at room temperature and sieved to a particle size of <0.125 mm before testing. Two grams of dried, sieved tailings were mixed in distilled water for 22 h with a magnetic stirrer, after which the pH of the suspension was determined. The suspension was then treated with 1 M HCl until its pH reached 2–2.5 and the mixtures were back-titrated to a pH of 8.3. Total sulphur content was determined by ICP-MS analysis.

Powder X-ray traces were conducted on a Siemens D5000 diffractometer using a Cu Kα radiation source (40 kV and 40 mA) over the range 2θ = 5–90° using a step size of 0.02° and scan rate of 1° per minute. Crystalline minerals present at proportions of >2 wt% were qualitatively determined.

From the primary ore and tailings, fifteen samples were prepared as polished sections and examined by optical and scanning electron microscopy for phase identification and textural analysis at the Luleå University of Technology. The electron microscope used was a Zeiss Merlin FEG-SEM equipped with energy- and wavelength-dispersive spectrometers. An accelerating voltage of 20 kV and beam current of 200–1000 pA were used for the analysis.

3.2. Leaching tests

Environmental assessment leaching tests (batch and weathering cell) were conducted to evaluate the behaviour of As in the tailings. Batch leaching tests (BLT) were performed to assess the leaching of selected elements from the tailings over the short term. Weathering cell tests (WCT) were conducted in duplicate to simulate the long-term weathering of the tailings over extended periods of time and to determine the kinetic release of specific elements.

Batch leaching tests (BLT) were conducted on tailings in triplicate according to the SS-EN 12457-1 standard (SS, 2003). Tailings (100 g, dry weight) were placed in acid-washed bottles (1500 ml) together with 1000 ml of milliQ H₂O to generate a liquid/solid ratio of 10 (L/S = 10). The samples were agitated for 24 h in a rotary shaker (10 rpm). The leachates were then filtered through a 0.45-mm Filtrrop S non-pyrogenic Sterile-R syringe filter (cellulose acetate membrane) into acid-washed bottles and stored cold (4 °C) in darkness until analysis. The pH, redox potential (Eh) and electrical conductivity (EC) of the tailings were determined using unfiltered samples. The chemical compositions of the water samples were analyzed as described in the “Sample analysis” section.

In the weathering cell test (WCT), a modified version developed by Cruz et al. (2001) was used to simulate accelerated weathering of the tailings and assess the reactivity of their mineral content over time. This protocol was selected because it enhances evaporation and reduces the degree of saturation of the tested media, avoiding reactivity inhibition. Approximately 70 g of tailings was placed on a paper filter in a Buchner-type funnel. The samples were exposed to weekly cycles, involving...
one day of leaching, three days of ambient air exposure, a second
day of leaching and finally two days of air exposure. The samples
were leached by covering them with 50 ml of milliQ H₂O for
approximately 2 h and then recovering the leachates by applying
a vacuum to the funnel. The pH, Eh and EC of the leachates were
measured after filtration; the chemical composition of the water
samples was analyzed as described in the section entitled “Sam-
ple analysis”. Duplicate tailings samples (Tailings 1 and 2) were
leached. The experiment was conducted over a period of 31
cycles (217 days).

Arsenic speciation was assessed using the modified sequential
extraction scheme described by Dold (2003). In each extraction
sequence, 2 g of tailings was placed in an acid-washed round-
bottomed centrifuge tube with a capacity of 60 ml and extracted
with seven different solutions in succession as listed in Table 1.

After each extraction, the suspensions were subjected to centri-
fugation at 1200 rpm for 15 min. The leachate was then filtered using
a 0.45 μm syringe filter with an acetate cellulose membrane into
acid-washed (60 ml) plastic bottles. The samples were stored cold
(4 °C) in darkness until analysis. The solid residues were washed
with milliQ H₂O to remove all traces of the previous extraction
solution before each step in the sequence after the first. Finally,
the filtrates from each extraction step were submitted for total ele-
ment analysis. Their chemical compositions were determined as
described in the “Sample analysis” section.

3.3. Modelling – PHREEQC

Speciation-solubility calculations were performed with the geo-
chemical code PHREEQC (Parkhurst and Appelo, 1999) using the
Waterqf database. Element concentrations, redox-potential (Eh)cline (KAlSi3O8). Jarosite (KFe3(SO4)2(OH)6) was present in small amounts and no crystalline phases of As were found. The relative standard deviation of S in each fraction was 12.6–33.8%. The relative standard deviation of S in each fraction deviated by less than 10% from the average. How-

### 4. Results

#### 4.1. Tailings and ore characteristics

According to the XRD-analyses, the major tailings mineral assemblage in Svartliden consisted of quartz (SiO2), tremolite (Ca2Mg3Fe5.5Al0.5Si8O22(OH2)), albite (NaAlSi3O8) and microcline (KAlSi3O8). Jarosite (KFe3(SO4)2(OH)6) was present in small amounts and no crystalline phases of As were found. The relative proportions of the minerals were calculated from the peak heights of the XRD spectra. The dominant elements in the tailings and ore were Al, As, Ca, Cr, Cu, Mn, Ni, P, Pb and Zn. The total sulphur contents of the tailings and ore were 2.1 ± 0.05 and 2.5 ± 0.23 wt%, respectively. Low proportions of iron inorganic carbon (0.19 ± 0.03 wt%, Table 2) and a NIP of less than 20 kg CaO/m³ (−60.8 ± 1.32), showed that tailings could be considered acid-generating. The As contents of the tailings and ore were 1070 ± 30 and 4703 ± 781 mg/kg, respectively (Table 2).

The solid samples were analyzed for major and minor elements by the accredited laboratory. For the determination of As, Cd, Co, Cr, Cu, Mn, Ni, P, Pb and Zn were determined by high resolution inductively coupled plasma–mass spectrometry (HR-ICP-MS), whereas Al, Ca, Fe, K, Mg, Na and S were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Before analysis, samples were acidified with super-pure nitric acid using 1 ml of acid per 100 ml of sample. Analyses of HR-ICP-MS and ICP-AES were performed using modified versions of US Environmental Protection Agency (US EPA) methods 200.8 and 200.7, respectively.

The solid samples were analyzed for major and minor elements by the accredited laboratory. For the determination of As, Cd, Co, Cr, Cu, Mn, Ni, P, Pb and Zn, samples were dried at 50 °C and digested with 7 M nitric acid in closed Teflon vessels in a microwave oven. Other elements were determined after fusion with lithium metaborate, followed by dissolution in dilute nitric acid. The solutions were subjected to centrifugation and diluted before analysis. For data quality control, two in-house reference materials were analyzed in parallel with the solid samples. The dry matter content of the tailings samples were determined in triplicate by drying the samples in an oven at 105 °C for 24 h according to Swedish standard SS 028113-1 (SSI, 1981).

#### 4.2. Sequential extraction tests

Sequential extractions were conducted on tailings and ore samples in triplicate. In ore samples, analyzed contents of As, Fe and Ca in each fraction deviated by less than 10% from the average. However, the standard deviation of S in each fraction was 12.6–33.8% (Fig. 5), with the largest variation measured in the secondary sulphide fraction. Results (Fig. 2) showed that most (98 wt%) of the As in the ore was associated with the primary sulphide fraction and approx. 1 wt% with the residual fraction (silicates). The majority (75 wt%) of the Fe was associated with the residual fraction but lesser (16.7 wt%) quantities were associated with primary sulphides, Fe-oxides (5.6 wt%) and the adsorbed–exchangeable–carbonate (AEC) fraction (1.8 wt%). Most of the S (71 wt%) was associated with the primary sulphide fraction, with smaller (15 wt%) quantities associated with secondary sulphides and the residual fraction (12 wt%). A small proportion (3.1 wt%) of the Ca in the ore was associated with the AEC fraction and primary sulphides (2.8 wt%), but the majority (93 wt%) was associated with the residual fraction. Total contents of As and S differed (2654 and 10,344 mg/kg) in these samples, indicating a large difference from the chemical composition analyses of the ore (Table 2). The non-existence of S-silicates and Ca-sulphides in natural environ-

#### 4.1.1. Scanning electron microscopy

Results from SEM showed the occurrence of gold in ore samples and grains of arsenopyrite in tailings samples (Fig. 2). No arsenic-bearing Fe-precipitates were detected, due to low content of As in tailings (less than 1 wt%). Indications of a hydrous ferric oxide (HFO)-rim enclosing As-sulphide grains could be detected (Fig. 2d).
ments implies that the sulphide fraction of S and silicate fraction of Ca were underestimated.

Results from the sequential extractions of tailings (Fig. 4) suggested that the majority of As (94.6 wt%) was co-precipitated with secondary Fe (III) minerals, whereas 2.5 ± 1.3 wt% occurred as primary sulphides. A minor proportion of As (0.8 wt%) was associated with the AEC fraction. The majority of Fe was associated with the residual fraction (61 wt%) and Fe (III) oxy-hydroxides (30 wt%), but a smaller proportion was associated with primary sulphides (3.6 wt%). Most of the S was associated with the primary sulphide
fraction (37 wt%) and water-soluble fraction (35 wt%); smaller quantities were associated with the AEC (11 wt%) and Fe (III) oxy-hydroxides (7.0 wt%). The proportion of Ca in the residual fraction was (88 wt%), whereas the rest was associated with the water-soluble fraction (7.4 wt%) and primary sulphides (3.8 wt%). The non-existence of Ca-sulphides in natural environments suggests that the silicate fraction of Ca was underestimated.

4.2.2. Batch leaching tests

The leachate from the BLT had an electrical conductivity (Ec) of 2.86 mS/cm due to its high contents of S (532 mg/l), Ca (360 mg/l), Fe (650 mg/l), Mg (34.7 mg/l) and Al (60.3 mg/l) (Table 3). It was also quite highly oxidized (Eh: 347 ± 3 mV). The tailings leachate had a pH of approx. 3 (Table 3) and could be classified as acid mine drainage (AMD) according to INAP (2009).

4.2.3. Weathering cell tests

The WCT of the tailings exhibited good reproducibility with only small differences between runs. The cumulative release of As from the tailings was 1.52 ± 0.06 mg/kg and the concentrations of As ranged from 22 to 554 µg/l. Similar trends were initially observed for the release of As, Fe, Ca and S: the concentrations of all four elements decreased gradually during the first few weeks of leaching. The concentrations of As and Fe increased but leaching of Ca remained low throughout the remainder of the leaching period. After 80 days, the release of As increased and concentrations of S and Fe increased in tandem once the pH fell below 4.5 (Fig. 5).

4.2.4. Modelling – PHREEQC

The dissolution of ferrihydrite was most extensive at the end of the WCT and coincided with increased leaching of As. Gypsum was the most dominant Ca-mineral and was under saturated during the WCT (Fig. 6).

5. Discussion

Based on results from the sequential extraction tests (Figs. 3 and 4), the cyanidation process appeared to have redistributed the majority of As originating from the dissolution of arsenopyrite into secondary phases. Our studies suggested that multiple mechanisms of As attenuation could occur within oxidized tailings at the studied site. Thus, the release of As from these cyanidation tailings can be attributed to various processes, including (1) dissolution of water-soluble and exchangeable As-species; (2) oxidation and

<table>
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<th>Element</th>
<th>Unit</th>
<th>Ca mg/l</th>
<th>360 ± 12</th>
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<tr>
<td>Fe mg/l</td>
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<td>K mg/l</td>
<td>1.61 ± 0.11</td>
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<tr>
<td>Mg mg/l</td>
<td>347 ± 0.9</td>
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<tr>
<td>Na mg/l</td>
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<td>Si mg/l</td>
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<td>Al mg/l</td>
<td>60.3 ± 11.2</td>
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<tr>
<td>S mg/l</td>
<td>532 ± 26</td>
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<td>Mn mg/l</td>
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<td>Zn mg/l</td>
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<td>Ba µg/l</td>
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<td>Cd µg/l</td>
<td>16.7 ± 0.5</td>
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<td>Co µg/l</td>
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<td>Cr µg/l</td>
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<td>Cu µg/l</td>
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<tr>
<td>Ec mS/cm</td>
<td>2.86 ± 0.11</td>
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Fig. 5. Evolution of pH and release of Ca, Fe, S and As from Svartliden gold mine tailings over time during the WCT.

Fig. 6. Evolution of As-release and Saturation Index (SI) of gypsum, goethite and ferrihydrite during the WCT.
dissolution of arsenopyrite; and (3) precipitation and dissolution of As-bearing Fe-hydrates.

5.1. Presence of water-soluble and exchangeable species of As in tailings

The initial period of the WCT (approx. until the 80th day) was characterized by low As release, a pH of 4.5–5.5. At this stage, As-release could derive from the most soluble phases of As (water-soluble and AEC) which constitute of a small proportion (0.8%) or the total content of As. Modelling suggested however, that the release of As at this stage could be due to the dissolution of poorly crystalline As-bearing Fe-hydrates (Fig. 6).

