Arsenic mobility in the Cu-W-As tailings in SW Finland

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ABSTRACT

The Ylöjärvi Cu-W-As mine in SW Finland operated 1943-1966, producing 4 Mt of tailings. Arsenic (As) is leached from the tailings under slightly acidic to neutral conditions. A geochemical and mineralogical study was conducted to investigate the occurrence and mobility of As within the tailings. The mineralogy and elemental distribution of twelve tailings samples were studied by scanning electron microscopy with energy dispersive spectrometry, electron microprobe analysis and sequential extractions. These extractions successively targeted water-soluble, adsorbed-exchangeable-carbonate, Fe precipitate, Fe oxide, and sulfide phases. The primary source of As in the unoxidized tailings is arsenopyrite (up to 7000 mg/kg), whereas the oxidized surface layer is nearly depleted in arsenopyrite and other sulfide minerals (< 73 mg/kg As). A cemented layer at 110 cm depth with elevated As concentrations contained intensively altered arsenopyrite and secondary phases; dissolved As is partially retained by iron hydroxides and iron arsenates within the oxidized and cemented layers. Arsenic concentrations up to 3700 mg/kg were observed in these secondary phases filling tailings voids. Relatively low As concentrations (average 75 mg/kg) were observed in the first two extraction steps targeting easily mobilized As. However, elevated As concentrations are gauged in the surrounding surface waters and groundwater with up to 3 mg/L and 10 mg/L, respectively. Arsenic transportation in surface waters is also reflected by elevated As concentrations in the lake sediments and nearby peat bog. Arsenic leaching remains active half of a century after mine closure; this process is expected to continue for decades, and perhaps centuries, to come.

Key Words: iron arsenate, Fe (oxy)hydroxide

INTRODUCTION

Arsenic is a principal contaminant in many mining areas, especially in gold, copper and uranium mines (Donahue et al., 2000; Bodénan et al., 2004; Salzsauler et al., 2005). It is a natural constituent of the bedrock and is mainly found in sulfides and sulfosalts such as pyrite (FeS_2), arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (AsS). In the natural state, they are relatively unchanged, but once the ore containing these minerals is ground and processed, they are more prone to alteration. Oxidation of arsenopyrite by oxygen is greatly enhanced under alkaline conditions (e.g., Nicol and Guresin, 2003), though arsenopyrite is stable under anaerobic and alkaline pH conditions. 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. Once dissolved, the mobility of arsenic in the tailings and in its surroundings depends on the speciation and prevailing physicochemical conditions.

Previous studies (Carlson et al., 2002; Parviainen et al., 2006) documented that high arsenic (As) concentrations are present in the surface water and groundwater surrounding the Ylöjärvi Cu-W-As mine in SW Finland. A geochemical and mineralogical study was conducted to investigate the occurrence and mobility of As within the Ylöjärvi tailings.

MATERIALS AND METHODS

Site description

The Ylöjärvi Cu-W-As mine operated from 1943 to 1966, producing 4 Mt of tailings. Arsenopyrite concentrate, containing a total of 563 t As, was recovered over five years of production (Puustinen, 2003); most of the arsenopyrite was dumped in the two tailings areas of 4 and 19 ha (Figure 1). The open pit and underground galleries are situated at the SW end of Lake Parosjärvi from which water was used for ore processing. Underground galleries below Lake Parosjärvi were filled with tailings. The host rock is a brecciated tuffite with a matrix composed of tourmaline and ore minerals including arsenopyrite (Himmi et al., 1979). Regionally, the background values of arsenic in the bedrock and soils are higher than on average in Finland, but the principal source of As contamination in the area is the mine tailings. As is leached from the tailings under near-neutral pH conditions, leading to As transport into surface waters and groundwater. According to Carlson et al. (2002), arsenic concentrations range from 4 to 3000 μg/L and from 100 to 10 000 μg/L in surface water and groundwater, respectively. The mining impact is reflected also as high As concentrations in the nearby peat bogs and in the lake sediment records, because surface runoff water flows directly to the peat bog; there are several seepage points around the bigger tailings area (Carlson et al., 2002; Parviainen et al., 2006).

The groundwater table is encountered approximately 3 m from the tailings surface and the average depth of the pile is 9 m. The natural soil below the tailings consists of peat and sandy till.

