Occurrence and mobility of As in the Ylöjärvi Cu–W–As mine tailings

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A B S T R A C T

Fifteen tailings samples were investigated for mineralogy by scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), 12 for geochemical distribution by sequential extractions successively attacking water-soluble, adsorbed-exchangeable-carbonate, Fe (oxy)hydroxide, Fe oxide and sulfide fractions, as well as 13 tailings pore water and two groundwater samples for geochemical composition and physicochemical conditions at the former Ylöjärvi Cu–W–As mine in SW Finland. Mineralogical observations and sequential extractions demonstrated the depletion of arsenopyrite and other sulfide minerals from the superficial and deeper coarse-grained tailings resulting in high concentrations of As in pore water and groundwater beneath the tailings heap (5140 and 14 500 μg L⁻¹, respectively), and lowering the pore pH (from ca. 7.8 to 5.3). The solubility of As was controlled by pH (and Eh) as well as precipitating Fe(III) (oxy)hydroxides and Fe(III) arsenates. Although these phases are an important sink for As, it accumulates in the percolating water. Further acidification of the tailings after the consumption of scarce neutralizing calcite is probable and will affect the stability of the remaining arsenopyrite and As-bearing secondary phases.

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1. Introduction

Arsenic (As) is a principal contaminant in many mining areas, especially in gold, copper, and uranium mines (Bodénan et al., 2004; Da Pelo et al., 2009; Donahue et al., 2000; Salzsauler et al., 2005). It is a natural constituent of the bedrock and is mainly found in sulfides and sulfosalts such as pyrite (FeS₂), arsenopyrite (FeAsS), orpiment (As₂S₃), and realgar (As₄S₄) (Smedley and Kinniburgh, 2002). In the natural state under low Eh and high pH conditions, they are relatively unchanged and natural alteration may occur slowly, but once the ore containing these minerals is ground, processed and deposited in tailings facilties exposed to air and rainwater, the alteration is significantly enhanced. Arsenopyrite oxidation occurs according to Reaction 1:

\[
4\text{FeAsS} + 13\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 4\text{SO}_4^{2−} + 4\text{H}_2\text{AsO}_4^{−} + 4\text{H}^+. \tag{1}
\]

Walker et al. (2006) documented that the oxidation rate of arsenopyrite in circumneutral conditions is not oxygen dependent, as is the case for other sulfide minerals. However, Yunmei et al. (2007) reported dependence on dissolved oxygen in the oxidation rate of arsenopyrite. Another metallurgical study revealed that the oxidation of arsenopyrite by oxygen is greatly enhanced under alkaline conditions (Nicol and Guresin, 2003). Once dissolved, the mobility of arsenic in tailings and their surroundings depends on the speciation and prevailing physicochemical conditions. Each of the As species has its own characteristics; from among the most common species, As⁺³, is more mobile and at the same time is more toxic than As⁵⁺ (Smedley and Kinniburgh, 2002).

Previous studies (Bilaletdin et al., 2007; Carlson et al., 2002; Parviainen et al., 2006) have documented that high As concentrations are present in the surface water and groundwater surrounding the Ylöjärvi Cu–W–As mine tailings (containing on average 0.46 wt.% of As, 13.2 wt.% of Fe and 1.34 wt.% of S; Himmi et al., 1979) in SW Finland. Therefore, a geochemical and mineralogical study was carried out to investigate the tailings and pore water within the tailings, especially in the vadose zone tailings where active oxidation occurs. The main focus of this paper is the occurrence and mobility of As in the Ylöjärvi mine tailings as a source of contamination in view of future remedial actions or attempts to mitigate As release to the environment.
2. Material and methods