5.2. Stability of As-sulphides in tailings

The sequential extraction tests showed that a small quantity (2.5 ± 1.3 wt%) of As was associated with primary sulphides. Observations in SEM confirmed the presence of As-sulphides (Fig. 7c and d). This means that a small proportion of the As and acid release from the tailings may be controlled by the dissolution of As-sulphides. As-sulphides is generally stable under reducing conditions at pH values of 2–12 but is oxidized under near-surface oxidizing conditions at pH > 5 (Blowes et al., 1998) (reaction (2)):

\[
\text{FeAsS(s)} + 1.5\text{H}_2\text{O} + 2.75\text{O}_2(aq) \\
\rightarrow \text{Fe}^{3+} + \text{H}_2\text{AsO}_4(aq) + 5\text{SO}_4^{2-}
\]  

However, at pH values > 5, Fe\(^{3+}\) rapidly oxidizes to Fe\(^{4+}\), undergoes hydrolysis and precipitates as Fe(OH)\(_3\) (HFO:s) (reaction (3)). Thus, HFO:s may form rims on the surfaces of the As-sulphide grains. Such rims form rapidly under alkaline conditions (Bhargava et al., 2007). Indications of HFO-rims on these grains imply a coating that retards the minerals’ further oxidation (Belzile et al., 2004; Asta et al., 2013). The evolution of pH and redox conditions in tailings has important implications for the long-term stability of As-bearing phases. The evolution of the pH in tailings is mainly governed by the presence of pyrrhotite and calcite. Pyrrhotite is the main sulphide mineral in the Svartliden ore (Scrubia, 2013). The sequential extraction tests suggested that the content of Fe-sulphides in the tailings was approx. 5.8 wt% and the sulphide and sulphate contents of the tailings accounted for 44% and 56% of the total S, respectively. A minor part of the total S and As in the tailings was released during the WCT (22.8% and 0.1% respectively). Until the 110th day of the WCT, CaS-molar ratios < 1 in the leachates and modelling (Fig. 6) suggesting the dissolution of gypsum formed during treatment of the tailings slurry (reaction (1)). Towards the end of the
test period (217 days), the pH of the leachate fell to <3.5 and concentrations of As, Fe and S increased (Fig. 5). The Fe/S molar ratio in the leachate increased to ~0.8 by the end of the WCT, suggesting that pyrrhotite oxidation could destabilize As-bearing Fe-hydrates further. As-release in the tailings had an oxidation of pyrrhotite, As-release increased while As-bearing Fe-hydrates were destabilized. As-release in the tailings had an increasing trend while pH was lowered and the proceeding of pyrrhotite oxidation could destabilize As-bearing Fe-hydrates further.

Acknowledgements

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The use of low binder proportions in cemented paste backfill – effects on As-leaching

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The use of low binder proportions in cemented paste backfill – Effects on As-leaching

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**Abstract**

Gold is extracted by cyanide leaching from inclusions in arsenopyrite at a mine in the north of Sweden. The major ore mineral assemblage consists of pyrrhotite and arsenopyrite–loellingite. Arsenopyrite is assumed to be oxidized during cyanidation and the stability of secondary As-phases needs to be assessed. One way of managing such tailings is to convert them into a monolithic mass by using a method called cemented paste backfill (CPB). In CPB, tailings are traditionally mixed with water (typically 25% by weight) and small amounts (3–7%) of binders, and backfilled into excavated underground areas. To investigate the release of arsenic (As) from CPB prepared from As-rich tailings, tailings containing approx. 1000 ppm of As, mainly in the form of As-bearing iron (Fe)-precipitates (FEP), were mixed with small quantities (1–3%) of biofuel fly ash (BFA), ordinary cement, and water to produce monolithic CPB masses. CPB-recipes were designed to meet the strength demand of 200 kPa, stated by the mine operators. Tank leaching tests (TLT) and the weathering cell test (WCT) were used to compare the leaching behavior of As in unmodified tailings and CPB-materials. Results from the leaching tests (TLT and WCT) showed that the inclusion of As-rich tailings into a cementitious matrix increased leaching of As. This behavior could partially be explained by an increase of pH where As sorbed to FEPs becomes unstable. In the CPB mixtures, small (>1%) proportions of the total As in the solid material was released from less acid-tolerant species (i.e. Ca-arsenates and As bonded to cementitious phases). Unmodified tailings generated an acidic environment in flooded conditions at which As-bearing FEPs were stable. Acid was added to the crushed CPB materials during later stages of the WCTs to mimic the effects of weathering. This increased the leaching of Fe and had minor effects on that of As but did not affect S-leaching.

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1. Introduction

In sulfide gold ores, fine gold particles mainly occur as inclusions in sulfide minerals such as arsenopyrite. Cyanidation has been the dominant gold extraction technology since the 1970s. Prior to cyanidation, the ore is milled and pH is raised in the resulting slurry to avoid conversion of cyanide ions into the toxic cyanide gas of HCN (Hinton et al., 2003). While arsenopyrite is assumed to be oxidized during gold enrichment, mobility of arsenic in cyanidation slurries is governed by the relative abundance of secondary As-phases, namely arsenates (Craw et al., 2003). Arsenates are soluble in alkaline conditions (Craw et al., 2003) that prevail during cyanidation, so slurries produced in this way must be treated to immobilize As before being discharged into tailings facilities. This problem is commonly addressed by the addition of a iron sulfate salt (\(\text{Fe}_2(\text{SO}_4)_3\)) to the cyanidation slurries aiming to form stable As-bearing Fe-precipitates (FEP) (Wilkie and Hering, 1996) (reaction (1)).

\[
2\text{H}_2\text{AsO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{FeAsO}_4(s) + 3\text{CaSO}_4 + 2\text{H}_2\text{O}(s) + 6\text{H}_2\text{O}
\] (1)

Arsenopyrite usually co-exists with other sulfide minerals such as pyrrhotite and pyrite (Genkin et al., 1998). These minerals can be oxidized on contact with atmospheric oxygen and water, producing an acid leachate called acid mine drainage (AMD) (INAP, 2009). In general, arsenic bearing FEP with a Fe/As-molar ratio of >3 are stable in the pH range 4–8 (Riveros et al., 2001). The co-occurrence of As-bearing FEPs and sulfide minerals could therefore pose difficulties for tailings remediation. Cemented paste backfill (CPB) is a method where tailings are converted into a monolithic mass by the addition of low proportions (3–7%) of binders. CPB focuses on being a geotechnical support to underground conditions.
mine cavities increasing operational benefits for the mining industry. CPB offers moreover on the minimization and/or enhancement of the quality of percolating water (Coussy et al., 2011; Benzaazoua et al., 2004c). CPB is typically formed using cement as the binder material and usually has a water content of 20–25%; this level of water is required to enable the transport of the initially-formed paste through pipe networks (Landriault, 2001). Because large mines may produce millions of tonnes of tailings, the cost of the cement used when forming CPB can be substantial, and many studies have therefore explored the scope for using alternative binders or otherwise minimizing the amount of cement used in CPB (Benzaazoua et al., 2004a; Peyronnard and Benzaazoua, 2012). Granulated blast furnace slag (GBFS) and biofuel fly ash (BFA) have successfully been used to partially replace cement in CPB due to their pozzolanic and alkaline properties (Coussy et al., 2011; Benzaazoua et al., 1999, 2002). It is generally believed that alkaline materials (fly ashes and slags) increase the mobility of As, but some results indicate that they may decrease its mobility by promoting the formation of stable Ca-As complexes (Hartley et al., 2004; Porter et al., 2004; Botte and Brown, 1999).

Studies of Benzaazoua et al. (2004a), Coussy et al. (2011), and Randall (2012) has successfully used CPB to immobilize arsenopyrite, scorodite, and spiked As in natural and synthetic CPB. Proportions of binders used in these studies were 4–7% with a strength demand of 0.5–1 MPa. The mechanisms suggested for the stability of As in these cases were: formation of Ca-arsenates, the entrapment of As in the cemenitious matrix by sorption onto calcium-silicate-hydrates (C-S-H), or substitution of As into the crystal lattice of secondary cemenitious minerals. However, CPB has also been evaluated as backfill of non-load bearing construction or tailing dams (Yin et al., 2014; Deschamps et al., 2011, 2008). In such cases the strength of the CPB-material is of less concern but aims to prevent the release of metal ions and minimize AMD still remains. So, where less strength is needed in the CPB-material, how does it affect the leaching of arsenic? A former study of Cruz et al. (2001) has shown that low proportions of binders could be insufficient to suppress the generation of acid mine drainage. It is therefore important to investigate the chemical stability of As-bearing FEP in CPB materials where iron sulfides are occurring. At lower strength demands, proportions of binders used in CPB materials could be reduced. The aim of this study was, therefore, to evaluate the behavior of As in CPB-materials with low proportions of binders and its response to weathering and flooded conditions. In this study, mine operators considered that a compressive strength of 200 kPa was sufficient for the CPB-material. Recipes for CPB-materials are listed (in Table 3) and were also chosen by considering economic criteria minimizing the binder proportions. The effect of cementation on As-leaching was evaluated by comparing CPB-materials and unmodified tailings.

2. Materials and methods

2.1. Tailings characteristics

At a mine in Svartliden, Sweden, gold is extracted by cyanidation from inclusions in arsenopyrite (FeAsS), which is predomi-

Table 1 Results from ABA test, ICP-AES analyses of S and As, particle size distribution, (n = 3), (SD) in the Svartliden tailings.

<table>
<thead>
<tr>
<th>Element</th>
<th>Units</th>
<th>Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids (TS)</td>
<td>%</td>
<td>89.0 ± 0.4</td>
</tr>
<tr>
<td>SO₄</td>
<td>% of TS</td>
<td>5.5 ± 1.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>% of TS</td>
<td>4.0 ± 0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>% of TS</td>
<td>16.7 ± 0.25</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>% of TS</td>
<td>16.7 ± 0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>% of TS</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>% of TS</td>
<td>3.1 ± 0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>% of TS</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>% of TS</td>
<td>0.8 ± 0.03</td>
</tr>
<tr>
<td>F₂O₅</td>
<td>% of TS</td>
<td>0.24 ± 0.01</td>
</tr>
<tr>
<td>TiO₂</td>
<td>% of TS</td>
<td>0.16 ± 0.00</td>
</tr>
<tr>
<td>As</td>
<td>mg/kg TS</td>
<td>1070 ± 30</td>
</tr>
<tr>
<td>S</td>
<td>mg/kg TS</td>
<td>20.93 ± 4.93</td>
</tr>
<tr>
<td>AP</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>NP kg CaCO₃</td>
<td></td>
<td>4.48 ± 1.31</td>
</tr>
<tr>
<td>MNP kg CaCO₃</td>
<td></td>
<td>60.6 ± 1.32</td>
</tr>
<tr>
<td>D₅₀</td>
<td>mm</td>
<td>6.15 ± 0.03</td>
</tr>
<tr>
<td>D₉₀</td>
<td>mm</td>
<td>91.0 ± 2.7</td>
</tr>
<tr>
<td>Dₙ₅₀</td>
<td>mm</td>
<td>195.8</td>
</tr>
</tbody>
</table>

water samples from the leaching tests were analyzed by an accredited laboratory (ALS Scandinavia, Luleå, Sweden) to determine their elemental composition. The samples’ contents of As, Cd, Cr, Cu, Mn, Ni, P, Pb, and Zn were determined using inductively coupled plasma sector field mass spectroscopy (ICP-SFMS) while their contents of Al, Ca, Fe, K, Mg, Na, and S were determined by ICP-AES. Before analysis, samples were acidified with 1 ml of super pure nitric per 100 ml of sample. The ICP-SFMS and ICP-AES analyses were conducted in the accredited EPA method 200.8 and 200.7, respectively (USEPA, 1991). Solid samples of the binders used to form the CPB materials were also analyzed and minor elements by the accredited ALS Analytical laboratory. Their contents of As, Cd, Co, Cu, Ni, Pb, S, and Zn were determined after drying samples at 50 °C and then digesting them with 7 M nitric acid in closed Teflon vessels in a microwave oven. Other elements were determined after fusion with lithium metaphosphate followed by dissolution in diluted nitric acid. The solutions were centrifuged and diluted before analysis. For quality control of the data, two in-house reference materials were analyzed in parallel with the solid samples. The ICP-AES analyses were conducted according to the modified EPA method 200.7.
2.2. Paste backfill samples preparation and mechanical strength

Two types of binders were tested in different paste mixtures: Portland cement (Ordinary Portland Cement, or CE) and biofuel fly ash (FA) from a biofuel incineration plant located in Lycksele, Sweden. Tailings (TA) were mixed with the binders and distilled water was then added slowly until a water content of 25–30 wt.% was achieved. The proportions of tailings and binders (Table 3) were targeted to achieve the desired hardened strength of 200 kPa while minimizing the binder content of the CPB.

CE and FA mixed with tailings were poured into plastic bottles (diameters of 50 mm, and weighed to determine their densities, samples were then cut into pieces with lengths of 100 mm and approximately 70 g of the resulting material was placed on a lids of the tanks such that the tailings were fully immersed in the water. Duplicate experiments were conducted for each CPB material and for the unmodified tailings, so in total six samples were leached. The leachate was removed and the tank was charged with the same volume of fresh distilled water after 6 h, 1 day, 2.25 days, 4 days, 9 days, 16 days, 36 days and 64 days. In all cases, the leachate was stirred manually before collection and analysis. The collected leachates were filtered through a 0.45 mm membrane filter after which their pH, Eh and conductivity were measured and their elemental composition was determined by ICP-AES.

The mass transfer of As from the tailings and CPB materials was calculated using Eq. (2), as specified in the EA NEN 7375:2004 standard:

\[ M_i = \frac{(C_i \times V_i) \times A}{L} \]

2.3.1. Flooded monoliths – Tank leaching test (TLT)

Tests were conducted according to the Dutch standard EA NEN 7375:2004, which examines leaching from a monolithic block. CPB samples were removed from their bottles after 31 days of curing and shaped into regular cylinders. The resulting monoliths were then placed inside tanks on 2 cm tall plastic supports, after which the tanks were charged with distilled water until there was a 2 cm water head surrounding the CPB sample and a liquid/solid (LS) ratio of 10 cm³ of solution per cm² of exposed solid was established. Reference samples (tailings) were placed in paper filter bags with 1 mm pores inside nylon filters, which were hung from the lids of the tanks such that the tailings were fully immersed in the water. Duplicate experiments were conducted for each CPB material and for the unmodified tailings, so in total six samples were leached. The leachate was removed and the tank was charged with the same volume of fresh distilled water after 6 h, 1 day, 2.25 days, 4 days, 9 days, 16 days, 36 days and 64 days. In all cases, the leachate was stirred manually before collection and analysis. The collected leachates were filtered through a 0.45 mm membrane filter after which their pH, Eh and conductivity were measured and their elemental composition was determined by ICP-AES.

