Reprocessing historical tailings for possible remediation and recovery of critical metals and minerals – The Yxsjöberg case

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Cover photo: The conceptual framework for reprocessing historical tailings, which was employed in this thesis' research work.
With the increasing consumption of primary mineral resources, mining waste has also increased, thus requiring the mining industry to address the growing environmental concerns. Waste rock and tailings are potential secondary sources of critical raw materials currently in short supply in the European Union and a source for environmental issues like acid mine drainage. Therefore, reprocessing such tailings to recover critical metals and minerals is a supply risk-reducing measure and an approach to remediation.

As a country with an active metal mining industry, Sweden is exploring historical tailings repositories for possible remediation and recovery of critical metals and minerals. The challenge is that information about the tailings material and the repositories is frequently limited. In this thesis, a conceptual framework has been defined and employed to systematically generate relevant information and knowledge about the Smaltjärnen tailings repository of the Yxsjöberg historical tungsten mine in the Bergslagen district, Sweden. The conceptual framework for developing effective and efficient methods to recover critical metals and minerals from historical tailings has been divided into six steps: (i) Identification and exploration; (ii) Repository characterization; (iii) Tailings characterization; (iv) Metallurgical test work; (v) Process design and analysis; and (vi) Residue management.

The Smaltjärnen tailings repository’s historical tailings were generated in the period 1935 to 1963, from primary ore of average grade 0.3–0.4 wt.% WO$_3$, 0.2 wt.% Cu and 5–6 wt.% fluorite. The exploited minerals were scheelite for W, which was also the main mineral of interest in this thesis, chalcopyrite for Cu and fluorite. The repository is estimated to have about 2.2 million tons of tailings, and covers an area of 26 hectares.

A site-specific sampling strategy and technique was identified, and based on the observed lithology, tailings particles were studied to understand their distribution across the repository. Methods for tailings characterization were identified involving drill core screening, particle size analysis, chemical analysis, X-ray diffraction, and mineral liberation analysis. Based on a comprehensive literature survey, an assessment of earlier processes from which the Yxsjöberg tailings were produced, and combined with characteristics of the tailings, possible separation methods were pre-selected, including dry low-intensity magnetic separation and high intensity magnetic separation, enhanced gravity separation using a Knelson concentrator, and froth flotation. From the metallurgical test work, possible reprocessing flowsheets were then determined. In addition, an innovative mechanochemical leaching process, referred to as leaching while grinding was tested.

Historical tailings in the Smaltjärnen repository contain critical raw materials including W and CaF$_2$ but also minerals of environmental concern as pyrrhotite and pyrite, in the dominating particle size fraction ~600 to +149 μm. The average WO$_3$ concentration in these tailings based on the sampled locations was 0.15 %, giving approximately 3300 tons of WO$_3$. Scheelite recovery was enhanced using a Knelson concentrator, with the highest WO$_3$ recovery of 76.4 wt.% in the first rougher concentrate. With the maximum recovery of W attainable via the mechanochemical method of leaching while grinding at 90%, approximately 2970 tons of WO$_3$ would be recovered in the leachate for subsequent processing.
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Author’s contributions:

**Paper I** – conceptualization, methodology, validation, formal analysis, investigation, resources, data curation, writing (original draft preparation) and visualization.

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**Paper III** – conceptualization, methodology, validation, formal analysis, investigation, resources, data curation, writing (original draft preparation) and visualization.

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INTRODUCTION

1 Background and objectives

The mining industry has a critical role to play in the achievement of the United Nations (UN) Sustainable Development Goal (SDG) 12 (“ensure sustainable consumption and production patterns”) because it is a huge consumer of natural resources especially mineral resources, and generates one of the largest waste streams (mining wastes) in the world [1,2]. The largest stream of these mining wastes are tailings, classified as processing wastes, and usually stored in piles, large surface impoundments (tailings dams) and other tailings storage facilities (TSF) [1,3,4]. The huge consumption of primary mineral resources has resulted in having depleted high-grade deposits and moving towards low-grade deposits, while the increased generation of mining wastes has led to a demand on the mining industry to address growing environmental concerns. Historical tailings (HT) are potential secondary sources of critical raw materials (CRMs) currently in short supply in the European Union (EU) [5], and there is a need for environmental intervention on the repositories as most of them already exhibit environmental issues like acid mine drainage (AMD) [1]. This is because relatively high minerals and metals content characterize HT due to less efficient extraction methods and/or relatively low metal prices at the time of production [4]. Therefore, reprocessing of such tailings to recover CRMs is not only a supply risk-reducing measure but also an approach to remediation [5–8]. This holistic approach will contribute towards a circular economy and environmental sustainability in the mining industry.

Countries with active metal mining like Sweden are exploring historical tailings repositories for possible remediation and recovery of critical metals and minerals but the challenge is the limited information and knowledge gaps about the material and the repositories [6,7]. In this thesis, a conceptual framework has been defined and employed to systematically generate relevant information and knowledge about the Smaltjärnen TSF of the Yxsjöberg historical tungsten mine in the Bergslagen district, Sweden. The conceptual framework is aimed at developing effective and efficient methods to recover critical metals and minerals from HT while leaving a stable and environmentally safe residue. With this approach and aim, the ERA-MIN project REMinE (Improve Resource Efficiency and Minimize Environmental Footprint) linked to this thesis, was going to achieve its vision of decreasing the amount of harmful wastes by reprocessing. Therefore, the REMinE project took a holistic approach in dealing with historical mining wastes from different mine sites, namely the Smaltjärnen TSF in Yxsjöberg, Sweden, the Cabeço do Pião tailings dam in Portugal [9], and the Sasca Montana tailings management facility in Romania [10].

In this thesis, the Smaltjärnen TSF in Yxsjöberg, Sweden was used as a case study to investigate the reprocessing of historical tailings for possible remediation and recovery of critical metals and minerals. The tailings in the Smaltjärnen TSF contain some of the CRMs cited for supply risk and economic importance for the EU, in elevated concentrations; tungsten (W), fluorite (CaF₂), beryllium (Be) and bismuth (Bi) (Figure 1) [5,11]. With its crucial role in a circular economy, materials criticality has become a topic of increasing international interest [12]. Therefore, the research in this thesis also gained the support of other international projects (IRTC – International Round Table on Materials
Criticality) because the Yxsjöberg case study is a good example of how the supply risk-reducing measure in materials criticality could contribute to a circular economy in the mining industry [13].

Of the four CRMs found in the HT under study, W is an element of interest; thus, reference will be made to it more than the other elements. It has unique characteristics such as having the highest melting point of all metals, high density and low reactivity/toxicity, which make it a suitable and irreplaceable metal in the production of hard, tough, durable and corrosion resistant tools essential in modern technologies [14–16]. According to the 2015 risk list of the British Geological Survey, W has a relative supply risk index of 8.1 on a scale of 1 to 10, which is ranking sixth behind rare earth elements that have the highest risk [17]. Primarily, it is produced from scheelite (CaWO₄) and wolframite ((Fe,Mn)WO₄) mineral ores with 0.08-1.5% tungsten trioxide (WO₃) grade [14,18]. These tungsten minerals are friable in nature compared to the associated gangue minerals; hence, fine W particles are excessively generated during comminution processes (crushing and grinding). The generated fine W particles are lost to tailings due to the failure of separation methods used earlier to recover W minerals [14,19]. In low-grade ores, W losses to the tailings are enhanced because fine mineral particles such as scheelite particles are either lost as liberated fine particles due to the required fine grinding or as unliberated particles if the grinding is insufficient. Therefore, new techniques that would help to reduce such losses during beneficiation and/or recover W from tailings need to be developed [14,19,20].
The amount of minerals and/or metals that remain in tailings depends mainly on the separation and extraction methods employed, and the processing efficiencies. The design and selection of these processing methods are primarily based on the mineralogical characteristics of ores: (i) Identities of major, minor and trace minerals; (ii) Compositions of minerals that bear on the process; (iii) Quantities of minerals; (iv) Particle and grain size distributions and textures of the minerals; (v) Mineral liberations; and (vi) Surface coatings on minerals [21,22]. These mineralogical characteristics are also essential when considering tailings for reprocessing because they have a link to the metallurgical performance of process flowsheets to be developed [23–25].

Like ore bodies, HT repositories can be subdivided into different volumes with a similar set of textural and compositional properties and hence metallurgical performance, also referred to as geometallurgical units/domains [23]. Contrary to primary ore deposits, the structure and characteristics of a tailings repository is anthropogenic and determined by a number of factors, including depositional environment, discharge (spigotting) point, the method of slurry entry into the impoundment, discharge rate, the density of the discharged slurry, particle size and mineralogical composition [3]. The visible effects of these factors are stratification, including graded and cross-bedding of the tailings. Coarser and heavier particles tend to settle near the discharge point while the finer and lighter particles settle further away. Therefore, if certain minerals occur in a particular particle size, they may segregate and accumulate in the repository locations [3].

Different geometallurgical and/or process mineralogical approaches have been used to reprocess tailings or process ores [24–29]. These approaches improve the mineral production prediction, including mining waste (waste rock and tailings) amounts and their composition. Based on this, appropriate waste management measures can be determined at the inception of the mining operation to attain improved environmental outcomes and circular economy aspirations [30]. This approach enhances resource knowledge from the processing perspective hence lowering operational risk related to repository unknown variation [31]. Using such an integrated approach allows for a better understanding of the characteristics and metallurgical performance of the tailings [29], but it is only a part of the conceptual framework required to investigate the reprocessing of historical tailings holistically and systematically.

Therefore, in order to develop effective and efficient methods to recover critical metals and minerals from the Yxsjöberg historical tungsten tailings in the Smaltjärnen TSF thereby leaving a stable and environmentally safe residue, a conceptual framework was defined and employed based on the following research questions:

1) What are the major steps and tasks necessary for reprocessing historical tailings?
2) What effective and efficient reprocessing methods can be employed to remediate and recover critical metals and minerals from the Yxsjöberg historical tungsten tailings?

Based on these research questions, a research approach was developed resulting in the work presented in this thesis. Relevant information and knowledge about the Smaltjärnen TSF of the Yxsjöberg historical tungsten mine in the Bergslagen district, Sweden, were systematically generated, and used to develop tailings reprocessing methods, thus providing a conceptual framework that could be applied even to other HT repositories. With mine waste management being a key part of the mining value chain, the conceptual framework employed in this thesis would also be used to plan how mining
waste should be deposited as a future secondary source of metals and minerals, and what information should be archived.

2 The Conceptual Framework

Investigating a historical tailings repository for holistic reprocessing requires a systematic approach that encompasses resource knowledge from the processing and environmental perspective. The conceptual framework for reprocessing historical tailings to remediate the repository and/or recover critical metals and minerals is divided into six steps with defined tasks (Figure 2).

In order to have relevant information and knowledge in each of the six steps, it is important to identify the relevant stakeholders that can provide a multidisciplinary input. In the identification and exploration step, some initial information such as the primary ore geology and production plans may be available from national geological surveys, technical literature, and particularly the mine’s production archives. Otherwise, it would have to be generated from the comprehensive exploration of the tailings repository itself. Anyhow, knowledge of the primary ore, which helps to assess the effect and extent of weathering on the repository, would still be lacking while both primary and altered secondary minerals are present.
Critical in all these steps is having representative samples of the tailings for analysis and evaluation; hence determining effective sampling techniques is vital. It is also important to note that the sampling strategy and suitable technique are usually site-specific because each tailings repository is unique and the reasons for the sampling vary due to (i) exploration purposes, (ii) environmental concerns and (iii) secondary resources potential [7]. In the tailings characterization step, the latter two determine the methods to be selected and the sequence to be followed, and hence the sub-steps of remediation and recovery of critical metals and minerals.

For metallurgical test work, tailings characterization results referring to both sub-steps (remediation, and recovery of critical metals and minerals) are vital for determining possible reprocessing methods and assessing metallurgical performance. However, it is also important to understand the processes from which the tailings were produced, the composition of the initial products, how and where they were discharged. Therefore, having initial process flowsheets and information about the lithology of the repository in the first two steps of this conceptual framework is essential for planning metallurgical test work. It also enhances the use of multidisciplinary approaches like the geometallurgical and/or process mineralogical approaches, which are beneficial for such complex materials with heterogeneity issues.

Findings from metallurgical test works are then used to design suitable process flowsheets that would allow for the reprocessing of historical tailings to remediate the repository and/or recover critical metals and minerals. However, the developed process’ sustainability needs to be assessed, and the generated residue needs to be stable and environmentally safe. The residue management helps to ensure that the reprocessing of historical tailings does not create another problem but offers a long-term solution.

Therefore, using this conceptual framework, the Yxsjöberg case was explored to remediate and recover critical metals and minerals. A methodology to further understand the physical, chemical and mineralogical properties of the Yxsjöberg HT, how they are distributed in the TSF, and to determine the process options for reprocessing was established.
3 The Smaltjärnen tailings repository in Yxsjöberg

The Smaltjärnen TSF is located in Bergslagen, Central Sweden, historically one of the most important mining areas in northern Europe regarding tungsten ores. The Yxsjöberg tungsten tailings were produced from ore that was mined at the Yxsjö Mines, during operation from 1935 to 1963. The exploited minerals were scheelite for W, chalcopyrite for Cu and Fluorite (CaF$_2$), from crude ore with an estimated average grade at 0.3-0.4 %WO$_3$, 0.2 %Cu and 5-6 %CaF$_2$ [32,33]. The scheelite grain size in the ore was 0.2-4.0 mm and 90 wt.% of the ore was liberated at an average grain size of 0.4 mm.

![Figure 3. Smaltjärnen TSF in Yxsjöberg, Sweden. The yellow arrows from the decommissioned Yxsjö processing plant indicate the gravity flow of the discharged tailings from the hilltop.](image)

The concentrate recoveries at that time were 50-70 wt.% for scheelite, 50 wt.% for fluorite and 25 wt.% for chalcopyrite meaning that a considerable amount of these valuable minerals ended up in the tailings [33]. The Yxsjö processing plant had three main divisions namely gravity separation, magnetic separation, and flotation, from which tailings were generated and randomly discharged into the Smaltjärnen TSF (Figure 4). Tailings deposition was done through several pipes, thus producing homogenous layers of tailings equally distributed over the repository surface’s width. No data were available that could be used to link these layers to the former production schedule.
The Smaltjärnen TSF is estimated to have about 2.2 million tons of tailings and covers an area of 26 hectares, with elemental concentrations of 1-2 %S, 0.02-0.2 %Cu, 0.02-0.3 %W, 0.02-0.04 %Sn and 0.02-0.03 %Be. This TSF does not have dam walls or complete vegetation cover to prevent the tailings from being washed into the Smaltjärnen Lake at the foot of the repository; the remains of what seems to have been an embankment made of wood shows a failure to contain the tailings thus allowing erosion (Figure 5). Therefore, environmental concerns are inevitable as seepage from the tailings through the dilapidated embankment into the surface waters, and air and soil pollution through dust generation are evident [3].
4 Characterization and reprocessing options

4.1 Repository characterization

The Smaltjärnen TSF was sampled by collecting drill core samples from nine different locations. Samples were collected mainly along the main discharge flow directions (Figure 6). The red dots represent the individual drill core sampling locations and the numbering of the sampling locations was based on the sequence of sampling in each sampling campaign. The first four locations were distinguished by _1 and _2, meaning 1_1 was in the first campaign while 1_2 was in the second campaign. For locations 1_2 to 7, a percussion drill rig was used with plexiglass tubes (40 mm diameter and 1.2 m length each tube) to hold the sample. The site visit helped to come up with a site-specific sampling strategy and technique. The strategy was to locate the discharge points and sample the repository according to the discharge flow directions (Figure 6). It was assumed that the distribution of the material in the horizontal plane happened in a uniform way resulting in similar profiles in the vertical plane when following the discharge downhill. Based on that, sampling was mainly done along a line in a downhill direction (longitudinal section) with control points to the left and to the right (transverse section). Table 1 summarizes the 17 sampling points out of which eight (1_2, 6 to 6F) were used for preliminary testing of feasible processing methods.

Figure 6. Drill core sampling locations on the Smaltjärnen TSF are represented by red dots that are connected by white arrows for direction order of interpolated longitudinal section views. The yellow squares show two discharge points, and the yellow lines show the repository limit.
Table 1. Summary information of points on the Smaltjärnen TSF.

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>Sampling Points GPS Coordinates</th>
<th>Altitude (m)</th>
<th>Number of drill holes</th>
<th>Drill hole depth (m)</th>
<th>Number of drill cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_1</td>
<td>60.041669, 14.771031</td>
<td>307</td>
<td>1</td>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
<td>2_1</td>
<td>60.040194, 14.775531</td>
<td>309</td>
<td>1</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>1_2</td>
<td>60.041778, 14.775325</td>
<td>306</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>2_2</td>
<td>60.040792, 14.776211</td>
<td>314</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>60.042189, 14.771242</td>
<td>291</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>60.040769, 14.774017</td>
<td>305</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>60.040069, 14.774878</td>
<td>305</td>
<td>2</td>
<td>4.8</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>60.042656, 14.775217</td>
<td>303</td>
<td>7</td>
<td>2.4</td>
<td>14</td>
</tr>
<tr>
<td>6A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6B</td>
<td></td>
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<td></td>
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<td>6C</td>
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<tr>
<td>6D</td>
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<td>6E</td>
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<tr>
<td>6F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.042911, 14.774928</td>
<td>315</td>
<td>2</td>
<td>2.4</td>
<td>4</td>
</tr>
<tr>
<td>7A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The drill cores were screened based on the differences in color and granulometry in the cores, with the split into smaller samples representing tailings layers in a particular location of the repository. This approach was taken in order to have a clear understanding of layers represented in each drill core; after characterization, the particle size and minerals dominant in a given layer and their effect on the pre-selected separation methods would then be known. This understanding is important because the layers are an indication of how tailings deposition took place in the repository, variations in mineralogy and process parameters during the production period. The variations in the tailings layers in the different locations were also observed on-site in excavated sections (Figure 7). Drill core vertical profiles showing the different tailings layers in the selected locations of the repository are shown in Figure 8.

Figure 7. Photos of excavated sections of the Smaltjärnen TSF showing variations in the tailings layers.
Figure 8. Variations in vertical profiles for the 17 sampling locations; each color represents a layer of the drill core, and its compacted thickness in the tailings repository as shown in the photo to the far right.

4.2 Tailings characterization

A holistic approach that considers the environmental consequences of reprocessing historical tailings as secondary resources is desired. Therefore, both sub-steps of remediation and recovery of critical metals and minerals were considered in selecting methods and sequence of characterizing the Smaltjärnen tailings.

In order to characterize the tailings samples physically (moisture content, texture, and particle size distribution), chemically (elemental composition), and mineralogically (modal mineralogy, mineral locking, and liberation), the samples were first dried in air at 105 °C for 48 hours. The dried samples were then split into sub-samples using a riffle splitter. Figure 9 shows pictures of the dried tailings samples for drill cores 1_1, 1_2 and 6, with each sample representing a layer in the drill core. Therefore, in addition to the number indicating the sample location, an extra set of numbers indicates each drill core layer. Drill core samples were characterized by using various selected analysis methods (Figure 10).

Figure 9. Dried tailings samples for drill core 1_1 with layers 1_1-1 to 1_1-10, drill core 1_2 with layers 1_2-1 to 1_2-11, and drill core 6 with layers 6-1 to 6-3, showing variability in color and texture.
Mineral Liberation Analysis (MLA) was conducted on each layer and each particle size fraction of the selected drill cores from location 6 (Table 2) using the Scanning Electron Microscope equipped with the MLA 3.1.3.612 software suite from FEI (SEM – FEI Quanta 650 MLA-FEG: FEI Company, Hillsboro, OR, USA). Both sample preparation and MLA were done at the Helmholtz Institute Freiberg for Resource Technology in Germany. For the results presented in this thesis, the Grain-based X-ray Mapping (GXMAP) MLA measurement mode was employed. The MLA Dataview v3.1.4.686 software (3.1.4.686, FEI Company, Hillsboro, OR, USA, 2014) was used to evaluate the MLA data.

Table 2. Summary of MLA sample protocol.

<table>
<thead>
<tr>
<th>Sieve fraction (µm)</th>
<th>Number of specimens</th>
<th>Number of samples</th>
<th>Total MLA specimens</th>
<th>Sample ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-1190</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>6-1, 6-2, 6F-1</td>
</tr>
<tr>
<td>300-600</td>
<td>3</td>
<td>4</td>
<td>12</td>
<td>6-1, 6-2, 6-3, 6F-1</td>
</tr>
<tr>
<td>149-300</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>6-1, 6-2, 6F-1</td>
</tr>
<tr>
<td>75-149</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>6-1, 6-2, 6-3, 6F-1</td>
</tr>
<tr>
<td>&lt;75</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>6F-1</td>
</tr>
</tbody>
</table>
4.3 Physical separation tests

Based on the tailings characterization, a comprehensive literature survey and the assessment of processes from which the Yxsjöberg tailings were produced, possible separation methods were pre-selected, including magnetic separation, and enhanced gravity separation. Tailings samples from location 1_2, which had 11 different layers were used, with each layer being tested as a separate sample so that variations in metallurgical performance could be observed. The Knelson Concentrator (Figure 12) was selected because it is a more advanced gravity separation method than the shaking tables that were used at the time these tailings were produced. It uses enhanced gravity separation (EGS) where a centrifugal force is applied to enhance the differential settling velocities between heavy and light particles (<80,000+10 µm), which is good for efficient recovery of heavy fines such as scheelite fines in these tailings [35]. As for magnetic separation, dry low-intensity magnetic separation (LIMS) and dry high-intensity magnetic separation (HIMS) were selected (Figure 11) because it was desired to separate the strongly and/or weakly magnetic minerals, such as pyrrhotite responsible for AMD [11], from other minerals in the tailings. For water conservation, and separation of tailings particles >75 µm, dry magnetic separation was preferred to wet separation. Detailed feed specifications and process operating parameters are given in the appended paper II.

Figure 11. The simplified flowsheet of the magnetic separation process.

Figure 12. The gravity separation process using the Knelson concentrator.
4.4 Flotation tests

Froth flotation was considered to be an alternative method to EGS for recovering fine (<75 µm) scheelite from the tailings under study. At the time these tailings were produced, scheelite flotation was unsuccessful as its separation from other Ca-bearing minerals like fluorite failed due to similar flotation properties [36]. This challenge of scheelite selectivity still exists, and research on performance of different reagents is ongoing [37], therefore, two new collectors (Berol 8313 and Atrac 2600) were considered [38]. Some preliminary froth flotation tests were done on the <75 µm tailings fraction from location 6 (where more drill cores were collected). For covering variations in the metallurgical performance concerning the sampling points, tests were run on samples from seven points 6 to 6F (as given in Table 1).

A batch mini-flotation machine called Clausthal flotation cell was selected as small sample amounts are needed to run tests in this cell, and the flotation test protocol is summarized in Figure 13. Collectors NaOl, Berol 8313 (a formulation containing fatty acid and nonionic), and Atrac 2600 (a synthetic anionic collector with different active components), with SS as the depressant, were used as flotation reagents. Nouryon provided technical guidelines for the preparation of Berol 8313 and Atrac 2600 aqueous solutions [39]. For pH regulation, 1.0 M HCl (hydrochloric acid) and 1.0 M NaOH (sodium hydroxide) were used. Specifications for flotation parameters, reagents and dosages are given in Table 3. The flotation products were chemically analyzed at ALS Scandinavia AB using the ICP-SFMS method.

Dosages for NaOl with SS were based on a more recent study about selective flotation of scheelite from calcite [40], while for new collectors Berol 8313 and Atrac 2600 the recommended dosage range by Nouryon was 100-400 g/t with SS up to 400 g/t [41]. Berol 8313 was “developed for the direct flotation of scheelite”, is “suitable for direct flotation of fluorite”, and is a “formulation for complex difficult to float ores and/or hard process water” especially in the direct flotation of phosphate where Atrac 2600 is also indicated to have a key benefit of improved selectivity [23].

![Figure 13. Flotation test protocol.](image-url)
Table 3. Summary of flotation parameters.

