

# Secondary gypsum and HFO affected the mobility of critical metals (Be & W) in historical skarn tailings, Yxsjöberg, Sweden

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## Abstract

Beryllium (Be) and tungsten (W) are both classified as Critical Raw Materials (CRM), but their geochemistry in near-surface environments is not well understood. The mobility is largely dependent on the stability of hosting minerals. Uptake of Be and W in secondary gypsum and hydrous ferric oxides (HFO) on the shore of Smaltjärnen skarn tailings, Sweden, was studied with sequential extraction, low-vacuum SEM-EDS and DXRD (Differential X-ray Diffraction). The results showed that W was hosted to HFO, while Be adsorbed/co-precipitated temporarily with secondary gypsum. Gypsum was dissolved upon rainfall and Be was released to the surface water while W settled to the sediments a few hundred meters from the mine site. The future of TSM (Total Suspended Matter) monitoring is discussed.

## Introduction

The EU is striving for a higher domestic production of CRM, e.g., Be and W, to secure that the European Green Deal is reached by 2050 (European Commission, 2023a). On March 16th, 2023, The European Commission published an updated list of CRM together with the Critical Raw Materials ACT, stressing the importance to implement domestic production of CRM in Europe (European Commission, 2030a, b). The CRM Act also states the need to increase efforts to mitigate any adverse impact regarding environmental protection related to CRM mining. To achieve sustainable mining, environmental standards must be high, minimizing adverse effects on ecosystems and human health. Inadequate mine waste storage and closure can result in negative consequences on water quality downstream of the mine site and generate expensive remediation costs. However, the geochemical knowledge regarding Be and W is too limited to determine which precautions that should be taken. Without this knowledge, mine waste and water management containing Be and W might be insufficient, and reclamation to “pre-mining conditions” after mine closure may be unachievable. Even though mineral processing aims for a high recovery, metal extraction is unlikely

to reach 100%, generating concentrations of CRM in the tailings. The poor knowledge of Be and W geochemistry can adversely impact groundwater due to element leaching. Beryllium has been identified as the most toxic element in the periodic table if inhaled by dust, and other exposure pathways are not sufficiently studied to be excluded as toxic (Taylor *et al.*, 2003). Tungsten is classified as an emerging contaminant of concern (US EPA 2014).

The risk of having groundwater polluted with Be and W highly depends on the stability of hosting minerals and the surrounding geochemical environment. The mobilities of Be and W in mine tailings are affected by co-precipitation with secondary minerals and their stabilities. Gypsum and hydrous ferric oxides (HFO) are common secondary minerals in mine waste, either formed naturally in skarn tailings (Hällström *et al.*, 2018) or produced by liming in sulfidic tailings. Researchers have mainly focused on adsorption/co-precipitation of metals with HFO, while studies regarding uptake in gypsum are lacking. Studies regarding co-precipitation of Be and W to secondary minerals in field are limited, but some have been completed in the laboratory (Gustafsson, 2003).

Both Be and W have previously been considered as immobile elements (Koutsospyros *et al.* 2006; Taylor *et al.* 2003), but Hällström (2021) found that both elements were released from their primary minerals in W-skarn tailings in Yxsjöberg and transported to the groundwater in high concentrations. The groundwater drains at the shore of the tailings, where secondary minerals have precipitated. In this study, the adsorption/co-precipitation of Be and W to secondary gypsum and HFO was studied.

## Study site

At the Smaltjärnen repository, 2.8 million tons of tailings from a W-skarn deposit in Yxsjöberg, Sweden (1918-1989) have been stored open to the atmosphere for more than 50 years (fig. 1b). In 1993, a cover of sludge was placed on the tailings to suppress dust. The height difference between the industrial area and downstream lake Smaltjärnen is 15 – 20 m with a relatively uniform slope, except at the shore where it flattens out (fig.