The mass transfer of As from the tailings and CPB materials was calculated using Eq. (2), as specified in the EA NEN 7375:2004 standard:

\[ M_i = \frac{(C_i \times V_i) \times A}{L} \]

2.3.2. Accelerated weathering – Weathering cell test (WCT)

A modified version of the WCT developed by Cruz et al. (2001) was used. The CPB samples (hardened for 31 days) were crushed and approximately 70 g of the resulting material was placed on a paper filter in a Buchner-type funnel. The samples were then

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Water soluble</th>
<th>Exchangeable</th>
<th>Fe (III) hydroxide</th>
<th>Fe (III)-oxides</th>
<th>Secondary sulfides</th>
<th>Primary sulfides</th>
<th>Residual</th>
<th>Total (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>7.39 ± 0.35</td>
<td>0.50 ± 0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.84 ± 0.10</td>
<td>3.77 ± 0.02</td>
<td>87.5 ± 4.1</td>
<td>45.258 ± 2522</td>
</tr>
<tr>
<td>Fe</td>
<td>0.09 ± 0.003</td>
<td>0.29 ± 0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.23</td>
<td>3.59 ± 0.26</td>
<td>6.1 ± 3.1</td>
<td>121.772 ± 4122</td>
</tr>
<tr>
<td>As</td>
<td>0</td>
<td>0.81 ± 0.06</td>
<td>94.6 ± 3.2</td>
<td>1.81 ± 0.09</td>
<td>0.02</td>
<td>2.75 ± 0.38</td>
<td>0.03 ± 0</td>
<td>997 ± 50</td>
</tr>
<tr>
<td>S</td>
<td>35.0 ± 2.5</td>
<td>0.8 ± 0.8</td>
<td>6.99 ± 0.55</td>
<td>5.36 ± 0.36</td>
<td>4.41 ± 0.26</td>
<td>37.5 ± 2.7</td>
<td>0.00 ± 0</td>
<td>14.259 ± 1379</td>
</tr>
</tbody>
</table>

Using a Perkin Elmer Optima DV 5300 instrument, and the ICP-SFMS analyses were conducted according to the modified EPA method 200.8 using a Thermo Scientific Element instrument.

Table 2
Specifications of As and S in tailings and ore from Svartliden, extraction scheme adopted from Dold (2003) (values in % of total content) (n = 3, ±SD).

Table 3
Composition of tested cemented paste backfill mixtures (values reported in wt.%)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>FA</th>
<th>CE</th>
<th>H2O</th>
<th>Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA 5</td>
<td>5</td>
<td>25</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>FA 15</td>
<td>15</td>
<td>25</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>CE 2.2</td>
<td>3</td>
<td>2</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>CE 3</td>
<td>10</td>
<td>26</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>CE 3</td>
<td>3</td>
<td>26</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>CE 5</td>
<td>5</td>
<td>25</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>CE–FA 1:2</td>
<td>2</td>
<td>26</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>11</td>
<td>89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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. Leaching was performed with 50 ml of deionized water at a time over approximately 2 h, after which the leachate was recovered by applying suction to the funnel. The pH, Eh and conductivity of the leachates were measured and their elemental composition was analyzed by ICP-AES after filtration. Duplicate weathering tests were performed for each CPB sample, so 4 cells were set up. The test was conducted over a period of 32 cycles (217 days). During cycles 13–18, 1 M HCl was added to consume the buffering minerals within the CPB materials and stimulate the formation of acid mine drainage (AMD).

3. Results

3.1. The characteristics of the binder materials used for CPB

3.1.1. Elemental composition of the binder materials

See Table 4.

3.1.2. Characterization of binder material and CPB mixtures

The composition of the CPB mixtures was adjusted to achieve the desired hardened strength of 200 kPa while minimizing the amount of binder used.

3.1.3. Mechanical strength (Unconfined Compressive Strength, UCS)

The mixtures of CE 1 wt.% and CE (2 wt.%)-FA (1 wt.%) gained a mechanical strength of approx. 200 kPa with a minimal proportion of binders and were chosen for further studies. The CE mixture achieved the highest compressive strength, exhibiting a value of 214 kPa after 60 days' curing (see Fig. 1).

3.2. Leaching tests

3.2.1. Tank leaching test (TLT)

The highest As concentrations released during a leachate renewal cycle for CE, CE–FA, and unmodified tailings were 41.3 mg/m², 13.7 mg/m², and 1.6 mg/m², respectively. The largest renewal cycle for CE, CE–FA, and unmodified tailings were 214 kPa after 60 days' curing (see Fig. 1).

The highest As concentrations released during a leachate renewal cycle for CE, CE–FA, and unmodified tailings were 41.3 mg/m², 13.7 mg/m², and 1.6 mg/m², respectively. The largest renewal cycle for CE, CE–FA, and unmodified tailings were 214 kPa after 60 days' curing (see Fig. 1).
tailings was approx. 3.2. In WCT, conducted with unmodified tailings, leaching of As, Fe and S increased while pH <3.5 (Fig. 4).

4. Discussion

4.1. As-leaching in unmodified tailings

As-bearing FEP with Fe/As-ratios <3 are stable at a pH of 4–8 (Riveros et al., 2001). The pH-stability range increases with higher Fe/As-ratios and the presence of Ca$^{2+}$ and Zn$^{2+}$ (Yakutunc et al., 2008). However, as suggested by sequential extraction tests (Table 2), small proportions of As-sulfides were still present in the tailings and could contribute to an As-release. At more acidic (pH < 4) conditions, oxidation of arsenopyrite and pyrrhotite are accelerated (Blowes et al., 1998). The tailings released relatively small quantities of As during the TLT when pH 3.8–5.7. The As-release was not correlated with pH and standard calculations suggest that the evolution of arsenic leaching in tailings during TLT was dominantly a wash-off-effect where arsenic was rinsed off from the tailings surface (Voglar and Leštan, 2013). Saturated conditions during the TLT limited potential for direct sulfide oxidation by oxygen. So, initial leaching of As could be due to a presence of As (II) in the tailings pore water existing as a consequence of incomplete pre-oxidation of As (III) to As(V) during the tailings treatment process. The As release declined and were almost diminished after the 2nd extraction in the TLT. A reddish crust formed on the surface of the tailings mid-way through the TLT. This was assumed to be due to the formation of an enclosing iron-oxide-precipitate reducing permeability and the rate of weathering enhancing the wash-off effect.

In the WCT, leaching of As increased most extensively when pH decreases below 3.5 in the end of the test (Fig. 4). At this stage, the Fe/S molar ratio in the leachate increased to >4.8, suggesting that pyrrhotite had been oxidized over the course of the experiment. In unsaturated conditions prevailing during WCT leaching of As could originate from the destabilization of As-bearing FEP and the oxidation of As-sulfides that remains in the tailings at small quantities (2.75 ± 0.38 wt.%).

4.2. The use of low binder proportions in CPB – Effects on As-leaching

In cementitious environments, the reactivity of arsenopyrite becomes quickly passivated but pyrrhotite remains active (Benzaazoua et al., 2004a). This would suggest that As-leaching in CPB-materials largely originate from secondary As-phases. The pH-variation in the TLT is related to leaching of Ca$^{2+}$ from the
dissolution of the cementitious binders. The oxidation of Fe-sulfides in cementitious media consumes hydroxyl ions (OH\(^{-}\)) and could contribute to the excessive release of sulfates in leachates as well as the precipitation of Fe-oxides (Benzaazoua et al., 1999) (reaction (3)). Iron tends to precipitate in the water/sample interface while sulfates are released into the leachate.

\[
4\text{FeS}_2 + 15\text{O}_2 + 16\text{OH}^{-} \rightarrow 4\text{Fe}^{3+} + 8\text{SO}_4^{2-} + 2\text{H}_2\text{O}
\]  

At pH <9, all hydrated cement phases are assumed to have been dissolved, resulting in the formation of expansive gypsum and ettringite (Benzaazoua et al., 1999) increasing As, Ca, and Si contents of the leachate. C-S-H surfaces contain SiO\(_2\) moieties that can repel the anionic arsenic species formed under alkaline conditions (10–13). The mechanism of As bonding to C-S-H has been related to the availability of Ca\(^{2+}\), which acts as a charge-balancing counter ion that increases the positive charge on surfaces amenable to As-binding, the normally positively charged C-S-H-surfaces may become negatively charged if the Ca/Si-ratio falls below 1.2 (Phenrat et al., 2005). However, the availability of Ca\(^{2+}\) may also increase the surface charge on the surfaces of FEPs and increase their ability to adsorb As(V), especially at pH <9 (Wilkie and Hering, 1996). The availability of Ca\(^{2+}\) therefore strongly affects the immobilization of As in cementitious systems.

Cementation reduced the Fe contents of the TLT leachates relative to those observed for the tailings, but increased leaching of S, Ca, As and the leachate pH. As-leaching from the CPB materials during the TLT was initially lower than that from the tailings. This may have been due to the ability of cementitious oxides (especially MnO) to oxidize As (III) to As(V) (Cornelis et al., 2008). Leaching of As from CPB materials was most intensive when the pH fell from 10 to 8 at the end of the TLT (Fig. 2). In alkaline conditions during TLT (pH 7.7–10.4), arsenic could have desorbed from FEPs and re-precipitate as Ca-arsenates, sorbed onto calcium-silicate-hydrates (C-S-H), or substituted for SO\(_4^{2-}\) in the crystal lattice of secondary cementitious minerals (i.e. gypsum, ettringite). The mechanism of As leaching from CPB materials (CE and CE–FA) was different to that in the tailings. Initially, cementation hindered water to percolate through the CPB-materials and the release of As would have occurred by rinsing the surfaces of the monoliths. However, as the cementitious phases dissolved (indicated by a Si-release) (Fig. 2), permeability increased and As-leaching became more diffusion-driven where As could spread through the CPB-matrix. This is corroborated by calculations performed according to the TLT standard (Table 5). Consequently, the release of As from CE and CE–FA indicate that no plateau was reached, so the release of As could have continued after the 64-day experimental period. The amount of As released from CE–FA was greater than that from CE–FA during TLT, probably because the greater content of binder material in CE–FA allowed less water to percolate to the matrix and increased the availability of Ca\(^{2+}\). The release of As from CE–FA was more strongly correlated with that of Si (Fig. 5) than was the case for CE, suggesting that more arsenic was associated with C-S-H (Coussy et al., 2011).
The greater leaching of As from CE compared to CE–FA could therefore be due to the lower levels of Ca\(^{2+}\) in the former but may also be partially due to the formation of greater quantities of Ca-arsenates. These Ca-arsenates are stable at pH >10 but become very soluble at lower pH values (Benzaazoua et al., 2004a).

As in TLT, the release of As in CE during the WCT was greater than that from CE–FA when the pH fell from 10 to 8. However, this pH change was more rapid during WCT, occurring within 10 days of the start of the experiment. The mechanisms of As leaching during WCT differed from those for TLT because the exposed surface area in WCT is greater and the sample is more susceptible to oxidation. Surficial conditions could have a negative effect on As-leaching in the CPB-materials while carbonation (which depends on the availability of CO\(_2\)) is known to have a destabilizing effect on Ca-arsenates (Krause and Ettel, 1989) and cementitious phases (Benzaazoua et al., 2004). Weathering during WCT increased the availability of Ca\(^{2+}\) in CPB-leachates, which may have increased the positive charge on the FEP surfaces.

### 4.3. The effect of accelerated weathering on the stability of As in CPB materials

The addition of acid to leachate solutions during the later stages of the WCT was conducted to simulate accelerated weathering and determine its effects on As leaching. The addition of acid increased the leaching of As, Fe, Si, and Ca but had no significant effect on that of S (Figs. 4 and 6).

Arsenic released from the cementitious phases could potentially be re-adsorbed onto FEP surfaces, the high sulfate concentrations formed under these conditions would compete with As(V) species.

---

**Fig. 4.** Evolution of the leachate pH and cumulative leaching of S, Ca, Fe, As and Si from tailings, CE and CE–FA between days 52 and 217 of the weathering cell tests (average values presented).

**Fig. 5.** Changes in the Si and As contents of the TLT leachates produced from CE–FA and CE.
for FEP binding (Frau et al., 2010). This negative effect could be counteracted by the co-adsorption of Ca++, which may function as a multi-adsorbent for As at pH values of 4–9 (Gia and Demopoulos, 2005; Wilkie and Hering, 1996). The cumulative release of As and Fe from CE was greater than from CE-FA. This suggests that the higher binder content introduces more Ca++, which could enhance the ability of FEP to adsorb As. Fe-precipitates originated from sulfide oxidation at alkaline conditions (reaction (3)) could have formed permeable crusts covering the sulfide minerals surfaces retarding its further oxidation (Belzile et al., 2004; Asta et al., 2013).

4.4. Future aspects concerning the use of CPB based on As-rich tailings from cyanidation

Most of the As in the tailings were present as As-bearing FEP: S As(III) which constituted approximately 95% of the total As. Arsenic in these precipitates is sensitive to reducing, extreme acidic or alkaline environments. Arsenic dissolutions under reductive environment may contribute to the As release into solution when the management of tailings are not adequately designed. Although, results from the tailings TLT showed that As-bearing FEPs may be stable under acidic and oxidizing conditions common to the tailings piles. Increased molar Fe/S-ratios (up to 0.8) in the WCT indicated that more extensive pyrrhotite oxidation generating acidic conditions may increase As-leaching on a long term basis. Results from TLT suggested that the addition of binders may increase As-leaching on a short term basis. However, the addition of binders increased the tailings' acid-neutralizing capacity and introduced more Fe precipitates into the tailings matrix, both of which may reduce the potential for sulfide oxidation. Pyrrhotite oxidation is not obstructed, but in alkaline conditions, Fe may precipitate on the surfaces of sulfide grains retarding its further oxidation. Consequently, it may have had a lower positive charge density on its FEP and C-S-H surfaces, reducing their capacity for As adsorption. Unmodified tailings generated an acidic environment in which As-bearing FEPs were stable. A crust of Fe-oxides enclosing the unmodified tailings was formed during flooded conditions, which decreased the surface area susceptible for oxidation. In the CPB mixtures, small (≤15%) proportions of the total As in the solid material was released.