<table>
<thead>
<tr>
<th>Air flow rate (mL/s)</th>
<th>Agitation speed</th>
<th>Liquid volume (mL)</th>
<th>% Solids</th>
<th>Collector</th>
<th>Collector dosage</th>
<th>Depressant</th>
<th>Depressant dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6</td>
<td>265</td>
<td>190</td>
<td>20</td>
<td>NaOl</td>
<td>3 x 10^{-4} mol/L</td>
<td>SS</td>
<td>300 mg/L</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Berol 8313</td>
<td>100 g/t</td>
<td>SS</td>
<td>400 g/t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Atrac 2600</td>
<td>100 g/t</td>
<td>SS</td>
<td>400 g/t</td>
</tr>
</tbody>
</table>

4.5 Hydrometallurgical tests

4.5.1 Conventional leaching tests

A scheelite flotation concentrate (75.0 %WO₃) from the decommissioned Yxsjöberg processing plant was used to run conventional leaching tests (Figure 14) to get an indication of how this high-grade material responds to alkali leaching before the low-grade HT in this study could be tested. For each experiment, 15 g of scheelite concentrate was used. Prior to leaching, the concentrate was washed with acetone to avoid agglomeration of the concentrate in the concentrated (10 M) NaOH solution (300 mL). Leaching tests were conducted at 38°C, 60°C, 80°C and 100°C. Each test was run for six hours, and leachate samples were collected every hour. The leachate was then analyzed for W, and W recovery was calculated.

![Figure 14. Conventional leaching laboratory setup for scheelite concentrate.](image)

4.5.2 Leaching while grinding tests

An innovative mechanochemical leaching process, referred to as leaching while grinding (LWG) was tested after running conventional leaching tests with scheelite concentrate as indicative tests. This process was considered because it was desired to use a more efficient and sustainable process in which
higher W recoveries would be attainable even when compared to the physical separation and flotation methods. Grinding improves the leaching kinetics as scheelite reactivity increases, and surface area increases with particle size reduction [42,43].

Initial LWG tests were conducted at 38, 60 and 80°C using the scheelite concentrate (10 g), and 200 mL concentrated (10 M) NaOH solution. For HT, the feed material for these tests was from location 6, and 26 grams of tailings sample was used for each experimental run based on the ball-to-powder ratio (BPR) of 50 [44], with the particle size distribution of –600 to +75 μm, and average density of 3.35 g/cm3 determined using a pycnometer. Mill and media parameters were as given in Table 4. The LWG tests for HT were designed (Table 5) using the Design-Expert® software (12.0.12.0, Stat-Ease, Minneapolis, United States, 2020), and the experimental setup was as shown in Figure 15. The design had 16 completely randomized runs (Table 6), with W recovery as the response. The real values for temperature, digestion time, and liquid/solid ratio coded low (-1) were 60°C, 4 hours, and 0.8, while coded high (+1) were 98°C, 6 hours, and 1.0, respectively.

<table>
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<th>Media</th>
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<tr>
<td>Stirrer speed (rpm)</td>
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<tr>
<td>Ball filling volume (mL)</td>
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<tr>
<td>Density (g/cm³)</td>
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<td>Mass (g)</td>
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<td>Volume (cm³)</td>
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<tr>
<td>Ball size (mm)</td>
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<td>BPR</td>
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<td>+1 ↔ +1.00</td>
<td>0.0000</td>
<td>1.03</td>
</tr>
<tr>
<td>B</td>
<td>Digestion time</td>
<td>hours</td>
<td>Numeric</td>
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</tr>
<tr>
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<td>Liquid/solid ratio</td>
<td>ratio</td>
<td>Numeric</td>
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<td>B:Digestion time</td>
<td>C:Liquid/solid</td>
<td>D:Stirrer speed</td>
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Figure 15. Leaching while grinding experimental setup.
5 Results and discussion

The results for the ‘identification and exploration’ step of the conceptual framework (Figure 2) formed the initial part of the methodology for this research as the foundation for understanding the Smaltjärnen HT, and executing the subsequent steps for reprocessing.

- It is important to identify the relevant stakeholders that can give a multidisciplinary input to the conceptual framework for reprocessing historical tailings. For the Yxsjöberg case, the disciplines included mineral processing, applied geochemistry, and geophysics.
- For current and future tailings repositories, the proposed conceptual framework can also be used as a checklist to ensure that all relevant information is systematically archived for future reference.

5.1 Repository characterization

Based on the location of the discharge points, the observed southward flow of tailings into the Smaltjärnen Lake, the altitude information and layering of the drill cores, two interpolated longitudinal section views of the repository were constructed (Figure 16). From the depositional environment observed in the two longitudinal section views, the three locations 1_1, 1_2 and 6 provided preliminary representative samples of tailings near discharge points (locations 1_1 and 6), and lower-level areas where larger volumes of tailings flow from surrounding higher-level areas and accumulate in several layers (location 1_2).

![Figure 16. Interpolated longitudinal section views of the repository show the depositional environment and the tailings thickness variation on the TSF: Left – direction order 7, 6, 1_2, 2_2 and 2_1; Right – direction order 3, 1_1, 4 and 5.](image)
5.2 Tailings characterization

5.2.1 Physical and chemical characterization

Variations in the physical and chemical properties were observed in the different layers and locations of the repository. In order to illustrate the particle size variation in the three selected locations of the repository, the determined $D_{80}$ values for the layers in each drill core are plotted against the depth (Figure 17). It was observed that particles in drill core 1_1 are generally coarser than those in drill cores 1_2 and 6. This can be explained by particle segregation and settling in the TSF, as drill cores 1_1 and 6 were sampled near the spigotting points containing coarser particles, while drill core 1_2 was further away from both outlets, and at a lower altitude [3]. The observed disparity in particle size distribution across the tailings repository indicates geometallurgical domains that may have different metallurgical performances [23] as well as affects the choice of reprocessing methods. For instance, in location 1_1, further grinding may be required as minerals of interest may be locked up in coarse tailings particles.

![Figure 17. Variation of $D_{80}$ values with depth.](image)

Particle size distribution (PSD) curves for the three drill cores were determined using all the layers in each drill core. In all drill cores, the dominating particle size fractions were –600 to +300 µm and –300 to +149 µm (Figure 18). Drill cores 1_2 and 6 had more fines (<75 µm) than drill core 1_1. This disparity in particle size reveals the effect of the depositional environment on particle distribution across the repository coupled with variations in mineralogy and/or process parameters such as grinding size during the production period of 1936 to 1963.
Figure 18. PSD curves for the three drill cores.

Similarly, elemental concentrations and mass distributions in the six particle size fractions were determined in each drill core from locations 1_1, 1_2 and 6 (Figure 19, Figure 20 and Figure 21). The elements of high concentration were W, Cu, S, Sn, Zn, Be, and Bi. The weighted average elemental concentrations in each layer were calculated from the particle size fractions' elemental concentrations and subsequently for the entire drill core. Using the weighted average elemental concentrations, and the total mass of tailings in each particle size fraction, elemental mass distributions were then also calculated. Except for drill core 1_1, which had a very small amount of material in <75 µm size fraction thus having a different particle size range starting from <149 µm for chemical analysis, all elements were highest in particle size fraction –600 to +297 µm followed by –297 to +149 µm. Therefore, for reprocessing these HT, additional steps for ensuring sufficient mineral liberation need to be considered for such coarse tailings particles.

Figure 19. Elemental concentrations (left), and mass distributions (right) in the different particle size fractions of drill core 1_1.
Elemental concentrations and mass distributions were also varying at different depths of the TSF (Figure 22 and Figure 23). Sulphur depletion because of oxidation was expected in this TSF, with the depletion decreasing from top to bottom, due to the long storage period. Observing the S depletion trend for drill core 1_2, there would be three possible main deposition and oxidation periods where S is seen to have a significant stepwise increase in depth; the first being for the depth 296–483 cm, second 145–295 cm, and third 0–144 cm. Based on the alteration index of minerals and pH/EC in the tailings, the upper section—oxidized acidic zone (pH < 5.5)—showed that pyrrhotite was completely replaced by hydrous ferric oxides (HFOs), calcite depleted, and occasional yellow rims around scheelite grains [45]. These trends also show possible mineralogical variations with regard to sulphur content over the production period of 1936 to 1963. The chemical analysis also confirmed that the material in the bottom layer of drill core 6 was not typical of the tailings as the concentrations and distributions of all the main elements were extremely low.
Figure 22. WO$_3$ concentration (left) and mass distributions (right) at different depths of locations 1_1, 1_2 and 6.

Figure 23. Sulphur concentration (left) and mass distributions (right) at different depths of locations 1_1, 1_2 and 6.

These variations in chemical composition would have an effect on the grades and recoveries of the concentrates that may be produced from the reprocessing of these HT. For process and product optimization, varying process parameters and blending of tailings may be necessary. Therefore, based on the physical and chemical characterization of the Smaltjärnen TSF, the variations occurring in the different layers of the drill cores revealed the variability at different depths and locations of the TSF.

Figure 24 summarizes the weighted average elemental concentrations and D$_{80}$ values in the three locations. Location 1_1 has higher concentrations of WO$_3$, Cu, Sn, Zn, Be and Bi than locations 1_2 and 6, and location 6 has the highest S concentration. Taking the average WO$_3$ and Cu concentration in these three tailings locations to be 0.15 % and 0.11 %, respectively, and applying them to the estimated 2.2 million tons of tailings in this repository gives approximately 3300 tons of WO$_3$ and 2512 tons of Cu.
Conclusions:

- The coarser particle size fractions (−600 to +149 μm) have the highest amount of elements of high concentration which are W, Cu, S, Sn, Zn, Be, and Bi.
- Approximately 3300 tons of WO$_3$ is contained in the estimated 2.2 million tons of tailings in Smaltjärnen TSF, at an average WO$_3$ concentration 0.15 %.
- Physical and chemical variations occur at different depths and locations of the Smaltjärnen TSF, hence for process and product optimization, varying process parameters and blending of tailings from the different locations may be necessary.

5.2.2 Mineralogical characterization

Effective separation of valuable minerals and safe disposal of the remaining residue requires a detailed understanding of the mineralogical, geochemical and bulk physical properties of the tailings [4,46]. Therefore, bulk mineralogical characterization of the tailings was conducted using XRD to identify mineral phases in particle size fractions −1190 to +600 μm, −600 to +300 μm, −300 to +149 μm, −149 to +75 μm and <75 μm of drill core 6. The analysis was also used to assess variations in mineralogical composition in the different locations of the repository by comparing location 6 to location 1_2 where studies were done earlier [11,47]. The dominating silicate minerals diopside, hedenbergite, albite, ferro-actinolite, oligoclase and quartz were present in all particle size fractions, and repository locations. Minerals of economic interest fluorite, scheelite, wolframite and chalcopyrite were also identified (Figure 25) in all particle size fractions but it was noted that except for fluorite the other three minerals could only be found in the candidate list by using restrictions when executing the
‘search & match’ function in HighScore Plus software. Therefore, prior knowledge of the mineral composition of the primary ore [32,33,48] from which these tailings were generated was essential in identifying such mineral phases.

Figure 25. XRD pattern view of selected mineral phase patterns that matched the peak list and were accepted in particle size fraction –600 to +300 µm of layer 6-1 in drill core 6.

The tailings particles were initially analyzed using optical microscopy, and the fluorescence property of scheelite was used to identify the scheelite grains. The blue filter was found to be effective for distinguishing scheelite from other minerals of similar luminance and brightness, such as bismuthinite (Figure 26). The distinction between scheelite and bismuthinite particles was verified using SEM-EDS chemical composition. It was observed that scheelite occurs as both fine and coarse mineral grains. Its grains in the tailings fine fraction (<75 um) are liberated, whereas those in the coarse fraction are not.
Figure 26. Micrographs with a blue filter showing scheelite particles texture and liberation in various particle size fractions.

More mineralogical studies were conducted using SEM-EDS on different drill core layers, and BSE images of samples showing mineral phases and analytical spots (spectra) were obtained (Figure 27). Using element-to-mineral conversion (EMC) in HSC chemistry software and knowledge of minerals known to be present in the tailings, the minerals were identified based on each spectrum's chemical composition. Other minerals identified include hedenbergite, albite, actinolite, andradite, quartz, bismuthinite, chalcopyrite, magnetite, pyrite, pyrrhotite and sphalerite.
Since in the physical and chemical characterization, it was observed that to reprocess these HT, sufficient mineral liberation needed to be considered for such coarse tailings particles, MLA was thus conducted on five particle size fractions of drill cores 6 and 6F. Location 6 was picked for this analysis because of its higher sulphur concentration compared to the other locations 1_1 and 1_2. Based on the XRD analysis findings, mineral phases to be targeted in MLA were specified, and MLA was used to assess the host minerals for the elements of high concentration and economic interest, as given in Table 7, together with their average modal mineralogy and densities [49]. Fluorine (F), a hazardous element, was not included in the ICP–SFMS chemical analysis protocol, but with MLA, it was mostly (99.67%) contained in the critical mineral fluorite.

### Table 7. Summary of the main minerals of economic interest in the tailings with their densities.

<table>
<thead>
<tr>
<th>Element of high concentration</th>
<th>Main Mineral</th>
<th>Average Modal Mineralogy (Wt.%)</th>
<th>Mineral Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Scheelite</td>
<td>0.092</td>
<td>5.9 - 6.12</td>
</tr>
<tr>
<td>Cu</td>
<td>Chalcopyrite</td>
<td>0.310</td>
<td>4.1 - 4.3</td>
</tr>
<tr>
<td>Sn</td>
<td>Cassiterite</td>
<td>0.002</td>
<td>6.8 - 7</td>
</tr>
<tr>
<td>Zn</td>
<td>Sphalerite</td>
<td>0.000</td>
<td>3.9 - 4.2</td>
</tr>
<tr>
<td>Be</td>
<td>Danalite</td>
<td>0.460</td>
<td>3.43</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuthinite</td>
<td>0.018</td>
<td>6.8 - 7.2</td>
</tr>
<tr>
<td>F</td>
<td>Fluorite</td>
<td>3.930</td>
<td>3.01 - 3.25</td>
</tr>
</tbody>
</table>

Minerals distribution in the different particle size fractions was assessed in terms W, S and Ca-bearing minerals as these were considered critical in the selection of reprocessing methods. The two layers (6-1 and 6-2) of drill core 6 were analyzed to investigate and compare the mineral occurrences in the samples with slightly different chemical compositions and weathering state. It was observed
that other than scheelite, a substantial amount of W (≈30 wt.%) was related to wolframite in particle size fraction –300 to +149 μm (Figure 28 (left)). Unlike scheelite, wolframite is a dense and paramagnetic mineral; hence its beneficiation techniques include gravity and/or magnetic separation meaning if magnetic separation is employed before gravity separation, W from wolframite in this sample would be lost to the paramagnetic fraction [50]. Therefore, to recover this W from the paramagnetic fraction, gravity separation may be required as a subsequent step to process this fraction.

With regard to AMD, pyrite and pyrrhotite were notably the acid-generating sulphide minerals, with pyrrhotite reacting much faster than pyrite [51,52] hence the much lower S distribution observed in pyrrhotite. It was observed that the upper layer (6-1) has a higher S distribution in pyrite and pyrrhotite than layer 6-2, meaning less oxidation has occurred in the upper layer compared to the layer underneath, which also shows a higher S distribution in the secondary minerals gypsum and Fe sulphate (Figure 28 (right)). Gypsum is mostly in size fractions –600 to +300 μm (≈1.2 wt.%) and –1190 to +600 μm (≈3.6 wt.%) while Fe sulphate is mostly in size fractions –300 to +149 μm (≈4.7 wt.%) and –149 to –75 μm (≈8.0 wt.%) (Figure 29). This means that layer 6-2 was exposed to weathering before layer 6-1 was deposited, and the liberated smaller particles have been more susceptible to weathering due to the larger surface area. The acid produced by the oxidation of pyrrhotite was neutralized by calcite and hence the depletion of the two minerals in layer 6-2 (Figure 28 (right) and Figure 30) [11]. Another critical aspect of AMD with these historical tailings is the enhanced mobility of toxic elements like Be to ground and surface water, which even though it is not environmentally regulated in Sweden, has a very high concentration compared to the American recommended standard for groundwater [53]. Beryllium was observed to be only contained in the unusual mineral danalite, which is also one of the main sulphur-bearing minerals in these tailings (Figure 28 (right)).

![Figure 28. Tungsten-bearing minerals with W distribution (left), and S-bearing minerals with S distribution (right) in different particle size fractions of layers 6-1 and 6-2 in drill core 6.](image)
Figure 29. Tailing particles containing pyrrhotite sorted by total mineral area.
Figure 30. Calcium-bearing minerals with Ca distribution in particle size fraction –600 to +300 µm of layers 6-1 and 6-2 in drill core 6.

In the fine size fraction (<75 µm), minerals with elements of high concentration were analyzed, and scheelite was found to be the main W-bearing mineral. Main Ca-bearing minerals included fluorite, garnet-andradite, the most abundant mineral (28.25 wt.%), and ilvaite (Figure 31).

Figure 31. Modal mineralogy for minerals with elements of high concentration in particle size fraction <75 µm of layer 6F-1 in drill core 6F.
Figure 32. Tailings particles in <75 μm size fraction, containing scheelite, wolframite, fluorite and chalcopyrite, sorted by total mineral area.
The most abundant S-bearing mineral was Fe sulphate (8.50 wt.%), which is a secondary mineral resulting from the weathering of sulphide minerals like pyrrhotite (3.40 wt.%) and chalcopyrite (0.22 wt.%). This shows that tailings particles in the <75 µm size fraction were susceptible to weathering, and with Fe sulphate forming on the mineral surfaces of chalcopyrite (Figure 32), it would have an adverse effect on the froth flotation for this sulphide mineral if it was the target mineral.

As was observed in optical microscopy, MLA particle images also showed that scheelite occurs as both fine and coarse mineral grains. The grains in the tailings fine fraction (<75 µm) are liberated (Figure 32), whereas those in coarser fractions (>75 um) are mostly non-liberated, with a few liberated (Figure 34). Therefore, since there is a higher distribution of W in size fractions >149 um, the liberation of scheelite and wolframite in coarser fractions will be necessary for better recovery of W. In the primary skarn ore, the fairly coarse-grained scheelite was associated with the pyroxene skarn characterized by xenomorphic hedenbergite (normally >200 µm) while the fine-grained scheelite was associated with the amphibole skarn mainly consisting of hornblende [48]. Concerning Figure 34, hedenbergite is associated with ilvaite, garnet-andradite, and fluorite, while hornblende is associated with quartz and calcite [54].

Agglomerated tailings particles were observed in the coarsest fraction –1190 to +600 µm, with gypsum as the binder (Figure 29 and Figure 34). The modal mineralogy showed that both critical minerals (scheelite and fluorite) and minerals of environmental concern (pyrite and pyrrhotite) are present in these agglomerated tailings particles but in very low quantities (<1 wt.%) except for fluorite and pyrite (=2 wt.%). This means that in order to recover and/or separate the critical minerals from the minerals of environmental concern, regrinding for increasing liberation will be required.

Mineral locking for scheelite was assessed in both layers, and particle size fractions. In both layers, scheelite was more liberated in size fraction <149 µm, but since most of the tailings particles were in size range –600 to +149 µm, it was important to assess the locking of scheelite in this particle size range (Figure 33). Therefore, for reprocessing, scheelite needs to be liberated from the binary and ternary or greater particles in order to enhance its recovery.

![Figure 33. Mineral locking for scheelite in different particle size fractions of layers 6-1 and 6-2 in drill core 6.](image)
Figure 34. Tailing particles containing scheelite sorted by total mineral area.
Further assessment of the minerals locked with scheelite revealed that scheelite locking is mostly with the Ca-bearing minerals ilvaite, fluorite and garnet-gross-andradite meaning if froth flotation is considered as a reprocessing method option, the challenge of selective flotation of scheelite from the Ca-bearing minerals needs to be taken into consideration [37,55,56]. Other minerals of interest concerning magnetic separation locked with scheelite included wolframite and Fe-oxide (may be magnetite and/or hematite but not distinguishable in MLA) as they would contribute to scheelite losses to the magnetic fractions. Chalcopyrite is also observed to be locked with scheelite; hence if not liberated, it may be lost with scheelite in the magnetic fraction of magnetic separation or lost to the scheelite concentrate in gravity separation. This analysis with a processing perspective in the tailings characterization step is essential for subsequent conceptual framework steps for reprocessing historical tailings.

The degree of scheelite locking with other minerals was further assessed by looking at its liberation in terms of the free surface of the particle (Table 8) thus enhancing the understanding of how much of the scheelite grain surfaces in the tailings particles are liberated, and the mineral distribution in each class. Comparing the two size fractions, it was observed that in the coarse fraction, only 9.8% of scheelite grains were totally liberated in the tailings particles, while in the fine fraction 70.7%. Therefore, the coarse tailings particles would require fine grinding to liberate the >80% scheelite surfaces, especially that the tailings particles are complex with scheelite locked with several other minerals.

Table 8. Scheelite degree of liberation by free surface in particle size fraction <75 μm of layer 6F-1 of drill core 6F, and –600+300 μm of layer 6-2 in drill core 6.

<table>
<thead>
<tr>
<th>20% Liberation classes</th>
<th>Distribution of scheelite (%) in particle size fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;75 μm</td>
</tr>
<tr>
<td>0% (not exposed)</td>
<td>0.0</td>
</tr>
<tr>
<td>0% &lt; x ≤ 20%</td>
<td>1.1</td>
</tr>
<tr>
<td>20% &lt; x ≤ 40%</td>
<td>5.0</td>
</tr>
<tr>
<td>40% &lt; x ≤ 60%</td>
<td>10.6</td>
</tr>
<tr>
<td>60% &lt; x ≤ 80%</td>
<td>7.5</td>
</tr>
<tr>
<td>80% &lt; x &lt; 100%</td>
<td>5.1</td>
</tr>
<tr>
<td>100%</td>
<td>70.7</td>
</tr>
</tbody>
</table>

Conclusions:

- The coarser particle size fractions (–600 to +149 μm) have the highest volume of critical minerals (scheelite and fluorite) and minerals of environmental concern (pyrite and pyrrhotite).
- W, Cu, S, Sn, Zn, Be, Bi, and F are hosted mainly in scheelite, chalcopyrite, pyrrhotite, cassiterite, sphalerite, danalite, bismuthinite, and fluorspar, respectively.
Pyrite and pyrrhotite are the main acid-generating sulphide minerals, with pyrrhotite reacting much faster than pyrite, and the liberated smaller particles have been more susceptible to weathering due to the larger surface area.

Scheelite occurs as both fine and coarse mineral grains in the tailings; fine fraction (<75 um) are liberated while those in coarser fractions (>75 um) are mostly non-liberated, with a few liberated.

5.3 Physical separation

Tailings characterization was essential in the pre-selection of possible reprocessing methods. With remediation and recovery being the focus of the HT reprocessing, minerals of economic interest, and minerals of environmental concern were both considered in the metallurgical test work. Scheelite was the main mineral of economic interest for W; hence its separation from these HT was the initial consideration in the reprocessing. Since scheelite is a dense mineral, the densities of other minerals present in the tailings were also considered, as given earlier in Table 7, especially that gravity separation was a possible separation method [35]. On average, the tailings particle density was approximately 3.2 g/cm³. For remediation, the separation of pyrrhotite, which is a weakly-to-strongly magnetic main Fe–sulphide mineral responsible for AMD, was desired; thus, magnetic separation was also considered.

5.3.1 Magnetic separation

The two layers (1_2-4 and 1_2-8) of drill core 1_2 were individually used for magnetic separation. The three products from the magnetic separation using LIMS and HIMS, namely ferromagnetic, paramagnetic and non-magnetic fractions, had significant visual (color) differences, with the non-magnetic fraction dominated by the orange, brown and white colored minerals (Figure 35). Based on the knowledge of minerals known to be present in these HT and using EMC, the light-colored minerals in the non-magnetic fraction were identified to be mainly albite, fluorite, calcite, scheelite and biotite.