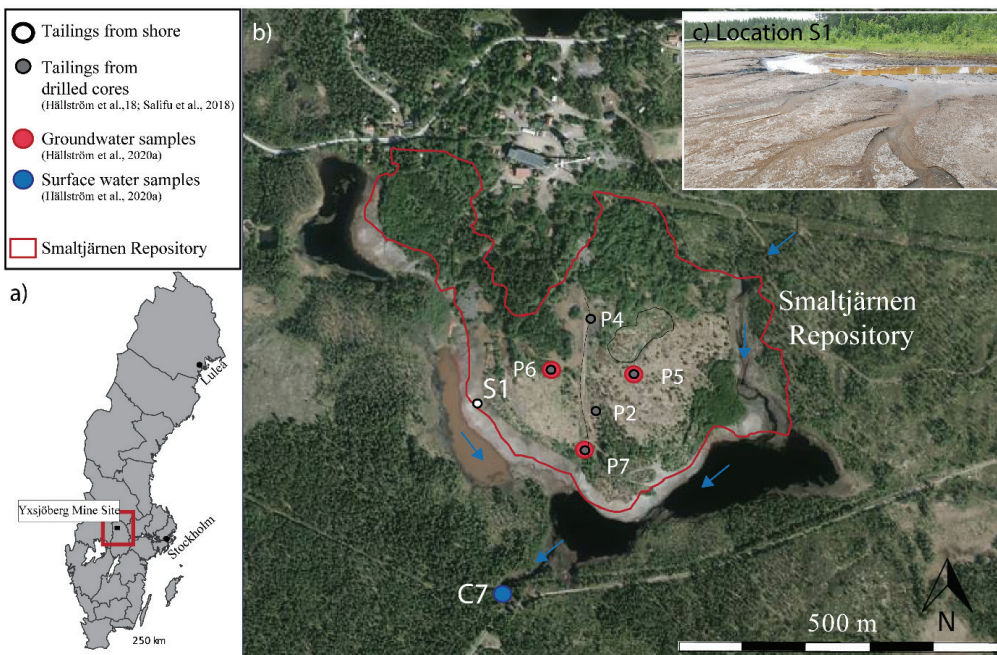
1c). The average Be and W concentrations in the tailings were 284 and 960ppm, respectively. The tailings contained 88 wt% of silicates, and lower quantities of fluorite ( $\text{CaF}_2$ ), calcite ( $\text{CaCO}_3$ ), pyrrhotite ( $\text{Fe}_{(1-x)}\text{S}$ ), pyrite ( $\text{FeS}_2$ ), scheelite ( $\text{CaWO}_4$ ), danalite [ $\text{Be}_3(\text{Fe}_{4.4}\text{Mn}_{0.95}\text{Zn}_{0.4})(\text{SiO}_4)_{3.2}\text{S}_{1.4}$ ] (Hällström *et al.*, 2018). Hällström *et al.* (2019) found that several geochemical zones have developed with depth in the tailings due to sulfide oxidation and calcite neutralization (fig. 5).

## Method

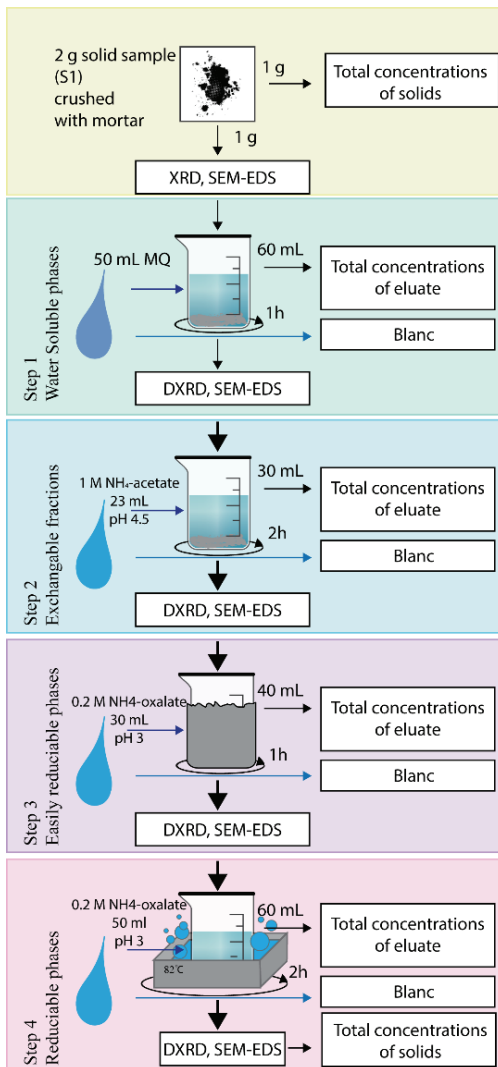
The tailings at the shore of Smaltjärnen Repository were identified covered by HFO and secondary gypsum in several areas on the shore (fig. 1c). A combination of sequential extraction, low vacuum SEM-EDS and DXRD was used to study the adsorption of Be and W to the secondary minerals.