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Paper III

Lowering the water saturation levels in cemented paste backfill mixtures – effect on the release of Arsenic

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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 \( \text{H}_2\text{O}_2 \) and \( \text{O}_2 \)) 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; Deschenes et al., 1998; Pakstne 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)).

\[
2\text{H}_2\text{AsO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{FeAsO}_4(s) + 3\text{CaSO}_4 + 2\text{H}_2\text{O} + s + 4\text{H}_2\text{O}
\]

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 \( \text{Ca(OH)}_2 \)) containing amorphous ferric arsenates (Paktun 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 (Brekke et al., 2009; Kesimal et al., 2005; Bengaazoua 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 lussilignite 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 (Bélisle 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)) (Bengaazoua et al., 1999). In CPB mixtures based on tailings from a cyanide leaching process (CT), sulphates could also originate from the destruction of cyanide (INCO SO4-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 (Brekke et al., 2009). This phenomenon is referred to as a sulphate attack (Bengaazoua 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 sulphide CPB materials, the dissolution of these cementitious binders contributes to neutralization of the acidity generated from the oxidation of sulphides (reactions (2) and (3)).

\[
\begin{align*}
\text{Fe}_3\text{O}_4 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{(OH)}_2+2\text{SO}_4^{2-} + 4\text{H}^+ \\
\text{Ca(OH)}_2 + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \\
\text{Ca}_2\text{Al}_2\text{(SO}_4\text{)}_3 \cdot 12\text{H}_2\text{O} + 2\text{Ca}^{2+} + 2\text{H}_2\text{O} & \rightarrow \text{Ca}_2\text{Al}_2\text{(SO}_4\text{)}_3 \cdot 12\text{H}_2\text{O}
\end{align*}
\]

Previous studies have shown that CPB can immobilize As (Bengaazoua et al., 2004a; Coussy et al., 2011, 2012) in tailings. In these studies, cement based CPBs 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 (Bengaazoua 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 denitrified water to simulate an initial underground storage of a monolithic mass. 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 SiO2 + Al2O3 + Fe2O3 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>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Tailings</th>
<th>FA</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>wt% of DS</td>
<td>55.0 ± 4.9</td>
<td>34.6 ± 1.3</td>
<td>20.6 ± 0.8</td>
</tr>
<tr>
<td>Al2O3</td>
<td>wt%</td>
<td>4.69 ± 0.04</td>
<td>10.7 ± 0.6</td>
<td>5.61 ± 0.43</td>
</tr>
<tr>
<td>CaO</td>
<td>wt%</td>
<td>4.83 ± 0.25</td>
<td>14.1 ± 1.0</td>
<td>50.3 ± 1.8</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>wt%</td>
<td>16.7 ± 0.6</td>
<td>13.9 ± 1.0</td>
<td>2.91 ± 0.05</td>
</tr>
<tr>
<td>K2O</td>
<td>wt%</td>
<td>0.02 ± 0.03</td>
<td>2.99 ± 0.08</td>
<td>0.83 ± 0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>wt%</td>
<td>3.24 ± 0.01</td>
<td>2.94 ± 0.08</td>
<td>4.00 ± 0.17</td>
</tr>
<tr>
<td>MnO</td>
<td>wt%</td>
<td>0.14 ± 0.01</td>
<td>0.50 ± 0.03</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>Na2O</td>
<td>wt%</td>
<td>0.82 ± 0.03</td>
<td>1.24 ± 0.08</td>
<td>0.65 ± 0.07</td>
</tr>
<tr>
<td>P2O5</td>
<td>wt%</td>
<td>0.24 ± 0.01</td>
<td>2.25 ± 0.05</td>
<td>0.06 ± 0.00</td>
</tr>
<tr>
<td>TiO2</td>
<td>wt%</td>
<td>0.18 ± 0.00</td>
<td>0.54 ± 0.01</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>sAs</td>
<td>wt%</td>
<td>2.10 ± 0.50</td>
<td>1.27 ± 0.02</td>
<td>1.00 ± 0.02</td>
</tr>
</tbody>
</table>

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 SO4-air process, H2O2, Fe2(SO4)3 and lime to immobilize As and destroy toxic cyanides. Hydrogen peroxide (H2O2) and Oxygen gas (O2) is added aiming to oxidize arsenopyrite and pyrrhotite to facilitate the cyanide dissolution of gold. The pH of the outlet water is restricted to 6–8.5, Fe2(SO4)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 SiO2 + Al2O3 + Fe2O3 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.

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with the Dutch standard EN 7375:2004. CPB duplicate samples were removed from the bottles after 31 or 446 days and shaped into regular cylinders. The liquid/solid (L/S) ratio was fixed at 4:1 to ensure the compressive strength of 200 kPa was sufficient for the CPB-material. CPB-materials with a minimal proportion of binders were used (Table 3 for proportions). Tailings were mixed with the binders (CE and FA) and distilled water was slowly added to 20% (w/w). The CPB mixtures (CE and CE-FA) were prepared as described in Hamberg et al. (2015). A slump test was not conducted while only 15 kg of tailings was available for analyses and experiments. Mixtures of CE and CE-FA were cured for 31 days or 446 days (hereafter referred to as CE31, CE446, CE-FA31, and CE-FA446). CE31 and CE-FA31 were kept at +25 °C in dark, room-temperature conditions until the 446th day. These conditions were chosen to enhance the formation of an unsaturated area at the surface of the CPB-mixtures as found in Ouellet et al. (2003). The curing period was terminated while local desaturation areas appeared at the surfaces of the CPB-mixtures. A curing period of 31 days were chosen based on results from the studies of Ercikdi et al., (2009; Huang et al., 2011). In CPB’s with low proportions of binders (less than 5 wt. %) the hydration of cement is assumed to be nearly completed after 30 days and the strength does not change much afterwards (Ercikdi et al., 2009; Huang et al., 2011). Increasing the curing period to more than a year could mean a strength loss in the CPB-material, especially when containing sulphide/sulphate rich tailings (Kesimal et al., 2005).  

2.1. Preparation of the CPB-materials

In the study of Hamberg et al. (2015), mine operators considered that a compressive strength of 200 kPa was sufficient for the CPB-material. CPB-materials with a minimal proportion of binders were used (Table 3 for proportions). Tailings were mixed with the binders (CE and FA) and distilled water was slowly added to 20% (w/w). The CPB mixtures (CE and CE-FA) were prepared as described in Hamberg et al. (2015). A slump test was not conducted while only 15 kg of tailings was available for analyses and experiments. Mixtures of CE and CE-FA were cured for 31 days or 446 days (hereafter referred to as CE31, CE446, CE-FA31, and CE-FA446). CE31 and CE-FA31 were kept at +25 °C at approximately 80% humidity (similar to underground conditions according to Bensaazouma et al., 2004b), under dark conditions, until the 31st day of curing. As for CE446 and CE-FA446, these samples were cured at the same conditions as CE31 and CE-FA31 until the 31th day, while the subsequent curing was conducted at approx. 60% humidity, in darkness, at room-temperature conditions until the 446th day. These conditions were chosen to enhance the formation of an unsaturated area at the surface of the CPB-mixtures as found in Ouellet et al. (2003). The curing period was terminated while local desaturation areas appeared at the surfaces of the CPB-mixtures. A curing period of 31 days were chosen based on results from the studies of Ercikdi et al., (2009; Huang et al., 2011). In CPB’s with low proportions of binders (less than 5 wt. %) the hydration of cement is assumed to be nearly completed after 30 days and the strength does not change much afterwards (Ercikdi et al., 2009; Huang et al., 2011). Increasing the curing period to more than a year could mean a strength loss in the CPB-material, especially when containing sulphide/sulphate rich tailings (Kesimal et al., 2005).

2.2. Leaching tests

2.2.1. Tank leaching test (TLT)

A TLT is suitable for monolithic (low permeability) materials, where the leaching fluid flows around the material, thereby providing the driving force for maintaining leaching. This test provides a mechanism for evaluating the surface area-related (i.e. diffusion-controlled) release that occurs at the external boundary of the material. Results are therefore expressed as mass released on a surface area (mg/m²) and tests on the CPB samples (CE-FA and CE-FA) were conducted in accordance with the Dutch standard EN 7375:2004. CPB duplicate samples were removed from the bottles after 31 or 446 days and shaped into regular cylinders. The liquid/solid (L/S) ratio was fixed at 10 cm³ water/cm² of exposed solid for all samples to ensure that the duplicated samples were leached under the same conditions (Coussy et al., 2011). The leachate was removed and the tanks was charged with the same volume of fresh distilled water after 6 h, 1 day, 2.25 days, 4 days, 9 days, 16 days, 36 days and 64 days. The overall experimental set-up is described by Hamberg et al. (2015). The 446-day-cured CE monoliths were disintegrated and placed in paper filter bags, with 0.45-μm-sized pores, inside nylon sample holders. The bags were changed on a weekly basis and hung from the lid of each tank to ensure that the disintegrated CE mixtures were fully immersed in the water. The mass transfer of As from the tailings and CPB materials was calculated using Eq. (1), as specified in the EA NEN 7375:2004 standard:

\[ M_t = (C_t \times V_t)/A \]

where \( M_t \) (mg/m²): mass of As released during the leaching period i, \( C_t \) (mg/L): As concentration during period i, \( V_t \) (L): leachate volume associated with period i, and \( A \): specimen surface area exposed to the leachate (m²). The apparent diffusion coefficient of As was determined by plotting the logarithm of the cumulative Mt (for times preceding and including the i-th period) against the logarithm of the time elapsed since the start of the experiment.

2.2.2. pH-dependent leaching test

The protocol of the test was inspired by previous studies of Glass and Buesfeld (1999) and Peyronnard et al. (2009). Materials from the outermost areas of CE-FA446 and CE446 were crushed into a pulverized material, divided into 12.5-g sub-samples, and placed in acid-cleaned plastic bottles. The aim of the test was to estimate the release of As in response to a decrease in the pH of the CPB material. The acid-cleaned bottles containing CE-FA446 and CE446 were filled with 50 mL of nitric acid solution with the aim of achieving a liquid/solid ratio (L/S) of four. Duplicates were included for three HNO₃ concentrations (pH 6, 4, and ∼2.7) associated with each CPB recipe. The amount of nitric acid added to each bottle was based on preliminary test results that revealed a correlation between nitric-acid addition and the pH. The pH ranged from 8 to ∼2.7 corresponding to the normal pH of the semi-alkaline cementitious samples of CE446, CE-FA446 and unmodified tailings, respectively. The bottles were stirred for 8 days to reach a constant pH, and then leachates were filtered with 0.45 μm polypropylene membranes on a Buchner filter.

2.2.3. Sequential extraction test

A sequential extraction test, adapted from Dold (2003), was conducted on crushed, pulverized, CPB materials (taken from the CPB-surfaces) and the fraction of As associated with certain target phases in CE446 and CE-FA446 was compared. The obtained results were then compared with those of a sequential extraction test (Hamberg et al., 2015) conducted on unmodified tailings (see Table 4).
3. Results

3.1. Tank leaching test (TLT)

The release of elements experienced small deviations in the duplicated samples, averaged values is therefore presented. More As is released in CE31 than in CE446 (Fig. 1), where more Si, Ca, and S are released. As-release in CE31 is lower than that in CE446 at the beginning of the test, but increases thereafter. Maximum As concentrations of 32 mg/m² (0.32 mg/L) for CE31 and 6 mg/m² (0.06 mg/L) for CE446 occur at the 8th and 1st extraction, respectively, of the leachate renewal cycle. In addition, opposite trends are observed for the pH evolution of CE31 and CE446, where a low initial value of 3.2 increases to 6.2 during the last extraction (Fig. 1). The pH of CE31, in contrast, has a high initial value of 9.3 which decreases to 7.7 during the last extraction (Fig. 1). During the leachate renewal cycle of CE-FA, the highest concentrations of As (14 mg/m² and 12 mg/m² for CE-FA31 and CE-FA446, respectively) are released at the 8th extraction. As in the case of CE, more Si, Ca, and S are released in aged CE-FA-materials (CE-FA446) than in fresh CE-FA. The pH evolution of CE-FA446 is similar to that of CE446, i.e. the initial value of 5.2 increases to 7.7 at the 8th extraction. In the case of stored CPB-materials, the amount of As leached from CE-FA during the TLTs increases with time, whereas the amount leached from CE decreases. Similar amounts of Ca and S are released from CE446 and CE-FA446, but a significantly higher amount of Fe is released from CE446, especially while pH is lower than 4.5. A lower amount of Ca, S, and As is released from the unmodified tailings than from CE31, CE446, CE-FA31, and CE-FA446. However, a higher amount of Fe-leaching occurs in these tailings than in CE31, CE446, CE-FA31, and CE-FA446 (Fig. 1).

The occurrence of higher molar ratios (Ca/S) in the TLT-leachates, compared with those in the unmodified tailings from fresh CE31, indicates that Ca is derived from an additional source, besides gypsum. As in the case of CE31, molar ratios (Ca/S) of TLT-leachates from CE-FA31 are larger than those of the unmodified tailings, again indicative of an additional source of Ca. The occurrence of alkaline conditions suggests that cementitious phases have dissolved in CE-FA31 (Fig. 2). Moreover, Ca/S molar ratios corresponding to CE446 and CE-FA446 are lower than those associated with CE31 and CE-FA31 (Fig. 2).