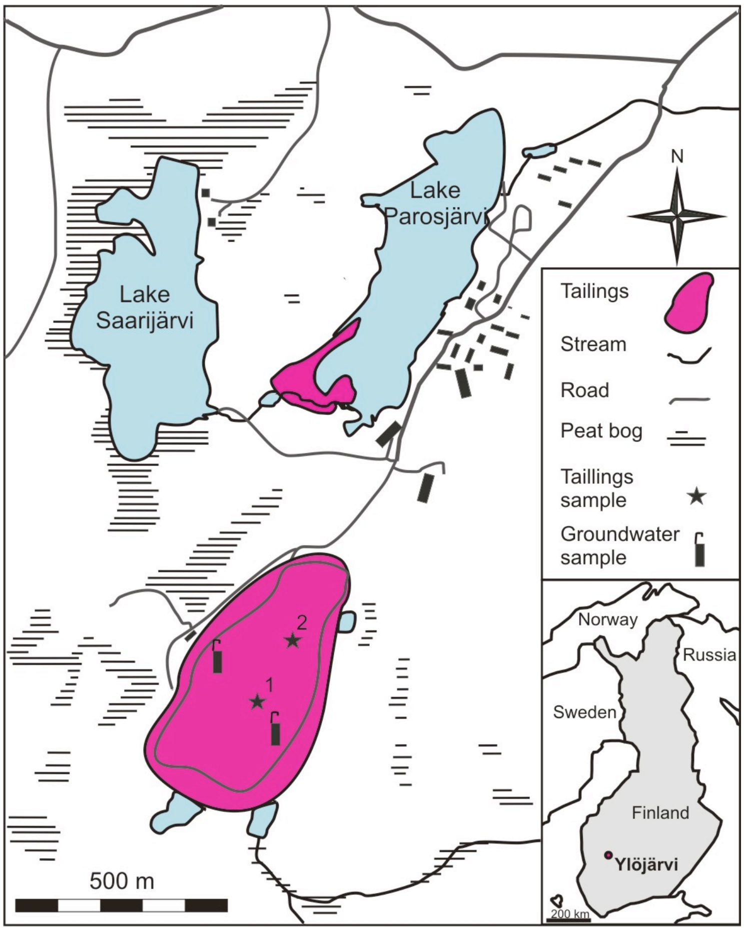

Figure 1. Map of the studied area.

Sampling and analysis

Twelve tailings samples were collected from two locations at approximately 50 cm intervals extending from the surface to a depth of 250 cm (Figure 1). Samples were named 1a-e and 2a-g, where "a" represents the surface sample. Sample 2d represents a cemented layer in the boundary of fine and coarse grained material at 110 cm depth. The samples were immediately frozen, and subsequently thawed and dried at room temperature at the laboratory. The mineralogy and elemental distribution were studied by reflected-light microscopy, scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), electron microprobe analysis (EMPA) and sequential extractions. These extractions successively targeted water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe precipitate, Fe oxide, and sulfide phases (modified from Hall et al., 1996; Dold 2003). In addition to primary oxide minerals, the Fe oxide fraction includes residual secondary Fe (oxy)hydroxides from the previous extraction step.

For tailings pore water sampling, 11 undisturbed drill core samples were collected in 17 cm long, 5 cm diameter glass fiber tubes. These samples were also frozen immediately. Tailings pore water was extracted in the laboratory with a squeezing technique using an under-pressure pump. Redox potential (Eh) and pH were measured with a Mettler Toledo portable pH/Eh meter, and electrical conductivity (EC) with a WTW multiline Pocket Meter.

RESULTS AND DISCUSSION

Mineralogical observations

The gangue minerals are quartz, plagioclase, potassium feldspar, tourmaline, biotite, chlorite, sericite, and epidote with some accessory apatite and titanite (Himmi et al., 1979). The sulfide minerals are pyrrhotite [$Fe_{(1-x)}S$], chalcopyrite ($FeCuS_2$), arsenopyrite (FeAsS), and pyrite (FeS_2). The surface samples are depleted in these minerals, as shown in the sequential extractions (Figure 2). Samples 1a and 2a show very low concentrations of As, Cu, and S in the sulfide fraction. Observations by SEM-EDS showed no remaining sulfide grains in these samples and in sample 2b, and high alteration of arsenopyrite in the cemented layer (Figure 3). Samples 2e through 2g, from below the cemented layer, had a coarser (sandy) grain size; pyrrhotite and pyrite were the only sulfide minerals showing moderate alteration on the grain boundaries. Some scheelite ($CaWO_4$), magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), monazite [(Ce, La, Nd)PO_4], and a U mineral were found. According to the sequential extractions, calcite ($CaCO_3$) is present, but is consumed from the surface samples and in the coarse-grained samples (Figure 2). Al hydroxides are scarce and aluminosilicates do not present visible alteration; hence, they do not play a significant role in the neutralization process of the tailings.