2.1. Site description

The Ylöjärvi Cu–W–As mine operated from 1943 to 1966, exploiting chalcopyrite (CuFeS$_2$), scheelite (CaWO$_4$), and arsenopyrite (FeAsS). The ore deposit is located in the Tampere Schist Belt in SW Finland and the host rock is a brecciated tuffite with a matrix composed of tourmaline and ore minerals, including pyrrhotite (Fe$_{1-x}$S), chalcopyrite, arsenopyrite, scheelite, and minor pyrite (FeS$_2$) (Himmi et al., 1979). Sphalerite (ZnS), galena (PbS), cubanite (CuFe$_2$S$_3$), mackinawite ((Fe,Ni)S$_{0.9}$), molybdenite (MoS$_2$), and some oxides [magnetite (Fe$_3$O$_4$), ilmenite (FeTiO$_3$), cassiterite (SnO$_2$)] are found as accessory minerals, and minute concentrations of uraninite (UO$_2$), native bismuth, silver and gold have also been detected (Himmi et al., 1979). The gangue minerals are quartz, plagioclase, potassium feldspar, tourmaline, biotite, chlorite, sericite, epidote, and scarce calcite, with some accessory apatite and titanite (Himmi et al., 1979). According to these authors, the amount of tourmaline in the mill feed ranged from 13 to 16%.

The mine produced 4 Mt of tailings during its operation, 2.8 Mt of which was dumped in two tailings areas of 4 and 17 ha, and about 1.1 Mt was used to fill the open pit and underground galleries situated at the SW end of Lake Parosjärvi (Fig. 1) (Kukkonen, 1967). In the larger tailings area, inaugurated in 1952, the average depth of the pile is 9 m. The natural soil below the tailings consists of peat and glacial sandy till. Runoff waters from the tailings area flow into the Lake Parosjärvi which is connected to a 7 km-long water course ending up in the Lake Näsijärvi (255 km$^2$). Tampere, the third largest city in Finland by its population (213217 inhabitants in 2010), resides by the Lake Näsijärvi. According to Parviainen et al. (in press), metal loading in the receiving water course changed in composition and intensity during and after active mining period; the metal accumulation in the lake sediment records peaked during mining and the metal concentrations gradually decreased after mine closure. However, the recent top sediments show concentrations above the pre-mining level implying continuous drainage waters from the Ylöjärvi mining area.

Arsenopyrite concentrate, containing a total of 563 t of As, was recovered over 5 years of production from 1949 to 1953 (Puustinen, 2003); most of the time, arsenopyrite was discarded and ended up in tailings. According to Himmi et al. (1979), during the final 7 years of production, 2.51 Mt of mill feed contained on average 11 546 t of As, 17 068 t Cu, 502 t Co, 427 t Zn, 301 t Mo, 100 t Ni, and 90 t Pb, and the S content was 33 600 t (1.34%). The true amount of elements discarded is probably much higher, because the mine was active and produced mill feed during a total of 23 years.

2.2. Sampling and analysis

Sampling was carried out in December 2008. Twenty undisturbed and continuous tailings samples were collected in two drill core profiles (1 and 2 in Fig. 1) from the surface to 250 cm and 200 cm depth, respectively, in sealed 17-cm-long (5 cm Ø) glass fiber tubes with a Norwegian type piston sampler. Two parallel drill cores were taken from both profiles, and the sample tubes were frozen immediately and named as 1a–l and 2a–j, where “a” represents a surface sample. Fifteen samples were selected for mineralogical observations, 12 for sequential extractions and 13 samples for pore water studies (Table 1). Previously, in November 2007, two test pits had been

![Fig. 1. Map of the study area showing the sampling locations for drill core profiles and groundwater wells.](image-url)
Fe (oxy)hydroxides from the previous extraction step (e.g., goethite [FeO(OH)] and jarosite). The fifth and final extraction step (sulfide fraction) attacked primary sulfide minerals along with organics and secondary Cu sulfides with KClO3 and a HCl leach followed by boiling with 4 M HNO3. The extracts were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for Bi, Li, Rb, Se, Th, Tl, U, and W, and by inductively coupled atomic emission spectrometry (ICP-AES) for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, and Sb. In addition, the observations on polished sections and sequential extraction methods employed on 12 tailings samples collected in November 2007 were used in this study. These samples were prepared and analyzed as described in Parviainen and Loukola-Ruskeeniemi (2009), and a more detailed description of the methodology can be found in Parviainen (2009).

The grain-size distributions of the tailings were determined by laser diffraction (Mastersizer 2000; Malvern Instruments Ltd., UK) and specific surface areas were measured using the BET N2(1) absorption method (Brunauer et al., 1938).