A plot with a slope ($r_c$) of < 0.4 is expected for the surface wash-off process, where surface-captured As is released from the surface of the CPB material. The slope is defined as the logarithm of the total mass of
As transferred plotted against the logarithm of the time elapsed during the experiment. Conversely, diffusion-controlled As release should yield a linear plot with a slope of 0.4–0.6. Calculations performed in accordance with the EN 7375:2004 standard, revealed that As leaching from CE446 and CE31 results from a wash-off-effect and is diffusion controlled (Table 5), respectively. The sharp initial increase in the As concentration of leachates from the CE-FA446 samples is attributed to mass transfer-controlled processes, whereas As release during the later stages of the experiment results mainly from diffusion.

3.2. Sequential extraction test

Crushing CE446 and CE-FA446 prior to the sequential leaching tests revealed dry (bright), superficial regions which could be associated with a low degree of water saturation. Results from the corresponding sequential extractions (Fig. 3) showed that the addition of cementitious binders leads to slight modification of As fractionation, compared with that of the unmodified tailings. Furthermore, compared with that of the unmodified tailings, the fraction of As associated with (i) amorphous Fe(III) oxy-hydroxides in CE446 and CE-FA446 is lower, (ii) the AEC fraction in the cementitious mixtures (especially in CE-FA446) is higher, (iii) Fe(III)-oxides in CE446 and CE-FA446 is higher and unaltered, respectively, and (iv) low-solubility phases (sulphides, silicates) in the CPB-materials is unaltered. Sequential extraction tests on fresh CPB-mixtures were impossible due to unexpected changes in the unmodified tailings.

3.3. pH-dependent leaching test

At pH ≠ 6, more As is released from CE-FA446 than from CE446. At pH = 4 and pH = 2.7, leaching of Fe from CE-FA446 is lower than and similar to, respectively, that from CE446. Conducting a pH-dependent leaching test on fresh CPB-mixtures were impossible due to unexpected changes in the unmodified tailings.

4. Discussion

4.1. Lowering the water saturation levels in CPB-mixtures – Effect on the stability of As

In Hamberg et al. (2016), results from a sequential leaching test suggested that most (95%) of the As in the unmodified tailings is associated with Fe(III)-oxy-hydroxides. As-bearing Fe(III) oxy-hydroxides formed during the tailing treatment process are stable at pH values of 4–8 (Riveros et al., 2001). This As-phase account for 85–90 wt.% of the total As in CE446 and CE-FA446. Specifically, the fraction of As associated with crystalline Fe-phases in CE446 and with the AEC fraction is higher than that of the tailings. This is also true of As associated with the AEC fraction of CE-FA446 (Fig. 3). However, the fraction of As-sulphides in the CPB materials is unaltered compared with that of the tailings (Fig. 3), and is indicative of a low oxidation rate of Arsenopyrite. The re-distribution of As phases in CE446 could mean that a larger proportion of crystalline As-Fe precipitates and less acid tolerant precipitates.
As-species (Fig. 3) has formed compared to that in unmodified tailings. However, these results should be interpreted with precaution whilst changes in the distribution of As is lower than 10% (Tessier et al., 1979).

The As content of the Svartliden are varies significantly (100–1000 ppm), suggesting that Fe-As precipitates with various Fe/As molar ratios have formed in the tailings (Hamberg et al., 2016). As species having an Fe/As molar ratio of 1–1.5 are considered co-precipitated, but adsorbed As species dominate at Fe contents (of the As-Fe precipitates) corresponding to Fe/As-ratios of > 1.5 (Paktunc et al., 2003). However, cyanide leaching of gold ores under semi-neutral/alkaline conditions could also promote the formation of Ca-Fe arsenates from Fe- and As-rich process solutions. Yukonite is a highly soluble Ca-Fe-arsenate while arsenosiderite is stable at pH 3.5–7.5 in gypsum-saturated solutions (Paktunc et al., 2015). In Hamberg et al. (2016), As-release from unmodified tailings is low at pH > 3.5 and is therefore probably not governed by Yukonite. The pH-stability field of arsenosiderite overlaps that of iron-arsenates (Paktunc et al., 2015; Riveros et al., 2001), that could be associated with the Fe(III)-oxy-hydroxide-fraction (Parviainen et al., 2012). So, the stability of As in tailings could therefore be controlled by the solubility of iron-arsenates and arsenosiderite.

In Hamberg et al. (2016), rims of Fe-oxides that could sequester arsenates (AsV) were detected on arsenopyrite grains. Several studies have shown that adsorbed As(V) can transform into a Ca-arsenate in a cementitious matrix (Jing et al., 2003; Vandecasteele et al., 2002; Coussy et al., 2012), as in the case of CE446 and CE-FA446. The introduction of alkaline conditions (resulting in desorption of adsorbed As) and an increase in the Ca content of pore water (through the addition of a Ca-rich, soluble binder) may increase the solubility of Fe-As precipitates over a wide range (3–12) of pH values (Swash and Monhemius, 1995; Drabeka et al., 2009). Ca-arsenates formed under alkaline conditions are known to be thermodynamically unstable in the presence of atmospheric carbon dioxide or carbonate ions (Riveros et al., 2003; Krause and Ettel, 1985; Benzaazoua et al., 2004b). The higher amount of As associated with the AEC fraction of CE446 and CE-FA446, compared with that of the unmodified tailings, results possibly from the formation of Ca-arsenates (Punturro and Cinnamelli, 2010). The proportion of As associated with the AEC fraction, is larger in CE-FA446 compared to that in CE446 (Fig. 3) and is therefore more susceptible to dissolution in an acid medium. This may have resulted in the greater stability of As in CE446 than in CE-FA446 during the pH-dependent leaching test (Figs. 2 and 4); especially in the acidic range. This poses a risk for destabilization of a large fraction of As, due to sulphide-mineral components in the CPB mixtures.

4.2. Lowering water saturation levels in CPB-mixtures – effect on As leaching

In general, tailings material used in CPB-mixtures must contain at least 15 wt.% of fine particles (< 20 μm in size) in order to retain sufficient water to form a paste (Landriault, 2003). In case of CT, this proportion stands for 19 wt.% during the TLT, As leaching from the CPB mixtures is higher, regardless of curing conditions (time and water saturation), than that of the unmodified tailings. Lowering the water saturation level in the CPB-mixtures yields higher and lower As leaching from CE-FA and CE, respectively (Fig. 1). During the TLT, As release from CE-FA and CE, respectively (Fig. 1). During the TLT, As release from CE-FA and CE, respectively (Fig. 1). During the TLT, As release from CE446- and CE-FA446-leachates are lower than those of CE31 and CE-FA31 and increases during the TLT. The evolution of As-release from CE-FA31, CE-FA446, and CE31 suggests that physical encapsulation (Bowell, 2014), and the formation of Ca-, Ca-Fe-, and As-species sorbed onto cementitious phases (Coussy et al., 2012). The occurrence of a diffusion-like transport mechanism of As in CE-FA31, CE-FA446, and CE31 (Table 5) suggests that physical encapsulation has been ineffective in decreasing As leaching. Ca-arsenates and cementitious As-phases formed in a CPB mixture may therefore dissolve in the presence of carbon dioxide and/or acidic conditions, thereby releasing As into solution (Benzaazoua et al., 2004b). As-release from CE31, CE-FA31 and CE-FA446 are largely dependent on the stability of cementitious phases. The stability of cementitious phases in the CPB mixtures is sensitive to reductions in pH that depends strongly on the sulphide-oxidation rate. Initial pH (pH 3–4) in CE446- and CE-FA446-leachates are lower than those of CE31 and CE-FA31 and increased during the TLT. Lowering the water saturation level at the end of the TLT, this results possibly from a more extensive sulphide oxidation that occurred while water saturation levels were lowered. Most of the acid generated from the CPB mixtures during TLT should originate from the oxidation of pyrrhotite. Benzaazoua et al. (2004b) showed that arsenopyrite surfaces can become rapidly passivized in cementitious environments. However, the surfaces of pyrrhotite grains remain active in a cementitious environment, leading to further pH-control of the CPB materials (Benzaazoua et al., 2004b). Pyrrhotite undergoes oxidation in the CPB mixtures, regardless of curing conditions (length and level of...
water saturation), and seems to increase As-release from CE-FA-mixtures while the opposite concern for CE-mixtures.

A presence of gypsum in unmodified tailings is suggested by water-soluble Ca and S (Dold, 2003). Ca/S molar ratios of > 1 for TLT leachates from CE31 and CE-FA31 (Fig. 2), are indicative of Ca-leaching from another source, besides gypsum, probably a cementitious phase. Ca/S molar ratios and pH of TLT-leachates from CE446 and CE-FA446 are lower than those of CE31 and CE-FA446 (Fig. 2) suggesting that some of the cementitious phases have dissolved while water saturation levels decreased as the curing time was prolonged. This is especially evident for CE446 that disintegrated during the curing period. A comparatively low binder proportion (1 wt.%) in CE446 has probably been insufficient to maintain the stability of C-S-H (physical strength), during a more extensive sulphide oxidation. During the TLT, a low amount of As is released from CE446 and CE-FA446 in the acidic range. This amount increases with pH in CE-FA446, suggesting that As is released while the cementitious phases dissolve to buffer acidity from pyrrhotite oxidation. The release of cementitious As-phases manifested as a simultaneous release of As and Si (Coussy et al., 2011) (Fig. 3) from CE31, CE-FA446 and CE31. In CE446, a simultaneous As-Si-release is less obvious (Fig. 3), instead, As could origin from the dissolution of Fe, which is comparatively more abundant (Fig. 2). During the TLT, a majority of As released from CE31, CE-FA31 and CE-FA446 is originated from cementitious As-phases that dissolves when binders are buffering acidity generated from pyrrhotite oxidation.

Coussy et al. (2011), suggested that As is more stable in CPB-mixtures containing larger amounts of lime, but also that fly-ash based CPBs are not suitable for the stabilization of As. These suggestions could to some extent be evident in this study while in the TLT, As-release is most abundant from CE-FA446. Lime content, is however, higher in CE-FA-mixtures (due to higher binder proportions) and As-release is less abundant in CE-FA31 compared to that in CE31. However, as water saturation levels are lowered As-release in CE-FA446 becomes more abundant than that from CE-FA31 and CE446. As-release from CE446 is lower and has a different release mechanism (wash-off) compared to that in CE31, CE-FA31 and CE-FA446 (Table 3). This might be due to the shape of CE446 which is granular rather than monolithic, but also due to higher stability of As in the acidic range compared to that in CE-FA446 (Fig. 4).

5. Conclusions

Management of cyanidation tailings by using CPB with a low fraction of binders results in increased leaching of As, regardless of curing conditions. Lowering the water saturation level in the CPB mixtures leads to the dissolution of cementitious phases. In CPB-mixtures with lower fractions of binders, this yields a reduction in As leaching, where most of the cementitious As phases dissolve to form relatively stable As species. Cementitious phases of As persist in CPB mixtures with a higher fraction of binders, this yields a reduction in As leaching, where leads to the dissolution of cementitious phases. In CPB-mixtures with lower fractions of binders, this yields a reduction in As leaching, where leads to the dissolution of cementitious phases. In CPB-mixtures with a lower fraction of binders, this yields a reduction in As leaching, where leads to the dissolution of cementitious phases. In CPB-mixtures with a higher fraction of binders, this yields a reduction in As leaching, where leads to the dissolution of cementitious phases. In CPB-mixtures with a higher fraction of binders, this yields a reduction in As leaching, where.

leaching of As. Nevertheless, adding a Ca-rich binder may destabilize initially formed As-Fe precipitates in unmodified tailings and thereby decrease the stability of As, especially in the acidic range. Maintaining high saturation levels is therefore essential for preventing acidic conditions and extensive As-release in CPB mixtures.

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References


Fig. 5. The release of As and Si from CE31, CE-FA31, and CE-FA446 during TLT.


The formation of unsaturated zones within cemented paste backfill mixtures -
Effects on the release of copper, nickel, and zinc

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The formation of unsaturated zones within cemented paste backfill mixtures—effects on the release of copper, nickel, and zinc

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Abstract
Flooding of cemented paste backfill (CPB) filled mine workings is, commonly, a slow process and could lead to the formation of unsaturated zones within the CPB fillings. This facilitates the oxidation of sulfide minerals and thereby increases the risk of trace metal leaching. Pyrrhotitic tailings from a gold mine (cyanidation tailing (CT)), containing elevated concentrations of nickel (Ni), copper (Cu), and zinc (Zn), were mixed with cement and/or fly ash (1–3 wt%) to form CT-CPB mixtures. Pyrrhotite oxidation progressed more extensively during unsaturated conditions, where acidity resulted in dissolution of the Ni, Cu, and Zn associated with amorphous Fe precipitates and/or cementitious phases. The establishment of acidic, unsaturated conditions in CT-CPB:s with low fractions (1 wt%) of binders increased the Cu release (to be higher than that from CT), owing to the dissolution of Cu-associated amorphous Fe precipitates. In CT-CPB:s with relatively high proportions of binder, acidity from pyrrhotite oxidation was buffered to a greater extent. At this stage, Zn leaching increased due the occurrence of fly ash-specific Zn species soluble in alkaline conditions. Irrespective of binder proportion and water saturation level, the Ni and Zn release were lower, compared to that in CT. Fractions of Ni, Zn, and Cu associated with acid-soluble phases or amorphous Fe precipitates, susceptible to remobilization under acidic conditions, increased in tandem with binder fractions. Pyrrhotite oxidation occurred irrespective of the water saturation level in the CPB mixtures. That, in turn, poses an environmental risk, whereas a substantial proportion of Ni, Cu, and Zn was associated with acid-soluble phases.