As desired, pyrrhotite, the main Fe-sulphide mineral in the tailings and responsible for AMD, was mainly in the ferromagnetic and paramagnetic fractions, with a minimum of 1.0 wt.% S in the non-magnetic fraction (Table 9). However, the desired separation of scheelite, fluorite, and chalcopyrite...
from the paramagnetic fraction was not achieved due to the insufficient liberation from pyrrhotite and/or to liberated small particles being entrapped and entrained. Tungsten could have also ended up in the paramagnetic fraction as wolframite [50].

Table 9. Products balance for magnetic separation.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight (g)</th>
<th>Grade (%)</th>
<th>Contents (g)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gram</td>
<td>%</td>
<td>W</td>
<td>S</td>
</tr>
<tr>
<td>1_2-4 Ferromagnetic</td>
<td>8.19</td>
<td>4.21</td>
<td>0.09</td>
<td>14.40</td>
</tr>
<tr>
<td>1_2-4 Paramagnetic</td>
<td>169.66</td>
<td>87.30</td>
<td>0.08</td>
<td>0.59</td>
</tr>
<tr>
<td>1_2-4 Non-Magnetic</td>
<td>16.50</td>
<td>8.49</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>1_2-4_Calculated Feed (&gt;75 μm)</td>
<td>194.35</td>
<td>100.00</td>
<td>0.09</td>
<td>1.14</td>
</tr>
<tr>
<td>1_2-8 Ferromagnetic</td>
<td>8.64</td>
<td>4.98</td>
<td>0.07</td>
<td>22.20</td>
</tr>
<tr>
<td>1_2-8 Paramagnetic</td>
<td>148.97</td>
<td>85.82</td>
<td>0.07</td>
<td>0.72</td>
</tr>
<tr>
<td>1_2-8 Non-Magnetic</td>
<td>15.98</td>
<td>9.21</td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
<td>1_2-8_Calculated Feed (&gt;75 μm)</td>
<td>173.59</td>
<td>100.00</td>
<td>0.07</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Assessing the particle sizes in the products in relation to what was in the feed, it was observed that 97 wt.% of the −600 to +297 μm particles, being the most abundant in these HT, were distributed to the paramagnetic fraction. This confirms that the minerals of interest, like scheelite, need to be further liberated from this particle size fraction in order to improve mineral separation by magnetic separation.

Conclusions:

- Sulphur is mostly recovered in the ferromagnetic and paramagnetic fractions, with only 1.0 wt.% in the non-magnetic fraction, meaning pyrrhotite, the main Fe–sulphide mineral in the HT responsible for AMD, separated to the desired magnetic fractions of the LIMS and HIMS.
- Due to insufficient liberation from pyrrhotite and/or to liberated small particles being entrapped and entrained, the desired separation of scheelite, fluorite, and chalcopyrite from the paramagnetic fraction could not achieved.

5.3.2 Gravity separation

The two layers (1_2-1 and 1_2-8) of drill core 1_2 were individually used for gravity separation tests with the Knelson concentrator, with two separation cycles for each sample. For comparison in metallurgical performance, these samples were quite similar in terms of mass distribution in the core, but slightly different in chemical composition, grain size, and exposure to weathering. The recovery of scheelite in each cycle product was assessed by the amount of W. It was observed that recovery of W in the concentrates was decreasing with an increasing number of separation cycles, with the highest recovery being 60.6 wt.% (76.4 wt. % WO$_3$) in concentrate 1 of layer 1_2-1 (Table 10). The decrease in W recovery with the increasing number of separation cycles was due to the decreasing amount of dense and coarse particles that contain W. In this regard, the comparison between the two layers
showed a higher W recovery in concentrate 1 for layer 1_2-1, which was coarser with higher W content than layer 1_2-8.

### Table 10. Products mass balance for gravity concentration products using Knelson concentrator.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight</th>
<th>Grade (%)</th>
<th>Contents (g)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_2-1 Concentrate 1</td>
<td>88.88</td>
<td>17.05</td>
<td>0.42</td>
<td>0.37</td>
</tr>
<tr>
<td>1_2-1 Concentrate 2</td>
<td>87.71</td>
<td>16.82</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>1_2-1 Tailings</td>
<td>344.83</td>
<td>66.13</td>
<td>0.04</td>
<td>0.15</td>
</tr>
<tr>
<td>1_2-1_Actual Feed (&lt;600 µm)</td>
<td>521.42</td>
<td>100.00</td>
<td>0.12</td>
<td>0.61</td>
</tr>
<tr>
<td>1_2-8 Concentrate 1</td>
<td>92.56</td>
<td>18.53</td>
<td>0.20</td>
<td>0.18</td>
</tr>
<tr>
<td>1_2-8 Concentrate 2</td>
<td>95.61</td>
<td>19.14</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>1_2-8 Tailings</td>
<td>311.47</td>
<td>62.34</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td>1_2-8_Actual Feed (&lt;600 µm)</td>
<td>499.64</td>
<td>100.00</td>
<td>0.08</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Even though the recovery of scheelite was favorable with this enhanced gravity separation, its separation from the other minerals would still be required as at least 30 wt.% of each main element was also recovered to the concentrate fraction. This means that minerals with lower densities than scheelite such as quartz, fluorite, calcite, chalcopyrite, pyrrhotite, and danalite were not fully separated from scheelite. Considering the coarseness of the particles in these samples, the insufficient mineral separation would be attributed to the insufficient liberation of the mineral particles.

Using products distribution in various particle sizes to further assess the concentration process, it was confirmed that the dense coarser (−600 to +297 µm) particles were distributed more to concentrate 1 than 2, while the dense finer (<75 µm) particles were higher in concentrate 2 than 1. Therefore, in order to minimize W losses in the fines to the tailing fraction, the particle size range of the feed material to the Knelson concentrator must be narrow; otherwise, many concentration cycles would be needed to optimize the recovery. In this initial metallurgical test work, the feed particle size range was −600 to +38 µm; however, for subsequent tests, division of this size range into narrower ones such as −600 to +297 µm, −297 to +149 µm, −149 to +75 µm, and −75 to +38 µm should be considered in order to improve the recovery and separation efficiency [35].

**Conclusions:**

- The recovery of scheelite was significantly favorable with enhanced gravity separation using the Knelson concentrator, with a maximum recovery of 76.4 wt.% WO₃ in the first rougher concentrate.
- To improve the recovery and separation efficiency, narrower size range such as −600 to +297 µm, −297 to +149 µm, −149 to +75 µm, and −75 to +38 µm should be considered.

### 5.4 Flotation

With a substantial amount of scheelite in the fine (<75 µm) fraction of HT, froth flotation was also selected as a possible reprocessing method [55]. Flotation tests to assess the possibility of recovering scheelite from Yxsjöberg HT showed that with SS (300 mg/L) as the depressant, the widely used fatty anionic acid collector NaOl at 3 x 10⁻⁴ mol/L concentration was not ideal for this material as both WO₃
grade and recovery was very low (Figure 36). On the contrary, collectors Berol 8313 and Atrac 2600 gave promising results, with Atrac 2600 at 400 g/t dosage giving the highest rougher concentrate WO₃ grade (1.13%) with 3.9 enrichment ratio (Table 11), WO₃ recovery (57.4%), and a higher scheelite selectivity against other Ca-bearing minerals.

![Figure 36. Concentrate WO₃ grade (left), mass and elemental recoveries (right) from HT flotation using different collectors and dosages.](image)

<table>
<thead>
<tr>
<th>Collector</th>
<th>NaOl 3×10⁻⁴ mol/L</th>
<th>Berol 8313 400 g/t</th>
<th>Berol 8313 100 g/t</th>
<th>Atrac 2600 400 g/t</th>
<th>Atrac 2600 100 g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed WO₃ grade (%)</td>
<td>0.28</td>
<td>0.32</td>
<td>0.29</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>Enrichment ratio</td>
<td>0.1</td>
<td>2.5</td>
<td>0.4</td>
<td>3.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

There are minimal differences in the concentrate WO₃ grades, and enrichment ratios for Atrac 2600 at dosages 400 g/t and 100 g/t shows. Therefore, a more technical evaluation was considered, and the Separation Efficiency (Es) for each of the Atrac 2600 dosages was calculated using the following formula given that recoveries, assays, and enrichment ratios were available [57]:

\[
E_s = R \left( \frac{C_m}{C_m - f} \right) \left( \frac{E_r - 1}{E_r} \right); E_r = \frac{C}{f}
\]

(1)

where \( R \) is % recovery of valuable constituent (WO₃) in concentrate, \( C_m \) is % assayed element (WO₃) in mineral (scheelite) being concentrated, \( f \) is % assayed element (WO₃) in feed, \( E_r \) is enrichment ratio, and \( C \) is % assayed element (WO₃) in the concentrate. Thus, \( E_s \) for scheelite concentration was determined using WO₃ as the valuable constituent. Based on the \( E_s \) values, Atrac 2600 at dosage 400 g/t had a better separation efficiency (42.8%) for scheelite flotation than its 100 g/t (15.6%).

Other elemental recoveries were also considered to assess W’s separation, with the desired outcome being as low recovery as possible. Cu and S, both of which are elements of economic importance but non-critical raw materials [5], were less recovered for Atrac 2600 meaning better separation from W than for Berol 8313 (Figure 36). The low S recovery also means that the main S-bearing minerals responsible for AMD, like pyrrhotite, would be separated to the tailings fraction as desired. Based on the MLA tailings characterization, the Fe sulfate observed on the mineral surfaces
of chalcopyrite (Figure 32) and pyrrhotite, and their low degree of liberation by free surface, would hinder flotation of such particles even in sulfide flotation. Therefore, these mineral particles would be depressed to the tailings fraction; thus, the need to further characterize the residue from the reprocessing of such historical tailings and assess the recycling potential such as being used as cement additives [58,59].

Therefore, Atrac 2600 at 400 g/t dosage was selected as the preferred collector to be used for further scheelite flotation tests to evaluate the metallurgical performance of different core tailings samples (6-1, 6A-1, 6A-2, 6B, 6C, 6D-1 and 6E-1). There was no significant difference in the mass recovery in five (6A-2, 6B, 6C, 6D-1 and 6E-1) out of the seven samples (Figure 37). Samples 6-1 and 6A-1 concentrate WO₃ grades and recoveries were significantly higher, and the selectivity of WO₃ against CaO was more evident than for the other five samples.

The concentrations of elements (Cu, Bi, Fe, and S) that were contained in the main sulfide minerals (chalcopyrite, bismuthinite, and pyrrhotite) were higher in samples 6A-2, 6B, 6C, 6D-1, and 6E-1 (Table 12), meaning the sulfide minerals were preferentially concentrated than scheelite, which was undesirable. To reduce the preferential concentration of sulfide minerals, and increase the collector’s efficiency for the scheelite flotation, sulfide flotation should precede scheelite flotation, especially that chalcopyrite also shows good selectivity from scheelite and pyrrhotite in all the samples [36,39,48]. Additionally, the concentrate WO₃ grade and recovery in scheelite flotation of the historical tailings under study may be enhanced by having rougher, scavenger, and cleaner flotation stages as was done in the Yxsjöberg scheelite flotation process [36,48].

Table 12. Concentrate assays for elements contained in the main sulfide minerals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (ppm)</th>
<th>Bi (ppm)</th>
<th>Fe₂O₃ (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-1</td>
<td>1460</td>
<td>1300</td>
<td>21.00</td>
<td>1.89</td>
</tr>
<tr>
<td>6A-1</td>
<td>1794</td>
<td>1450</td>
<td>17.00</td>
<td>2.38</td>
</tr>
<tr>
<td>6A-2</td>
<td>2593</td>
<td>2534</td>
<td>27.77</td>
<td>7.47</td>
</tr>
<tr>
<td>6B</td>
<td>2622</td>
<td>2084</td>
<td>23.70</td>
<td>4.63</td>
</tr>
</tbody>
</table>
The difference in metallurgical performance was not only for samples from different drill holes but also from the same drill hole with varying layers like samples 6A-1 (upper layer) and 6A-2 (bottom layer). For samples with less favorable responses, this difference could be attributed to low scheelite liberation by free surface and/or having wolframite, which cannot be recovered by flotation [36,50].

Conclusions:

- The new collectors Berol 8313 and Atrac 2600 performed better than the commonly used NaOl in mass recovery, WO$_3$ grade and recovery, and scheelite selectivity.
- Atrac 2600 at 400 g/t dosage had the highest rougher concentrate WO$_3$ grade (1.13%) with 3.9 enrichment ratio, WO$_3$ recovery (57.4%), and a better scheelite selectivity against other Ca-bearing minerals.
- At least two geometallurgical areas were observed in the Smaltjärnen repository location where samples for flotation were obtained; with Atrac 2600 at 400 g/t dosage, one area had a better metallurgical performance (rougher concentrate WO$_3$ grade of 1.15% at 48.2% WO$_3$ recovery) than the other (rougher concentrate WO$_3$ grade of 0.37% at 8.1% WO$_3$ recovery).
- Sulfide flotation should precede scheelite flotation in order to reduce the preferential concentration of sulfide minerals and increase the efficiency of Atrac 2600 collector for scheelite flotation.

5.5 Hydrometallurgical tests

5.5.1 Conventional leaching

The recovery of W from Yxsjöberg scheelite concentrate using concentrated NaOH (equation (2)) was assessed at different temperatures, and leaching time to get indications of its dependence on these two factors and how it varies with time.

$$\text{CaWO}_4(s) + 2\text{NaOH}(aq) \leftrightarrow \text{Na}_2\text{WO}_4(aq) + \text{Ca(OH)}_2(s)$$  \hspace{1cm} (2)

It was observed that W recovery was increasing with increasing temperature and leaching time (Figure 38), but at lower temperatures (38°C and 60°C) the change in W recovery over the 1-hour time intervals was minimal due to the low rate of reaction [60,61]. Leaching scheelite concentrate in concentrated NaOH solution could not give W recovery higher than 70% even after six hours of leaching at 100°C because the produced sodium tungstate (Na$_2$WO$_4$) crystallizes due to its low solubility in concentrated NaOH solution [62]. This meant that even with the excess NaOH due to the leaching process operating at a high NaOH/WO$_3$ ratio, and liquid/solid ratio, which promote the reaction (equation (2)) to proceed toward the right direction, W recovery to the leachate would still be low [61,62]. Therefore, this process was not economically and environmentally sustainable hence process improvement was essential.
Figure 38. Recovery of W from scheelite concentrate at different temperatures and leaching time in conventional leaching.

5.5.2 Leaching while grinding

As an improvement to the conventional leaching, grinding was introduced to deal with surface layers on scheelite particles, and increase the leaching efficiency. The mechanical activation of scheelite improves the leaching kinetics as its decomposition temperature is reduced, and surface area is increased with reducing particle size resulting from grinding [42,43]. The initial LWG tests with scheelite concentrate showed an increase in W recovery and a higher reaction rate of reaction at 38°C and 60°C but reduced W recovery at 80°C (Figure 39).

Figure 39. Recovery of W from scheelite concentrate at different temperatures and leaching time in LWG.
Compared to conventional leaching, W recovery was 4.8 times higher at 38°C, 1.8 times higher at 60°C, and 0.5 times lower at 80°C after six hours of leaching meaning the grinding improved the leaching kinetics for the lower temperatures, but it had an adverse effect at a higher leaching temperature. This means that grinding had a higher influence on scheelite leaching than temperature. When scheelite is mechanically activated by grinding, its reactivity increases, causing it to be leached faster, thus forming soluble Na₂WO₄ rapidly, and in a short time, the solution becomes saturated, leading to the precipitation of Na₂WO₄ until all the scheelite has reacted [63]. Therefore, at 80°C, the precipitation of Na₂WO₄ seems to occur just after an hour of leaching hence the lower W recovery than at the lower leaching temperatures (Figure 39).

Despite having improved leaching kinetics at lower leaching temperatures, W’s recovery after six hours of leaching was too low (36% at 60°C); hence, LWG process needed further improvement to make it more sustainable. Therefore, for HT leaching as an alternative reprocessing method to the earlier proposed physical separation and flotation, the LWG experiments were designed to assess the effect of liquid/solid ratio, temperature, digestion time, and stirrer speed on the W recovery from historical tailings. The notable difference from the earlier leaching experiments was in the amount of concentrated NaOH solution used that was determined by the selected liquid/solid ratio, and the two leaching stages; digestion with concentrated (10 M) NaOH solution, washing with diluted (1 M) NaOH solution, and sampling of the leachate could not be done during the leaching process [64]. Optimal conditions were then determined and applied to both HT, and scheelite concentrate as a high-grade material. Details of the experiment design are given in the appended paper IV.

The concentration of W in the leachate was used to calculate the W recovery (main design response) from the historical tungsten tailings (Figure 40).

![Figure 40. Design responses from the 16 different experimental runs: Concentration of W in leachate (left), and W recovery (right) from historical tungsten tailings.](image)

It was observed that the stirrer speed (D), temperature (A) and digestion time (B) had a positive effect meaning an increase in these main factor effects would increase the W recovery (Figure 41). The stirrer speed had the largest contribution of 58.5% because it reduces particle size thus increasing the surface area for increased reactivity of scheelite [60,65]. It also enhances mass transfer in the highly viscous NaOH digestion solution, and continuously removes the Ca(OH)₂ solid product layers that form on scheelite mineral particles as the accelerated rate-determining chemical reaction (equation (2) proceeds [61,62,66,67].
Despite temperature and digestion time also having a positive effect on W recovery, their interaction AB negative effect and contribution was larger than that of the individual factors. Similarly, the AD factor interaction had a negative effect with an even larger contribution (13.1%) than the AB factor interaction. With the mechanical activation of scheelite brought about by the grinding occurring simultaneously with the leaching in the LWG process in this study, one expected and desired advantage was reduced leaching temperature, which would then make the factor interactions AB and AD to have a positive effect on W recovery. Another advantage of the mechanical activation of scheelite is the shorter reaction time due to the increased rate of the forward reaction but if the digestion time goes beyond this reaction time, Na$_2$WO$_4$ saturation may occur and since its solubility is low in the 10 M NaOH digestion solution, crystallization would occur [42,61,62].

Therefore, having high temperature, which also increases the leaching rate, and high digestion time results in the negative effect of the AB factor interaction on W recovery to the leachate as it would remain in the solute as solid Na$_2$WO$_4$ especially if the NaOH dilution in the subsequent washing stage is insufficient for complete dissolution [18,64]. The digestion time encompassed time for both grinding the tailings particles, and NaOH digestion of scheelite hence a key factor in the mechanical activation of scheelite mineral grains, as is the stirrer speed but with a very small effect and contribution to W recovery. Since the feed material used in this study was coarse with a very low W grade, the grinding also enhanced the liberation of scheelite mineral grains in the tailings particles.

The liquid/solid ratio (C) factor had the second-highest effect and contribution to the W recovery but unlike the other three main factors, this factor had a negative effect on W recovery. This factor is especially critical for leaching scheelite from very low-grade material such as tailings because sufficient
fluidity of the digestion mixture should be attained such that even after digesting for a while at a given temperature, the mixture does not solidify. For such low W grade material, sufficient fluidity is not attainable using the NaOH stoichiometric ratio hence the NaOH is in excess, and the Na$_2$WO$_4$ crystallizes due to its limited solubility in such highly concentrated NaOH solution [61]. Therefore, the CD factor interaction equally has a negative effect unless an optimal liquid/solid ratio is employed.

An optimization criterion was determined for each factor and response (details in appended paper IV), with the most important goal being that of the response W recovery to be maximized. The best-suggested software solution was considered by assessing the 3D response surface (Figure 42).

![Figure 42. The 3D response surfaces for the best optimization solution to maximize W recovery from historical tungsten tailings using the LWG process: C = -1, D = 410 rpm.](image)

It was observed that maximum W recovery at 91.2% was best achieved at the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature at 60°C (Figure 42). This desired outcome confirmed the earlier analysis of the factors effect on W recovery that the mechanical activation of scheelite in the LWG process led to having a lower leaching temperature with the leaching process conducted in a simpler and less expensive reactor compared to using pressurized reactors such as autoclaves, and higher leaching temperatures above 100°C [42,60,62,64,66,68].

Compared to earlier leaching tests with scheelite concentrate, these LWG tests with HT proved to be more efficient and sustainable as much higher W recoveries were attainable even when compared to the physical separation and flotation methods. Verification tests were conducted based on the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature (60°C). The obtained mean W recovery for LWG using tailings was within the
model’s 95% prediction interval; hence, the model was confirmed (Figure 43). For LWG using the scheelite concentrate, the NaOH was not in excess as the 0.8 liquid/solid ratio was equivalent to the 1:2 CaWO₄/NaOH stoichiometric ratio hence the much lower W recovery. Therefore, for such high W grade material, optimizing the NaOH/WO₃ ratio would help improve W recovery [60–62,64,68]. The control experiment in which LWTG was employed proved that LWG was a better leaching process for the historical tungsten tailings under study as W recovery very low (5.5%).

![Bar chart showing mean verification results using factor settings of the best numerical optimization recommended solution.](image)

Figure 43. Mean verification results using factor settings of the best numerical optimization recommended solution.

The LWG process could be further improved by considering the energy conservation factor where other solutions on the 3D response surface (Figure 42) with digestion time less than 6 hours may be compared though the W recovery would be lower than 91.2%. Other factors that would also be considered for maximizing W recovery would be the dilution of NaOH solution in the washing stage as too much dilution favors the reverse reaction, and the duration of washing [64]. Therefore, characterization of the solute using XRD to determine in which phases the unleached W is found would be essential. If W is found in the Na₂WO₄ phase then the dissolution issue would have to be investigated. If W is found in the CaWO₄ phase then it would be either the scheelite digestion did not occur due to unliberated scheelite grains in the coarse tailings particles or the reverse reaction could have occurred during the washing stage due to over dilution of NaOH.

Based on the conducted LWG tests on the Yxsjöberg HT, a LWG process design for reprocessing historical tungsten tailings is proposed comprising the following steps (Figure 44):

i. Pre-mixing – historical tungsten tailings feed material is mixed with digestion concentrated NaOH solution.

ii. Digestion – pre-mixed feed added to heated attritor mill for digestion. Diluted NaOH solution is added after digestion has ended to wash out the digested slurry and grinding media.

iii. Leaching – diluted slurry is further washed with diluted NaOH solution so that the Na₂WO₄ is completely solubilized.
iv. Filtration – leachate goes for further processing to extract W and other elements. The residue is considered for recycling and/or disposal.

Figure 44. Proposed LWG process design for reprocessing historical tungsten tailings.

Conclusions:

- LWG was more efficient and more sustainable than conventional leaching, especially that the amount NaOH used was much lower, and W recovery was much higher at a lower leaching temperature.
- The most critical factors in the maximization of W recovery were the stirrer speed and the liquid/solid ratio, with an increase in the stirrer speed having a positive effect while the liquid/solid ratio had a negative effect.
- The maximum W recovery (91.2%) was attained at the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature (60°C).
- A low leaching temperature (60°C) was attainable due to the mechanical activation of scheelite resulting from the simultaneous grinding and leaching.
- Optimizing the liquid/solid ratio is critical for maintaining substantial fluidity in the digestion mixture for low W grade material such as the historical tailings used in this study.
- The dilution of NaOH solution in the washing stage, and the duration of washing would be other factors to optimize for subsequent optimization of W recovery.
- A slight reduction in the digestion time factor would optimize energy conservation factor.

5.6 Reprocessing options for the Yxsjöberg historical tungsten tailings

Based on the results of the tailings characterization, physical separation, flotation, and LWG tests, the reprocessing options for the Yxsjöberg HT are summarized (Figure 45). Since the tailings’
elemental and mass distribution was high in the coarser particle size fractions of ~600+149 μm, classification to separate the coarser tailings from the finer ones would be the first step. The first classification threshold is at <75 μm because from MLA, scheelite particles in this size fraction are mostly liberated. Also, during gravity separation, much of the <75 μm ended up in the tailings product; hence there is a need for prior separation. As earlier indicated, scheelite recovery from this particle size fraction would be best through froth flotation [55]. With the observed preferential concentration of sulfide minerals to scheelite in some HT samples, good chalcopyrite selectivity from scheelite and pyrrhotite in all HT samples, and the need to increase the efficiency of the collector for scheelite flotation, sulfide flotation should precede scheelite flotation; stepwise flotation will be essential [36,39,48]. For the tailings fraction >75 μm, the issue of mineral liberation is evident, hence regrinding will be required, but the generation of ultrafine particles should be minimized hence the liberation size for target minerals needs to be considered. With sufficient mineral liberation, having magnetic separation before gravity separation enhances the separation of magnetite (in addition to pyrrhotite) from scheelite; magnetite density (5.15 g/cm³) is close scheelite density (6.01 g/cm³) [49] hence their separation with gravity separation may not be efficient. Therefore, gravity separation would be applied to the non-magnetic product of magnetic separation. Leaching while grinding could be conducted without tailings classification and comminution, but it could also be done after physical separation processes, and/or flotation.