Thirteen samples for tailings pore water extraction were allowed to thaw at room temperature in the laboratory. Pore water was extracted with a squeezing technique using a vacuum pump and the extracts were filtered with a 0.45 μm membrane filter. Groundwater samples were collected from two existing monitoring wells installed during environmental studies at the Ylöjärvi mine (Carlson et al., 2002). The sampling depth was just beneath the tailings pile in the underlying bedrock/soil interface at 12.7 m from the tailings surface in monitoring well H4 and at 8.4 m in H5. The monitoring wells were pumped the day before sampling and allowed to settle for 24 h. The groundwater level in the wells was at 3.7 and 2.7 m, respectively. Two aliquots of groundwater samples were collected: 1) filtered and acidified samples for elemental analysis and 2) non-filtered and non-acidified samples for anion analysis.

Before elemental analysis, the pore water samples were digested with HNO3 in a water bath at 90 °C. These samples together with groundwater samples were analyzed by ICP-MS for Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Rh, Sb, Se, Th, Tl, U, V, Zn, and W, and by ICP-AES for B, Ca, Fe, K, Mg, Mn, Na, Si, Sr, and Tl at the accredited chemical laboratory Labtium Oy (www.labtium.fi). The pore water samples that were extracted in sufficiently large quantities (>15 mL) and groundwater samples were analyzed for Cl and SO4 by ion chromatographic (IC) determination with suppressed NaNO3/NaHCO3 elution. The redox potential (Eh) and pH were measured with a Mettler Toledo MP125 portable pH/Eh meter and an InLab combination pH sensor equipped with an ARGENTHAL™ Ag⁺ trap in KCI as a reference system, and electrical conductivity (EC) was measured with a WTW multiline P4 Pocket Meter. The redox potential was corrected to the standard hydrogen electrode (SHE).

The geochemical equilibrium model PHREEQC (version 2.17.5) (Parkhurst and Appelo, 1999) was applied in the interpretation of the water samples using the Watq4f and Llnl databases. The model was used to determine the aqueous species and saturation indices (SI) of relevant mineral phases. SI values <0 indicate that the mineral is undersaturated and should dissolve in solution, while minerals with SI values >0 are stable and expected to precipitate (oversaturated with respect to the solution).

3. Results

3.1. Mineralogical and geochemical observations on the tailings

The grain size of the tailings was generally fine in the order of magnitude of silt (60 to 90% of <63 μm), whereas a coarser layer with fine to medium sand (70% of 63–250 μm) was detected in samples 2h to 2j in profile 2. The specific surface area of the tailings varied from 0.18 to 1.03 m² g⁻¹, where the lowest value corresponds to sandy tailings and the highest value to fine tailings with a 90%
Fig. 2. Elemental distribution of Al, As, Ca, Co, Cu, Fe, Mg, S, U, W, and Zn (mg kg$^{-1}$, upper x-axis) according to the sequential extractions presenting 1) water-soluble, 2) adsorbed-exchangeable-carbonate (AEC), 3) Fe (oxy)hydroxide, 4) Fe oxide, and 5) sulfide fractions (bar graphs), and the pore water concentrations (Fe and W on a logarithmic scale) at corresponding depths (line graphs), as well as backscattered images of arsenopyrite grains from samples 1) 2c, 2) 2h and 3) 2i. The sequential extraction results corresponding to cores 1l and 2j are from the sampling in 2007 (D = sample depth in cm; S = sample).
fraction of silt and clay. On the boundary of fine and coarse tailings a compact cemented layer was detected (sample 2h 124 cm).

The results of the sequential extractions are presented in Fig. 2. In general, most of the trace elements had low total average concentrations (Co 12.4 mg kg\(^{-1}\), Cu 111 mg kg\(^{-1}\), Cd 9.0 mg kg\(^{-1}\), Ni 11.2 mg kg\(^{-1}\), Pb 1.2 mg kg\(^{-1}\), Zn 147 mg kg\(^{-1}\)), whereas As presented a higher concentration (2615 mg kg\(^{-1}\)).

According to the AEC fraction of the sequential extractions, calcite is present in the tailings (Fig. 2), but has been consumed from the surface and coarse-grained samples. Furthermore, the results of this fraction illustrate that only very small amounts of trace elements (As, Co, Cu, Ni, and Zn) and S (probably as SO\(_4\)) are bound to mineral surfaces by adsorption. Sulfur was the only exception in sample 1d, with a concentration of 2000 mg kg\(^{-1}\) in the AEC fraction.