Keywords Tailing management · Cement · Trace metal leaching

Introduction
Cyanide is typically used to extract gold occurring as inclusions in sulfide minerals, such as pyrrhotite and pyrite. In the cyanide leaching process, lime addition can avoid the formation of toxic cyanide species by reaching a pH of ≈ 10. In refractory gold ores, an oxidation step aimed at oxidizing the sulfide minerals enclosing the gold is usually performed prior to the cyanide leaching process (Mesa Espitia and Lapidus 2015). The goal of this step is to increase the availability of cyanide for dissolving the gold. However, this process is seldom 100% effective, and remnants of sulfide minerals often occur in tailings obtained through a cyanide leaching process (cyanidation tailing (CT)). These sulfides often contain trace metals such as copper (Cu), arsenic (As), and zinc (Zn). Furthermore, sulfide minerals exposed to atmospheric oxygen and water may become oxidized. These reactions (reaction 1) yield sulfate and an acid leachate, referred to as acid mine drainage (AMD), with a high content of metals (Blowes et al. 2003). Owing to the co-occurrence of these trace metals and the sulfide minerals, CT must be carefully handled to avoid pollution of the surrounding environment.

FeS2 + 15/4O2 + 7/2H2O → Fe(OH)3 + 2SO42− + 4H+(1)

Tailing management often aims to restrict the interaction of tailings with the environment. A commonly used method is by placing the tailings in underground engineered facilities. Managing of CT in underground workings often includes the use of a so-called “Cemented paste backfill” (CPB)

Highlights
- Pyrrhotite oxidation occurrence within CPB irrespective of the water saturation level
- Unsaturated conditions in CPB increased Cu and Zn leaching
- Using CPB increased proportion of Ni, Zn, and Cu associated to acid-intolerant phases
method. In CPB, low fractions (3–7 wt%) of cementitious binders are mixed with tailings and backfilled into underground facilities (Coussy et al. 2011). Using CPB can primary lead to the formation of a monolith that can serve as a geotechnical support to underground mine cavities, thereby increasing the operational benefits of the mining industry. Increasing the fraction of binders in a CT-CPB may yield intensified hydration and pozzolanic reactions, thereby enhancing the mechanical strength. The use of CPB could also prevent air intrusion into CT and thereby lower the sulfide-oxidation rate. Trace metal immobilization in CPB has been applied to a combination of physical encapsulation and chemical stabilization. Studies of Chen et al. (2009) and Paria and Yuet (2006) suggested that nickel (Ni) and chromium (Cr) can be encapsulated in the calcium-silicate-hydrate (C-S-H) structure. This physical encapsulation is largely dependent on the inherent strength of the CPB. The CPB strength results primarily from the abundance of C-S-H (Peyronnard and Benzaazoua 2012) formed by the addition of calcium-rich binders that hydrate in solution. In CT-based CPB materials (CT-CPB), dissolution of C-S-H contributes to neutralization of the acid formed by the oxidation of sulfides (reactions 1 and 2). Sulfide oxidation, gypsum dissolution, the cyanide leaching process, and/or the binders may generate sulfates in the CT and the CT-CPB mixtures. The stability of C-S-H in a CPB is governed by the sulfide and sulfate content, curing time as well as the type and fraction of binder material (Ercikdi et al. 2009; Kesimal et al. 2005; Benzaazoua et al. 2004). The cementitious phase reacts with sulfates, thereby forming expansive phases such as gypsum and ettringite (a sulfate attack, reactions 2 and 3) that may lead to a decrease in the inherent strength, generate cracks, and increase the availability of oxygen in the CPB material. A chemical stabilization may occur and the hydroxyl anions from this process may react with trace metals (i.e., Pb and Zn), forming hydroxides that can adsorb onto C-S-H. However, highly alkaline conditions (resulting from the release of OH−) could also increase the mobility of some trace metals (Cr, Pb, Zn, and Cu) (Kumpiene et al. 2008). Maintaining the stability of C-S-H is therefore essential from the viewpoint of trace metal mobility in a CT-CPB.

\[
\begin{align*}
\text{Ca(OH)}_2 + 2\text{SO}_4^{2−} + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{OH}^− \quad (2) \\
\text{Ca}_6\text{Al}_2\text{(SO}_4)\text{O}_4\cdot 12\text{H}_2\text{O} + 2\text{SO}_4^{2−} + 2\text{Ca}^{2+} & \rightarrow 2\text{H}_2\text{O} + \text{Ca}_6\text{Al}_2\text{(SO}_4)\text{O}_4\cdot (\text{OH})_2\cdot 2\text{H}_2\text{O} \quad (3)
\end{align*}
\]

Maintaining a high grade of water saturation in a CT-CPB will hinder sulfide oxidation and the subsequent sulfate attack on the C-S-H. In field conditions, a CT-CPB is typically flooded when mine operations are disclosed and the ground water has recovered to natural levels. Complete flooding of a CT-CPB-filled stope may take several years, and unsaturated zones may form within the CT-CPB (Ouellet et al. 2006). This will increase the risk of a significant sulfide oxidation to occur within the CT-CPB. A previous study of Kesimal et al. (2005) showed that the strength of a CPB material (especially sulfide-rich CT-CPB) could decrease by more than 50% during prolonged (>1 year) curing. Cruz et al. (2001) have shown that low fractions of binders may be insufficient to prevent the occurrence of AMD. Knowledge of trace metal and sulfide mineral mobility in CT-CPB is therefore essential for the prediction/management of contaminant release over an extended period of time. In some underground workings, the strength of the CT-CPB material is of less concern, but aims to minimize water percolation and enhancing trace metal stability still exist. So, when less strength is needed in the CPB material, how does it affect the leaching of trace metals? CT from a gold mine in the north of Sweden was to be managed by the use of a CPB application, whereas the strength demand was set to 0.2 MPa by the mine operator. The overall aim of this study was to determine whether a low-strength CPB (0.2 MPa) could be an environmentally friendly option for managing tailings (obtained through a cyanide leaching process) with elevated concentrations of Cu, Ni, and Zn.

As part of the overall aim, primary objectives of the study were to

- Evaluate the effect of using low-strength CT-CPB mixtures on the release of Ni, Cu, and Zn;
- Determine the effect of unsaturated conditions in low-strength CT-CPB mixtures on leaching of these elements.

The results of this study may increase knowledge of the preparation/management of CPB mixtures for use in mine facilities with slow recovery of natural groundwater levels.

**Materials and methods**

Tailings and ore were collected from a gold mine in the north of Sweden. The ore was considered refractory as the gold occurred as inclusions in co-occurring sulfide minerals. According to personnel at the site, hydrogen peroxide (H₂O₂) was added in the 1st step of the cyanide leaching process, with the aim of oxidizing the sulfide minerals. This oxidation will increase the availability of cyanide for gold dissolution. Effluents from the H₂O₂ step were treated with lime (to maintain a pH of 10) to avoid the formation of hazardous cyanide species. Subsequently, Fe(SO₄)₃ addition continued until a pH of ~8 was reached for the outlet water. Portland cement (CE) and biofuel fly ash (FA) were tested as cementitious binders for the preparation of various cemented paste mixtures. The ash was provided from a biofuel incineration plant located near to the mine site and could be classified as a class C fly ash (SiO₂ + Al₂O₃ + Fe₂O₃ ≥ 60 wt%).
weight (wt%), according to ASTM C618-05 (2005). The main elements and total content of Cu, Ni, S, and Zn in the CT, ore, CE, and FA are presented in Table 1.

In Hamberg et al. (2016), X-ray diffraction (XRD) and scanning electron microscopy combined with energy dispersive spectroscopy (SEM-EDS) revealed that pyrrhotite and arsenopyrite were the main Fe- and As-sulfide minerals in the CT. Quartz constituted the main mineral (~80 wt%) in the studied tailings. Tremolite, albite, and microcline each accounted for <5 wt% of the tailings, and no Cu-, Ni-, or Zn-carrying minerals were found. The acid-base accounting (ABA) test was conducted in Hamberg et al. (2015) and showed that the tailings were considered to be acid generating with an acid potential (AP) of 65.3, neutralization potential (NP) of -4.5. This rendered a net neutralization potential (NNP) of -60.5. Calculation performed in Hamberg et al. (2016) suggested that the sulfide and sulfate content in CT accounted for 44 and 56 wt%. These estimations were based on the suggestions of Dold (2003), which encountered the sulfate content to be the amount of S released in steps 1–4 during the sequential extraction test. The sulfide content was equal to total S released in step 5–6.

Sample analysis

The pH of the water samples was measured on unfiltered samples. The pH of the water samples was measured on unfiltered samples. The paste-pH was measured by a method suggested by Sobek et al. (1978) and Page et al. (1982). Twenty grams of solids were mixed with 20 g of deionized water, stirred for 5 s, and then left for 10 min before pH was measured. A pH meter called “Meterlab PHM201” pH-Eh meter calibrated against standard buffers at pH 4.01 and 7.0 was used. Element compositions in the water samples were analyzed by a laboratory accredited by the Swedish board of accreditation and conformity assessment (SWEDAC). Total contents of Cu, Ni, and Zn were determined by high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS), whereas Al, Ca, Fe, K, Mg, Na, and S were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Prior to analysis, samples were acidified with super-pure nitric acid using 1 mL of acid/100 mL of sample. Analyses of HR-ICP-MS and ICP-AES were performed using modified versions of the US Environmental Protection Agency (US EPA) methods 200.8 and 200.7, respectively.

Solid samples were analyzed for major and minor elements by the accredited laboratory. For the determination of Cu, Ni, S, and Zn, samples were dried at 50 °C, digested with 7 M nitric acid in closed Teflon vessels, and treated in a microwave oven. Concentrations of other elements were determined after fusion with lithium metaborate, followed by dissolution in dilute nitric acid. The solutions were subjected to centrifugation and diluted before analysis. For quality control, two in-house reference materials were analyzed in parallel with the solid samples. The dry matter content of CT, CE, and FA samples were determined in triplicate by drying the samples in an oven at 105 °C for 24 h according to Swedish standard SS 028113-1 (SIS 1981).

Preparation of CT-CPB mixtures

Mixtures (desired strength 0.2 MPa) were designed with minimal fractions of binders (see Table 2). The tailings were mixed with the binders (CE and FA), and ~25 wt% of distilled water was slowly added (see Table 2 for the composition of the CT-CPB mixtures (CE and CE-FA)). The preparation is described in detail by Hamberg et al. (2015). CT-CPB mixtures of CE and CE-FA were cured for 31 or 446 days (referred to as CE31, CE446, CE-FA31, and CE-FA446 hereafter). CE31 and CE-FA31 were kept at room temperature at ~80% humidity under dark conditions, until the 31st day. In

| Table 1: Total content of elements and pH in the ore, tailings, fly ash, and cement (a selection from 31 elements is presented) (n = 3, ± SD) |
|---|---|---|---|
| | Ore | CT | Fly ash | Cement |
| Total solids (TS) | 99.97 ± 0.06 | 89.0 ± 0.4 | 95.2 ± 0.7 | 99.4 ± 0.0 |
| SiO₂ | 38.3 ± 0.9 | 55.0 ± 4.9 | 34.6 ± 1.3 | 20.6 ± 0.8 |
| Al₂O₃ | 1.74 ± 0.07 | 4.69 ± 0.04 | 10.7 ± 0.6 | 5.61 ± 0.45 |
| CaO | 4.26 ± 0.09 | 4.83 ± 0.25 | 14.1 ± 1.0 | 50.3 ± 1.8 |
| Fe₂O₃ | 12.6 ± 0.5 | 16.7 ± 0.6 | 13.9 ± 1.0 | 2.81 ± 0.05 |
| K₂O | 0.32 ± 0.00 | 0.92 ± 0.03 | 2.89 ± 0.08 | 0.83 ± 0.05 |
| MgO | 2.38 ± 0.07 | 3.24 ± 0.01 | 2.54 ± 0.08 | 4.00 ± 0.17 |
| 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 |
| S | 25,367 ± 2363 | 20,933 ± 493 | 13,700 ± 200 | 9960 ± 219 |
| Zn | 10.6 ± 1.5 | 25.0 ± 0.4 | 374 ± 10 | 149 ± 3 |
| Paste-pH | N.D | 5.03 ± 0.25 | 13.2 ± 0.6 | 12.7 ± 0.3 |

N.D not determined
addition, CE446 and CE-FA446 were cured under the same conditions as CE31 and CE-FA31 until the 31st day, and subsequently at ~60% humidity, in the dark, under room temperature conditions until the 446th day. These conditions were chosen to enhance the formation of an unsaturated region at the surface of the CPB mixtures, as described by Ouellet et al. (2006). The curing period was terminated when brighter (drier) regions (compared with those in the bulk) formed on the surfaces of the CPB mixtures.

Leaching tests

Flooded monoliths—tank leaching test

Tank leaching tests (TLTs) were conducted, in accordance with 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 setup is described in Hamberg et al. (2015). CE 446 fell apart upon contact with water and, therefore, placed in paper filter bags (with 0.45-μm pores) inside nylon sample holders. The filter bags containing the granular CT and CE mixtures were changed upon each leachate renewal and were fully immersed in the water. In addition, the 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, and Ni from CT and the CT-CPB materials was calculated from (as specified in the EA NEN 7375:2004 standard):

$$M_i = \frac{C_i \times V_i}{A}$$  \hspace{1cm} (4)

Where, $M_i$ (mg/m²): mass of the element released during leaching period $i$; $C_i$ (mg/L): element concentration for period $i$; $V_i$ (L): leachate volume for period $i$; and $A$: specimen surface area (m²) exposed to the leachate. The apparent diffusion coefficient of Cu, Fe, S, Ca, Zn, and Ni was determined by plotting the logarithm of the cumulative release $M_i$ until the $i$th period against the logarithm of the time elapsed since the start of the experiment. A plot with a slope ($r_c$) of $<0.4$ is expected for the surface wash-off process, where surface-captured elements are released from the surface of the CT-CPB. The slope is defined as the logarithm of the total mass of the transferred elements plotted against the logarithm of the time elapsed during the experiment. Conversely, diffusion-controlled release should yield a linear plot with a slope of $0.4-0.6$, and dissolution controls the release if the slope is $>0.6$.

