

# Metal Release from Acidic and Near-Neutral pH-Conditions in Historical W, Cu and F Skarn Tailings at Yxsjöberg, Sweden

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## Abstract

Weathering products stored in the pore water and/or as easily soluble salts in historical skarn tailings containing Be, Bi, Cu, W, and Zn, were released in water soluble fraction in the upper-most acidic tailings, at the visual oxidation front (1.5m), and/or below 2.5m (pH>7). Thus, there is a risk that these metals can pollute receiving waters by neutral mine drainage. Re-mining the tailings could be a suitable remediation method that would both reduce the environmental impact and simultaneously support the supply of metals.

**Keywords:** Tungsten, Beryllium, Bismuth, Skarn tailings, water soluble fractions, Re-mining

## Introduction

Tailings generated from mining activities in the ancient past can pose a risk to the water quality in the vicinity of the repository due to reckless disposal and long-term storage (Hudson-Edwards et al., 2011). This is if metals in high concentrations are released from their hosting minerals due to changing geochemical conditions (Lindsay et al., 2015). The extent of metal downward movement in the tailings is dependent on adsorption and (co-)precipitation processes (Lee et al., 2002). Elements captured in secondary minerals that are water soluble pose a high risk of being transported in the tailings along with the release from primary weathering processes, and leak out to the ground- and surface water in the vicinity of the repository. Most of the environmental studies related to mine waste have been focused on sulfidic deposits and acid mine drainage, while little attention has been paid to tailings from skarn ore deposits and neutral mine drainage. Skarn tailings can contain several elements of potential concern such as e.g. Be, Bi, Cu, W, and Zn, together with Fe-sulfides and carbonates (Meinert et al., 2005). The sulfides can enhance the mobility of metals in the tailings due to sulfide oxidation reducing the pH (Blowes et al., 2003), and the carbonates can form neutral mine drainage if the abundance is large enough to neutralize the acidity and immobilise metals generated from the sulfides

(Lindsay et al., 2015). Studying the long-term effects of metal release in skarn tailings is of great importance. In Smaltjärnen's repository at Yxsjöberg, 2.8 Mt of tailings from a former W, Cu, and fluorite mine have been stored more than 50 years. The tailings are in direct contact with the atmosphere and Lake Smaltjärnen (Fig.1a). Total concentrations of 134 samples from four vertical cores through the tailings showed an average content of Be, Bi, Cu, Sn, Zn, W, and S in the tailings of 284, 495, 946, 559, 301, and 960 ppm, and 1.2 wt.%, respectively (Hällström et al., submitted). Pyrrhotite was the dominating sulfide in the tailings together with lower amounts of chalcopyrite and bismuthinite. The unusual mineral danalite ( $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$ ) contained approximately 40% of all Be and Zn, and 2% of all Mn in the tailings (Hällström et al., submitted), and is considered to be more easily weathered than other Be-minerals (Taylor et al., 2003). Scheelite was the main W-mineral (Hällström et al., submitted). The long-term storage had resulted in pyrrhotite oxidation down to 2.5 m depth and depletion of calcite in the upper 1.5 m subsequent with formations of gypsum and hydrous ferric oxides (HFO). A distinctive change in color was found at 1.5m depth in the tailings (Fig.1c), which is referred to as the visual oxidation front. Hydrous ferric oxides (HFO) had colored the tailings reddish-brown above the oxidation front, and dark-grey tailings were



present below. A detailed description of the site and mineralogy can be found in Hällström et al. (submitted). Earlier studies have shown that the groundwater has a pH in-between 7-9 and that the surface water has a pH around 6. Elevated concentrations of Ca, S, Be, and Zn has previously been found in the groundwater (Höglund et al., 2004).