Fe and As constitute secondary minerals with concentrations of up to 27700 mg kg\(^{-1}\) and 2800 mg kg\(^{-1}\), respectively, in the Fe (oxy)hydroxide and Fe oxide fractions. Arsenic in these phases was found to be especially abundant in the surface samples and in the cemented layer (2h 124 cm). The sequential extraction method used in this study (after Dold, 2003) is not arsenic specific, but SEM-EDS studies revealed that As appears in unidentified Fe arsenates and in smaller concentrations in Fe (oxy)hydroxides (Fig. 3).

The Fe (oxy)hydroxides contained only traces of S (average S 0.3 wt.%). Fig. 3 shows both types of secondary precipitates at the depth of approximately 45 cm and in the interface of coarse-grained material (124 cm), as well as a coated mineral surface with filaments of bacteria at the depth of 165 cm. Fig. 2 demonstrates that As principally occurs in the secondary minerals of the Fe (oxy)hydroxide fraction throughout the profiles, and also in the primary sulfide fraction in deeper samples. In general, As and Fe were only detected in relatively low concentrations (averaging 105 mg kg\(^{-1}\) and 190 mg kg\(^{-1}\), respectively) in the easily mobilized (i.e., water-soluble and AEC) fractions. The sequential extraction results from 2007 also show that the highest As and Fe concentrations in Fe (oxy)hydroxide and Fe oxide fractions appeared in the surface samples (top most 10 cm) and in the cemented layer (2d) in the interface of the coarse-grained layer, which were also depleted in the primary sulfide phases (Parviainen and Loukola-Ruskeeniemi, 2009).

Table 2
Sample depth, pH, redox potential (Eh), electric conductivity (EC), and concentrations of relevant elements, Cl, and SO\(_4\) for the pore water and groundwater samples (na = not analyzed).

<table>
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<th>Sample</th>
<th>Depth (cm)</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>EC (µS/cm)</th>
<th>Al (µg L(^{-1}))</th>
<th>As (µg L(^{-1}))</th>
<th>Ba (µg L(^{-1}))</th>
<th>Cd (µg L(^{-1}))</th>
<th>Co (µg L(^{-1}))</th>
<th>Cr (µg L(^{-1}))</th>
<th>Cu (µg L(^{-1}))</th>
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the major sulfide minerals, showing moderate alteration at the grain boundaries in the coarser samples. Furthermore, some scheelite, magnetite, ilmenite, monazite [(Ce,La,Nd)PO₄], sphalerite, baryte (BaSO₄), and a U mineral (probably uraninite) were found. If the sequential extraction method is not uraninite or scheelite specific, it is difficult to interpret the U- and W-bearing phases. However, as illustrated in Fig. 2, U (average 18 mg kg⁻¹) and W (average 94 mg kg⁻¹) exhibited moderate total concentrations; the dominant U phases were encountered in the AEC and Fe (oxy)hydroxide fractions, whereas W was not present in the easily mobilized phases.

3.2. Geochemical observations of the water samples

The physicochemical conditions and elemental concentrations of the tailings pore water and groundwater samples are presented in Table 2 and in Figs. 4 to 7. In the tailings pore water, pH values ranged from 4.9 to 8.8 with an average of 6.3. In the first 2 m of the tailings, the pH was 5.7 on average, but 8.8 in the deeper tailings below 2 m in the first profile, and 7.7 just above the coarser layer in the second profile. The redox value (Eh) varied from 286 to 362 mV in the near surface profile, and dropped to close to 220 mV in the deeper samples. However, in samples 2h and 2j, consisting of coarser material, Eh rose again to about 350 mV. The pH and Eh were strongly correlated (R²=0.74) (Fig. 4). EC increased as a function of depth from 270 to 2600 μS/cm in the pore water samples. In the groundwater samples the pH ranged from 6.6 to 7.1, Eh from 193 to 222 mV, and EC was above 900 S/cm. SI values ranging from 270 to 2600 μS/cm.