### Five step sequential extraction

The sequential extraction combined the methodologies by Dold (2003) and Hall *et al.*



**Figure 1** The Smaltjärnen tailings are located in Yxsjöberg/ Sweden (a), and the tailings have been deposited inside the red line from 1912–1963 (b). Intact core samples (P2, P4, P5, P6 and P7), groundwater (P5, P6, P7) and surface water samples (C7) have been sampled previously (Hällström *et al.*, 2020a). In this study secondary gypsum and HFO from the tailings shore (c) were sampled at S1 (b). The map was collected from [www.eniro.se](http://www.eniro.se) at 2022-12-05.



**Figure 2** Step sequential extraction scheme together with analysis of total concentrations, blanks, SEM-EDS and DXRD.

(1996). The first four steps of sequence B as in Dold (2003) were conducted and the final step included total digestion of the solid residue after the extraction. The tailing sample (S1) was crushed and homogenized with a mortar. One gram of the sample was used as starting material for the sequential extraction and 1 g was sent to ALS Scandinavia for analysis of total concentrations. The laboratory procedures and analysis performed are summarized in figure 2. In Step 1 (water soluble phases), milliQ water was added in a L/S ratio of 1:50. The sample was shaken

for one hour and centrifuged 10 minutes with 2800 rpm, and afterwards decanted and filtered with a syringe through 0.45  $\mu\text{m}$  cellulose filter. The material was rinsed two times with 5 mL of milliQ, centrifuged for 10 minutes and decanted as described above. A total of 60 mL eluate was collected from the sample.

In Step 2 (Exchangeable phases), 23 mL of 1 M  $\text{NH}_4$ -acetate was added to the solid residue from step 1. The sample was shaken for two hours, and then the same procedure was done as described for step 1 for removing the eluate and rinsing the sample. A total of approximately 30 mL eluate was collected from the sample.

Step 3 (Easily reducible phases) was performed in the dark by wrapping aluminum foil around the sample container. 30 mL of 0.2 M  $\text{NH}_4$  oxalate, with pH 3, was added to the sample. The sample was shaken for one hour, then the same procedure for removing water and rinsing as described for the two previous steps were performed. A total of approximately 40 mL was collected for analysis.

In Step 4, the same reagent as for step 3 was used, and 50 mL was added to the residue. The sample was placed in an 82 OC water bath for two hours and was shaken every 30 minutes. Then it was centrifuged, decanted, and rinsed twice. Approximately 60 mL fluid was collected for analysis.

### Mineralogy

Between each step of the sequential extraction, the residues of S1 were studied with SEM-EDS mapping and DXRD. The SEM-EDS measurements were carried out with a high-resolution Zeiss Merlin FEG-SEM at Luleå University of Technology. The samples were uncoated and investigated in low vacuum, with a WD (working distance) = 8.5 mm, EHT = 20 kV.

XRD measurements were performed on the grinded, homogenized sample residues with a PANalytical Empyrean X-ray diffraction diffractometer, utilizing Cu-K $\alpha$  radiation. For the first analysis on the dry, powdered, sample (before the sequential extraction), the analysis was performed with 45 kV, using a 10 mm mask, ¼ anti-

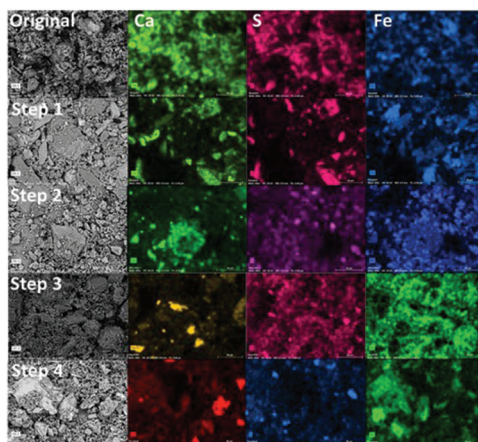
scatter, 1/ programmable, and anti-scatter RM5.7 (detector side). For the recording of the semi-dry residual samples from the leaching a 5 mm mask was used while the rest of the parameters were the same. The mineral identification was performed with the HighScore Plus Version 3 software package, utilizing XRD reference patterns from ICSD-2016.