Figure 45. Reprocessing options for the Yxsjöberg historical tungsten tailings.
6 Conclusions

In this thesis, a conceptual framework was defined and employed to systematically generate relevant information and knowledge about the Smaltjärnen tailings repository of the Yxsjöberg historical tungsten mine in the Bergslagen district, Sweden. The conceptual framework aimed to develop effective and efficient methods to recover critical metals and minerals from historical tailing while leaving a stable and environmentally safe residue. It was defined and employed by addressing the formulated research questions, and the following were the findings and conclusions:

1) What are the major steps and tasks for reprocessing historical tailings?
   - Define a systematic approach that encompasses resource knowledge from the processing and environmental perspective. In this study, the defined conceptual framework was the approach.
   - Identify the relevant stakeholders that can provide a multidisciplinary input to the framework.
   - Determine site- and material-specific techniques for sampling, characterization, and reprocessing.

2) What effective and efficient reprocessing methods can be employed to remediate and recover critical metals and minerals from the Yxsjöberg historical tungsten tailings?
   a) What are the elements and minerals of economic interest, and environmental concern?
      - Identify relevant characterization methods, and define the sequence.
      - Verify that the tailings characterization information from previous related studies is consistent with that of samples in the current study as variations may occur from one repository location to another. In this study, the following was confirmed:
        - Elements and minerals of economic interest – W from scheelite, Cu from chalcopyrite, Sn from cassiterite, Zn from sphalerite, Be from danalite, Bi from bismuthinite, and Fluorite (CaF$_2$).
        - Elements and minerals of environmental concern – Be from danalite for toxicity to ground and surface water, and pyrrhotite and pyrite for AMD.
      - Based on the average WO$_3$ concentration of 0.15%, 3300 tons of WO$_3$ is contained in the estimated 2.2 million tons of tailings in Smaltjärnen TSF.
   b) What elemental recoveries are attainable with the reprocessing methods employed?
      - Select possible reprocessing methods based on the tailings characteristics.
- The dominating particle size fraction was ~600 to +149 μm, in which scheelite was mostly unliberated, but was mostly liberated in the fine (<75 μm) fraction.
- Pyrrhotite has weathered much faster than pyrite, with the liberated smaller (<149 μm) particles being more susceptible to weathering due to the larger surface area.
- Employed reprocessing methods, and attained elemental recoveries of interest were as follows:
  - Magnetic separation was aimed at having the lowest amount of S in the non-magnetic fraction to signify separation of Fe-sulphide minerals responsible for AMD from minerals like scheelite. A minimum of 1.0 wt.% S was recovered to the non-magnetic fraction.
  - Gravity separation was aimed at recovering scheelite, and maximum of 76.4 wt.% WO₃ was recovered in the first rougher concentrate, with the rest lost to the tailing fraction as fine scheelite.
  - Flotation was aimed at recovering fine (<75 μm) scheelite, and a maximum of 57.4 wt.% WO₃ was recovered in the rougher concentrate.
  - Leaching while grinding was an innovative method that has not been used before to recover W from the tailings in this study. With this method, physical separation and flotation of scheelite would not be required prior to W extraction, and the consumption of NaOH would be low compared to conventional leaching. A maximum of 91.2% W was recovered in the leachate, which would amount to approximately 2970 tons of WO₃ from the Smaltjärnen TSF.

c) Is tailings reprocessing a possible remediation option?
  - Yes but economic feasibility needs to be assessed.

The conceptual framework employed in this thesis would also be used to plan how mining waste should be deposited as a future secondary source of metals and minerals, and what information should be archived.
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PART II – PAPERS
Paper I
Systematic characterization of historical tailings for possible remediation and recovery of critical metals and minerals – The Yxsjöberg case

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Abstract: As the need to address environmental concerns in mining and the demand for critical metals and minerals increase, historical tailings are among the mining waste repositories being sought after. However, there is only limited information available about such repositories, and hence there is a need to fill these knowledge gaps. In this paper, a conceptual framework is proposed for how relevant information about historical tailings can be generated and structured in a systematic manner. The case of the closed Yxsjöberg mine in Sweden is used to demonstrate how this framework is being used. A site-specific sampling strategy and technique was identified, and based on the observed lithology, tailings particles were studied to understand their distribution across the repository. Using Mineral Liberation Analysis (MLA), the modal mineralogy, mineral associations, and mineral liberation by particle size of the tailings were determined. The Smaltjärnen tailings repository of Yxsjöberg has potential for critical metals and minerals, including tungsten (W) and fluorite (CaF₂) but also contains minerals of environmental concern as pyrrhotite and pyrite. It has on average 0.15 % WO₃ concentration in the sampled locations, indicating approximately 3300 tons of WO₃ in the repository. Scheelite mineral grains are mostly (>50 wt.%) locked in binary and ternary or even more complex tailings particles in the dominating particle size fraction –600 to +149 μm. Mineral locking is mostly with calcium-bearing minerals ilvaite, fluorite and garnet-gross-andradite. Pyrrhotite has been the most reactive acid-generating mineral, and hence is more depleted than pyrite in the weathered locations. The heterogeneity of tailings across the repository suggests a possible existence of geometallurgical domains that require further assessment to evaluate their metallurgical performance. The obtained information and knowledge about these tailings will hereinafter be used to develop sustainable processes for remediation and recovery of the critical metals and minerals.

Keywords: Yxsjöberg; Tungsten; Scheelite; Acid Mine Drainage; Characterization; Mineral Liberation Analysis
1. Introduction

Tailings are volumetrically one of the largest waste streams in the world covering a substantial amount of the earth’s surface in the form of piles, large surface impoundments (tailings dams) and other tailings storage facilities (TSF) (Hudson-Edwards et al., 2011; Lottermoser, 2011, 2010). They are generated by the mining industry where they are classified as processing wastes, with possible severe environmental impacts due to the high concentrations of elements (e.g. As, Be, Bi and W) and compounds (e.g. sulphur-containing minerals pyrrhotite and pyrite). For historical tailings, the severe environmental impact is likely because the less efficient extraction methods and/or relatively low metal prices at the time of active mining led to leaving relatively high minerals and metals in these mine wastes (Lottermoser, 2011). However, as primary ore resources are becoming depleted and lower in grade, historical tailings are increasingly considered potential secondary sources. Their potential as secondary sources is particularly interesting in the case of the critical metals and minerals currently in short supply in the European Union (EU) (Commission, 2017). Therefore, countries with active metal mining like Sweden are exploring mine wastes such as historical tailings not only for as a supply risk-reducing measure but also to identify and quantify harmful elements and minerals (Hallberg and Reginiussen, 2019; Sädbom and Bäckström, 2018). However, the challenge with exploring mine wastes such as historical tailings is the limited information and knowledge gaps about the material and the repositories thus requiring continued multidisciplinary research to understand and manage these wastes sustainably (Hallberg and Reginiussen, 2019; Hudson-Edwards et al., 2011; Sädbom and Bäckström, 2018).

The structure and characteristics of a tailings repository are determined by a number of factors including depositional environment, discharge (spigotting) point, the method of slurry entry into the impoundment, discharge rate, the density of the discharged slurry and mineralogical composition (Lottermoser, 2010). The visible effects of these factors are stratification, including graded and cross-bedding of the tailings. Coarser and heavier particles tend to settle near the discharge point while the finer and lighter particles settle further away. Therefore, if certain minerals occur in a particular particle size, they may segregate and accumulate in particular locations of the repository (Lottermoser, 2010). Based on the depositional environment, historical tailings repositories can be subdivided into different volumes with a similar set of textural and compositional properties and hence metallurgical performance, also referred to as geometallurgical units/domains (Lotter, 2011). Different geometallurgical and/or process mineralogical approaches have been used to reprocess tailings or process ores (Brough et al., 2013; Evans et al., 2011; Lotter et al., 2018, 2013; Tungpalan et al., 2015b; Whiteman et al., 2016).

The geometallurgical concept, which is a cross-disciplinary approach involving both geology and mineral processing, improves the prediction of mineral production, including mining waste (waste rock and tailings) amounts and their composition. Based on this, appropriate waste management measures can be determined at the inception of the mining operation to attain improved
environmental outcomes and circular economy aspirations (Tayebi-Khorami et al., 2019). This approach enhances resource knowledge from the processing perspective hence lowering operational risk related to repository unknown variation (Lund and Lamberg, 2014). For a historical tailings repository, several geometallurgical domains may exist depending on the type of primary ore, processing methods that generated the tailings, method of deposition of the tailings into the impoundments, and the weathering history of the tailings.

Using such an integrated approach allows for a better understanding of characteristics and metallurgical performance of the tailings (Tungpalan et al., 2015a), but it is only a part of the conceptual framework required to investigate the reprocessing of historical tailings in a holistic and systematic manner. The framework presented here has been adopted in the ERA-MIN project REMInE (Improve Resource Efficiency and Minimize Environmental Footprint) dealing with historical mine wastes from different mine sites, namely the Smaltjärnen historical tungsten ore tailings repository in Yxsjöberg, Sweden, the Cabeço do Pião tailings dam in Portugal (Figueiredo et al., 2018), and the Sasca Montana tailings management facility in Romania (Filcenco-Olteanu et al., 2017). The Yxsjöberg case consists of two tailings repositories Smaltjärnen and Morkulltjämen of which the former is the focus of this study.

Earlier investigation (Mulenshi et al., 2019) on the selection of feasible methods for reprocessing the Yxsjöberg historical tailings was based on the tailings characterization using only bulk mineralogy analysis techniques X-ray diffraction (XRD) and element-to-mineral conversion (EMC). However, the findings revealed that for the processing methods to be optimised, it was necessary to further characterize the tailings using microanalysis methods to enhance understanding of mineral grains of interest in the tailings particles. Therefore, in this current study, the historical tailings are further characterized using Mineral Liberation Analysis (MLA), and tailings characterization is shown to be an essential step to metallurgical testing in the conceptual framework for reprocessing historical tailings.

The proposed conceptual framework for reprocessing historical tailings is defined as a systematic way to generate relevant information and fill the knowledge gaps about historical tailings repositories. The Yxsjöberg case is used to demonstrate how this conceptual framework is being applied for the possible recovery of critical metals and minerals from the Smaltjärnen historical tailings as secondary sources, and remediation of the repository.
2. The conceptual framework for reprocessing historical tailings

The proposed conceptual framework for reprocessing historical tailings to remediate the repository and/or recover critical metals and minerals is divided into six steps with defined tasks and sub-steps with associated tasks (Figure 1). In order to have relevant information and knowledge in each of these steps, it is important to identify the relevant stakeholders that can provide a multidisciplinary input. In the identification and exploration step, some initial information such as the primary ore geology and production plans may be available from national geological surveys, technical literature, and the mine’s production archives. Otherwise, it would have to be generated from the exploration of the tailings repository itself. Anyhow, knowledge of the primary ore, which helps to assess the effect and extent of weathering on the repository, would still be lacking while both primary and altered secondary minerals are present.

![Figure 1. The conceptual framework for reprocessing historical tailings.](image)

Critical in all these steps is having representative samples of the tailings for analysis and evaluation hence determining effective sampling techniques is vital. It is also important to note that the sampling strategy and suitable technique are usually site-specific because each tailings repository is unique and the reasons for the sampling vary due to (i) exploration purposes, (ii) environmental concerns and (iii) secondary resources potential (Sädbom and Bäckström, 2018). In the tailings
characterization step, the latter two determine the methods to be selected and the sequence to be followed, and hence the sub-steps of remediation and recovery of critical metals and minerals.

For metallurgical test work, tailings characterization results from both sub-steps (remediation, and recovery of critical metals and minerals) are vital for determining feasible reprocessing methods and assessing metallurgical performance. However, it is also important to understand the processes from which the tailings were produced, the composition of the initial products, how and where they were discharged. Therefore, having initial process flowsheets and information about the lithology of the repository in the first two steps of this conceptual framework is good for planning metallurgical test work. It also enhances the use of multidisciplinary approaches like the geometallurgical and/or process mineralogical approaches, which are beneficial for such complex materials with heterogeneity issues.

Findings from metallurgical test works are then used to design suitable process flowsheets that would allow for the reprocessing of historical tailings to remediate the repository and/or recover critical metals and minerals. However, the sustainability of the developed process needs to be assessed, and the generated residue needs to be stable and environmentally safe. The residue management helps to ensure that the reprocessing of historical tailings does not create another problem but offers a long-term solution.

In this study, the focus has been put on the first three steps of this conceptual framework and how the information and knowledge developed for the Yxsjöberg case has or will be used in the subsequent steps.

3. The Yxsjöberg mine tailings case

The Yxsjöberg historical tungsten ore tailings repositories (Smaltjärnen and Morkulltjämen) are located in the Bergslagen mining region of south-central Sweden. This region has had numerous mining activities for centuries, and historical tailings are among the large volumes of mine waste that resulted. The tailings in the Smaltjärnen repository, which this study is based on, were deposited in the period 1935 to 1963, while those in the Morkulltjämen repository were from 1969 to 1989 (Höglund et al., 2004; Hübner, 1971; Rothelius, 1957). These tailings are among the Bergslagen mine wastes that have been identified as potential secondary sources for critical metals and minerals that are in short supply in the EU, but there is need to build knowledge about them (Hallberg and Reginiussen, 2019; Sädbom and Bäckström, 2018). Therefore, the proposed conceptual framework for reprocessing historical tailings (Figure 1) is applied to the Yxsjöberg case to enhance information and knowledge about the Smaltjärnen repository not only for recovery of critical metals and minerals but also for remediation of environmentally harmful elements and minerals in these tailings.
3.1 Step 1: Identification and exploration

The initial information for the tasks in this step of the conceptual framework was obtained from available very old literature, archived mine records, and reports mostly done in conjunction with the Geological Survey of Sweden (SGU).

Figure 2 shows the location of the Smaltjärnen tailings repository and the decommissioned processing plant in Yxsjöberg. The primary ore from which the Smaltjärnen tailings were generated was mined at the Yxsjö Mines and had an average ore grade of 0.3-0.4 wt.% WO₃, 0.2 wt.% Cu and 5-6 wt.% fluorite (Hübner, 1971; Rothelius, 1957). The exploited minerals were scheelite for W, chalcopyrite for Cu and fluorite, and their respective concentrates were produced in three main sections of the Yxsjö processing plant, namely gravity separation, magnetic separation, and flotation (Figure 3). However, a considerable amount of these valuable minerals ended up in the tailings due to low concentrate recoveries (50-70 wt.% for scheelite, 50 wt.% for fluorite and 25 wt.% for chalcopyrite). More details about the processing products, estimated volume, and elemental concentrations are given in earlier publications (Hällström et al., 2020a; Mulenshi et al., 2019).

Figure 2. Smaltjärnen TSF in Yxsjöberg, Sweden. The yellow arrows from the decommissioned Yxsjö processing plant indicate the gravity flow of the discharged tailings from the hilltop.
Figure 3. Simplified flowsheet of the Yxsjö processing plant from which the tailings were generated and then randomly discharged onto the Smaltjärnen repository. The aerial photo of the repository shows drill core sampling locations represented by red dots, the yellow squares show two discharge points, and the yellow lines show the repository limit. (Hübner, 1971; Rothelius, 1957).

3.2 Step 2: Repository characterization

A site visit of both the decommissioned Yxsjö processing plant and the Smaltjärnen repository by a team of researchers from multiple disciplines (mineral processing, applied geochemistry and geophysics) helped to understand and verify some of initial information from the identification and exploration step. The visit also helped to come up with a site-specific sampling strategy and technique. The strategy was to locate the discharge points and sample the repository according to the discharge flow directions (Figure 2). It was assumed that the distribution of material in the horizontal plane happened in a uniform way resulting in similar profiles in the vertical plane when following the discharge downhill. Based on that, sampling was mainly done along a line in downhill direction (longitudinal section) with control points to the left and to the right (transverse section).

The repository surface is mostly without a vegetation cover and there are no dam walls to prevent the tailings from being washed into the Smaltjärnen Lake at the foot of the repository. Environmental concerns are thus unavoidable as seepage of tailings occurs through the dilapidated wooden embankment into the surface waters, and air and soil pollution through dust generation is evident. Therefore, some sampling points were selected near already sunk boreholes (Höglund et al., 2004) so that the effect of these tailings on ground and surface water could be further investigated. The strategy also included using sampling techniques that would minimize exposing large areas of unweathered tailings to weathering conditions but enhance understanding of the repository lithology. Therefore, two
types of equipment were tested for sampling: a Cobra hand drill with an open gauge steel tube (40 mm diameter and 1 m length) for sample holding, and a percussion drill rig from Envix Nord AB with plexiglass tubes (40 mm diameter and 1.2 m length each tube) for sample holding. The latter was the preferred sampling equipment, and hence the Smaltjärnen repository was sampled by collecting drill core samples from nine different locations (Figure 3). Details about the numbering of the sampling locations are given in Mulenshi et al., 2019. For this paper, three sampling locations (1_1, 1_2 and 6) were investigated in more detail (Table 1).

Table 1. Information about sampling locations.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Sampling Points GPS Coordinates [DMS (degrees, minutes, seconds)]</th>
<th>Altitude with tailings (m)</th>
<th>Number of drill holes</th>
<th>Drill hole depth (m)</th>
<th>Number of drill cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_1</td>
<td>60°02’30.0”N 14°46’15.7”E</td>
<td>307</td>
<td>1</td>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
<td>2_1</td>
<td>60°02’24.7”N 14°46’31.9”E</td>
<td>309</td>
<td>1</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>1_2</td>
<td>60°02’30.4”N 14°46’31.2”E</td>
<td>306</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>2_2</td>
<td>60°02’26.9”N 14°46’34.4”E</td>
<td>314</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>60°02’31.9”N 14°46’16.5”E</td>
<td>291</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>60°02’26.8”N 14°46’26.5”E</td>
<td>305</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>60°02’24.2”N 14°46’29.6”E</td>
<td>305</td>
<td>2</td>
<td>4.8</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>60°02’33.6”N 14°46’30.8”E</td>
<td>303</td>
<td>1</td>
<td>2.2</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>60°02’34.5”N 14°46’29.7”E</td>
<td>315</td>
<td>2</td>
<td>2.4</td>
<td>4</td>
</tr>
</tbody>
</table>

The lithology of the repository was studied through screening of the collected drill core samples. Each drill core was subdivided, vertically, into layers based on color and granulometry. This approach was taken in order to have a clear understanding of the layers represented in each drill core. The layers are an indication of how tailings deposition took place in the repository, variations in mineralogy, and process parameters during the production period. To have an approximate thickness of layers in the tailings repository, the thickness of each observed compacted layer was measured using a measuring tape. Vertical profiles in the selected locations of the repository were constructed with each color representing a layer in the drill core and its compacted thickness (Figure 4). In total, 10, 11 and 3 layers were observed in sampling locations 1_1, 1_2 and 6, respectively, with sampling location 1_2 having the longest drill core of approximately 5 meters.
3.3 Step 3: Tailings characterization

A holistic approach that takes into consideration the environmental consequences of reprocessing historical tailings as secondary resources is desired. Therefore, both sub-steps of remediation and recovery of critical metals and minerals were considered in the selection of methods and sequence of characterizing the Smaltjärnen tailings.

In order to characterize the tailings samples physically (moisture content, texture, and particle size distribution), chemically (elemental composition), and mineralogically (modal mineralogy, mineral locking, and liberation), the samples were first dried in air at 105 °C for 48 hours. The dried samples were then split into sub-samples using a riffle splitter. Figure 5 shows pictures of the dried tailings samples for drill cores 1_1, 1_2 and 6, with each sample representing a layer in the drill core. Therefore, in addition to the number indicating the sample location, there is an extra set of numbers indicating the layers in each drill core.
conceptual framework (Figure 6). For more details about sample preparation and characterization of drill core samples, refer to earlier publication (Mulenshi et al., 2019).

Mineral Liberation Analysis (MLA) was conducted on each layer of the selected drill core 6 in each particle size fraction using the Scanning Electron Microscope equipped with the MLA 3.1.3.612 software suite from FEI (SEM – FEI Quanta 650 MLA-FEG: FEI Company, Hillsboro, OR, USA). Both sample preparation and MLA were done at the Helmholtz Institute Freiberg for Resource Technology in Germany. For the results presented in this paper, the Grain-based X-ray Mapping (GXMAP) MLA measurement mode was employed. The MLA Dataview v3.1.4.686 software (3.1.4.686, FEI Company, Hillsboro, OR, USA, 2014) was used to evaluate the MLA data.

4. Characterization results and discussion

The results with regard to the identification and exploration step of the conceptual framework (Figure 1) are already given above as they form the foundation for understanding the Smaltjärnen historical tailings and selection of characterization methods. Therefore, in this section, the results of the repository and tailings characterization steps are presented.
4.1 Repository characterization

Based on the location of the discharge points, the observed southward flow of tailings into the Smaltjärnen Lake, the altitude information and layering of the drill cores, two interpolated longitudinal section views of the repository were constructed (Figure 7 a-b). From the depositional environment observed in the two longitudinal section views, the three locations used in this study provide preliminary representative samples of tailings near discharge points (locations 1_1 and 6), and lower-level areas where larger volumes of tailings flow from surrounding higher-level areas and accumulate in several layers (location 1_2). Transverse sections between sampling locations were also constructed (Figure 7 c-d) to compare the effect of the depositional environment on tailings volume and layering on the TSF.

Figure 7. Interpolated longitudinal and transverse section views of the repository show the depositional environment and the tailings thickness variation on the TSF.

4.2 Tailings characterization

Physical and chemical variability was observed in the different layers and locations of the repository. In order to understand the particle size variation in the three selected locations of the repository, D$_{50}$ values for the layers in each drill core were determined (Table 2). It was observed that particles in drill core 1_1 are generally coarser than those in drill cores 1_2 and 6. This can be explained by particle segregation and settling in the TSF, as drill cores 1_1 and 6 were sampled near the spigotting points containing coarser particles, while drill core 1_2 was further away from both outlets, and at a lower altitude (Lottermoser, 2010).
The drill core 1_1 layer at the depth between 31 and 70 cm shows a significantly coarser ($D_{50} = 1065 \, \mu m$) tailings layer than the other layers in the same drill core. The bottom layer was the coarsest ($D_{50} = 1830 \, \mu m$) in drill core 6 but had material that was not typical for the tailings, which were comparatively coarse and much darker in color; hence, the only chemical analysis could confirm the observation. The longest drill core 1_2 had two layers that were significantly fine with $D_{50}$ values of 259 and 227 $\mu m$ at depths 303 and 483 cm, respectively. The above disparity in particle size distribution across the tailings repository indicates geometallurgical domains that may have different metallurgical performances (Lotter, 2011) as well as affects the choice of reprocessing methods. For instance, in location 1_1, further grinding may be required as minerals of interest may be locked up in coarse tailings particles as observed in MLA particle images to be shown later in Figure 14 and Figure 16.

Particle size distribution (PSD) in the three drill cores was determined using all the layers in each drill core. In all drill cores, the dominating particle size fractions were $-600$ to $+300 \, \mu m$ and $-300$ to $+149 \, \mu m$ (Table 2). Drill cores 1_2 and 6 had more fines ($<75 \, \mu m$) than drill core 1_1. This disparity in particle size reveals the effect of the depositional environment on particle distribution across the repository coupled with variations in mineralogy and/or process parameters such as grinding size during the production period of 1936 to 1963.