Figs. 5 and 6, respectively, show the major and trace element concentrations of the pore water samples as a function of sample depth. Additionally, Fig. 7 presents both the pore water and groundwater results as a function of Eh. The metal and metalloid concentrations varied according to: Al 17–28 700 μg L⁻¹, As 32–145 500 μg L⁻¹, Cd 1–41 μg L⁻¹, Co 1–3770 μg L⁻¹, Cr 1–6 μg L⁻¹, Cu 1–3240 μg L⁻¹, Mo 0.3–209 μg L⁻¹, Ni 3–1880 μg L⁻¹, Pb 1–13 μg L⁻¹, U 1–82 μg L⁻¹, Zn 7–12 200 μg L⁻¹, W 1–88 μg L⁻¹, and Fe 0.99–159 mg L⁻¹. Cl and SO₄ concentrations ranged from 1.2–31 mg L⁻¹ and 104–1970 mg L⁻¹, respectively. The major elements in Fig. 5 and trace elements in Fig. 6 form two differently behaving groups: Al, Fe, Cd, Co, Cu, Ni, Pb, and Zn increased with rising Eh values, whereas As, Mo, U, and W showed the opposite tendency. The first group of cations exhibited higher concentrations at lower pH values, as they do not adsorb in more acidic conditions, while the concentrations of the second group of oxyanions increased with rising pH (Dzombak and Morel, 1990).

According to thermodynamic calculations in PHREEQC, As(V) (H₂AsO₄⁻, HAsO₂⁻, H₂AsO₄⁻, and Fe(III) (FeO(OH)₂, Fe₂O₃(OH)₂, and Fe(OH)₃) was the dominant species in all samples, including the groundwater samples. Arsenite concentrations were extremely low in all samples and even zero in sample 2h. As and Fe presented a weak negative correlation (R² = 0.55 in profile 1 and R² = 0.40 in profile 2 excluding sample 2j). In addition, As was negatively correlated with Eh values (R² = 0.52), but had a strong positive correlation with pH (R² = 0.72) in the pore water samples. Fe showed statistically insignificant correlations: a very weak positive correlation with Eh (R² = 0.09), and a very weak negative correlation with pH (R² = 0.06). Other cations (e.g. Cu and Zn) were more closely correlated with Eh (Fig. 7).

Based on the calculations in PHREEQC, the pore water and ground- water samples throughout were oversaturated with respect to a variety of Al, Mg and Fe oxides, hydroxides and hydroxysulfates. For instance, ferrihydrite, goethite, jarosite, and schwertmannite presented Si values >1 (Table 3). Scorodite (FeAsO₄·2H₂O) was undersaturated or near equilibrium. According to the model, an As-bearing phase, Ba₅As₂O₈ was suggested to be stable in all samples excluding 1b and 1c. However, it is probably less important with respect to the fate of arsenic, as the concentration of Ba in the water samples was rather low (as compared to 38-fold higher concentrations of As). Interestingly, a phase equivalent to arenathemite (KUO₂, AsO₄) also suggested to be undersaturated in samples 2f and 2j. Gypsum was undersaturated in all samples except for 1j and 1l, in which it was in equilibrium (SI = 0.07). Other sulfates such as bierbite (CoSO₄·7H₂O), chalcantite (CuSO₄·5H₂O), melanterite (FeSO₄·7H₂O), epsomite (MgSO₄·7H₂O), and goilarite (ZnSO₄·7H₂O) were undersaturated. Sulfide oxidation was supported by PHREEQC, with SI values ranging from −235 to −330 for arsenopyrite, chalcopyrite and pyrite and from −155 to −186 for pyrrhotite. The lowest SI values were encountered in samples 1b, 1c, 2h and 2j, implying the lowest stability of sulfide minerals.