## Results

The results showed enriched concentration of Be in Step 1 and 2, together with high release of Ca and S. Modelling with PhreeQC indicated a saturation of gypsum in the eluate after Step 1, explaining the high content of Ca and S after Step 2 of the sequential extraction. Tungsten was released in step 3 and 4 together with high concentrations of Fe.

Low vacuum SEM-EDS measurements of the samples showed that Ca and S occurred together in the starting material, and that they were present all over the sample (fig. 3). Iron was also present in high content. After Step 1 (water soluble fractions), much Ca and S had disappeared while Fe still was present in high amounts. However, Ca and S were still found together in the tailings. After Step 2 (Exchangeable fractions), Ca and S were no longer found together in the sample and Fe remained intact. After Step 3 (easily reducible fractions) small areas of Ca were present in the sample and S was only found in low quantities showing similar patterns as Fe. After step 4 (reducible fractions) the content of Fe decreased.

The XRD measurement identified monoclinic gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; Gp), ferrohornblende (Fe2-hbl) and hedenbergite (Hd) in the starting material (fig. 4). Ferrohornblende and hedenbergite are primary minerals from the ore (Hällström *et*



*Figure 3 Low vacuum SEM-EDS mapping between each step of the sequential extraction shows a decrease in Ca and S after step 2, and Fe after step 3.*

*al.*, 2019). The main peak of gypsum reached 1500 counts. Rietveld refinement estimated gypsum to account for 94% of the minerals in the sample. After Step 1 in the sequential extraction, peaks of gypsum, calcite, hedenbergite and ferrohornblende were present. Gypsum was still the dominating mineral (82%) even though it is supposed to dissolve by water.

After Steps 2,3,4 of the sequential extraction, gypsum was completely dissolved, and ferrohornblende and hedenbergite were the dominating minerals. Hydrous ferric oxides could not be identified with the XRD measurements in any of the steps of the sequential extraction.

## Discussion

The shore at Smaltjärnen repository acts as a chemical barrier, scavenging Be temporarily and W more permanently by adsorption/co-precipitation with gypsum and HFO,

*Table 1 Major and trace elements released from Step 1, 2, 3, 4 and in the residue in the sequential extraction.*

	Major elements mg/kg					Trace elements mg/kg	
	Al	Ca	Fe	Mn	S	Be	W
Step 1	360	36600	32,4	66	30000	13	0.002
Step 2	360	36000	93	69	29400	13	0,01
Step 3	680	68	4800	200	960	1.8	100
Step 4	660	72	31200	174	2100	3	114
Residue	27000	92000	150000	6000	8400	200	2600



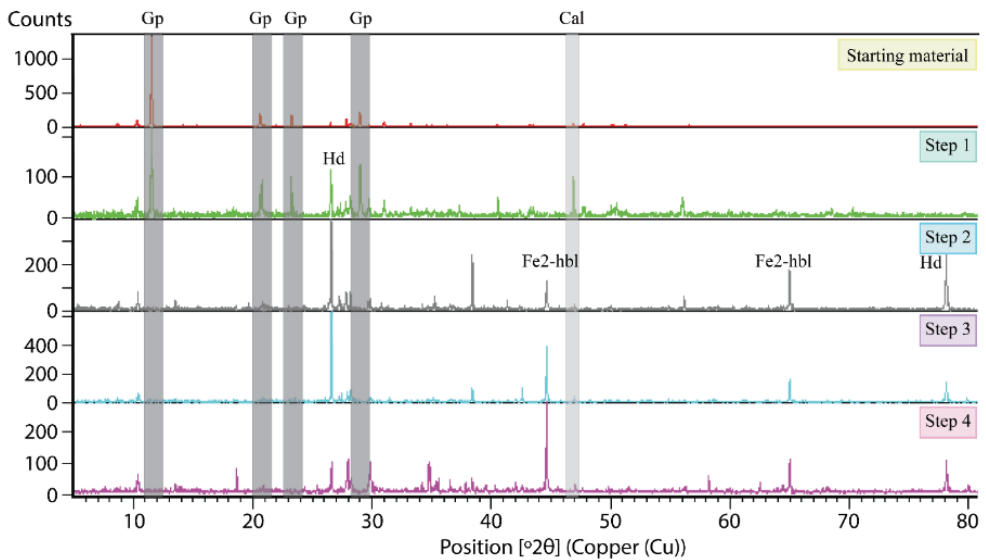


Figure 4 DXRD analysis between each step of the sequential extraction showed decreased peaks of gypsum after step 2, hydrous ferric oxides could not be identified with XRD. Gp = gypsum, Cal = calcite, Fe<sub>2</sub>-hbl = Ferrohornblende, Hd = Hedenbergite.