As received from the chemical analysis, the elements of high concentration were W, Cu, S, Sn, Zn, Be and Bi. The weighted average elemental concentrations in each layer (Table 2) were calculated from the elemental concentrations in the particle size fractions, and subsequently for the entire drill core. Using the weighted average elemental concentrations [Figure 8 (a) and (c)] and the total mass of tailings in each particle size fraction, elemental mass distributions [Figure 8 (b) and (d)] were then also calculated. Except for drill core 1_1, which had a very small amount of material in $<75 \, \mu m$ size fraction thus having a different particle size range starting from $<149 \, \mu m$ for chemical analysis, all elements were highest in particle size fraction $-600$ to $+297 \, \mu m$ followed by $-297$ to $+149 \, \mu m$. 
Figure 8. Elemental concentrations (a) and (c), and mass distributions (b) and (d) in the different particle size fractions of drill core 1_1 (left) and 6 (right).

Elemental concentrations and mass distributions also vary with depth and across the repository. The highest WO$_3$ concentration was observed in drill core 1_1 (Table 2). In all the three drill cores, the highest WO$_3$ concentration was between 88 and 153 cm depth. These highest WO$_3$ concentrations were 0.27, 0.22 and 0.16 % in drill cores 1_1, 1_2 and 6, respectively. However, in terms of the mass distribution of WO$_3$ in the various layers of the drill cores, the concentration may be high, but the actual quantity is small. It is observed that for drill core 6, most of the WO$_3$ ($\approx$70 wt.%) is contained in the upper layer (0-111 cm), while for drill core 1_2 it is between 175 and 295 cm with 32 wt.% of the total WO$_3$. For drill core 1_1, the depth (31-70 cm) had the highest mass distribution of WO$_3$ (21 wt.%).

Table 2. $D_{80}$ values, PSD, concentration and distribution of WO$_3$ and S in drill cores 1_1, 1_2 and 6 at different depths in the repository.
Sulphur depletion because of oxidation was expected in this TSF, with the depletion decreasing from top to bottom, due to the long storage period. Both concentration and mass distribution of sulphur in each drill core were analyzed. In all the three drill cores, the highest S concentration was between 88 and 153 cm depth, as was the case for WO$_3$. These highest S concentrations were 1.89, 1.85 and 3.05 % in the drill cores 1_1, 1_2 and 6, respectively. In Table 2, it can be seen that for drill core 6, 57 wt.% of the S is contained in the upper layer (0-111 cm) while for drill core 1_2, it is between 175 and 295 cm with 28 wt.% of the total S. In drill core 1_1, the depth (151-190 cm) had the highest mass distribution of S at 24 wt.%. Besides sulphur oxidation, these variations may also be attributed to mineralogical changes during production, and a detailed analysis of the sulphur depletion trend on location 1_2 is given in our earlier publication (Mulenshi et al., 2019). The chemical analysis
also confirmed that the material in the bottom layer of the drill core 6 was not typical of the tailings as the concentration and distribution of all the main elements was extremely low.

Chemical composition variability in different locations of the Smaltjärnen TSF would have an effect on the concentrate grades and recoveries. Subsequently, process and product optimization practices such as process parameter variation and blending of tailings before reprocessing would be necessary.

Figure 9 summarizes the weighted average elemental concentrations and Dₘ₀ values in the three locations. Location 1_1 has higher concentrations of WO₃, Cu, Sn, Zn, Be and Bi than locations 1_2 and 6, and location 6 has the highest S concentration. Taking the average WO₃ and Cu concentration in these three tailings locations to be 0.15 % and 0.11 %, respectively, and applying them to the estimated 2.2 million tons of tailings in this repository gives approximately 3300 tons of WO₃ and 2512 tons of Cu.

Bulk mineralogical characterization of the tailings was conducted using XRD to identify mineral phases in particle size fractions −1190 to +600 μm, −600 to +300 μm, −300 to +149 μm, −149 to +75 μm and <75 μm of drill core 6. The analysis was also used to assess variations in mineralogical composition in the different locations of the repository by comparing location 6 to location 1_2 where studies were done earlier (Hällström et al., 2018; Khavari, 2018). The dominating silicate minerals diopside, hedenbergite, albite, ferro-actinolite, oligoclase and quartz were present in all particle size fractions, and repository locations. Minerals of economic interest fluorite, scheelite, wolframite and chalcopyrite were also identified (Figure 10) in all particle size fractions but it was noted that except for fluorite the other three minerals could only be found in the candidate list by using restrictions
when executing the ‘search & match’ function in HighScore Plus software. Therefore, prior knowledge of the mineral composition of the primary ore (Hübner, 1971; Rothelius, 1957; Siirak et al., 1978) from which these tailings were generated was essential in identifying such mineral phases.

![Figure 10. XRD pattern view of selected mineral phase patterns that matched the peak list and were accepted in particle size fraction –600 to +300 μm of layer 6-1 in drill core 6.](image)

To understand the tailings particles further, MLA was carried out on particle size fractions –1190 to +600 μm, –600 to +300 μm, –300 to +149 μm, and –149 to +75 μm of drill core 6. Particle size fractions –600 to +300 μm and –300 to +149 μm are discussed in more detail because tailings in the Smaltjärnen repository are mostly in these size fractions. Location 6 was picked for this analysis because of its higher sulphur concentration compared to the other drill cores. Based on the XRD analysis findings, mineral phases to be targeted in MLA were specified, and MLA was used to assess the host minerals for the elements of high concentration and economic interest, as given in Table 3, together with their average modal mineralogy and densities (Barthelmý, 2012).

**Table 3. Summary of the main minerals of economic interest in the tailings with their densities.**
It is observed that the higher WO$_3$ concentration in the second layer (6-2) of drill core 6 (Table 2) is not totally from scheelite as a substantial amount of W (∼30 wt.%) is related to wolframite in particle size fraction –300 to +149 μm (Figure 11). Contrary to scheelite, wolframite is a dense and paramagnetic mineral hence its beneficiation techniques include gravity and/or magnetic separation (Yang and Niemistö, 2017) meaning W from wolframite in this sample would be lost to the paramagnetic fraction in the process flowsheet proposed for separation of valuable minerals from the Yxsjöberg historical tailings (Mulenshi et al., 2019). Therefore, to recover this W from the paramagnetic fraction, gravity separation may be required. This analysis with a processing perspective in the tailings characterization step is essential for subsequent steps in the conceptual framework for reprocessing historical tailings.

<table>
<thead>
<tr>
<th>Element of high concentration</th>
<th>Main Mineral</th>
<th>Average Modal Mineralogy (Wt.%)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Scheelite</td>
<td>0.092</td>
<td>5.9 - 6.12</td>
</tr>
<tr>
<td>Cu</td>
<td>Chalcopyrite</td>
<td>0.310</td>
<td>4.1 - 4.3</td>
</tr>
<tr>
<td>Sn</td>
<td>Cassiterite</td>
<td>0.002</td>
<td>6.8 - 7</td>
</tr>
<tr>
<td>Zn</td>
<td>Sphalerite</td>
<td>0.000</td>
<td>3.9 - 4.2</td>
</tr>
<tr>
<td>Be</td>
<td>Danalite</td>
<td>0.460</td>
<td>3.43</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuthinite</td>
<td>0.018</td>
<td>6.8 - 7.2</td>
</tr>
<tr>
<td>F</td>
<td>Fluorite</td>
<td>3.930</td>
<td>3.01 - 3.25</td>
</tr>
</tbody>
</table>

Figure 11. Tungsten-bearing minerals with W distribution in different particle size fractions of layers 6-1 and 6-2 in drill core 6.
The two layers (6-1 and 6-2) of drill core 6 were analyzed to investigate and compare the mineral occurrences in the samples with slightly different chemical composition and weathering state. Six main sulphur-bearing minerals (Figure 12) and nine main calcium-bearing minerals (Figure 13) were identified. With regard to acid mine drainage (AMD), pyrite and pyrrhotite are notably the acid-generating sulphide minerals, with pyrrhotite reacting much faster than pyrite (Blowes et al., 2003; Jamieson, 2011) hence the much lower S distribution observed in pyrrhotite (Figure 12).

It was observed that in both particle size fractions, the upper layer (6-1) has a higher S distribution in pyrite and pyrrhotite than layer 6-2, meaning less oxidation has occurred in the upper layer compared to the layer underneath. However, in terms of secondary minerals in layer 6-2, gypsum is mostly in size fractions –600 to +300 μm (≈1.2 wt.%) and –1190 to +600 μm (≈3.6 wt.%) while Fe sulphate is mostly in size fractions –300 to +149 μm (≈4.7 wt.%) and –149 to +75 μm (≈8.0 wt.%) (Figure 14). This means that layer 6-2 was exposed to weathering before layer 6-1 was deposited, and the liberated smaller particles are more susceptible to weathering due to the larger surface area. The acid produced by the oxidation of pyrrhotite was neutralized by calcite and hence the depletion of the two minerals in layer 6-2 (Figure 13 and Figure 14) (Hällström et al., 2018).

Another critical aspect of AMD with these historical tailings is the enhanced mobility of toxic elements like Be to ground and surface water, which even though it is not environmentally regulated in Sweden, has a very high concentration compared to the American recommended standard for groundwater (Hällström et al., 2020b). Beryllium was observed to be only contained in the unusual mineral danalite, which is also one of the main sulphur-bearing minerals in these tailings. The
danalite mineral grains were mostly non-liberated (>80 wt.%) and locked with the Ca-bearing (ilvaite, garnet-andradite, and fluorite), and Fe-bearing (Fe oxide, Fe sulphate, pyrite and pyrrhotite) minerals. This means that when reprocessing these tailings, danalite would end up in the process fractions where these minerals report such as the magnetic fraction (with pyrrhotite and pyrite) in magnetic separation (Mulenshi et al., 2019), and froth flotation tailings (with Ca-bearing minerals) in scheelite froth flotation (Gan, 2019). Therefore, as AMD prevention measures are taken during the deposition of such process fractions, the mobility of toxic elements like Be would also be addressed.

![Elemental distribution](image)

Figure 13. Calcium-bearing minerals with Ca distribution in particle size fraction –600 to +300 µm of layers 6-1 and 6-2 in drill core 6.
Figure 14. Tailing particles containing pyrrhotite sorted by total mineral area.
Based on the MLA particle images (Figure 16), scheelite and wolframite occur as both fine and coarse mineral grains. The grains in the tailings fine fraction (<75 µm) are liberated, whereas those in coarser fractions (>75 µm) are mostly non-liberated, with a few liberated. Therefore, since there is a higher distribution of W in size fractions >149 µm (Figure 8), the liberation of scheelite and wolframite in coarser fractions will be necessary for better recovery of W. In the primary skarn ore, the fairly coarse-grained scheelite was associated with the pyroxene skarn characterized by xenomorphic hedenbergite (normally >200 µm) while the fine-grained scheelite was associated with the amphibole skarn mainly consisting of hornblende (Siirak et al., 1978). With reference to Figure 16, hedenbergite is associated with ilvaite, garnet-andradite, and fluorite, while hornblende is associated with quartz and calcite (Hudson Institute of Mineralogy, 2020).

Agglomerated tailings particles are observed in the coarsest fraction ~1190 to +600 µm, with gypsum as the binder (Figure 14 and Figure 16). The modal mineralogy (Figure 15) shows that both critical minerals (scheelite and fluorite) and minerals of environmental concern (pyrite and pyrrhotite) are present in these agglomerated tailings particles but in very low quantities (<1 wt.%) except for fluorite and pyrite (≈2 wt.%). This means that in order to recover and/or separate the critical minerals from the minerals of environmental concern, regrinding for increasing liberation will be required.

Figure 15. Agglomerated minerals with modal mineralogy in particle size fraction ~1190 to +600 µm of layer 6-2 in drill core 6.
Figure 16. Tailing particles containing scheelite sorted by total mineral area.
Mineral locking for scheelite was assessed in both layers, and particle size fractions. In both layers, scheelite was more liberated in size fraction –149 µm but since most of the tailings particles were in size range –600 to +149 µm, it was important to assess the locking of scheelite in this particle size range. It was observed that in layer 6-1, scheelite was mostly liberated (≈50 wt.%) in size fraction –300 to +149 µm while in size fraction –600 to +300 µm, scheelite is mostly locked (≈80 wt.%) in ternary or greater particles (Figure 17). For layer 6-2, scheelite was mostly locked (≈60 wt.%) in binary particles in fraction –300 to +149 µm while in size fraction –600 to +300 µm, scheelite is mostly locked (≈60 wt.%) in ternary or greater particles. Therefore, for reprocessing, scheelite needs to be liberated from the binary and ternary or greater particles in order to enhance its recovery in the proposed process flowsheet (Mulenshi et al., 2019). Further assessment of the minerals locked with scheelite (Figure 18) revealed that locking is mostly with the Ca-bearing minerals ilvaite, fluorite and garnet-gross-andradite meaning if froth flotation is considered as a reprocessing method option, the challenge of selective flotation of scheelite from the Ca-bearing minerals needs to be taken into consideration (Foucaud et al., 2020; Gan, 2019). Other minerals of interest concerning magnetic separation locked with scheelite included wolframite and Fe-oxide (may be magnetite and/or hematite but not distinguishable in MLA) as they would contribute to scheelite losses to the magnetic fractions (Mulenshi et al., 2019). Chalcopyrite is also observed to be locked with scheelite hence if not liberated, it may be lost with scheelite in the magnetic fraction of magnetic separation or lost to the scheelite concentrate in gravity separation (Mulenshi et al., 2019).

Figure 17. Mineral locking for scheelite in different particle size fractions of layers 6-1 and 6-2 in drill core 6.
Figure 18. Minerals in ternary or greater locking with scheelite in particle size fraction –300 to +149 µm of layers 6-1 and 6-2 in drill core 6.

The degree of scheelite locking with other minerals was further assessed by looking at its liberation in terms of the free surface of the particle (Table 4). The mineral locking for scheelite shown in Figure 17 and Figure 18 can be linked to liberation classes, thus enhancing the understanding of how much of the scheelite grain surfaces in the tailings particles are liberated and the mineral distribution in each class. For instance, looking at layer 6-2 and size fraction –600 to +300 µm, it is observed that 78% of scheelite grains have ≤20% of their surfaces liberated in the tailings particles, while 11% are completely unexposed. Therefore, such tailings particles would require fine grinding to liberate the >80% scheelite surfaces, especially that the tailings particles are complex with scheelite locked with several other minerals.

Table 4. Scheelite degree of liberation by free surface in particle size fraction –600 to +300 µm of layer 6-2 in drill core 6.

<table>
<thead>
<tr>
<th>20% Liberation classes</th>
<th>Distribution of scheelite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% (not exposed)</td>
<td>10.99</td>
</tr>
<tr>
<td>0% &lt; x ≤ 20%</td>
<td>78.27</td>
</tr>
<tr>
<td>20% &lt; x ≤ 40%</td>
<td>0.96</td>
</tr>
<tr>
<td>40% &lt; x ≤ 60%</td>
<td>0.00</td>
</tr>
<tr>
<td>60% &lt; x ≤ 80%</td>
<td>0.00</td>
</tr>
<tr>
<td>80% &lt; x &lt; 100%</td>
<td>0.00</td>
</tr>
<tr>
<td>100%</td>
<td>9.78</td>
</tr>
</tbody>
</table>
5. Conclusions

A conceptual framework for reprocessing historical tailings has been proposed and applied to the case of the closed Yxsjöberg mine in order to enhance the systematic generation of relevant information and filling of the knowledge gap about the Smaltjärnen tailings repository. The results will generally help in the recovery of critical metals and minerals from historical tailings as secondary raw material sources, and in the environmental remediation of such repositories. The following section summarizes the findings and conclusions.

- It is important to identify the relevant stakeholders that can give a multidisciplinary input to the conceptual framework for reprocessing historical tailings. For the Yxsjöberg case, the disciplines included mineral processing, applied geochemistry, and geophysics.

- For current and future tailings repositories, the proposed conceptual framework can also be used as a checklist to ensure that all relevant information is systematically archived for future reference.

- Based on the findings in the tailings characterization step, informed decisions can be made on how to proceed with the subsequent steps (metallurgical test work, and process design and analysis) in the conceptual framework for reprocessing historical tailings.

- The variability in the tailings across the repository is an indication of the presence of possible geometallurgical domains within this repository and hence the need for subsequent metallurgical testing to assess the effect on metallurgical performances.

- The distribution of tailings particle across the repository is influenced by the depositional environment, variations in mineralogy, dispersity properties and process parameters during the production period.

From the Yxsjöberg study, several case-specific conclusions can be drawn:

- The coarser particle size fractions (−600 to +149 μm) have the highest volume of critical minerals (scheelite and fluorite) and minerals of environmental concern (pyrite and pyrrhotite). In this particle size range, scheelite mineral grains are mostly (>50 wt.%) locked in binary and ternary or greater (complex) tailings particles. This being a consistent observation in the locations under study shows a possible underlying processing issue in the Yxsjöberg beneficiation processes. Therefore, further grinding of the tailings will be required to liberate scheelite for enhanced separation.

- Scheelite is mostly locked with Ca-bearing minerals ilvaite, fluorite and garnet-gross-andradite, meaning that if froth flotation is considered as a beneficiation option for reprocessing the Smaltjärnen historical tailings, flotation reagents that would improve selective flotation of scheelite from the Ca-bearing minerals will be essential.

- The average WO$_3$ concentration in the sampled locations is 0.15 %, and applying this to the estimated 2.2 million tons of tailings in this repository gives approximately 3300 tons of WO$_3$. 
Acknowledgments: Our sincere gratitude goes to the late Niclas Strandberg (AB Yxsjö Industriservice), who was the owner of the Yxsjöberg mining site for his support of the project.

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Paper II
Characterization and Beneficiation Options for Tungsten Recovery from Yxsjöberg Historical Ore Tailings

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Abstract: Repositories of historical tungsten mining tailings pose environmental risks, but are also potential resources for valuable metals. They still contain large tonnages of useful minerals and metals, reflecting the inefficient extraction methods and/or low metal prices at the time they were mined. The focus of this study is to evaluate the technical viability of reprocessing the tailings to recover some of the contained valuable minerals and metals, as well as reducing the negative environmental impact associated with the tailings. Geometallurgical studies were conducted on drill core samples taken from the Smaltjärnen tailings repository of the closed Yxsjöberg tungsten mine, Sweden. The collected samples were characterized physically, chemically, and mineralogically. Knelson concentrator dry low- and high-intensity magnetic separation methods were tested as potential beneficiation methods. The tailings are dominated by the −600 to +149 µm particles. The highest concentration of tungsten (W) was 0.22% WO$_3$. Using a Knelson concentrator, scheelite (main W mineral) recovery was enhanced, with 75 wt.% tungsten recovered in the 34 wt.% heavy concentrate. Only 1.0 wt.% sulphur (S) reported to the non-magnetic fraction. Based on the findings, a methodology and a preliminary process flowsheet for reprocessing the tailings is proposed.

Keywords: historical tailings; Tungsten; Scheelite; geometallurgical approach; characterization; beneficiation; reprocessing

1. Introduction

Tungsten (W) is among the critical raw materials with significant economic importance and high supply risk for the European Union [1]. According to the 2015 risk list of the British Geological Survey, tungsten has a relative supply risk index of 8.1 on a scale of 1 to 10, which ranks sixth behind rare earth elements that have the highest risk [2]. Primarily, tungsten is produced from scheelite and wolframite ores with 0.08–1.5% tungsten trioxide (WO$_3$) [3]. These tungsten minerals are friable in nature compared to the associated gangue minerals; hence, fine tungsten particles are excessively generated during the necessary comminution processes. The fine tungsten particles are lost to tailings due to the failure of commonly used separation methods to recover fine tungsten minerals particles [3,4]. Thus, for critical raw materials with a high supply risk such as tungsten, old tailings storage facilities (TSF) are potential sources for additional production. Globally, historical tailings (HT) recycling is being considered as a supply risk-reducing measure [1]. Apart from being potential resources, HT repositories also pose environmental risks [5–7]. Hence, there is need for a holistic reprocessing approach in which not only the valuable minerals will be recovered, but also the environmental risk will be reduced, leaving an inert and environmentally safe residue [7].
HT repositories can be considered as geometallurgical units based on the definition of being “an ore type or group of ore types that possess a unique set of textural and compositional properties from which it can be predicted that they will have similar metallurgical performance” [8]. Accordingly, various geometallurgical and/or process mineralogical approaches have been used to investigate process tailings or processed ores [6,9–13]. TSF may have several geometallurgical units depending on what type of primary ore and which process streams the tailings were generated from, how the deposition was done (randomly or systematically), and the weathering that could have occurred over time. Concerning weathering, sulphide minerals are prone to oxidation, especially near the tailings surface, resulting in a series of reactions that produce acidic pore water and ferric-bearing secondary precipitates that may contain high concentrations of metals, either co-precipitated with or adsorbed onto ferric (oxy) hydroxides [14,15]. For tungsten tailings, low pH due to acid pore water in the tailings increases W affinity for hydrous ferric oxides (HFOs), and when it forms polyoxyanion species, its mobility in the aquatic environment is enhanced [16]. Therefore, for HT with a long storage period, these geochemical changes may alter the chemical composition of tailings compared to the primary ore from which they were produced [17]. This may lead to the reprocessing flowsheets and metallurgical performances of tailings being different from those of primary ores from which they were initially produced. Moreover, the amount of valuable minerals in HT depends largely on the initially employed beneficiation methods and their efficiencies. For instance, for high density ores such as scheelite ores, gravity separation and flotation methods are conventionally used, and depending on the associated minerals, magnetic separation may also be used [18]. Because of the excessive generation of fine scheelite particles which are partly lost to the tailings during comminution, advanced multi-stage gravity separation techniques, good for processing fine particles, should be considered in order to efficiently recover heavy fines during reprocessing of the tailings [19].

In this study, historical tailings from the Smaljärnen TSF at the closed Yxsjöberg tungsten mine in Middle Sweden were analyzed and tested in a case study that investigated the feasibility of reprocessing the tailings not only as a supply risk-reducing measure, but also as a possible remediation method. In addition to tungsten, other elements of economic importance and with elevated concentrations in the tailings under study include copper (Cu), fluorspar (CaF$_2$), sulphur (S), tin (Sn), zinc (Zn), beryllium (Be), and bismuth (Bi) [20]. Eventual extraction of these elements and safe disposal of the remaining residue require a detailed understanding of the mineralogical, geochemical, and bulk physical properties of the tailings [7,21]. Preliminary mineralogical and geochemical studies of the tailings revealed that W, Cu, F, S, Sn, Zn, Be, and Bi are hosted mainly in scheelite, chalcopyrite, fluorspar, pyrrhotite, cassiterite, danalite (both Zn and Be), and bismuthinite, respectively [20]. The analyses also showed that pyrrhotite was the main Fe–sulphide mineral responsible for acid mine drainage (AMD) and need to be sequestered from the bulk tailings as a remediation measure.

The objectives of the current study are (1) to propose a methodology to understand further the properties (physical, chemical, and mineralogical) of the Yxsjöberg HT and how these are spatially distributed in the TSF, and (2) to determine the processing options for the tailings. These objectives will be achieved through (1) TSF characterization (sequential characterization of tailings), (2) metallurgical test work (selection of feasible reprocessing methods, e.g., physical separation), and (3) process design and analysis (flowsheet design). The results of this initial study will be decisive for the development of methods for separating valuable and environmentally deleterious minerals from HT, leaving a stable environmentally safe residue.

2. Materials and Methods

2.1. The Yxsjöberg Mine

One of the most important mining areas in northern Europe with regard to tungsten ores has been the Bergslagen district in Middle Sweden, where the Yxsjöberg historical tungsten ore tailings repository is located. The tailings in this study were produced from the ore that was mined at the Yxsjöberg
mine from 1935 to 1963, with average ore grades of 0.3–0.4 wt.% WO₃, 0.2 wt.% Cu, and 5–6 wt.% fluorspar [22,23]. The exploited minerals were scheelite for W, chalcopyrite for Cu and fluorspar. This repository is estimated to have about 2.2 million tons of tailings and covers an area of 26 hectares, with elemental concentrations of 1–2 wt.% S, 0.02–0.2 wt.% Cu, 0.02–0.3 wt.% W, 0.02–0.04 wt.% Sn, and 0.02–0.03 wt.% Be. The scheelite grain size in the ore was 0.2–4.0 mm and 90 wt.% of the ore was liberated at 0.4 mm particle size. The concentrate recoveries at that time were 50–70 wt.% for scheelite, 50 wt.% for fluorspar, and 25 wt.% for chalcopyrite, and a considerable amount of valuable minerals ended up in the tailings [23]. The Yxsjöberg processing plant had three main sections, namely gravity separation, magnetic separation, and flotation, from which tailings were generated and discharged onto the Smaltjärnen tailings repository (see Figure 1). Tailings deposition was done through several pipes, thus producing homogenous layers of tailings equally distributed over the width of the repository surface. No data were available that could be used to link these layers to the former production schedule.