4. Discussion

4.1. Mineral alteration in the tailings

Sulfide oxidation occurs in the vadose tailings of the Vöjšari Cu-W-As mine, lowering the pore water pH and releasing Fe, trace elements (including As) and SO₄ into solution. Himmis et al. (1979) described low S concentrations in the mill feed (1.34 wt.%), but the S content in the sulfide fraction of the sequential extractions was even lower (concentrations ranging from 0 to 0.22 wt.%) average 0.06 wt.%) than the supposed original tailings. This implies that primary sulfides have been consumed from the top layer and sulfide oxidation has progressed to some degree throughout the sampling depth (Fig. 2). The concentrations of most of the sulfide-bound elements in the sulfide fraction increased downward, while the sulfide oxidation rate was expected to decrease as a response to limited oxygen transport at greater depths. However, in the interface of coarser-grained tailings in core 2h (2d in Parvainen and Loukola-Ruskeeniemi, 2009) the oxidation processes had been activated...
again because of the increased transport of oxygenated water into the layer with coarser material. For instance, As was almost depleted in the sulfide fraction in core 2h, and arsenopyrite grains in this sample showed more advanced alteration than in cores 2c (above) and 2i (below) (Fig. 2). Here, the pH dropped to 5.3 and Eh rose to ca. 350 mV. In samples below 150 cm, unoxidized arsenopyrite and other sulfides were found to remain, being prone to future oxidation. PHREEQC also indicated that the sulfides were prone to alteration in all samples: in general the oxidation susceptibility slightly decreased downward, but intensified once again in samples 2h and 2i (Table 3). The Fe and most of the sulfide-bound elements (Cd, Co, Cu, Ni, Pb, Zn) peaked in the pore water samples in which the lowest Si values for sulfides were detected, suggesting the higher alteration rate.

Acid production by sulfide oxidation in the tailings is mainly regulated by calcite, even though it is not a very abundant mineral in the tailings. Fig. 2 illustrates the consumption of calcite in supercritical samples and again in the deeper samples of profile 2. So far, the pH has remained relatively high because of the very low S content and subsequently moderate acid production, as well as the high neutralization capacity of calcite. Bodénan et al. (2004) and Johnson et al. (2000) reported that even small amounts of calcite can be very important in controlling pH in near-neutral areas. Nevertheless, the depletion of calcite from the vadose tailings will eventually lower the pore water pH. Aluminosilicates did not present visible alteration; hence, they do not seem to play a significant role in the neutralization process of the tailings. They only become important in acid-neutralization processes at very low pH values (<1.3), whereas the dissolution of Al hydroxides buffers the pH at 4.0–4.3 (Blowes and Ptacek, 1994; Jurjovec et al., 2002). Therefore, Al hydroxides are expected to start buffering the pH when calcite has been consumed from the tailings. Considering the low carbonate content of the tailings, the pH is expected to gradually decrease further, as could already be observed in the samples with higher alteration (Fig. 2 and Table 2).

Many studies have shown that the oxidation of arsenopyrite is enhanced in acidic conditions (Corkhill and Vaughan, 2009, and references therein), and Jones et al. (2003) and Corkhill et al. (2008) reported that oxidation occurs more rapidly and to a greater extent in the presence of bacteria common in acid mine drainage. Therefore, considering the future lowering of the tailings pore pH in the vadose layer, the remaining arsenopyrite grains are expected to dissolve intensively, contributing to the arsenic contamination in surface and groundwater bodies of the Ylöjärvi mine area over the long term.

4.2. Arsenic mobility

In pore water samples from the Ylöjärvi tailings, As and Fe concentrations showed a weak negative correlation, even though the fate of As in the tailings and acid mine drainage (AMD) environment is commonly controlled by Fe. According to Bednar et al. (2005), total concentrations of As and Fe did not show a direct correlation in the studied As-containing AMD, but As species instead changed as a function of the water chemical properties Eh, pH, and the Fe(III) concentration. The authors also stated that high pH mine waters and groundwater do not always follow the redox predictions as well as low pH AMD samples. The ability of Al, Fe, and Mn to remove As from solution under oxidizing to slightly reducing conditions is well known (Smedley and Kinniburgh, 2002), and the common Fe (oxy) hydroxides have a positively charged surface area in the measured pH range of the tailings from 4.9 to 8.8 (Cheng et al., 2009); for instance, goethite and ferricydrate can adsorb and/or co-precipitate As oxyanions upon precipitation. In waters with high As concentrations, Fe(III) arsenates may also precipitate (Smedley and Kinniburgh, 2002).