respectively (fig. 5). The groundwater of the tailings contained high concentrations of Ca, Fe, and S (615, 50, 590 mg/L, respectively), primarily released from pyrrhotite oxidation (Fe, S) and calcite neutralization (Ca) in the upper parts of the tailings (Hällström *et al.* 2021). The groundwater in the tailings flows out at the shore and makes the tailings saturated. On the shore, secondary gypsum has tentatively formed due to evaporation and HFO has formed due to oxidation of Fe<sup>2+</sup> where the groundwater meets the atmosphere.

Sequential extraction combined with XRD and SEM showed that Be preferentially adsorbs/co-precipitates with secondary gypsum. Thus, elevated concentrations of Be, Ca and S released during the first step in sequential extraction were correlated with removal of gypsum peaks in the XRD spectra and decreasing appearance of Ca and S during SEM-EDS mapping. This is interesting since Be previously has been considered to have high affinity for HFO (Taylor *et al.* 2003). Correlated concentrations of Be, Ca and S in surface water downstream of the tailings

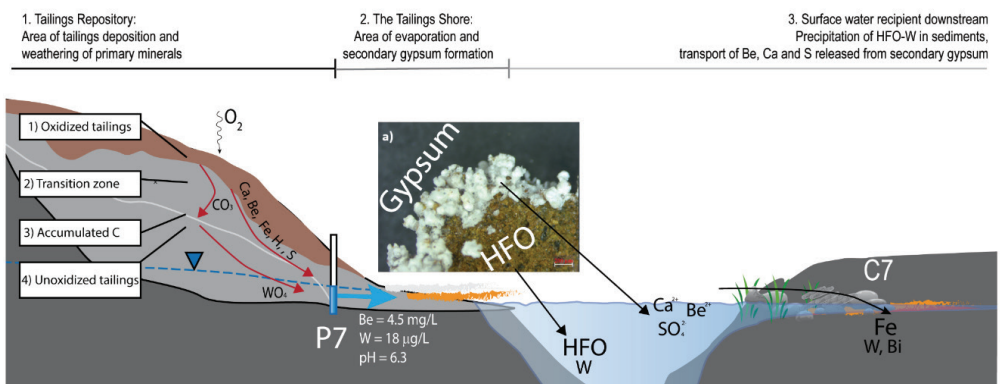


Figure 5 A schematic figure illustrating 1. Be and W mobility from different zones in the tailings to groundwater, 2. Uptake by secondary gypsum and HFO at the shore of the tailings, and 3. Be released to surface water downstream and settling of W with HFO.

suggest that secondary gypsum has been dissolved due to snowmelt or rainfall and released Be in high concentrations. Tungsten released from weathering of scheelite in the tailings was mainly associated to HFO according to the sequential extraction. Both Fe and W were found as suspended matter in the surface water, and erosion from the shore has probably transported the particles there. Tungsten settled into the sediment close to the mine site, while Be was transported in concentrations above guideline values from aquatic organism for more than 5 km from the site. This shows that the stability of the secondary minerals formed at the shore plays an important role regarding the impact on surface water quality.

## Conclusions

This study shows that Be preferentially adsorbs/co-precipitates with secondary gypsum, while W has high affinity for HFO. Tungsten settled to the sediments a few hundred meters from the repository together with HFO and does not pose a threat to ecosystems. A strong correlation between dissolved Be, Ca and S in high concentrations in surface water downstream the mine site showed that gypsum only acted as a temporary sink for Be. Gypsum dissolved upon rainfall and decreased the surface water quality. Co-precipitation of Be with gypsum has not been seen in the field before and is interesting since Be is assumed to have high affinity for HFO. This needs to be taken into consideration when evaluating methods for remediation of mine waste containing Be and W.

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