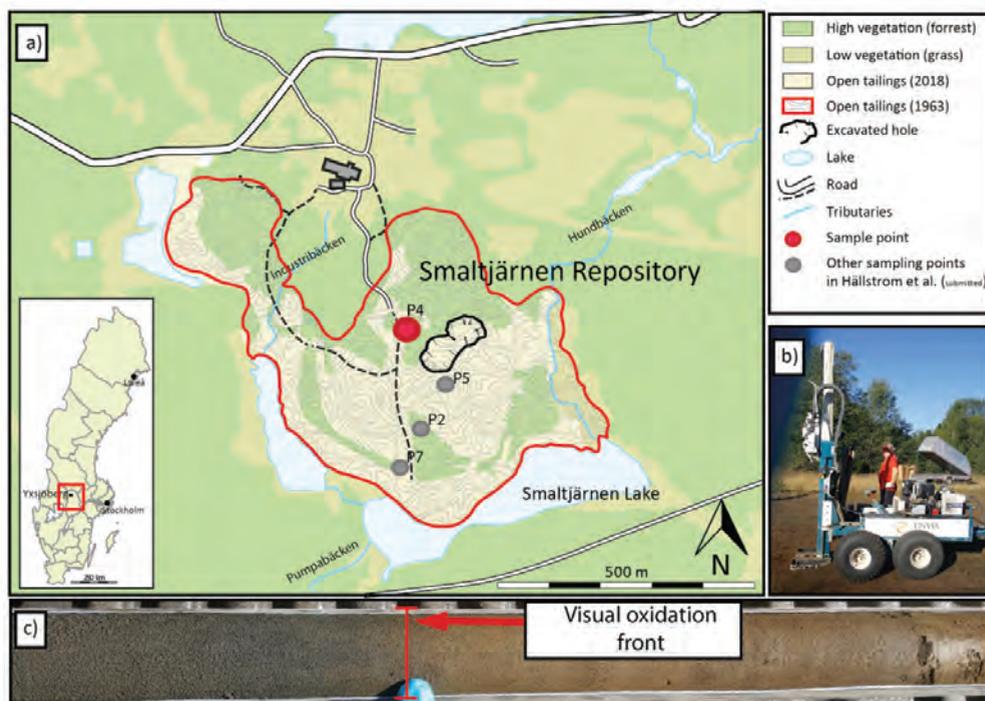
In this study, the weathering products stored in the pore water and/or as easily soluble salts in the tailings of Yxsjöberg were analyzed with depth in one representative core (P4) from Hällström et al. (submitted), with emphasis on Be, Bi, Cu, W, and Zn. The results were coupled with the chemical composition and mineralogical studies from Hällström et al. (submitted) to evaluate the risk of elements leaching to receiving waters, and the suitability of re-mining as remediation method.

## Method

The vertical core (P4) of 6 m has been sampled with percussion drilling through the tailings, and 50 subsamples of 10 – 30 cm were col-

lected and analyzed for total concentrations (Hällström et al., submitted).

The water soluble fractions of 14 subsamples of P4 were analyzed according to the first step of Dold (2003). A sample of 2.5 g was mixed with 125 ml milliQ water (0.055  $\mu\text{S}/\text{cm}$ ) and shaken for 1 hour. The eluates were filtered through 0.22  $\mu\text{m}$  cellulose acetate membrane filters, using a vacuum Sterifil® Aseptic System and Holder from Merck Millipore. The filters had been pre-washed with 5% acetic acid for 72 h and left in milliQ water for 24 h (Ödman et al., 1999). Samples were sent to ALS Scandinavia, Luleå, for screening analysis of 71 elements with an inductively-coupled plasma sector field mass spectrometer (ICP-SFMS), and anion analysis of sulfate, fluoride, and chloride with ion chromatography (CSN ISO 10304-1, CSN EN 16192). pH in the eluates were measurements with pHEnomenal MU 6100H and the electrode pHEnomenal 111 (662-1157), which was calibrated prior to the measurements with standard buffer solutions 4, 7 and 10. The electrical conductivity (EC) electrode



**Figure 1.** a) The water soluble fractions in tailings from Smaltjärnen Repository was studied with depth in one, out of four vertical cores (P4: marked in red) sampled with percussion drilling (b). c) The visual oxidation front in P4 was seen at 1.5m depth.



was controlled with a KCl-standard (1413  $\mu\text{S}/\text{cm}$ ) prior the measurements.