The prevailing pH–Eh conditions in the tailings pore water are close to the As(III)/As(V) boundary, but arsenic is the prevailing arsenic species according to PHREEQC. The highest As concentrations (2530 to 5150 μg L−1) in the pore water samples were encountered in the cores where unoxidized arsenopyrite remained and there were only minor accumulations of secondary Fe(III) minerals, whereas the lowest concentrations (31.9 to 61.3 μg L−1) were recorded in samples with a high level of alteration of arsenopyrite and important accumulations of Fe(III) (oxy)hydroxides and Fe(III) arsenates (Fig. 2). In contrast, Fe did not show a clear trend and did not correlate well with either pH or Eh. Particularly in pore water sample 2h, which represents the interface of fine and coarse material, the difference in the behavior of As and Fe was evident; As presented minimal concentrations, while Fe strongly increased. Arsenic pore concentrations decrease as a consequence of precipitating secondary phases, which were most abundant in sample 2h (124 cm), shown as high concentrations of As and Fe in the Fe (oxy)hydroxide fraction, but Fe did not follow a clear pattern (Fig. 2). Here, the trace element cations (e.g. 191 μg L−1 of Co, 2050 μg L−1 of Cu, 158 μg L−1 of Ni, and 12 200 μg L−1 of Zn) increased as a response to the higher Eh values and lower pH, under which conditions they are more soluble (Fig. 6) (Dzombak and Morel, 1990). In the deeper pore water samples, the As content increased again in the absence of secondary Fe(III) phases. The highest concentrations were measured in the groundwater samples, with up to 14 500 μg L−1 As. Bodénan et al. (2004) examined the behavior of arsenic in gold-ore mill tailings and observed the highest As concentrations (up to 95 000 μg L−1) in the groundwater with a slightly lower Eh (ca. 15–150 mV) than in Ylöjärvi and in near neutral conditions (pH 7.4–7.6). There, the major As species was arsenite. Previous studies on the surface water and groundwater quality have demonstrated that arsenic concentrations transported from the Ylöjärvi tailings area exceed manifold the threshold value for drinking water (10 μg L−1) (Bilaletdin et al., 2007; Carlson et al., 2002; Parviainen et al., 2006). According to Carlson et al. (2002), AMD toe seepage in all directions from the Ylöjärvi tailings area presented low pH values ranging from 3.4 to 4.8 (average 4.0) and relatively low As concentrations from 4.0 to 137 μg L−1 (average 44 μg L−1, excluding one seepage point with up to 3000 μg L−1 of As) in comparison to the present pore water and groundwater results (average 1700 and 9600 μg L−1, respectively). Accordingly, Fe concentrations were much lower in the seepage waters (from 0.1 mg L−1 to 40 mg L−1, average 8.2 mg L−1) than in the current study (average 13 and 27 mg L−1, respectively). This is due to the fact that ferrous iron comes into contact with air in the seepage points, it oxidizes and hydrolyzes, lowering the pH conditions and making As less soluble. Arsenic is scavenged by the forming Fe (oxy)hydroxides; hence, its concentrations in the Fe precipitates from the seepage points were elevated, ranging from 0.32 to 7.4 wt.% (average 1.7 wt.%) (Carlson et al., 2002; Kumpulainen et al., 2007). According to Kumpulainen et al. (2007), the Fe-bearing precipitates at the seepage points consist of schwertmannite, goethite and ferricydrate. The impact of runoff waters is also reflected in higher than average As concentrations in the nearby peat bogs and in the lake sediment records (Carlson et al., 2002; Parviainen et al., in press).
4.3. Role of secondary Fe(III) phases and changing pH–Eh conditions

As a consequence of sulfide oxidation, secondary As-bearing Fe(III) (oxy)hydroxides and Fe(III) arsenates form (Fig. 3). The lack or exiguity of S in the Fe (oxy)hydroxide and Fe oxide fractions of the sequential extractions and the SEM results imply that Fe(III) hydroxysulfates such as jarosite and schwertmannite are not present in notable amounts among the secondary minerals, even though their presence was suggested by PHREEQC. In the pH range (4.9–8.8) of the Ylöjärvi tailings, goethite (acidic to neutral conditions; Bigham et al., 1996) and ferrihydrite (pH>5; Bigham et al., 1992, 1996) are the most probable Fe(III) (oxy)hydroxides in the tailings.