Gypsum ($CaSO_4$) is a common secondary mineral throughout the profile and is shown as elevated concentrations of Ca and S in the water-soluble fraction. Fe and As constitute secondary minerals with concentrations of up to 7800 mg/kg and 3700 mg/kg, respectively, in the Fe precipitate and oxide fractions. Arsenic in these phases is especially abundant in the surface samples and in the cemented layer. The sequential extraction methods used in this study (after Dold, 2003) are not arsenic specific, but SEM-EDS and EMPA studies showed that As appears in an unidentified iron arsenate (average As 27.6 wt.%, Fe 27.7 wt.% and O 29.4 wt.%) and smaller concentrations (generally < 3 wt.%) in Fe (oxy)hydroxides (Figure 3). Figure 3 shows both types of secondary precipitates in the cemented layer, whereas, for example, only Fe (oxy)hydroxides are present in samples 2e and 2g. In the easily mobilized fractions (*i.e.* water-soluble and AEC), As appears only in low concentrations, averaging 75 mg/kg. However, sample 1b contains 250 mg/kg of water-soluble As.

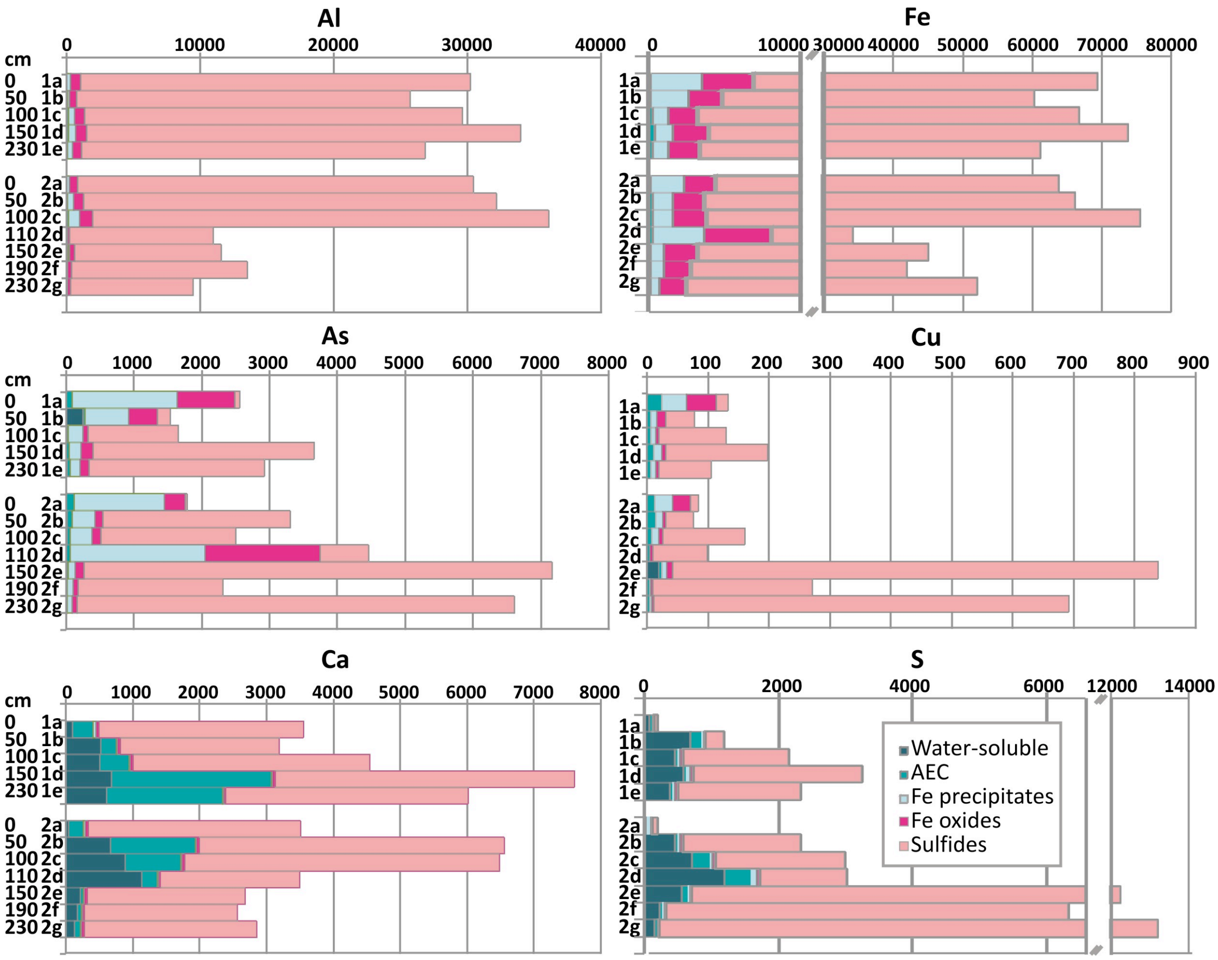

Figure 2. Elemental distribution of Al, As, Ca, Fe, Cu and S according to the sequential extractions presenting water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe precipitate, Fe oxide and sulfide fractions.