## Results

In the water soluble fractions, pH was higher than 7 below the oxidation front (1.5 m) and less than 5 in the oxidized upper-most tailings (Fig. 2). The electrical conductivity (EC) was anti-correlated with pH, with a maximum of 0.88 mS/cm at 0.3 m depth. Calcium, S, and  $\text{SO}_4$  in the water soluble fractions were highest in the upper-most samples, and the concentrations decreased with depth with an

exception of a small increase at 3.6 m (Fig.2). The correlation between the molality of Ca and S ( $R^2=0.997$ ), and between S and EC ( $R^2=0.993$ ), showed that gypsum regulated EC in the water soluble fraction throughout the profile. Copper was released in highest concentrations in the upper-most samples (max: 780  $\mu\text{g}/\text{L}$ ) and a second peak of released at the visual oxidation front (Fig.2). Aluminum, Be, K, Mg, Mn, Na, and Zn were released in the highest concentrations at, or just above, the visual oxidation front (1.5 m, depth). Aluminum, Be and Zn were not re-

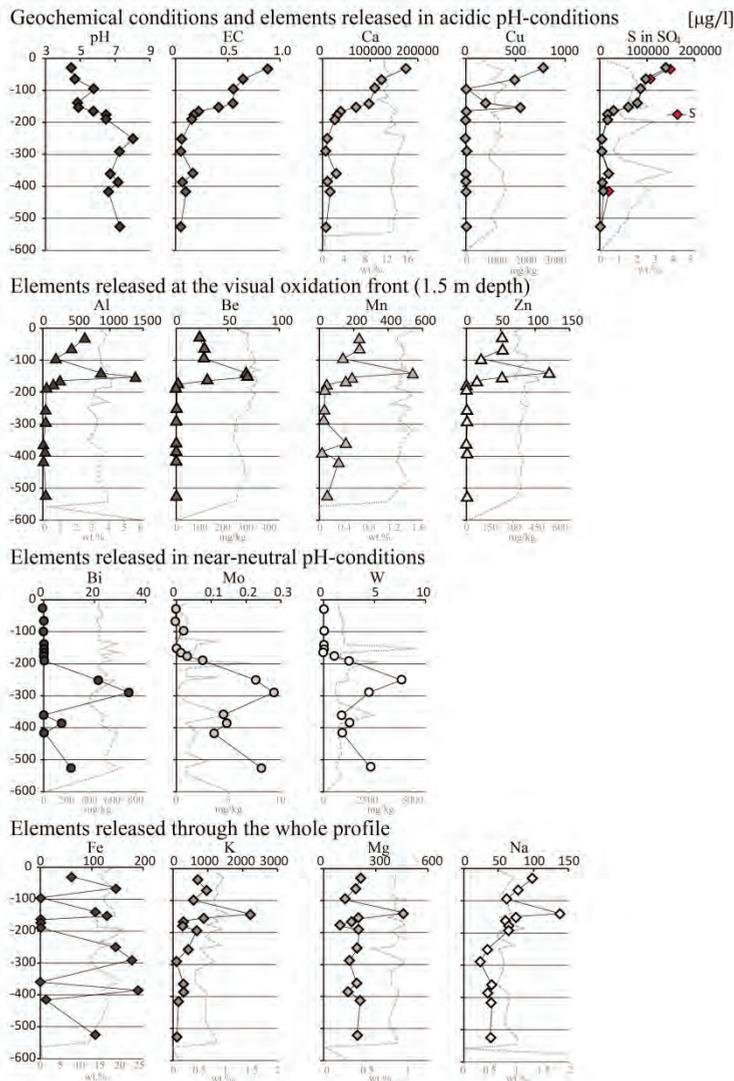


Figure 2. The water soluble fractions with depth in P4 is in  $\mu\text{g}/\text{L}$  and EC is in mS/cm. Total solid concentrations from Hällstrom et al. (submitted) are shown in grey dotted lines in mg/kg or wt.%.



leased below 2 m depth, whilst low concentrations of K, Mg, Na, and Mn was released through the whole profile. Manganese was water soluble at 3.6 m depth similar to Ca and  $\text{SO}_4$ . Bismuth, Mo, and W were released below 2.5 m depth. The highest concentrations were released between 2.5 – 3 m and lower concentrations were released between 3.5 – 4 m. Bismuth was released in the highest concentrations (max: 30  $\mu\text{g/L}$ ), followed by W (max: 10  $\mu\text{g/L}$ ). The released concentrations of Fe were varying through the whole profile with elevated concentrations in the upper-most samples, at the visual oxidation front and below 2.5 m depth. A maximum of 190  $\mu\text{g/L}$  Fe at 2.5 m depth were released, which corresponds to a release of 9.5 mg/kg Fe from the tailings. This is only a small fraction compared to the total concentration in the tailings, 14.9 wt.% (Hällström et al., submitted).