As shown in the previous section, the mobility of As is controlled by pH and precipitating Fe(III) phases, which are an important sink for As. However, at present the Fe(III) (oxy)hydroxides and Fe(III) arsenates within the tailings do not retain As efficiently enough to exclude it from solution, but it accumulates in the percolating pore waters and groundwater. Changing physicochemical conditions may cause the existing As-bearing secondary phases to re-dissolve, making them an additional source of As besides arsenopyrite. Therefore, it is important to understand the effect of changing pH–Eh conditions, for example after remedial actions (e.g. reductive dissolution after capping; Ribet et al., 1995) or during the natural evolution of the tailings pile (e.g. further acidification) to predict the stability of the secondary minerals. Al-Abed et al. (2007) noted the importance of pH in As and Fe dissolution from iron-rich mineral processing waste. At low (pH~4) and high pH levels (pH>8), As-bearing Fe (oxy)hydroxides were leached more effectively, whereas at intermediate pH values the solubility dropped and the Fe (oxy)hydroxides seemed to be more stable. In this study, the variation in Eh
4.4. Sequential extractions

The results from the sequential extractions correlated well with the mineralogical observations by SEM, and depicted the zones with oxidation of sulfide minerals as well as zones with accumulation of secondary Fe(III) precipitates. However, the sequential extractions did not give unequivocally answer to all the questions and the results are possibly ambiguous. For instance, high concentrations of Al, Ca, Fe, and Mg in the fifth extraction step infer to the dissolution of some less resistant silicate minerals (e.g. biotite, chlorite, sericite) in this extraction step. For example, the Fe concentrations in the sulfide fraction were elevated and similar in all samples, and did not show the typical and evident depletion of Fe-bearing sulfides in the surface samples detected in the S concentrations of the sulfide fraction and in electron microscopy.

Furthermore, the sequential extractions cannot unambiguously impart the origin of the dissolved mineral phases. Even though the results suggest the presence of gypsum and other water-soluble sulfates, the concentrations of Ca, S and small amounts of trace elements (As, Co, Cu, Ni, and Zn) encountered in the water-soluble fraction derived probably from the efflorescent sulfate minerals that formed upon drying of the samples. The high pore water concentrations of these elements (up to 3590 μg L⁻¹ As, 324 mg L⁻¹ Ca, 3770 μg L⁻¹ Co, 1790 μg L⁻¹ Cu, 562 μg L⁻¹ Ni, 6330 μg L⁻¹ Zn, and 1780 mg L⁻¹ SO₄ in the corresponding depths or just above) probably caused their tertiary precipitation. The geochemical equilibrium model PHREEQC also implied that the deposition of these phases is not in equilibrium in the tailings pore water conditions.

5. Conclusions

Almost half of a century after the Ylöjärvi mine ceased operation, arsenopyrite and other sulfide minerals are still dissolving from the vadose tailings, resulting in gradual acidification of the superficial tailings and the deposition of Fe(III) arsenates and As-bearing Fe(III) (oxy)hydroxides. Despite the fact that As is retained to some degree in these secondary phases, high As concentrations were detected in the tailings pore water and especially in the groundwater below the heap. The mobility of As in the vadose tailings is dependent on the physicochemical conditions (especially pH) and precipitating secondary Fe(III) phases. However, the behavior of Fe differs from that of As and does not seem to be controlled by either pH or Eh. The circum-neutral pH values and the slightly reductive conditions in the deeper fine tailings and in the groundwater below the tailings, as well as the lack of adsorbents favor the mobility and accumulation of dissolved As(V). Considering the lack of proper segregation of tailings from underlying natural subsoil, the risk of As contamination of the groundwater is considerable, as the concentrations are much higher than in the vadose tailings and the surface waters. Arsenic is also discharged through the seepage points from the tailings, where acid mine drainage is produced, and the precipitating Fe(oxy)hydroxides scavenge As.

At present, the tailings pH is buffered by scarce carbonates, but the consumption of the neutralizing calcite may change the pH conditions of the tailings. Sulfide oxidation and acid production are expected to

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At present, the tailings pH is buffered by scarce carbonates, but the consumption of the neutralizing calcite may change the pH conditions of the tailings. Sulfide oxidation and acid production are expected to
continue for decades and perhaps for centuries. Hence, the oxidation rate of primary arsenopyrite and the stability of secondary minerals capable of sequestering the As are likely to change in the long term.

In order to prevent the further release of contaminants and to mitigate the impact of the plume of low quality waters, some remedial actions should be taken. In the future, as speciation studies and research is recommended on the possibility for oxidation of the groundwater in order to precipitate Fe(III) phases and liming of the superficial tailings to prevent further acidification of the tailings and to enhance Fe(III) precipitation.

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References