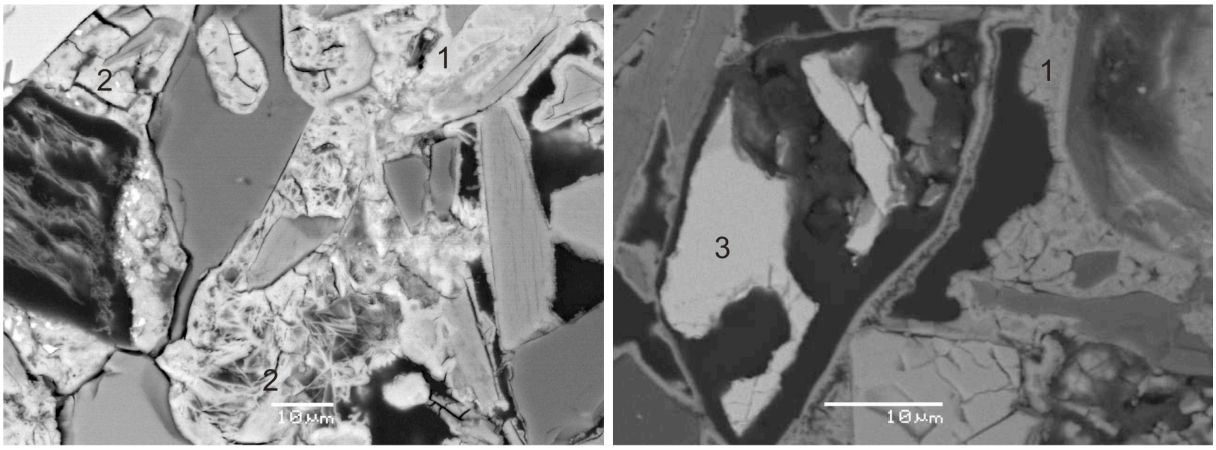

Figure 3. Backscattered images of 1) As-bearing Fe (oxy)hydroxide; 2) iron arsenate; and 3) altered arsenopyrite in the cemented layer (2d).

Tailings conditions

In the first two meters of the tailings, the pH is 5.7 and the Eh is 92 mV, on average (Figure 4). Just above the cemented layer in the second profile, the pH is 7.7 and Eh 3 mV. In the deeper tailings, the pH rises to 8.8 whereas Eh drops approximately to 0 mV. All pore water samples exhibited high electrical conductivity, increasing downwards from 0.3 to up to 2.6 mS/cm. According to Carlson et al. (2002), groundwater below the tailings, in the groundwater sampling points shown in Figure 1, has a neutral pH (6.5 to 7) with high electrical conductivity (1.1 mS/cm).

The acid production by sulfide oxidation is mainly regulated by the neutralization capacity of calcite even though it is not very abundant in the tailings. Bodénan et al. (2004) and Johnson et al. (2000) reported that even very small amounts of calcite can be very important in controlling pH in near-neutral areas. Calcite is being dissolved from the superficial tailings and also from the deeper coarser grained waste material in profile 2.