## Discussion

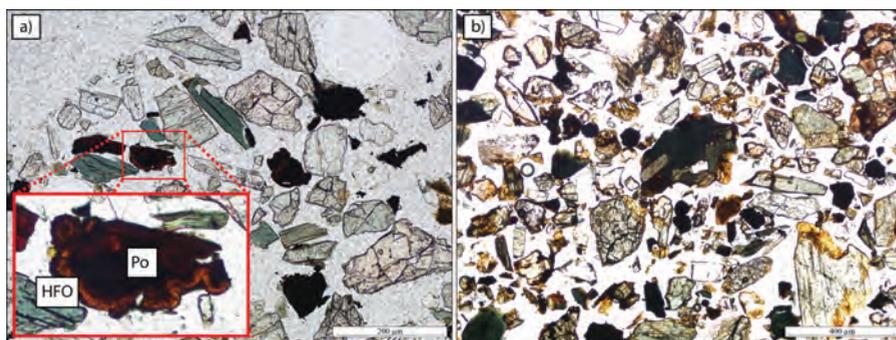
The long-term storage of tailings in ambient conditions has resulted in pyrrhotite oxidation down to 2.5 m depth, depletion of calcite and formations of HFO in the upper 1.5 m subsequent with reduced pH and increased electrical conductivity (Fig.2). At the visual oxidation front (1.5 m) pH was 4.9 and EC was 0.42 mS/cm. In the tailings, elements were released in elevated concentrations in either 1) the upper-most acidic tailings, 2) at the visual oxidation front (1.5 m), or 3) below 2.5 m in near-neutral pH-conditions (Fig.2). Only Fe was released in elevated concentrations in all three aforementioned settings. Gypsum dissolved by the water leaching test regulated EC throughout the profile, and the

increase of water soluble Ca and S at 3.6 m combined with mineralogical studies revealed that a second oxidized layer occurred. Thus, pyrrhotite was partly oxidized, calcite was altered and crystalline HFO were formed (Fig. 3a), which shows that the tailings at 3.6 m depth have been exposed to oxygen during a longer period of time in the past.

### *Elements released in acidic pH-conditions in the upper-most samples*

Oxidation of Fe-sulfides, subsequently decreased pH to 4.5, depletion of calcite and formations of gypsum and HFO has generated high concentrations of water soluble Ca, Cu, Fe, and S in the upper-most samples. Chalcopyrite is the main primary mineral for Cu and it was oxidized in the upper-parts of the tailings and covered with a thick rim of HFO (Hällström et al., submitted). Iron has previously been released from the oxidation of pyrrhotite, pyrite, and chalcopyrite, and has formed amorphous HFO around most mineral grains in the upper 1.5 m. The release of Cu and Fe are assumed to come from the pore water, or be loosely adsorbed to HFO or soluble Fe(II)salts. The total concentrations of Cu and Fe in the upper-most tailings are not decreasing considerably, which implies that released Cu and Fe in the acidic oxidizing conditions were not transported downwards.

The high concentrations of Ca and S in the water soluble fractions was due to the presence of secondary gypsum in upper-parts of the tailings. The occurrence was confirmed by mineralogical studies and gypsum had formed secondarily from the release of Ca from calcite and  $\text{SO}_4$  from pyrrhotite oxida-



**Figure 3.** a) At 3.6 m depth, secondary hydrous ferric oxides (HFO) were found around grains of magnetite, pyrrhotite (Po), and scheelite. b) At the visual oxidation depth (1.5 m depth) amorphous HFO were present around almost all mineral grains in the tailings.



tion (Hällström et al., submitted). The formations of secondary gypsum have decreased the transport of Ca and  $\text{SO}_4$  in the tailings, but high concentrations in the groundwater have, nevertheless, been found in previous studies (Höglund et al., 2004), and the solid content of Ca and S has both decreases from 1.5 m depth upwards (Fig.2). No other elements were following the same trends as Ca and  $\text{SO}_4$  in the upper-most samples, which imply that no trace elements were co-precipitated with gypsum.