Drill core samples were taken from nine different locations, shown in Figure 1b. Samples were collected mainly along the main discharge flow directions. The red dots represent the individual drill core sampling locations and the numbering of the sampling locations was based on the sequence of sampling in each sampling campaign. The first four locations were distinguished by _1 and _2, meaning 1_1 was in the first campaign while 1_2 was in the second campaign. For locations 1_2 to 7, a percussion drill rig from Envix Nord AB was used with plexiglass tubes (40 mm diameter and 1.2 m length each tube) to hold the sample. The sampled locations were selected based on the visual variations of the tailings in terms of color and granulometry, and the proximity to former discharge points (Figure 1). It should be noted that the drill core from sampling location 1_2 shown by the white arrow in Figure 1b is the focus of this study. This location is very close to the P4 sampling location referred to in the geochemical characterization of these historical tailings [20].

The actual sampling points in the selected locations were randomly picked, and a summary of the information about one sampling point used in this paper is given in Table 1. Screening of the drill core was done based on the differences in color and granulometry in the core, and the drill core was divided into sub-samples representing tailing layers in this particular location of the repository. The thickness of each observed compacted layer was noted to have its approximate thickness in the tailing repository. The vertical profile showing the different layers in the tailings in the selected location of the repository is shown in Figure 2. Each color represents a separate layer of the of the tailings and its compacted thickness. Eleven layers were observed at sampling point 1_2, where the total compacted tailing thickness in the 600 cm drill hole was approximately 500 cm. Since each plexiglass tube was only 1.2 m long, five pieces of drill cores were recovered from the drill hole.

**Figure 1.** (a) Processes from which the Yxsjöberg historical tailings were generated. (b) Drill core sampling locations on the Smaltjärnen tailings storage facilities (TSF) represented by red dots; the yellow squares show two discharge points, the yellow lines show the repository boundary, and the white arrow shows the focus area for this study.

### 2.2. Sampling and Sample Preparation

Drill core samples were taken from nine different locations, shown in Figure 1b. Samples were collected mainly along the main discharge flow directions. The red dots represent the individual drill core sampling locations and the numbering of the sampling locations was based on the sequence of sampling in each sampling campaign. The first four locations were distinguished by _1 and _2, meaning 1_1 was in the first campaign while 1_2 was in the second campaign. For locations 1_2 to 7, a percussion drill rig from Envix Nord AB was used with plexiglass tubes (40 mm diameter and 1.2 m length each tube) to hold the sample. The sampled locations were selected based on the visual variations of the tailings in terms of color and granulometry, and the proximity to former discharge points (Figure 1). It should be noted that the drill core from sampling location 1_2 shown by the white arrow in Figure 1b is the focus of this study. This location is very close to the P4 sampling location referred to in the geochemical characterization of these historical tailings [20].

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Prior to the physical and chemical analyses, the samples were dried at 105 °C for 48 h to ensure complete drying, as there was a large volume of sample in each drying pan. The dried samples were then split into subsamples using a riffle splitter. Figure 2 also shows respective pictures of the dried samples from sampling point 1_2. In order to account for the different layers, in addition to the numbering of the sampling location, a number was added to denote the layers from top to bottom of a drill core (i.e., 1_2-1 means the first (top) layer in drill core 1 of the second campaign).

One hundred and fifty grams split of dried samples were collected from each layer and analyzed using a RO-TAP® Sieve Shaker model RX-29 with five sieves to obtain six size fractions. The total amount of available samples from layers 1_2-5, 1_2-6, 1_2-7, and 1_2-10 was less than 150 g; hence, the samples were sieved without replication, which was done with the bigger samples to check that the split samples were representative of the whole layer sample.

2.3. Characterization of Drill Core Samples

The six size fractions obtained from the dry sieving were >1190 µm, −1190 to +600 µm, −600 to +297 µm, −297 to +149 µm, −149 to +75 µm, and <75 µm. Particle size distribution curves for each drill core layer and, subsequently, the entire drill core were determined. Using the Rosin–Rammler–Sperling–Bennett (RRSB) distribution function, the D80 of particle size was determined for each drill core layer, which gives more precise values than interpolating from the particle size distribution (PSD) curves. Small samples of approximately 15 g were split from each particle size fraction and bulk samples (1_2-5, 1_2-6, 1_2-7, and 1_2-10 layers that were less than 150 g) of each drill core layer were

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**Table 1. Information of sampling point 1_2.**

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>Sampling Points GPS Coordinates DD (Decimal Degrees)</th>
<th>Altitude (m)</th>
<th>Number of Drill Holes</th>
<th>Drill Hole Depth (m)</th>
<th>Number of Drill Cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_2</td>
<td>60.041778, 14.775325</td>
<td>306</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure 2.** Vertical profile at sampling point 1_2. On the far right is a photo of one of the five drill core pieces in the cut plexiglass tube and before dividing the core into subsamples.
chemically analyzed using the inductively coupled plasma–sector field mass spectrometry (ICP–SFMS) method. The “MG-2 + Bi Metals in waste” package analysis protocol, which included 10 oxides and 22 elements (namely SiO₂, Al₂O₃, CaO, Fe₂O₃, K₂O, MnO, Na₂O, P₂O₅, TiO₂, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Hg, Mo, Nb, Ni, Pb, S, Sc, Sn, Sr, V, W, Y, Zn, and Zr) was used.

The mineralogical composition was characterized by X-ray Diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer (PANalytical B.V., Almelo, The Netherlands). Drill core layers 1_2-1, 1_2-4, 1_2-8, and 1_2-9 were selected for this analysis as they had the highest mass distributions in this drill core, as shown in Figure 3. Small samples (i.e., less than 50 g) of these selected layers were pulverized in a ring mill to obtain the powder samples required for XRD analysis. The raw data obtained from the diffractometer were evaluated using the PANalytical X’Pert HighScore Plus v3.0 software (3.0d (3.0.4), PANalytical B.V., Almelo, The Netherlands, 2011).

![Drill core 1_2](image)

**Figure 3.** Mass distribution (%) of tailings layers in drill core 1_2.

A ZEISS Axiophot Fluorescent Microscope (ZEISS, Oberkochen, Germany) mounted with an Infinity HD Camera was used for optical microscopy to study the scheelite (as the main mineral of interest) particles in the tailings with regard to occurrence, texture, and liberation. The fluorescence property of scheelite mineral was used to identify the scheelite particles and the blue filter was found to be effective in distinguishing scheelite particles from other minerals of similar luminance and brightness, such as bismuthinite. For this study, a grain mount polished section was prepared from a composite sample comprising -3 g from each layer. The ZEISS MERLIN™ FE–SEM (Field Emission–Scanning Electron Microscope: ZEISS, Oberkochen, Germany) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) and Back Scattered Electron (BSE) imaging was used to study the minerals in the drill core layers 1_2-4 and 1_2-9, which were the two layers with enough sample material. BSE images were captured and analyzed using the INCA-Oxford Instruments software (5.05, Oxford Instruments, High Wycombe, England, 2014). The distinction between scheelite and bismuthinite particles was confirmed using SEM–EDS chemical composition.

The above characterization methods for the drill core samples are summarized in Figure 4.
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2.4. Physical Separation Test Work

Magnetic and gravity separation were pre-selected as feasible physical separation methods based on literature, tailings characteristics, and assessment of processes from which the Yxsjöberg HT were produced.

2.4.1. Magnetic Separation

Magnetic separation test was conducted on two samples from layers 1_2-4 and 1_2-8. The test was conducted on the +75 µm and required at least 150 g of material. The samples were tested using both dry low-intensity magnetic separation (LIMS) and high-intensity magnetic separation (HIMS). During the LIMS, the drum speed and feed rate were varied, and during the HIMS, it was the splitter position that was varied. The process was assessed by observing the uniformity in the color of the products. Table 2 summarizes the operating parameters of both methods. The flowsheet in Figure 5 shows the magnetic separation test.

Table 2. Magnetic separation operating parameters [24].

<table>
<thead>
<tr>
<th>Methods</th>
<th>Motor (0–100)</th>
<th>Vibrator (0–100)</th>
<th>Plane 1 (−5, +5)</th>
<th>Plane 2 (−5, +5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIMS</td>
<td>100</td>
<td>70</td>
<td>Fixed</td>
<td>N.A. (Not Applicable)</td>
</tr>
<tr>
<td>HIMS</td>
<td>Fixed</td>
<td>Fixed</td>
<td>3</td>
<td>−1</td>
</tr>
</tbody>
</table>
2.4.2. Gravity Separation

Samples 1_2-1 and 1_2-8 were tested separately for their susceptibility to gravity separation. The tests required less than 2 kg of the −600 to +38 µm fraction. A 58 mL laboratory scale Knelson concentrator at the Boliden AB laboratory was used, with operating parameters set as shown in Table 3.

Table 3. Knelson concentrator operating parameters [24].

<table>
<thead>
<tr>
<th>Drum Speed (rpm)</th>
<th>Centrifugal Force (G)</th>
<th>Fluidization Water Flow Rate (L/min)</th>
<th>Fluidization Water Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>60</td>
<td>3.5</td>
<td>2</td>
</tr>
</tbody>
</table>

The separation products were analyzed for their chemical composition at ALS Scandinavia AB in Luleå, Sweden using the ICP–SFMS method. Element-to-mineral conversion (EMC) algorithms of the HSC chemistry software (9.5.1, Outotec, Pori, Finland, 2018) were used to determine the minerals in the magnetic separation products based on their chemical composition.

3. Results and Discussion

3.1. Characterization of Drill Core Samples

The physical and chemical characterization of the HT showed variations occurring in the different layers of the drill cores, which revealed the variability at different depths of this repository location. In terms of moisture content, some of the upper tailing layers had higher moisture content than lower layers (Figure 6). This moisture variation results from varying grain size distribution in the tailing layers. It was observed that layers with significantly higher fraction of finer particles (1_2-6 and 1_2-11) had higher moisture content than the layers with relatively coarser particles. In order to illustrate particle size variation with depths, the determined D₈₀ values for the various layers of the drill core were plotted against the depth, as shown in Figure 7.

Layer 1_2-2, located between 87 and 144 cm depth, was significantly coarser (D₈₀ = 681 µm). On the other hand, layers 1_2-6 and 1_2-11 at 303 and 483 cm depth were significantly finer, with D₈₀ values of 259 and 227 µm, respectively. This variation in grain size distribution with depth is the first indication of the presence of different metallurgical units, which may have different metallurgical performances [8], and thus need to be characterized. The variability would likely have an effect on the choice of methods to be considered for reprocessing, such as further grinding to liberate minerals of interest that may be locked up in the coarse particles, as observed with optical microscopy.
Figure 6. Moisture content variation with depths.

Figure 7. Variation of D$_{80}$ values with depth. This graph type depicts the observed abrupt changes in the drill core layers.

The $-600$ to $+297$ µm and $-297$ to $+149$ µm were the dominating particle size fractions, except the two layers with higher proportions of finer fractions mentioned above (Figure 8). This variation in
particle size is indicative of varying process parameters, such as grinding size and/or changes in the mineralogy during the production period of 1936 to 1963.

![Particle Size Distribution (PSD) Curves](image)

**Figure 8.** PSD curves for the 11 drill core layers.

The chemical composition of the various particle size fractions was also determined. The major components were SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$, while W, Cu, S, Sn, Zn, Be, and Bi were the main trace elements. From the elemental concentrations in the particle size fractions, weighted average concentrations in each layer were determined and subsequently calculated for the entire drill core.

Figure 9 illustrates elemental concentrations and mass distributions for layer 1_2-4 as an example, which is the layer with the highest mass distribution of tailings in this drill core (compare Figure 3). Considering the drill core as a whole, W and Cu, as the main metals of interest, were observed to have high concentrations of 2329 mg/kg and 1427 mg/kg, respectively, in the fine (<75 µm) particle size fraction. All elements were high in the dominating particle size fractions mentioned earlier. Therefore, for purposes of reprocessing these HT, additional steps for ensuring sufficient mineral liberation need to be considered for such coarse tailings particles.

![Elemental concentration in drill core layer 1_2-4](image)

**Figure 9.** Elemental concentrations (left) and mass distributions (right) in the six particle size fractions for layer 1_2-4.
The chemical composition of the drill core was also varying with depth. The highest WO$_3$ concentration was 0.22 wt.% in layer 1_2-2 (between 87 and 144 cm), as shown in Figure 10. Since this was the layer with the coarsest tailings particles, it means that during the concentration processes shown in Figure 1a, most of the scheelite mineral particles should have been lost to these tailings as non-liberated particles. The highest Cu concentration was 1147 mg/kg in layer 1_2-8, at a much deeper depth between 313 and 365 cm. However, it is important to know the mass distribution of metals in the layers, because the concentrations may be high but the actual quantities would be small when the total metal content in the drill core is considered. Therefore, the mass distribution for each element in the layers was calculated as a percentage of the total elemental content in the drill core. Figure 11 shows the WO$_3$ and Cu mass distributions in the drill core. It shows that much of the WO$_3$ and Cu was contained at the depth between 174 and 295 cm, which contain 32 wt.% of the total WO$_3$ and 29 wt.% of the total Cu.

![Figure 10. WO$_3$ (left) and Cu (right) concentrations in the 11 drill core layers.](image)

![Figure 11. WO$_3$ (left) and Cu (right) mass distributions in the 11 drill core layers.](image)

Since these tailings have been stored in this repository for a long period, sulphur depletion due to oxidation was expected, with the depletion decreasing from top to bottom—even though this would also depend on other factors such as particle size and initial quantity. Therefore, both the concentration and mass distribution of sulphur in each layer was analyzed. The highest S concentration was also in layer 1_2-2 at 1.85%, as shown in Figure 12 (left). However, with regard to mass distribution, it was observed that much of the S was contained in layer 1_2-4 at the depth between 174 and 295 cm, with 28 wt.% of the total S.

Observing the S depletion trend for the drill core according to Figure 12 (right), there would be three possible main deposition and oxidation periods where S is seen to have a significant stepwise increase in depth; the first being for the depth 296–483 cm, second 145–295 cm, and third 0–144 cm. Based on the alteration index of minerals and pH/EC in the tailings, the upper section—oxidized acidic zone (pH < 5.5)—showed that pyrrhotite was completely replaced by HFOs, calcite depleted, and...
occasional yellow rims around scheelite [17]. These trends also show possible mineralogical variations with regard to sulphur content over the production period of 1936 to 1963.

Table 4 summarizes the concentrations of the seven main elements in the 11 layers and the weighted averages in the drill core. The variations in the elemental concentrations and distributions at different depths would have an effect on the grades and recoveries of the concentrates that may be produced from the reprocessing of the HT. Consequently, process parameters would need to be varied depending on what depth the tailings are obtained. For instance, in order to recover much of the W and Cu, the tailings at deeper depths (below 174 cm) must be treated. Blending of tailings before reprocessing may also be necessary for process and product optimization.

Table 4. Elemental concentrations in the layers and the drill core as a whole.

<table>
<thead>
<tr>
<th>Sample</th>
<th>WO₃ (%)</th>
<th>Cu (mg/kg)</th>
<th>S (%)</th>
<th>Sn (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Be (mg/kg)</th>
<th>Bi (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1_2-1</td>
<td>0.14</td>
<td>1024</td>
<td>1.54</td>
<td>554</td>
<td>311</td>
<td>267</td>
<td>454</td>
</tr>
<tr>
<td>Layer 1_2-2</td>
<td>0.22</td>
<td>1058</td>
<td>1.85</td>
<td>560</td>
<td>313</td>
<td>289</td>
<td>460</td>
</tr>
<tr>
<td>Layer 1_2-3</td>
<td>0.13</td>
<td>982</td>
<td>0.79</td>
<td>516</td>
<td>333</td>
<td>278</td>
<td>342</td>
</tr>
<tr>
<td>Layer 1_2-4</td>
<td>0.13</td>
<td>980</td>
<td>1.28</td>
<td>569</td>
<td>300</td>
<td>254</td>
<td>311</td>
</tr>
<tr>
<td>Layer 1_2-5</td>
<td>0.17</td>
<td>1060</td>
<td>1.25</td>
<td>590</td>
<td>305</td>
<td>249</td>
<td>298</td>
</tr>
<tr>
<td>Layer 1_2-6</td>
<td>0.16</td>
<td>777</td>
<td>0.72</td>
<td>709</td>
<td>309</td>
<td>239</td>
<td>286</td>
</tr>
<tr>
<td>Layer 1_2-7</td>
<td>0.13</td>
<td>1020</td>
<td>1.03</td>
<td>611</td>
<td>303</td>
<td>253</td>
<td>302</td>
</tr>
<tr>
<td>Layer 1_2-8</td>
<td>0.11</td>
<td>1147</td>
<td>1.81</td>
<td>528</td>
<td>313</td>
<td>237</td>
<td>418</td>
</tr>
<tr>
<td>Layer 1_2-9</td>
<td>0.07</td>
<td>910</td>
<td>1.17</td>
<td>600</td>
<td>102</td>
<td>204</td>
<td>454</td>
</tr>
<tr>
<td>Layer 1_2-10</td>
<td>0.11</td>
<td>1020</td>
<td>1.24</td>
<td>562</td>
<td>326</td>
<td>239</td>
<td>439</td>
</tr>
<tr>
<td>Layer 1_2-11</td>
<td>0.06</td>
<td>469</td>
<td>0.35</td>
<td>150</td>
<td>89</td>
<td>63.2</td>
<td>202</td>
</tr>
<tr>
<td>Drill core 1_2</td>
<td>0.12</td>
<td>981</td>
<td>1.33</td>
<td>558</td>
<td>251</td>
<td>241</td>
<td>390</td>
</tr>
</tbody>
</table>

Under the optical microscope, scheelite particles were observed in normal light and with a blue filter (Figure 13). The scheelite particles in the polished samples were both fine and coarse, as well as liberated and non-liberated, meaning that mineral liberation analysis would be essential in order to develop effective separation methods. Some particles showed rims, which were identified as hydrous ferric oxides [20]; hence, the recovery of such scheelite mineral particles may be hindered in processes like flotation where reagents need to have contact with the mineral particle, and also in magnetic separation where scheelite would end up being pulled to the paramagnetic fraction. Hence, pre-treatment methods such as scrubbing may be required. The main minerals in which the main elements W, Cu, S, Sn, Zn, Be, Bi, and F were contained were scheelite, chalcopyrite, pyrrhotite, cassiterite, danalite (both Zn and Be), bismuthinite, and fluorspar, respectively [20,24]
would enhance the separation of minerals like scheelite and chalcopyrite from pyrrhotite, which is the weakly-to-strongly magnetic. Magnetite, a ferromagnetic mineral, is also present, and as such, LIMS and HIMS were also considered as plausible processing methods. The magnetic separation where scheelite would end up being pulled to the paramagnetic fraction. Hence, pre-

3.2. Processing Properties

The Yxsjöberg tailings are fine particles (−600 to +38 µm) with high-density valuable minerals such as scheelite (6.01 g/cm$^3$) and bismuthinite (7 g/cm$^3$), and low-density gangue minerals such as quartz (2.62 g/cm$^3$) and calcite (2.71 g/cm$^3$) [25]. Therefore, enhanced gravity separation where a centrifugal force is applied to enhance the differential settling velocities between heavy and light particles (−80,000 to +10 µm) would be appropriate for these HT; thus, a Knelson concentrator was used [19]. The tailings have a high sulphur concentration, and the sulphur occurs mainly in pyrrhotite, which is weakly-to-strongly magnetic. Magnetite, a ferromagnetic mineral, is also present, and as such, LIMS and HIMS were also considered as plausible processing methods. The magnetic separation would enhance the separation of minerals like scheelite and chalcopyrite from pyrrhotite, which is the main Fe–sulphide mineral in the tailings responsible for AMD [20].

3.2.1. Magnetic Separation Tests

The two samples from layers 1_2-4 and 1_2-8 were used separately in magnetic separation tests. The three products from the magnetic separation, namely, ferromagnetic, paramagnetic, and non-magnetic fractions, had significant visual (color) differences, with the non-magnetic fraction dominated by the orange-, brown-, and white-colored minerals. Based on the knowledge of minerals known to be present in the samples and using EMC, the light-colored minerals in the non-magnetic fraction were identified to be mainly albite, fluorspar, calcite, scheelite, and biotite.

The desired outcome of the magnetic separation test was to have the valuable minerals (scheelite, fluorspar, and chalcopyrite) in the non-magnetic fraction of the HIMS, but the mass recovery to this fraction for both samples was very low, with the highest amount being only 9.2 wt.% from layer 1_2-8.
From Figure 14 and Table 5, it is observed that much of the W and Cu ended up in the paramagnetic fraction for both layers; meaning the separation of scheelite and chalcopyrite was not achieved as desired. This could be due to the insufficient liberation of scheelite and chalcopyrite minerals from pyrrhotite and/or to liberated small particles being entrapped and entrained by the paramagnetic particles. The insufficient liberation of scheelite was confirmed by the higher W recovery of 83.6 wt.% in the paramagnetic fraction, from the less coarse layer 1_2-8 which had more W retained in the −600 to +297 µm fraction as compared to layer 1_2-4. The paramagnetic fraction had the highest mass recoveries with 87.3 wt.% for layer 1_2-4 and 85.8 wt.% for layer 1_2-8, and based on EMC, approximately 40 wt.% and 30 wt.% of pyrrhotite was in this fraction, respectively, indicating that a high amount of pyrrhotite was ferromagnetic. Sulphur was mostly recovered in the ferromagnetic and paramagnetic fractions with only 1.0 wt.% in the non-magnetic fraction of layer 1_2-8, meaning that pyrrhotite, the main Fe–sulphide mineral in the tailings and responsible for AMD, was retained in the paramagnetic fraction, from the less coarse layer 1_2-8 which had more W retained in the −600 to +297 µm fraction as compared to layer 1_2-4. The paramagnetic fraction had the highest mass recoveries with 87.3 wt.% for layer 1_2-4 and 85.8 wt.% for layer 1_2-8, and based on EMC, approximately 40 wt.% and 30 wt.% of pyrrhotite was in this fraction, respectively, indicating that a high amount of pyrrhotite was ferromagnetic. Sulphur was mostly recovered in the ferromagnetic and paramagnetic fractions with only 1.0 wt.% in the non-magnetic fraction of layer 1_2-8, meaning that pyrrhotite, the main Fe–sulphide mineral in the tailings and responsible for AMD, was retained in the desired magnetic fractions of the LIMS and HIMS. For both layers, the mass recovered by the LIMS was very low, with the highest amount being only 5.0 wt.% from layer 1_2-8. This could indicate a low amount of the ferromagnetic mineral magnetite in the tailings. But considering the high recovery of Fe₂O₃ in the paramagnetic fraction, it could also mean that a larger amount of magnetite was locked up with pyrrhotite and/or other non-paramagnetic minerals, such as cassiterite, danalite, bismuthinite, fluorspar, calcite, and quartz.

Assessing the particle sizes in the products in relation to what was in the feed, it was observed that 97 wt.% of the −600 to +297 µm particles, being the most abundant in these HT, were distributed to the paramagnetic fraction (Figure 15). This confirms that the minerals of interest, like scheelite, need to be further liberated from this particle size fraction in order to improve mineral separation by magnetic separation.
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### 3.2.2. Gravity Separation Tests

The two layers (1_2-1 and 1_2-8) of drill core 1_2 were individually used for gravity separation tests with the Knelson concentrator, with two separation cycles for each sample. For comparison in metallurgical performance, these samples were quite similar in terms of mass distribution in the core, but slightly different in chemical composition, grain size, and exposure to weathering. The recovery of scheelite in each cycle product was assessed by the amount of W (Figure 16). It was observed that recovery of W in the concentrates was decreasing with an increasing number of separation cycles, with the highest recovery being 60.6 wt.% in concentrate 1 of layer 1_2-1. The decrease in W recovery with increasing number of separation cycles was due to the decreasing amount of dense and coarse particles that contain W. In this regard, comparison between the two layers showed a higher W recovery in concentrate 1 for layer 1_2-1, which was coarser with higher W content than layer 1_2-8. This can be seen in the products mass balance calculations given in Table 6.