Sequential extraction test

Fractionation of Ca, Fe, S, Ni, Zn, and Cu was assessed using a modified sequential extraction scheme described by Dold (2003). In each extraction sequence, 2 g of CT, ore, CE446, and CE-FA446 were used and extracted with five different solutions consecutively. Materials from CE446 and CE-FA446 were taken from the outermost (brighter) regions with a lower water saturation level than the other regions. Overall details about the extraction procedure are presented in Hamberg et al. (2016).

Weathering cell test

Approximately 70 g of tailings was placed on a paper filter in a Büchner-type funnel. Duplicate samples were exposed to 31 weekly cycles (217 days), involving 1 day of leaching, 3 days of ambient air exposure, a second day of leaching, and two subsequent days of air exposure. The samples were leached by covering each with 50 mL of Milli-Q H₂O for ~2 h. The leachates were then recovered by applying a vacuum to the funnel. The pH, Eh, and EC of the filtered leachates were subsequently measured; the chemical composition of the water samples was determined as described in Hamberg et al. (2016).

pH-dependent leaching test

The pH-dependent leaching test was inspired by the previous study of Peyronnard et al. (2009). Surficial materials of CE-FA446 and CE446 were crushed into a pulverized material, divided into 12.5-g sub-samples, and placed in acid-cleaned plastic bottles. The aim of the test was to estimate the release of Cu, Ni, and Zn in response to a decrease in the pH of the CPB material. A more detailed description of the test is described in Hamberg et al. (2017). The pH ranged from 8 to ~2.7 corresponding to the normal pH of CE446, CE-FA446, and unmodified tailings, respectively. The bottles were stirred for 8 days to reach a constant pH, and then leachates were filtered with 0.45-μm polypropylene membranes on a Büchner filter.
Speciation-solubility calculations were performed with the geochemical code PHREEQC (Parkhurst and Appelo 1999) using the ThermoDem database (Blanc et al. (2007), version V1:10, which includes cementitious phases inferred by Lothenbach et al. (2008). Element concentrations, redox potential (Eh), and pH in leachates from the TLT were used in these calculations.

**Scanning electron microscopy**

A JSM-IT 100 scanning electron microscopy (SEM), by JEOL, was used for the observation of particle morphology. Investigated samples were dried, powdered, and placed over a conductive carbon tape. Secondary electron detector (SED) mode, with high vacuum and acceleration of 10 kV, is used to obtain all the micrographs. The morphology is analyzed at different magnifications.

**Results**

**Sequential extraction test**

Sequential extractions were conducted on triplicate samples of ore, CT, CE446, and CE-FA446. A majority of all the analyzed elements in the ore were associated with the sulfide/residual fraction. Less than 30 wt% of Zn was associated with more soluble phases. The corresponding proportions of Cu, Ni, S, Ca, Fe, and Si associated with more soluble phases were 3–12 wt%. In the ore, there were no or very small amounts of analyzed elements associated with the water soluble phase. In CT, proportions of elements associated with the sulfide/residual fraction were lower compared to that in the ore, especially that of Ni. Instead, significant proportions of Ni (77 wt%), Cu (~ 10 wt%), Zn (~ 20 wt%), Ca (~ 8 wt%), and S (35 wt%) were associated with the water soluble fraction in CT. Concerning Fe and Si, minor amounts in CT were associated with the water-soluble phase. The proportions of Cu, S, and Fe associated with AEC, Fe(III)-oxy-hydroxide, and Fe(III) oxides in CT were higher compared to that in the ore, but unchanged for Zn and Si (Fig. 1). Total extracted amount of Cu was significantly higher in CT compared to that in the ore (Fig. 1). Detailed results from the sequential extraction tests are attached in an appendix Table 4.

In the CT-CPB mixtures, less proportions of Cu, Ni, and Zn were associated with the water-soluble fraction, compared to that in CT. The opposite concerned for S in CE-FA446. In general, higher proportions of Ni, Zn, Cu, Fe, S, Si, and Ca in CE-FA446 were associated with the AEC fraction, compared to that in CE446. This difference is most significant concerning Ca (Fig. 2). Proportions of Ni, Zn, Cu, Fe, S, Si, and Ca associated with Fe(III)-oxy-hydroxide and Fe(III) oxides in CT were higher compared to that in the ore (Fig. 1). Detailed results from the sequential extraction tests are attached in an appendix Table 4.

![Fig. 1](Fractionation of Ni, Zn, Cu, Fe, S, Si, and Ca in the ore and CT (average values presented, n = 3). Total content (n = 3; ± SD) of extracted elements in attached tables)
oxides were similar in CE-FA446 and CE446 (Fig. 2). Detailed results from the sequential extraction tests are attached in an appendix Table 4.

Compared with CT, CE and FA contained higher total concentrations of Ni and Zn. Similarly, Ni and Zn occurred with higher fractions in the CT-CPB mixtures (CE31, CE-FA 31, CE-FAA446, and CE446) than in the CT. An addition of CE increased the fraction of Ni by 1.8% in the CE mixture, compared to that in CT. The corresponding increase in CE-FA was 21.7 (Zn) and 3.0% (Ni).

Tank leaching test

In the TLT, small deviations are observed in results from the duplicated tests of CT, CE 31, CE 446, CE-FA 31, and CE-FA 446 and, therefore, average values are presented. The release of Fe, Ni, Zn, and Si from CT was significantly higher than that released from the CT-CPB materials. The opposite concerned for Cu, whereas higher amounts were released from CE446. In the CT-CPB materials, the largest amount of Fe, Ni, and Si was released from CE446 (Fig. 3), while the most abundant release of Zn was encountered from CE-FAA446. In all materials, the release of Cu and Fe evolved in a similar way and increased considerable during the first days (until the ninth day) of the TLT but was lowered toward the end. This was also somewhat true for the evolution of Ni and Zn. However, the Zn release in CE-FAA446 increased steeply during day 9–36 and was significantly lower in the last extraction. A Ni release from CE446 increased throughout the TLT (Fig. 3). The release of Si was most abundant in CT and increased steeply toward the end of the TLT. At the last extraction, the Si release from CE31, CE-FAA446, and CT increased, whereas the opposite occurred in CE-FA31. A Si release from CE446 increased throughout the TLT. The pH evolved in a similar way in CE31 and CE-FA31. In each case, the pH increased initially, stabilized at ~10–10.5, and dropped to 8 during the last extractions. The pH of CE446 and CE-FA446 were lower than those of CE31 and CE-FA31. Furthermore, the pH of CE446 increased initially and stabilized at a pH of 8. In CE446, pH increased throughout the TLT from 3 to ~6.

The saturation index of gypsum in CT decreased during the TLT. The saturation indexes of ferrihydrite in CE 446 and CE-FA 446 were negative (suggesting dissolution) during extractions 1–2, but positive during extractions 3–8. Furthermore, the saturation indexes of ferrihydrite in CT were negative during all extractions, except for extraction 4 (Fig. 4).

The results of the calculations based on the EA NEN 7375:2004 standard indicated that similar Cu and Ni leaching mechanisms operate in CE31 and CE-FA31 (Table 3). In the CT-CPB materials, the cumulative release of Zn from CE-FA31 and CE-FA446 was higher than that from CE31 and CE446. Similarly, more Fe and Cu were released from CE-FAA446 and CE446 than from CE31 and CE-FA31. The release of Cu from CE31 and
CE-FA31 occurred via diffusion induced by the dispersal of these elements from pore water. However, the release of Zn from the granular materials (CT and CE446) and the monoliths (CE-FA446, CE31, and CE-FA31) was induced by wash-off behavior and diffusion, respectively (Table 3).

Weathering cell test

After 217 days of the weathering cell tests, the cumulative release of Ni, Zn, Fe, and Cu from the CT-CPBs was lower than that from CT. More Cu was released from CE-FA than
from CE-FA, but the opposite was true for Ni and Zn. Similar pH trends were observed for CE and CE-FA. In both cases, the pH of the washings decreased from 11.4 (CE-FA) or 10.1 (CE) to a stable value of ~8 after 10 days (Fig. 4). Small deviations were observed in the results of the duplicated tests of CT, CE, and CE-FA, and, therefore, average values are presented. The release of Ni from the CT-CPB samples seemed to be correlated with changes in the pH (i.e., the maximum release occurred when the pH decreased from 11 to 8). Similar Zn and Cu evolution was observed in the CT-CPB samples, with maximum values occurring on the 10th day of the weathering cell test (WCT). The values then decreased until day 24, but then increased until day 52. The amount of Si decreased until the tenth day of the experiment, but increased thereafter. Prior to the addition of acid (after day 70), a low amount of Fe was released from the CT-CPBs.

After 70 days, acid was added to the leachate with the aim of consuming the buffering minerals in the CPB materials. Different amounts of acid (1 M HCl) were added over 77 days (between days 70 and 147) to each CPB material (CE 0.47 M H+ / kg TS and CE-FA 0.69 M H+ / kg TS). Consequently, the pH of each material decreased to ~4.5, i.e., the initial value in tandem with a pH decrease. The release of Cu and Fe increased with the addition of acid (after day 70), but increased thereafter. Prior to the addition of acid, a low amount of Fe was released from the CT-CPBs.

In Fig. 4, tabular-shaped particles with approximately length of 30–40 μm suggested the presence of gypsum (Myagkaya et al. 2016). In addition, typical gypsum morphology particles are detected in CE-446, Fig. 7a. From Fig. 7c, d, it was visible that tailings treated with CE and FA have developed needle-shaped morphology, typical of the hydrated cement paste phases, suggesting the formation of C-S-H and ettringite (Panchal et al. 2018). In addition, typical spherical shaped fly ash particles are observed in CE-FA446, Fig. 7d (Grau et al. 2015).

### Discussion

#### Unsaturated conditions in CT-CPB mixtures—effect on the solubility of cementitious binders

Immobilization of trace metals in cementitious mixtures has been applied to physical encapsulation and chemical stabilization (Chen et al. 2009; Paria and Yuet 2006; Benzaazoua et al. 2004). The physical strength is strongly dependent on the stability of cementitious C-S-H. Ideally, cementation will reduce the open porosity and obstruct water percolation through the CT-CPB mixtures. In these mixtures, the addition of cementitious binders was probably manifested as an increase in the amount of Ca and S associated with the AEC fraction (Dold 2003). Pyrrhotite oxidation generated sulfates that dissolved the binders, resulting in the formation of gypsum and ettringite (reaction 4) and, in turn, a reduction in the mechanical strength. Dissolution of this kind is suggested by the presence of C-S-H and ettringite in CE-FA446 (Fig. 7). The solubility of the cementitious phases increased at pH values of < 9 (Benzaazoua et al. 1999). The evolution of pH in leachates from all the CT-CPB mixtures during the TLT suggested that the cementitious phases have dissolved to some extent, especially in CE-446 that fell apart into a granular material. Cementitious phases were more abundant in CE-FA446 compared to that in CE446 that seems to contain more gypsum. The low strength of CE446 was probably also reflected in the larger amount of gypsum formed, as indicated by the higher fraction of water-soluble Ca and S (Dold 2003), compared with that of CE-FA446 (see Fig. 2).

#### Unsaturated conditions in CT-CPB mixtures—effect on the release of Ni, Cu, and Zn

According to Sciuba (2013), the major sulfide minerals in Svartliden consist of pyrrhotite (Fe7S8) and arsenopyrite experienced a different leaching pattern and was more abundant at pH 8 compared to that in pH 6 (Fig. 6).

### Table 3 Cumulative amounts of elements (in mg/m²) released via the dominant leaching mechanism during TLT

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT</td>
<td>8.0 DF</td>
<td>162 SW</td>
<td>199 SW</td>
</tr>
<tr>
<td>CE 446</td>
<td>35 SW</td>
<td>8.6 SW</td>
<td>8.9 SW</td>
</tr>
<tr>
<td>CE 31</td>
<td>2.7 DF</td>
<td>3.3 DF</td>
<td>31 DF</td>
</tr>
<tr>
<td>CE-FA 446</td>
<td>7.7 DF</td>
<td>1.0 DF</td>
<td>124 DS</td>
</tr>
<tr>
<td>CE-FA 31</td>
<td>2.5 DF</td>
<td>1.5 DF</td>
<td>68 DF</td>
</tr>
</tbody>
</table>

DF = diffusion, SW = surface wash off, DS = dissolution
(FeAsS). However, traces of chalcopyrite (CuFeS₂), pyrite (FeS₂), and sphalerite (ZnFeS) are also found. No chalcopyrite, sphalerite, and Ni species was found during mineralogical analyses, but it is a common fact that mining processes is never 100% effective, so remnants of sulfides are probably present in CT. Results from the fractionation (Fig. 1) suggested that significant amounts of sulfides in the ore oxidized during the cyanide leaching process. A substantial fraction of Zn, Cu, and Ni from this process was re-distributed to water-soluble-species and/or co-precipitated with Fe-(oxy)-hydroxides. The cyanide leaching process yielded a pH of ≈ 8 for the outlet water. This value resulted from the addition of lime and consequent formation of metal hydroxides (i.e., Cu(OH)₂, Zn(OH)₂, and Ni(OH)₂) (Donahue et al. 2000; Hidmi and Edwards 1999). These hydroxides are stable under pH-neutral, oxidized conditions (Karapınar 2016; Kumpiene et al. 2008). In CT, pyrrhotite oxidation products leads to acidic conditions (pH: 3.5–5.0) in TLT-leachates (Fig. 3) that probably dissolved a majority of these hydroxides. A majority of the Zn, Ni, and Cu were rinsed of the surface via a wash-off-effect in CT (Table 3) whereas initially high amounts of these elements decreased toward the end TLT (Fig. 3). This evolution is typical for a wash-off-effect, probably induced by the formation of a reddish crust on the surface of CT mid-way through the TLT. The crust was assumed to be an enclosing iron-oxide precipitate. As hydroxides of Ni,
Cu, and Zn dissolves, these could be re-adsorbed onto Fe precipitates, but this process becomes less effective in acidic conditions. In addition, Ni release and Zn release were more than ten times higher than the Cu release in the CT. This may have resulted from the fact that Cu is readily adsorbed onto Fe precipitates at a pH of 4, whereas

![Fig. 6](image_url) The release of Ni, Cu, Fe, and Zn (expressed in mole) during the pH-dependent leaching test (averaged release, n = 2)

![Fig. 7](image_url) SEM micrographs of CT (a), CE446 (b), and CE-FA446 (c, d)

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other metals (i.e., Ni and Zn) remain in the solution (Dzombak and Morel 1990).