#### *Elements released at the visual oxidation front (1.5m depth)*

Weathering of silicates and danalite has generated water soluble Be, K, Mg, Mn, Na, and Zn in elevated concentrations at, or just above, the visual oxidation front (1.5 m, depth). In the unoxidized tailings, K was mainly found in biotite and orthoclase, Na in oligoclase, and Mg in biotite, chlorite, ferrohornblende, and hedenbergite. Beryllium, Zn, and Mn were all hosted by danalite ( $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$ ), and the results indicated that ongoing weathering occurred at 1.5 m depth. Thus, the concentrations of Be had decreased stepwise with 40% from 351 mg/kg at 1.5 m to 250 mg/kg at 0.3 m, suggesting that danalite had already been weathered there. No strong accumulation peaks of Be were present deeper down in the tailings and Be, Zn, and Mn have previously been found in high concentrations in the groundwater of the repository (Höglund et al., 2004). The release of Al, K, Mg, and Na throughout the profile shows that silicate minerals have been weathered throughout the tailings profile but the most intense weathering occurred at the visual oxidation front. Weathering of silicates throughout the tailings was confirmed by mineralogical studies. Copper and Fe was also released in high concentrations at this depth. Compared to the release in the upper-most tailings, peaks of Cu or Fe were present at 1.6 m depth, coinciding with formations of blue secondary minerals, which is assumed to be a Cu-enrichment (Hällström et al., submitted). This implies that Cu has been transported downwards in the tailings due to low pH (4.5) and enriched when pH was above 5.5. Copper has not been found in high concentrations in the groundwater (Höglund et

al., 2004), even though up to 780  $\mu\text{g/L}$  were detected in the water soluble fraction in the tailings.

#### *Elements released in near-neutral pH-conditions*

A noteworthy downward transport of Bi, Mo, and W has occurred below 2.5 m depth where pH was higher than 7. Elevated concentrations in the water soluble fractions coinciding with low concentrations in the solid phases between 2.5 – 3.6 m for Bi, and between 2 – 3.6 m for Mo and W (Fig.2). The geochemical behaviors of Bi and W in tailings are poorly studied (Hällström et al., submitted), and their hosting minerals (bismuthinite and scheelite, respectively) has previously been considered as stable minerals (Bokii and Anikin, 1956; Jung et al., 2002). The few studies that exist about W, tentatively says that the release from scheelite in groundwater is due to anion exchange by  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  (Atademir, 1979), or  $\text{SiO}_2$  (Marinakis and Kelsall, 1987). The highest concentrations in water soluble phase of the tailings were found at 3 m depth, where secondary carbonates were formed (Hällström et al., submitted). Water soluble concentration of W and Mo were below the detection limit in tailings above 1.5m where HFO were present. Low concentrations of water soluble W and Mo were also coinciding with the oxidized layer of tailings at 3.6 were presence of HFO around grains of pyrrhotite, magnetite, and scheelite was observed (Fig.3a). Tungsten and Mo are known to form oxyanions with high affinity for HFO at pH <8 and remain in solution at pH >9 (Gustafsson, 2003). Bismuth is considered to be an immobile element due to its ion potential (Ball et al., 1982) but the element still showed similar trends as W and Mo.

### **Conclusions**

This study showed that metals of potential concern (Be, Bi, Cu, W, and Zn) were released in both acidic and near-neutral pH-conditions of skarn tailings during long-term storage in ambient conditions. In the upper-most tailings, where pH was 4.5, Ca and S were released by gypsum dissolution, and Cu was tentatively desorbed from secondary minerals. At the visual oxidation front, silicate minerals such as orthoclase and oligo-



clase were being weathered together with the unusual mineral danalite ( $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$ ), which released Be, Zn, and Mn into the water soluble fractions. In the deep tailings, pH was near-neutral (7 – 8) and Bi and W were found in elevated concentrations in the water soluble fractions, possibly due to anion exchange with carbonates, but this needs to be investigated further. Iron had an important role due to the formation of hydrous ferric oxides in the tailings capturing elements released in the water soluble fractions in both the upper-most samples and at 3.6m depth. The elements that were released at the visual oxidation front (Be, Mn, and Zn) were found in highest concentrations in the groundwater in previous studies. The transport of Cu, Bi, S, and W in the tailings and their retention by secondary minerals makes them to a potential concern since changes of geochemical conditions can release them to the groundwater. This makes re-mining to a more suitable remediation method than other more conventional options such as covers.

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