![Figure 15](image1.png)

**Figure 15.** Magnetic separation products distribution over particle size ranges.

**Figure 16.** Gravity separation (Knelson concentrator) elemental and mass recoveries.

Even though the recovery of scheelite was significantly favorable with this enhanced gravity separation, it is important to look at the selectivity, i.e., its separation from the other minerals. From Figure 16, it is observed that in both samples, other than W, at least 30 wt.% of each main element was also recovered to the concentrate fraction. This means that quartz (2.62 g/cm$^3$), fluorspar (3.13 g/cm$^3$), calcite (2.71 g/cm$^3$), chalcopyrite (4.19 g/cm$^3$), pyrrhotite (4.61 g/cm$^3$), and danalite (3.43 g/cm$^3$) were not fully separated from scheelite, despite having much lower mineral densities than scheelite (6.01 g/cm$^3$). Considering the coarseness of the particles in these samples, the insufficient mineral separation would
be attributed to the insufficient liberation of the mineral particles. With regard to the tailing fraction, W distribution was considerably high at 32.7 wt.% in layer 1_2-8, which is an indication of relatively high scheelite distribution into the fine fractions. The scheelite particles may be liberated in the fine fractions but would still end up in the tailings because of the preferential concentration of coarser particles due to their combined effect of size and density, which are important in enhanced gravity separation.

Table 6. Products mass balance for gravity concentration products using Knelson concentrator.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight (gram)</th>
<th>Assays (mg/kg)</th>
<th>Contents (g)</th>
<th>Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_2-1 Concentrate 1</td>
<td>88.88</td>
<td>17.05</td>
<td>4190</td>
<td>0.37</td>
</tr>
<tr>
<td>1_2-1 Concentrate 2</td>
<td>87.71</td>
<td>16.82</td>
<td>992</td>
<td>0.09</td>
</tr>
<tr>
<td>1_2-1 Tailings</td>
<td>344.83</td>
<td>66.13</td>
<td>449</td>
<td>0.15</td>
</tr>
<tr>
<td>1_2-1_Actual Feed (−600 μm)</td>
<td>521.42</td>
<td>100.00</td>
<td>1178</td>
<td>0.61</td>
</tr>
<tr>
<td>1_2-8 Concentrate 1</td>
<td>92.56</td>
<td>18.53</td>
<td>1950</td>
<td>0.18</td>
</tr>
<tr>
<td>1_2-8 Concentrate 2</td>
<td>95.61</td>
<td>19.14</td>
<td>813</td>
<td>0.08</td>
</tr>
<tr>
<td>1_2-8 Tailings</td>
<td>311.47</td>
<td>62.34</td>
<td>402</td>
<td>0.13</td>
</tr>
<tr>
<td>1_2-8_Actual Feed (−600 μm)</td>
<td>499.64</td>
<td>100.00</td>
<td>767</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Using products distribution in various particle sizes to further assess the concentration process (Figure 17), it was confirmed that the dense coarser (−600 to +297 μm) particles were distributed more to concentrate 1 than 2, while the dense finer (<75 μm) particles were higher in concentrate 2 than 1. Therefore, in order to minimize W losses in the fines to the tailing fraction, the particle size range of the feed material to the Knelson concentrator must be narrow; otherwise, many concentration cycles would be needed to optimize the recovery. In this initial metallurgical test work, the feed particle size range was −600 to +38 μm; however, for subsequent tests, division of this size range into narrower ones such as −600 to +297 μm, −297 to +149 μm, −149 to +75 μm, and −75 to +38 μm should be considered in order to improve the recovery and separation efficiency [19].

Figure 17. Knelson concentrator products distribution over particle size ranges.

3.2.3. Proposed Process Flowsheet

Based on the preliminary results of the physical and chemical characterization, as well as processing tests, a process flowsheet is proposed (Figure 18). Given the high deportment of mass and economic
elements into the coarser particle size fractions (~600 to +149 µm), classification to separate the coarser tailings from the finer ones would be the first step. The threshold for such a classification should be <75 µm because, from optical microscopy and SEM observations, scheelite particles in this size fraction are liberated. Also, during gravity separation, much of the <75 µm ended up in the tailing product; hence, there is a need for prior separation. Basically, scheelite recovery from this particle size fraction would be best through froth flotation [26]. For the tailing fraction >75 µm, the issue of mineral liberation is evident; hence, regrinding will be required. However, more studies need to be done to determine the optimal mineral liberation size for scheelite in the tailings so that generation of ultrafine particles is minimized. With sufficient mineral liberation, having magnetic separation before gravity separation enhances the separation of magnetite (in addition to pyrrhotite) from scheelite; magnetite density (5.15 g/cm³) is close to that of scheelite (6.01 g/cm³) [25]; hence, their separation with gravity method may not be efficient. Therefore, gravity separation would be applied to the non-magnetic product of magnetic separation.

**Figure 18.** Preliminary process flowsheet proposed for separation of valuable minerals from the Yxsjöberg historical tailings (HT).

### 3.3. Proposed Methodology for HT Reprocessing

Based on the preliminary study presented in this paper and future work foresight, a methodology for reprocessing the Yxsjöberg HT is proposed (Figure 19). The methodology is divided into three main steps, namely, TSF characterization, metallurgical test work, and process design and analysis. Each of these steps has defined tasks, which represent sub-steps and methods to be undertaken in each step, e.g., characterization of tailings is a sub-step in the TSF characterization category, but it also has sub-steps
and methods as shown in Figure 4. The methodology is preliminary because, with further investigations on the tailings, sub-steps that are more specific may be added to the three methodology steps.

Figure 19. Preliminary methodology proposed for the reprocessing of Yxsjöberg HT.

4. Conclusions

In this study, a preliminary process flowsheet and a methodology for reprocessing the historical tailings from the historical Yxsjöberg tungsten mine has been proposed. The following are the main findings and conclusions:

- The tailings in the repository are vertically stratified, with layers having significant variation in particle size distribution and composition. The variation reflects variation in initial processing parameters (e.g., milling) and/or in mineralogy of the original run-of-mine ore. The chemical composition is high in the coarser particle size fraction range \( -600 \) to \( +149 \) \( \mu m \). With regard to texture and liberation, scheelite particles are both fine- and coarse-grained, liberated and non-liberated, meaning that mineral liberation analysis will be essential in the development of effective separation methods.

- \( W, \) \( Cu, \) \( S, \) \( Sn, \) \( Zn, \) \( Be, \) \( Bi, \) and \( F \) are hosted mainly in scheelite, chalcopyrite, pyrrhotite, cassiterite, danalite (both \( Zn \) and \( Be \)), bismuthinite, and fluor spar, respectively. \( W \) and \( Cu \) are the metals of interest, and their highest concentrations are 0.22 wt.% \( WO_3 \) and 0.11 wt.% \( Cu \), and averages are 0.12% and 0.1%, respectively.

- Sulphur was mostly recovered in the ferromagnetic and paramagnetic fractions, with only 1.0 wt.% in the non-magnetic fraction, meaning pyrrhotite, the main Fe–sulphide mineral in the HT responsible for AMD, separated to the desired magnetic fractions of the LIMS and HIMS.

- The recovery of scheelite was significantly favorable with enhanced gravity separation using the Knelson concentrator, with the highest \( W \) recovery of 60.6 wt.%.

5. Future Work

Since these characterization and processing findings only represent one location in the TSF, further geometallurgical studies are planned for samples from different locations, so that geometallurgical
units can be defined within the entire TSF. Additionally, quantitative mineralogical studies of the processing products are required in order to ascertain that minerals of economic interest and minerals of environmental concern in the tailings are separated as desired. The proposed process flowsheet will require further refinement as the processes become more defined and optimized, for instance, the sequence of minerals to be floated, and additional classification after comminution.


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Article

Recovery of fine scheelite from Yxsjöberg historical tungsten ore tailings

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Abstract: The recovery of scheelite from secondary sources like historical tailings using froth flotation is quite challenging. This is because the chemical weathering in the historical tailings affects the metallurgical performance of flotation. In this study, the possibility of recovering fine scheelite from Yxsjöberg historical tailings by flotation was investigated using different collectors (Sodium Oleate (NaOl) and two new collectors: Berol 8313 and Atrac 2600). Mineral Liberation Analysis (MLA) for tailings characterization showed that 71% of scheelite particles were fully liberated below 75 µm. The criteria of comparing mass recovery, WO3 grade and recovery, and selective separation of scheelite were used to assess collector performance. Atrac 2600 at 400 g/t dosage gave favorable results with the highest rougher concentrate WO3 grade (1.13%) with 3.9 enrichment ratio, WO3 recovery (57.4%), and a higher scheelite selectivity against other Ca-bearing minerals. The variations in the metallurgical performance of the different tailings samples revealed that at least two geometallurgical areas were present.

Keywords: Scheelite; Ca-bearing minerals; Characterization; Liberation; Collector; Depressant; Selectivity; Grade; Recovery

1. Introduction

The mining industry has a critical role to play in the achievement of Sustainable Development Goal (SDG) 12 ("ensure sustainable consumption and production patterns") because it is a huge consumer of natural resources especially mineral resources, and generates one of the largest waste streams (mine wastes) in the world [1,2]. Mine wastes tend to have high concentrations of elements and compounds that may cause severe environmental impacts. Hence, there is a need for the mining industry to keep improving its extraction processes to enhance resource efficiency and reduce the generation of such harmful waste. With the increased demand for metals like tungsten, which is among the European Union (EU) critical raw materials (CRMs), mine wastes such as historical tailings are being explored as a measure to decrease both the supply risk and the amount of harmful residues [3–5]. This measure entails developing effective methods for separating valuable minerals, extracting metals of interest from historical tailings, and leaving a stable and environmentally safe residue.

For tungsten, its recovery is primarily from scheelite and wolframite mineral ores with 0.08-1.5% tungsten trioxide (WO3) grade, commonly found in complex skarn deposits [6]. Gravity separation (high grade and coarse particles) and froth flotation (low grade and fine particles) have been typical beneficiation techniques for recovering tungsten minerals. Scheelite flotation is challenging due to complex Ca-bearing gangue associated minerals (mainly fluorite and calcite) that show similar surface properties as scheelite [7,8]. This challenge in scheelite flotation has led to continued research in this area. However, most scheelite flotation studies have been done using pure
materials with particle size <74 µm, and a variety of collectors and depressants (Table 1), and there is approximately no investigation on the flotation of tailings.

Table 1. Scheelite flotation conditions in various studies.

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle Size</th>
<th>Collector</th>
<th>Depressant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure scheelite and calcite</td>
<td>-74+37 µm</td>
<td>Dodecylamine (DDA) + NaOl</td>
<td>Acidified Water Glass (AWG)</td>
<td>[9]</td>
</tr>
<tr>
<td>Pure scheelite crystals and calcite</td>
<td>-74+37 µm</td>
<td>Octyl hydroxamic acid (HXMA-8) + NaOl</td>
<td>Sodium Silica (SS)</td>
<td>[10]</td>
</tr>
<tr>
<td>Scheelite ore (0.38% WO₃)</td>
<td>-120+19 µm</td>
<td>Oleic acid</td>
<td>SS/Fe(II)</td>
<td>[11]</td>
</tr>
<tr>
<td>Scheelite and calcite mineral crystals</td>
<td>-74+38 µm</td>
<td>NaOl</td>
<td>Calcium lignosulphonate (CLS) SS</td>
<td>[12]</td>
</tr>
<tr>
<td>Pure calcite and scheelite</td>
<td>-74+38 µm</td>
<td>DDA + NaOl</td>
<td>SS</td>
<td>[13]</td>
</tr>
<tr>
<td>Pure scheelite and pure fluorite</td>
<td>-74 µm</td>
<td>Sodium soap of fatty acids formulated from oxidized paraffin (731)</td>
<td>Sodium polyacrylate (PA-Na)</td>
<td>[14]</td>
</tr>
<tr>
<td>Pure mineral crystals of scheelite, calcite, and fluorite</td>
<td>-74+38 µm</td>
<td>NaOl</td>
<td>Dextran sulfate sodium (DSS)</td>
<td>[15]</td>
</tr>
<tr>
<td>Pure scheelite and calcite</td>
<td>-74+38 µm</td>
<td>NaOl</td>
<td>Sodium humate</td>
<td>[16]</td>
</tr>
<tr>
<td>Pure calcite, scheelite, and fluorite</td>
<td>-74 µm</td>
<td>Benzohydroxamic acid (BHA) with Pb(NO₃)₂ as an activator</td>
<td>SS</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Earlier studies about the Yxsjöberg historical tungsten ore tailings from the Smaltjärnen repository, in the Bergslagen mining region of south-central Sweden, have shown that a substantial amount of tungsten (W) is contained in the fine (<75 µm) particle size fraction [18]. With the high-density scheelite (6.01 g/cm³) being the main W-bearing mineral in these tailings, gravity separation is an ideal separation method, however, this fine fraction still ends up in the tailings product [18]. Therefore, froth flotation would be appropriate to recover scheelite from this fine fraction [19]. Yxsjöberg tailings are from tungsten skarn ores that are known to be associated with complex Ca-bearing gangue minerals, which have similar surface properties as scheelite; thus, scheelite selectivity in froth flotation is critical [7]. For historical tailings, the material complexity is further enhanced by the formation of secondary minerals due to chemical weathering, which may also affect the metallurgical performance in froth flotation. In this regard, froth flotation for historical tungsten tailings is not only about scheelite selectivity but also knowing their metallurgical performance in the commonly used scheelite flotation reagents (fatty acids as collectors with sodium silicate as a depressant) for primary ores.

In this study, the feasibility of recovering scheelite from Yxsjöberg historical tailings using froth flotation is investigated by comparing:

(i) Collector performance of NaOl (as a typical collector (Table 1)) with two new collectors (Berol 8313 and Atrac 2600);
(ii) Scheelite selectivity against other Ca-bearing minerals in the three collectors; and
(iii) Metallurgical performance of different tailings samples in the collector that shows favorable results.

2. Materials and Methods

2.1. Tailings characterization

Historical tailings samples for this study were taken from drill core samples collected from location 6 on the Smaltjärnen repository [20]. Compared to other locations studied on this repository, this selected location exhibited higher sulfur (S) concentration, which is of interest with regard to acid mine drainage (AMD), hence in addition to scheelite flotation, it is also important to observe how the S-bearing minerals like chalcopyrite perform in this process. The samples are thus denoted by 6 coupled with the letters A to F representing the different drill holes in that location, and the –1 being the uppermost layer in a drill core that is layered. The <75 µm particle size fraction was separated from each of the eight tailings samples (6-1, 6A-1, 6A-2, 6B, 6C, 6D-1, 6E-1 and 6F-1), and split into 47.5 g sub-samples for froth flotation tests. The sub-samples’ weight was based on the 20% solid by weight and 190 mL solution volume selected to run the flotation tests with the amount of material available.

The tailings samples, including the flotation products, were chemically analyzed using the inductively coupled plasma–sector field mass spectrometry (ICP–SFMS) method. Prior to conducting froth flotation tests, all the eight tailings samples were chemically analyzed and compared to assess their chemical variability (Figure 1). The average concentrations of W, CaO, and S were 2220 ppm, 15.3%, and 3.9%, respectively.

For mineralogical analysis, Mineral Liberation Analysis (MLA) was conducted on sample 6F-1 using the Scanning Electron Microscope equipped with the MLA 3.1.3.612 software suite from FEI (SEM – FEI Quanta 650 MLA-FEG: FEI Company, Hillsboro, OR, USA) before the flotation tests. Based on MLA outcomes, scheelite was the main W-bearing mineral at 0.35 wt.% distribution in the <75 µm size fraction, while wolframite was only 0.03 wt.%. Fluorine, a hazardous element, was mostly (99.67%) in the critical mineral fluorite, which was 3.45 wt.% in the sample. The most abundant S-bearing mineral was Fe sulfate (8.50 wt.%), which is a secondary mineral resulting from the weathering of sulfide minerals like pyrrhotite (3.40 wt.%) and chalcopyrite (0.22 wt.%). This shows that tailings particles in the <75 µm size fraction were susceptible to weathering, and with Fe sulfate forming on the mineral surfaces of chalcopyrite and pyrrhotite, it would have an adverse effect on the flotation of these sulfide minerals if they were the target minerals in the flotation (Figure 2, Table 2).
Figure 1. Elements of high concentration in the <75 µm size fraction of the eight tailings samples.

Figure 2. MLA particle images of the Yxsjöberg historical tungsten tailings showing how grains of minerals of interest in the <75 µm particle size fraction are associated.

Table 2. Mineral degree of liberation by free surface in particle size fraction <75 µm.

<table>
<thead>
<tr>
<th>20% Liberation classes</th>
<th>Scheelite</th>
<th>Wolframite</th>
<th>Fluorite</th>
<th>Chalcopyrite</th>
<th>Pyrrhotite</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% (not exposed)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>0% &lt; x ≤ 20%</td>
<td>1.1</td>
<td>1.8</td>
<td>0.9</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>20% &lt; x ≤ 40%</td>
<td>5.0</td>
<td>5.9</td>
<td>2.6</td>
<td>8.9</td>
<td>14.4</td>
</tr>
<tr>
<td>40% &lt; x ≤ 60%</td>
<td>10.6</td>
<td>11.1</td>
<td>5.2</td>
<td>12.0</td>
<td>18.8</td>
</tr>
<tr>
<td>60% &lt; x ≤ 80%</td>
<td>7.5</td>
<td>0.0</td>
<td>5.7</td>
<td>16.0</td>
<td>14.7</td>
</tr>
<tr>
<td>80% &lt; x &lt; 100%</td>
<td>5.1</td>
<td>0.0</td>
<td>2.2</td>
<td>7.4</td>
<td>3.0</td>
</tr>
<tr>
<td>100%</td>
<td>70.7</td>
<td>81.1</td>
<td>83.4</td>
<td>53.5</td>
<td>41.1</td>
</tr>
</tbody>
</table>
2.2. Flotation conditions

For flotation experiments to test collector performance, two tailings samples (6-1 and 6F-1) were used while the other six samples (6A-1, 6A-2, 6B, 6C, 6D-1 and 6E-1) were used to compare the metallurgical performance of the different tailings samples in the collector with favorable results. A batch mini-flotation device called Clausthal flotation cell was used and the flotation test protocol is summarized in Figure 3. Collectors NaOl, Berol 8313 (a formulation containing fatty acid and nonionics), and Atrac 2600 (a synthetic anionic collector with different active components), with sodium silicate (SS) as the depressant, were used as flotation reagents [21,22]. Berol 8313 and Atrac 2600 are produced by Nouryon. Berol 8313 has been developed for the direct flotation of scheelite. It is suitable for the direct flotation of fluor spar, and it is a formulation for complex difficult to float ores and/or hard process water. Atrac 2600 is also indicated to have a key benefit of improved selectivity for the same minerals [23]. For pH regulation, 1.0 M HCl (hydrochloric acid) and 1.0 M NaOH (sodium hydroxide) were used. Specifications for flotation parameters, reagents and dosages are given in Table 3. Reagent dosages (Table 3) were selected based on the literature [10,22].

![Figure 3. Simplified flotation test protocol.](image)

**Table 3. Summary of flotation parameters, reagents and dosages.**

<table>
<thead>
<tr>
<th>Air flow rate (mL/s)</th>
<th>Agitation speed (rpm)</th>
<th>Liquid volume (mL)</th>
<th>% Solids</th>
<th>Collector</th>
<th>Collector dosage</th>
<th>Depressant</th>
<th>Depressant dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6</td>
<td>265</td>
<td>190</td>
<td>20</td>
<td>NaOl</td>
<td>3 x 10^-4 mol/L</td>
<td>SS</td>
<td>300 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Berol 8313</td>
<td>100 g/t</td>
<td>SS</td>
<td>400 g/t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Atrac 2600</td>
<td>100 g/t</td>
<td>SS</td>
<td>400 g/t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400 g/t</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

Results of flotation tests indicated that the mass recovery of concentrate was higher in the presence of two new collectors (Berol 8313 and Atrac 2600) than the commonly used NaOl (Figure 4). With the highest collector dosage at 400 g/t, the mass recovery for Berol 8313 was only 3.3% higher than Atrac 2600; hence, the other criteria (concentrate WO₃ grade, recovery, and enrichment) were considered (Table 4 and Figure 4). Atrac 2600 gave the highest concentrate WO₃ grade (1.13%), WO₃ recovery (57.4%), and enrichment ratio (3.9).
Figure 4. Mass and elemental recoveries from tailings flotation using different collectors and dosages.

Table 4. Concentrate WO3 enrichment for different collectors and at varying dosages.

<table>
<thead>
<tr>
<th>Collector</th>
<th>NaOl 3×10⁻⁴ mol/L</th>
<th>Berol 8313 400 g/t</th>
<th>Berol 8313 100 g/t</th>
<th>Atrac 2600 400 g/t</th>
<th>Atrac 2600 100 g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed WO3 grade (%)</td>
<td>0.28</td>
<td>0.32</td>
<td>0.29</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>Concentrate WO3 grade (%)</td>
<td>0.03</td>
<td>0.80</td>
<td>0.12</td>
<td>1.13</td>
<td>0.95</td>
</tr>
<tr>
<td>Enrichment ratio</td>
<td>0.1</td>
<td>2.5</td>
<td>0.4</td>
<td>3.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Other elemental recoveries were also considered to assess their separation from W, with the desired outcome being as low recovery as possible. Cu and S, both of which are elements of economic importance but non-critical raw materials [3], were less recovered for Atrac 2600 meaning better separation from W than for Berol 8313 (Figure 4). The low S recovery also means that the main S-bearing minerals responsible for AMD, like pyrrhotite, would be separated to the tailings fraction as desired. Based on the MLA tailings characterization, the Fe sulfate observed on the mineral surfaces of chalcopyrite and pyrrhotite (Figure 2), and their low degree of liberation by free surface (Table 2), would hinder flotation of such particles even in sulfide flotation. Therefore, these mineral particles would be depressed to the tailings fraction; thus, the need to further characterize the residue from the reprocessing of such historical tailings, and assess the recycling potential such as being used as cement additives [24,25].

For scheelite flotation, having a lower recovery of other Ca-bearing minerals is essential, so CaO recovery was also assessed for both Berol 8313 and Atrac 2600 at 400 g/t dosage. Atrac 2600 still gave a more favorable result for CaO recovery (29.0%) than Berol 8313 (36.1%), meaning Atrac 2600 was more selective against other Ca-bearing minerals than Berol 8313. This observation about Berol 8313 and Atrac 2600 was consistent with the indicated key benefits [23,26]. Results show that at lower collector dosages of these two new collectors, scheelite selectivity was negligible. For NaOl, other Ca-bearing minerals, chalcopyrite and other S-bearing minerals were preferentially floated and higher than scheelite (Figure 4). These outcomes make NaOl the least favorable collector for this process.
Therefore, Atrac 2600 at 400 g/t dosage was selected as the preferred collector to be used for further scheelite flotation tests to evaluate the metallurgical performance of different core tailings samples (6-1, 6A-1, 6A-2, 6B, 6C, 6D-1 and 6E-1). The same criteria of comparing mass recovery, WO$_3$ grade and recovery, and other elemental recoveries were used (Figure 5). There was no significant difference in mass recovery in five (6A-2, 6B, 6C, 6D-1 and 6E-1) out of the seven samples. The five had a difference of only 1.5% between the highest and lowest mass recovery. As for the other two samples (6-1 and 6A-1) with much higher mass recoveries, there was a larger difference of 5.8% between them, but their concentrate WO$_3$ grades were only differing by 0.04%. Compared to the other five samples, 6-1 and 6A-1 concentrate WO$_3$ grades and recoveries were significantly higher, and the selectivity of WO$_3$ against CaO was evident.