In CE31 and CE-FA31, the dissolution of the cementitious phases increased the pH of the TLT leachates to alkaline (pH 8–10.5) levels. The diffusion-like behavior of Cu, Zn, and Ni suggests that these elements were transported from the CT-CPB pore water to the surrounding leachate. Heavy metals in a CPB matrix could occur as metal hydrated phases or metal hydroxides precipitated on C-S-H-surfaces (Li et al. 2001). In these cases, a metal release occurs as the C-S-Hs are dissolving, causing alkaline conditions in the CT-CPB-leachates. This phenomenon could result in the formation of anionic complexes with a low affinity for Fe precipitates in the pore water of CE31 and CE-FA31. A Ni and Cu release could then be induced by desorption from Fe precipitate surfaces (Kumpiene et al. 2008). The Zn release from the CT-CPB mixtures was approximately a tenfold higher than the Ni and Cu release and most extensive at pH levels of < 8 or > 10 (Fig. 3). A Zn release was probably governed by zinc hydroxides (Zn(OH)$_2$) that are amphoteric and mobile in both alkaline and acidic conditions (Malviya and Chaudhary 2006). Zinc hydroxides could gradually be transformed into cationic species (Zn$^{2+}$, Zn(OH)$^{+}$) as the pH decreased to < 10 and anionic species at pH > 10 (Degen and Kosec 2000). Anionic Zn species could then be released due to desorption from Fe precipitates. The Zn release may also originate from the fly ash that, compared to CT, contains substantially higher fractions of Zn (Table 1). In the CE-FA mixtures, fly ash could contain Zn attached to calcium alumino-silicate glass that is more soluble under alkaline than acidic conditions (Luo et al. 2011). That might explain a greater release of Zn, irrespective of binder fraction and the water saturation level. The Zn release from the CT-CPB was lower than that from CT, irrespective of the establishment of unsaturated zones in the CT-CPBs had a negligible effect on the Ni release, which was low during the TLT. The Ni release from CE446 was more abundant compared to that in CE-FA446. This could be due to a more abundant dissolution of amorphous Ni-bearing Fe phases and a comparatively lower pH (Figs. 3 and 4). The Zn release from the CT-CPB was lower than that from CT, irrespective of binder fraction and the water saturation level. As unsaturated zones formed in the CT-CPB mixtures, the Zn release from the CE-FA mixtures increased, while the opposite occurred in the
CE mixtures. A minor Zn release from CE446, compared with that from CE-FA446, could be due to a comparatively lower total content of Zn (Table 1), owing to the addition of a lower fraction of binder. Elements associated with the AEC fraction are often bound to carbonate phases that are sensitive to pH fluctuations. Carbonate phases formed under alkaline conditions are known to be thermodynamically unstable in the presence of atmospheric carbon dioxide (Benzaazoua et al. 2004). At the surface (with a lower water saturation level than the bulk) of CE446 and CE-FA446, carbonation resulting in dissolution of the cementitious phases may have occurred. In CE446, this yielded a reduction in Zn leaching, where most of the cementitious Zn phases on the surface dissolved, thereby forming more acid-tolerant species. A Zn decrease may have also resulted from the fact that the leachate/CPB contact area during a surface wash-controlled release (as in CE446) is lower than the area associated with a dissolution-like release (as in CE-FA446). In CE-FA446, more Zn is released at neutral pH than under acidic conditions (Fig. 3). That substantiates a Zn release from FA, which might contain Zn attached to calcium aluminosilicate glass that is more soluble under alkaline conditions than acidic, suggested by Lou et al. (Luø et al. 2011). By adding binders to CT, a significant fraction of Cu, Ni, and Zn might have been re-distributed from the water-soluble fraction to AEC phases in CE446 and CE-FA446. However, a large part of Zn, Cu, and Ni associated with the AEC fraction in CE446 and CE-FA446 could also originate from the binder themselves, as previously suggested in many studies (Pöykiö et al. 2011; Nurmesniemi et al. 2008; Świetlik et al. 2013). In these cases, maintaining high water saturation levels in the CT-CPB mixtures is essential to preventing the effects of ongoing pyrrhotite oxidation.

**Mobility of Ni, Cu, and Zn in CT and CT-CPB mixtures during accelerated weathering**

Ni release from CT seemed to be correlated with the water-soluble Ni phases. This initially high release decreased sharply and diminished toward the end of the WCT, in contrast to the Zn release that was low during the WCT. The Cu release seemed to be correlated with the Fe-release, increased rapidly as the pH dropped below 4 (Fig. 5). The pH increased after the binders were added. Moreover, the results from the fractionation suggested that a large fraction of water-soluble phases was re-distributed into AEC phases (Fig. 1), which are sensitive to pH fluctuations (Dold 2003). In the CT-CPBs, the Cu, Ni, and Zn release exhibited similar trends and the maximum levels occurred with a sharp decrease (from 11 to 8) in pH until day 10. The release of Cu, Ni, and Zn decreased when the pH of the CT-CPB leachates stabilized at 8 (Fig. 5). This suggested that these elements are released, owing to desorption from Fe precipitates and/or the dissolution of cementitious phases. When acid was added to the CT-CPBs, the cumulative release of Ni, Cu, and Zn from the CT-CPB mixtures was substantially lower than that from the CT. This may have resulted from the fact that the pH at the endpoint (3.2) of the CT leachates was lower than that (pH: 4.5) of the CT-CPB leachates. The reaction kinetics of the WCTs differed from that of the TLT. In this case, the solubility of Cu, Ni, and Zn depended mainly on the pH and, hence, the elements were probably released via the dissolution/precipitation phases in the weathered CPB samples.

**Conclusions**

Flooding of cemented paste backfill (CPB)-filled mine facilities is, commonly, a slow process where unsaturated zones may form within the CPB mass. Cyanidation tailings (CT) with elevated concentrations of Cu, Ni, and Zn and a pyrrhotite content of 1 wt% were managed by using CPB (CT-CPB). Two low strength (0.2 MPa) CPB mixtures were used, CE (tailings mixed with 1 wt% cement) and CE-FA (tailings mixed with 2 wt% of cement and 1 wt% of fly ash). Using a low strength CPB resulted in decreased leaching of Zn and Ni, regardless of water saturation level and binder proportion compared to that occurring in the CT. The establishment of unsaturated zones within the CT-CPBs leads to significant pyrrhotite oxidation, which resulted in acidity and, in turn, dissolution of the cementitious phases. At this stage, the mobility of Zn increased in tandem with pH in the CT-CPB mixtures. In CE mixtures, semi-acidic conditions established, Zn-release decreased whereas relatively stable Zn-species formed. In CE-FA mixtures, a dissolution of larger amounts of binders caused alkaline conditions to be established, and Zn release increased due to the solubility of fly ash-specific Zn species. A Ni release was low irrespective of binder proportions and unaffected by varying saturation levels. In CE, an establishment of unsaturated zones increased Cu release to be higher than that from CT. This increase resulted possibly from the formation of Cu phases that were less acid tolerant than those comprising the CT. The aforementioned results indicated that using a low strength CPB is not an environmentally friendly option for underground storage; otherwise, large amounts of Cu could be released.

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Table 4 Results from the sequential extraction test (results expressed in mg/kg, n = 3, ± SD)

<table>
<thead>
<tr>
<th>Ore</th>
<th>Water soluble</th>
<th>AEC</th>
<th>Fe(III) oxyhydroxides</th>
<th>Fe(III) oxides</th>
<th>Sulfides/residual</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca mg/kg</td>
<td>160 ± 3</td>
<td>1427 ± 115</td>
<td>–</td>
<td>–</td>
<td>44,652 ± 2980</td>
<td>46,249 ± 3111</td>
</tr>
<tr>
<td>Fe</td>
<td>1.58 ± 0.39</td>
<td>1968 ± 23</td>
<td>304±.83</td>
<td>2916 ± 57</td>
<td>97,606 ± 4689</td>
<td>105,506 ± 4693</td>
</tr>
<tr>
<td>Si</td>
<td>13 ± 1.1</td>
<td>57.5 ± 5.2</td>
<td>346 ± 17</td>
<td>643 ± 26</td>
<td>336,282 ± 1367</td>
<td>344,410 ± 9056</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02 ± 0.01</td>
<td>0.64 ± 0.03</td>
<td>–</td>
<td>–</td>
<td>22 ± 0.7</td>
<td>23 ± 1.0</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01 ± 0</td>
<td>5.1 ± 0.34</td>
<td>3.05 ± 0.11</td>
<td>0.65 ± 0.06</td>
<td>58 ± 1.4</td>
<td>67 ± 2.2</td>
</tr>
<tr>
<td>Zn</td>
<td>0.16 ± 0.17</td>
<td>2.37 ± 1.52</td>
<td>3.21 ± 1.55</td>
<td>1.37 ± 1.18</td>
<td>19 ± 0.2</td>
<td>51 ± 22</td>
</tr>
<tr>
<td>S</td>
<td>86.5 ± 0.5</td>
<td>0 ± 0</td>
<td>–</td>
<td>173 ± 21</td>
<td>10,084 ± 268</td>
<td>10,354 ± 304</td>
</tr>
<tr>
<td>CT</td>
<td>3346 ± 56</td>
<td>227 ± 29</td>
<td>–</td>
<td>41,684 ± 1691</td>
<td>45,258 ± 1666</td>
<td></td>
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<tr>
<td>Fe</td>
<td>41.4 ± 2.56</td>
<td>353 ± 3</td>
<td>36,495 ± 202</td>
<td>7561 ± 303</td>
<td>121,772 ± 2656</td>
<td>121,772 ± 2656</td>
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<tr>
<td>Si</td>
<td>21.7 ± 0.7</td>
<td>28.1 ± 0.4</td>
<td>960 ± 4</td>
<td>673 ± 22</td>
<td>342,727 ± 9023</td>
<td>337,341 ± 1370</td>
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<td>Cu</td>
<td>8.99 ± 0.69</td>
<td>0.82 ± 0.07</td>
<td>31.1 ± 0.8</td>
<td>–</td>
<td>54 ± 7.9</td>
<td>96 ± 8</td>
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<tr>
<td>Ni</td>
<td>36 ± 3</td>
<td>17.5 ± 0.42</td>
<td>3.7 ± 0.12</td>
<td>0.8 ± 0.08</td>
<td>4.5 ± 0.8</td>
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<tr>
<td>Zn</td>
<td>9.36 ± 0.96</td>
<td>2.92 ± 2.56</td>
<td>6.48 ± 0.18</td>
<td>2.7 ± 1.76</td>
<td>30 ± 16</td>
<td>51 ± 22</td>
</tr>
<tr>
<td>S</td>
<td>5268 ± 141</td>
<td>1626 ± 44</td>
<td>1053 ± 13</td>
<td>807 ± 136</td>
<td>6312 ± 991</td>
<td>15,066 ± 998</td>
</tr>
<tr>
<td>CE-FA446</td>
<td>2443 ± 132</td>
<td>11,915 ± 250</td>
<td>0 ± 0</td>
<td>39 ± 5.4</td>
<td>37,405 ± 2124</td>
<td>51,802 ± 1953</td>
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<tr>
<td>Fe</td>
<td>46 ± 0.4</td>
<td>1453 ± 212</td>
<td>2206 ± 198</td>
<td>1271 ± 24</td>
<td>278,818 ± 8801</td>
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<tr>
<td>Si</td>
<td>0 ± 0.0</td>
<td>28 ± 0.9</td>
<td>35 ± 2.1</td>
<td>0.3 ± 0.1</td>
<td>101 ± 3.9</td>
<td>165 ± 6.6</td>
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<tr>
<td>Cu</td>
<td>12 ± 1.7</td>
<td>21 ± 1.2</td>
<td>–</td>
<td>1.9 ± 0.2</td>
<td>33 ± 2.4</td>
<td>67 ± 1.7</td>
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<tr>
<td>Ni</td>
<td>1.1 ± 0.6</td>
<td>15 ± 2.4</td>
<td>22 ± 1.7</td>
<td>5.3 ± 0.5</td>
<td>15 ± 0.7</td>
<td>58 ± 2.1</td>
</tr>
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<td>S</td>
<td>2092 ± 100</td>
<td>2221 ± 183</td>
<td>200 ± 22</td>
<td>83 ± 17</td>
<td>16,700 ± 735</td>
<td>21,287 ± 805</td>
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<td>CE446</td>
<td>7378 ± 112</td>
<td>707 ± 38</td>
<td>0 ± 0</td>
<td>21 ± 0.6</td>
<td>38,119 ± 1327</td>
<td>43,560 ± 1339</td>
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<tr>
<td>Fe</td>
<td>25 ± 0.7</td>
<td>212 ± 5.7</td>
<td>2075 ± 30</td>
<td>917 ± 72</td>
<td>263,856 ± 7142</td>
<td>265,977 ± 5412</td>
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<tr>
<td>Si</td>
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<td>–</td>
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<tr>
<td>Ni</td>
<td>6766 ± 91</td>
<td>228 ± 31</td>
<td>73 ± 1.9</td>
<td>36 ± 2.2</td>
<td>14,680 ± 700</td>
<td>19,370 ± 4188</td>
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