Arsenic mobility

According to the geochemical distribution of As in sequential extractions, As is dissolved from the primary phases and retained to some extent in secondary phases. However, surface water and groundwater samples show that considerable amounts of arsenic are transported from the tailings area (Carlson et al., 2002; Parviainen et al., 2006; Bilaletdin et al., 2007). The prevailing pH-Eh conditions in the tailings pore water are close to the As(III)/As(V) boundary, and amorphous $Fe(OH)_3$ and scorodite ($FeAsO_4 \cdot 2H_2O$) are not expected to form as they are not stable, except for $Fe(OH)_3$, in the deeper layers and the tailings just above the cemented layer (Figure 4). Salzsauler et al. (2005) described a mobilization of As-bearing alteration products under reducing near-neutral conditions in arsenopyrite-bearing mine wastes, Snow Lake, Manitoba, Canada. These authors suggested that under conditions similar to those in the deeper unoxidized tailings of Ylöjärvi mine, Fe (oxy)hydroxides may precipitate, adsorbing and retaining As from solution. Bodénan et al. (2004) studied arsenic behavior in gold-ore mill tailings and found that the highest arsenic concentration were in low Eh (67 mV) groundwater with near neutral conditions. There, the major arsenic species was arsenite.

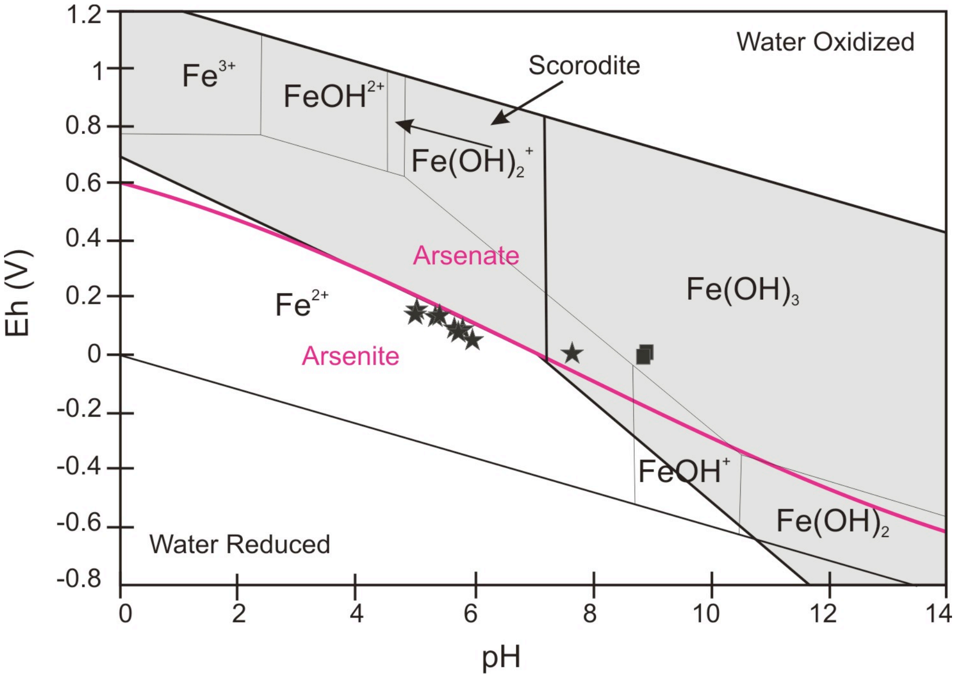

Figure 4. Iron speciation and arsenite/arsenate transition in a pH-Eh diagram. Grey areas mark the scorodite ($FeAsO_4 \cdot 2H_2O$) and $Fe(OH)_3$ fields according to Salzsauler et al. (2005). The stars correspond to the pore water samples in the upper 200 cm and the squares to the deeper tailings.

CONCLUSIONS

Almost half of a century after the Ylöjärvi mine was closed, arsenopyrite and other sulfide minerals are dissolving from the tailings pile, resulting in deposition of amorphous Fe arsenates and Fe (oxy)hydroxides. Despite the fact that As is retained to some extent in these secondary phases, they are not stable in the prevailing pH-Eh environment with slightly acidic to neutral pH and reducing conditions. As a consequence, high As concentration are measured in the surrounding surface waters and in the groundwater. At present, the tailings pH is buffered by carbonates, but the consumption of neutralizing calcite may change the pH conditions of the tailings. Sulfide oxidation and acid production is expected to continue for decades and perhaps for centuries. Hence, the stability of secondary minerals capable of sequestering the As is likely to change in the long run.

Further work is in progress to calculate the saturation indices for the pore water samples and to identify the secondary As phases.

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