Figure 5. Concentrate WO$_3$ grade (a), mass and elemental recoveries (b) from flotation of different tailings samples using Atrac 2600 at 400 g/t.

The other five samples had both WO$_3$ and CaO recoveries not exceeding 11%, with the CaO recoveries being slightly higher than the WO$_3$ recoveries. In addition, the concentrations of elements of interest (Cu, Bi, Fe, and S) that were contained in the main sulfide minerals (chalcopyrite, bismuthinite, and pyrrhotite) were higher than in samples 6-1 and 6A-1 (Table 5), meaning the sulfide minerals were preferentially concentrated than scheelite, which was undesirable. To reduce this preferential concentration of sulfide minerals and increase the efficiency of the collector for scheelite flotation, sulfide flotation should precede scheelite flotation, especially that chalcopyrite also shows good selectivity from scheelite and pyrrhotite in all the samples [22,27,28]. Additionally, the concentrate WO$_3$ grade and recovery in scheelite flotation of the historical tailings under study may be enhanced by having rougher, scavenger, and cleaner flotation stages as was done in the Yxsjöberg scheelite flotation process [27,28].

Table 5. Concentrate assays for elements of interest contained in the main sulfide minerals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (ppm)</th>
<th>Bi (ppm)</th>
<th>FeO$_3$ (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-1</td>
<td>1460</td>
<td>1300</td>
<td>21.00</td>
<td>1.89</td>
</tr>
<tr>
<td>6A-1</td>
<td>1794</td>
<td>1450</td>
<td>17.00</td>
<td>2.38</td>
</tr>
<tr>
<td>6A-2</td>
<td>2593</td>
<td>2534</td>
<td>27.77</td>
<td>7.47</td>
</tr>
<tr>
<td>6B</td>
<td>2622</td>
<td>2084</td>
<td>23.70</td>
<td>4.63</td>
</tr>
<tr>
<td>6C</td>
<td>2322</td>
<td>1903</td>
<td>21.19</td>
<td>4.77</td>
</tr>
<tr>
<td>6D-1</td>
<td>2421</td>
<td>1850</td>
<td>20.92</td>
<td>3.73</td>
</tr>
<tr>
<td>6E-1</td>
<td>2844</td>
<td>2228</td>
<td>24.04</td>
<td>4.96</td>
</tr>
</tbody>
</table>
The difference in metallurgical performance was not only for samples from different drill holes but also from the same drill hole with varying layers like samples 6A-1 (upper layer) and 6A-2 (bottom layer). Based on the test results of this study with Atrac 2600 at 400 g/t dosage, the weighted average rougher concentrate WO₃ grade for the geometallurgical area with samples 6-1, 6F-1 and 6A-1 would be 1.15% at 48.2% WO₃ recovery, while that with samples 6A-2, 6B, 6C, 6D-1 and 6E-1 would be 0.37% at 8.1% WO₃ recovery. Therefore, several enrichment stages would be required to attain the market-grade concentrate of between 15 to 75% WO₃ [6]. The difference in the metallurgical performance of these historical tailings samples with less favorable responses could be attributed to low scheelite liberation by free surface and/or having wolframite, which cannot be recovered by flotation [8,28]. Based on the tailings characterization using MLA (Figure 2), the non-liberated scheelite grains were mostly in binary tailings particles locked with wolframite and other Ca-bearing minerals like fluorite and garnet-andradite. Thus, selectivity would be hindered, as either the other Ca-bearing minerals would be floated together with scheelite to the concentrate, or scheelite would end up in the tails fractions with the depressed minerals. This is the most probable scenario for samples 6A-2, 6B, 6C, 6D-1 and 6E-1 because for the other samples on which MLA was conducted (6-1 and 6F-1), results show that fluorite had 83% of its grains totally liberated by free surface (Table 2), and the selectivity is evident in the recoveries of these samples. The dense and paramagnetic tungsten mineral wolframite also had a high percentage (81%) of its grains totally liberated, but due to having gravity and/or magnetic separation as the ideal beneficiation techniques [8], these grains are likely to end up in the tails when froth flotation is employed. If the WO₃ grade for samples 6A-2, 6B, 6C, 6D-1 and 6E-1 was mostly from wolframite, then that could be another reason for the varied WO₃ recoveries.

4. Conclusions

The feasibility of recovering scheelite from Yxsjöberg historical tailings using froth flotation was investigated, with the following as the main findings and conclusions:

- The new collectors Berol 8313 and Atrac 2600 performed better than the commonly used NaOl in mass recovery, WO₃ grade and recovery, and scheelite selectivity.
- Atrac 2600 at 400 g/t dosage gave more favorable results than Berol 8313. It gave the highest rougher concentrate WO₃ grade (1.13%) with 3.9 enrichment ratio, WO₃ recovery (57.4%), and a better scheelite selectivity against other Ca-bearing minerals.
- At least two geometallurgical areas were observed in the Smaltjärnen repository location where samples in this study were obtained; one area had a better metallurgical performance (rougner concentrate WO₃ grade of 1.15% at 48.2% WO₃ recovery) with Atrac 2600 at 400 g/t dosage than the other (rougner concentrate WO₃ grade of 0.37% at 8.1% WO₃ recovery).
- Sulfide flotation should precede scheelite flotation in order to reduce the preferential concentration of sulfide minerals and increase the efficiency of Atrac 2600 collector for scheelite flotation.


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**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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Paper IV
Mechanochemical treatment of historical tungsten tailings: leaching while grinding

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Abstract: Innovative tungsten (W) extraction techniques are continually being sought due to challenges of low leaching efficiencies despite using advanced processing units such as autoclaves operating high temperatures and pressures. Compared to conventional leaching, mechanochemical treatment improves the efficiency of leaching. Therefore, in this study, an innovative mechanochemical treatment method referred to as leaching while grinding (LWG) was employed as a reprocessing option to optimize W recovery from historical tungsten tailings. Experiments were run using the Regular Two-Level Factorial design to screen through the four factors stirrer speed, liquid/solid ratio, temperature, and digestion time, to assess their criticality and effects in the LWG process. The stirrer speed and the liquid/solid ratio were the most critical factors in the optimization of W recovery. The maximum W recovery (91.2%) was attained at the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature (60°C). The attained low leaching temperature (60°C) was due to the mechanical activation of scheelite resulting from the simultaneous grinding and leaching. For such low W grade material, liquid/solid ratio optimizing is critical for maintaining the digestion mixture fluidity, and for process environmental and economic sustainability regarding NaOH consumption, which was low.

Keywords: mechanical activation; scheelite; tailings; reprocessing; leaching; grinding

1. Introduction

Tungsten (W) is a critical raw material for the European Union [1], with scheelite (CaWO₄) and wolframite ((Fe,Mn)WO₄) being the most important tungsten ore minerals [2,3]. Over the years, different hydrometallurgical techniques have been used for W extraction from these ores, mostly from high-grade W concentrates, and synthetic concentrates (scraps) [2]. Different leaching reagents being either alkaline or acidic or a combination of the two applied at different stages of the leaching process, and reactors have been considered to enhance W extraction efficiency [4–6]. It was documented that mechanochemical treatment can improve the efficiency of leaching [7,8]. However, the mechanical activation (leaching while grinding-LWG) in the extractive metallurgy from primary or secondary resources has not been considered widely, and few applications are reported for the gold extraction [9–11]. Gold amalgamation (mill leaching) is an efficient practice in small mines [12]. For reducing the media and liner corrosion, mostly LWG is performed in alkaline conditions.

Zhao et al. [13] showed the advantages of hydroxide leaching of scheelite over carbonate processing usually done in autoclaves to include lower leaching temperature (150 to 170°C), and higher leaching solution concentration beneficial for the decomposition of W ores as sodium tungstate (Na₂WO₄) crystallizes earlier than the sodium hydroxide (NaOH). In this study, however, instead of using complex leaching reagents to deal with surface layers on scheelite particles and increase the leaching efficiency, LWG was used.
In this method, scheelite was mechanically activated and leached simultaneously in one reactor instead of conducting these steps sequentially in different reactors at varying operating conditions of temperature and pressure [7,8]. The mechanical activation of scheelite improves the leaching kinetics as its decomposition temperature is reduced, and the surface area is increased with reducing particle size resulting from grinding [7,8].

Therefore, in the current study, a concentrated NaOH solution was used to digest scheelite (equation (1) in historical tungsten tailings, which is a low W grade mining waste material, unlike the W ores or scheelite concentrates used in other studies [4,5,13–15].

\[
\text{CaWO}_4(s) + 2\text{NaOH(aq)} \leftrightarrow \text{Ca(OH)}_2(s) + \text{Na}_2\text{WO}_4(aq)
\]  

(1)

The tailings used in this study were also much coarser (>75 µm) than the scheelite concentrates used in other scheelite leaching studies; hence when selecting factors to optimize for the LWG process, factors that improve both scheelite leaching kinetics and grinding in a stirred media mill were considered [16,17]. The effects of leaching temperature, NaOH solution concentration, mineral particle size, liquid/solid ratio, and stirring speed are significant to the digestion of scheelite by NaOH, and the leaching rate [5,13,18]. These effects have been investigated in various studies using different statistical and graphical techniques [16,19], and in this study, this approach was also taken.

Indicative tests to compare conventional leaching to LWG at different temperatures were conducted on scheelite concentrate before the LWG test work in this study. W recovery was 4.8 times higher at 38°C, 1.8 times higher at 60°C, and 0.5 times lower at 80°C after six hours of leaching meaning that the grinding improved the leaching kinetics for the lower temperatures, but it had an adverse effect at a higher leaching temperature. This means that grinding had a higher influence on scheelite leaching than temperature. When scheelite is mechanically activated by grinding, its reactivity increases, causing it to be leached faster, thus forming soluble Na₂WO₄ rapidly, and in a short time, the solution becomes saturated, leading to the precipitation of Na₂WO₄ until all the scheelite has reacted [20].

Therefore, having characterized the historical tungsten tailings from the Smaltjärnen repository in Yxsjöberg, Sweden, and considered reprocessing options including magnetic separation, gravity separation and froth flotation [21,22], the LWG process employed in this current study was a more innovative method of reprocessing these historical tailings. With the simultaneous grinding of the tailings and leaching of scheelite, the comminution of the tailings particles would be further improved, scheelite mineral grains would be more liberated with increased surface area, and with the refreshing of surfaces, scheelite leaching would be enhanced.

The Regular Two-Level Factorial design for running experiments was picked to screen through the four factors stirrer speed, liquid/solid ratio, temperature, and digestion time, to assess their criticality and effects in the LWG process. The aim was to optimize the LWG process for W recovery from historical tungsten tailings.

2. Materials and Methods

2.1. Feed properties

The feed material was historical tungsten tailings samples collected from the Smaltjärnen repository in Yxsjöberg, Sweden [21]. In this study, 26 grams of tailings sample were used for each experimental run based on the ball-to-powder ratio (BPR) of 50 [17], with the particle size distribution of ~600 to +75 µm (Figure 1), and an average density of 3.35 g/cm³ determined using a He pycnometer. Chemical analysis was conducted using the inductively coupled plasma–sector field mass spectrometry (ICP–SFMS) method, while the bulk mineralogical phases in which the elements of high concentration were hosted were determined using X-ray diffraction (XRD). The feed material’s major elemental composition was CaO, Fe₂O₃ and SiO₂ at average concentra-
tions of 16.7%, 21.6% and 41.7%, respectively, while W (the element of interest in this study) was among the minor elements (Table 1).

![Cumulative particle size distribution](image)

**Figure 1.** Feed material (historical tungsten tailings) particle size distribution in three samples, showing similar distributions.

**Table 1.** Feed material minor elements of interest and their main host minerals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Average concentration (ppm)</th>
<th>Main mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>271</td>
<td>Danalite</td>
</tr>
<tr>
<td>Bi</td>
<td>363</td>
<td>Bismuthinite</td>
</tr>
<tr>
<td>Cu</td>
<td>988</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>S</td>
<td>14475</td>
<td>Pyrite, Pyrrhotite</td>
</tr>
<tr>
<td>Sn</td>
<td>564</td>
<td>Cassiterite</td>
</tr>
<tr>
<td>W</td>
<td>1125</td>
<td>Scheelite</td>
</tr>
<tr>
<td>Zn</td>
<td>263</td>
<td>Sphalerite</td>
</tr>
</tbody>
</table>

2.2. **Leaching procedure**

Leaching experiments were conducted in an insulated water-heated attritor mill with different parameters (Figure 2 and

![Leaching while grinding experimental setup](image)

**Figure 2.** Leaching while grinding experimental setup.

**Table 2.** Sodium hydroxide (NaOH) at 10 M, with an average pH of 13.56, was used to digest the tailings samples [18]. The liquid/solid ratio factor, temperature, digestion time, and stirrer speed were other factors investigated in this study to assess their effect on the W recovery from historical tailings in the LWG process. For the leaching procedure, experiments were designed using the Design-Expert® software (12.0.12.0, Stat-Ease, Min-
The Regular Two-Level Factorial Design was picked because of its effectiveness in “screening through many factors to find the critical few”, and the two-level full factorial was employed as it “permits estimation of all main effects and all interaction effects” [23].

Figure 2. Leaching while grinding experimental setup.

Table 2. Attritor mill and media parameters.

<table>
<thead>
<tr>
<th>Mill</th>
<th>Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (mL)</td>
<td>500</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.63</td>
</tr>
<tr>
<td>Stirrer speed (rpm)</td>
<td>205</td>
</tr>
<tr>
<td>Mass (g)</td>
<td>1285</td>
</tr>
<tr>
<td>Ball filling volume (mL)</td>
<td>350</td>
</tr>
<tr>
<td>Volume (cm³)</td>
<td>228</td>
</tr>
<tr>
<td>Ball size (mm)</td>
<td>–2.38 to +1.68</td>
</tr>
<tr>
<td>BPR</td>
<td>50</td>
</tr>
</tbody>
</table>

For factor level type, the stirrer speed was defined as ‘categoric’ because the attritor mill could only be run at two set speeds hence a range between the low and high level would not be available, as would the case for the other three factors defined as ‘numeric’ (Table 3). The digested tailings sample from each experimental run was then washed for 10 minutes in 300 mL NaOH leaching solution at 1 M concentration, which gives a higher Na₂WO₄ solubility [15]. The leachate was analyzed for W, including other metals and elements, using ICP–SFMS method, and W recovery was calculated.

Table 3. Experiment design factors and settings.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
<th>Units</th>
<th>Type</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Coded Low</th>
<th>Coded High</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Temperature</td>
<td>°C</td>
<td>Numeric</td>
<td>-1.0000</td>
<td>1.0000</td>
<td>-1 ↔ -1.00</td>
<td>+1 ↔ 1.00</td>
<td>0.0000</td>
<td>1.03</td>
</tr>
</tbody>
</table>
The experimental design involved 16 completely randomized runs (Table 4), with W recovery as the response. The real values for temperature, digestion time, and liquid/solid ratio coded low (-1) were 60°C, 4 hours, and 0.8, while coded high (+1) were 98°C, 6 hours, and 1.0, respectively. For the design post analysis, the best numerical optimization solution was picked to run two replicate verification tests; two tests were conducted using the tailings material. For the other two tests, scheelite concentrate with 66.2% WO₃ grade was used so that a comparison could be made to the indicative LWG tests that were conducted before the LWG tests in this study.

Table 4. Experiment design layout.

<table>
<thead>
<tr>
<th>Std</th>
<th>Run</th>
<th>A: Temperature °C</th>
<th>B: Digestion time hours</th>
<th>C: Liquid/solid ratio</th>
<th>D: Stirrer speed rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>410</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>205</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>205</td>
</tr>
<tr>
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<td>205</td>
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<td>1</td>
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<td>1</td>
<td>410</td>
</tr>
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<td>6</td>
<td>-1</td>
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<td>-1</td>
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</tr>
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<td>7</td>
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<td>-1</td>
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<td>10</td>
<td>12</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>410</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>205</td>
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<td>14</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>410</td>
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<td>410</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>205</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Factorial Design Analysis

3.1.1. Significant and insignificant factor effects

The concentration of W in the leachate was used to calculate the W recovery (main design response) from the tungsten tailings (Figure 3). The experiment design was evaluated on the reduced Two-Factor Interactions (2FI); the four main factors (A, B, C and D) and three 2FI (AB, AD and CD) terms were identified as significant factors which separated from the insignificant effects using the Half-Normal plot method (Figure 4). It was
observed that the stirrer speed (D), temperature (A) and digestion time (B) had positive effects meaning an increase in these main factors would increase the W recovery. The stirrer speed had the largest contribution of 58.5% because it relates to the particle size reduction, increases the surface area, and enhances the reactivity of scheelite [13,16]. It also enhances mass transfer in the highly viscous NaOH digestion solution and continuously removes the Ca(OH)₂ solid product layers that form on scheelite mineral particles as the accelerated rate-determining chemical reaction (equation (1) proceeds [5,9,14,15].

![Graph](image1)

**Figure 3.** Design responses from the 16 different experimental runs: (a) Leachate W grade (b) W recovery from historical tungsten tailings.

![Graph](image2)

**Figure 4.** The Half-Normal plot showing the selected significant factor effects.

Despite temperature and digestion time, also individually having a positive effect on W recovery, their interactions (AB) showed a negative effect, and this contribution was larger than that of the individual factors. Similarly, the AD factor interaction had a negative effect with an even larger contribution (13.1%) than the AB factor interaction; hence, it was important to observe these factor interactions for the optimizing model. With the mechanical activation of scheelite brought about by the grinding occurring simultaneously with the leaching in the LWG process in this study, one expected and
desired advantage was reduced leaching temperature which would then make the factor interactions AB and AD to have a positive effect on W recovery. Another advantage of the mechanical activation of scheelite is the shorter reaction time due to the increased rate of the forward reaction but if the digestion time goes beyond this reaction time, Na$_2$WO$_4$ saturation may occur and since its solubility is low in the 10 M NaOH digestion solution, crystallization would occur [5,7,15]. Therefore, having high temperature, which also increases the leaching rate, and high digestion time, results in the negative effect of the AB factor interaction on W recovery to the leachate. The recovery of W would be low because W would remain in the solute as solid Na$_2$WO$_4$ especially if the NaOH dilution in the subsequent washing stage is insufficient [2,18,20]. The digestion time encompassed time for both grinding the tailings particles, and NaOH digestion of scheelite hence a key factor in the mechanical activation of scheelite mineral grains, is the stirrer speed but with a very minimal effect and contribution to W recovery. Since the feed material used in this study was coarse with a very low W grade, the grinding also enhanced the liberation of scheelite mineral grains in the tailings particles.

The liquid/solid ratio (C) factor had the second highest effect and contribution to the W recovery but unlike the other three main factors, this factor had a negative effect on W recovery. This factor is especially critical for leaching scheelite from very low-grade material such as tailings because sufficient fluidity of the digestion mixture should be attained such that even after digesting for a while at a given temperature, the mixture does not solidify. For such low W grade material, sufficient fluidity is not be attainable using the NaOH stoichiometric ratio hence the NaOH is in excess, and the Na$_2$WO$_4$ crystallizes due to its limited solubility in such highly concentrated NaOH solution [5]. Therefore, the CD factor interaction equally has a negative effect unless an optimal liquid/solid ratio is employed.

3.1.2. Analysis of Variance (ANOVA)

Based on the above understanding of the selected effects, the model tested significant for the selected seven model terms using ANOVA, and the predictive model in coded terms was as follows:

$$W \text{ recovery} = 56.5595 + 2.78406 \times A + 1.68636 \times B - 7.56628 \times C + 14.5958 \times D - 3.81586 \times AB - 6.91214 \times AD - 2.81509 \times CD$$

(2)

The factor coefficients revealed the relative significance of the factors, with the stirrer speed (D) showing the highest impact on W recovery followed by the liquid/solid ratio (C) as was also observed in the analysis of the effects. The model showed a good fit as the R$^2$ adjusted and predicted values were in good agreement, with the difference less than 0.2 as recommended, and the model R$^2$ value being 0.964; hence the model was expected to provide good predictions for W recovery from historical tungsten tailings using the LWG process [24].

3.1.3. Optimization

An optimization criterion was determined for each factor and response, with the most important goal being that of the response W recovery to be maximized (Table 5).

<table>
<thead>
<tr>
<th>Name</th>
<th>Goal</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
<th>Lower Weight</th>
<th>Upper Weight</th>
<th>Importance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Temperature</td>
<td>is in range</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>B: Digestion time</td>
<td>is in range</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C: Liquid/solid</td>
<td>is in range</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>D: Stirrer speed</td>
<td>is in range</td>
<td>205</td>
<td>410</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>W recovery</td>
<td>maximize</td>
<td>26.611</td>
<td>91.182</td>
<td>10</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>
Solutions were given for the two combinations of categoric factor levels (205 and 410 rpm) of the stirrer speed, and the best solutions for each categoric factor level were considered by assessing the 3D response surfaces (Figure 5). It was observed that maximum W recovery at 91.2% was best achieved at the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature at 60°C (Figure 5a). This desired outcome confirmed the earlier analysis of the effect of the factors on W recovery that the mechanical activation of scheelite in the LWG process led to having a lower leaching temperature, with the leaching process conducted in a simpler and less expensive reactor compared to using pressurized reactors such as autoclaves, and higher leaching temperatures above 100°C [4,5,7,14,15,18]. With the low leaching temperature, the AB and AD factor interactions did not negatively affect the response (low W recovery) as the positive effects of the main factors B and D dominated.

![3D response surfaces](image)

**Figure 5.** The 3D response surfaces for the best optimization solution to maximize W recovery from historical tungsten tailings using the LWG process: (a) C = -1, D = 410 rpm, and (b) C = -1, D = 205 rpm.

The negative effects of the AB and AD factor interactions were evident in the solution (Figure 5b) that had the lowest stirrer speed (205 rpm), low liquid/solid ratio (0.8), shorter digestion time (4 hours), and high leaching temperature (96°C). Reducing both the stirrer speed and the digestion time to have high leaching temperature has a more negative effect on W recovery because the mechanical activation of scheelite is reduced. With the coarser tailings used in this study, particle size reduction, which is essential for increased scheelite reactivity [13,16] is less enhanced.

If the energy conservation factor was to be considered, other solutions on the 3D response surface in Figure 5a with digestion time less than 6 hours may be compared though the W recovery would be lower than 91.2%. Other factors that could also be considered for maximizing W recovery in this LWG process would be the dilution of NaOH solution in the washing stage as too much dilution favors the reverse reaction and the duration of washing [18]. Therefore, the solute characterization using XRD to determine in which phases the unleached W is found would be essential. If W is found in the Na2WO4 phase, then the dissolution issue would have to be investigated. If W is found in the CaWO4 phase, then it would be either that the scheelite digestion did not occur due to
unliberated scheelite grains in the coarse tailings particles, or the reverse reaction could have occurred during the washing stage due to over dilution of NaOH.

3.2. Design Post Analysis

The best numerical optimization recommended solution (highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature at 60°C) was used to conduct verification tests. For LWG using scheelite concentrate, the NaOH was not in excess as the 0.8 liquid/solid ratio was equivalent to the 1:2 CaWO₄/NaOH stoichiometric ratio; hence, the much lower W recovery. Therefore, for such high W grade material, optimizing the NaOH/WO₃ ratio would be more beneficial in improving W recovery [4,5,13,15,18]. The control experiment in which LWTG was employed proved that LWG was a better leaching process for the historical tungsten tailings under study as W recovery very low (5.5%).

![Mean verification results using factor settings of the best numerical optimization recommended solution.](image)

Figure 6. Mean verification results using factor settings of the best numerical optimization recommended solution.

4. Conclusions

This study aimed to analyze and optimize the LWG process for W recovery from historical tungsten tailings. Leaching tests were done with a stirred media mill at different conditions. Using the Regular Two-Level Factorial Design, the four factors, stirrer speed, liquid/solid ratio, temperature, and digestion time, were assessed for their criticality and effects in the LWG process. The following were the findings and conclusions:

- Compared to conventional leaching, the LWG in this study was more efficient and more sustainable especially that the amount NaOH used was much lower, and W recovery was much higher at a lower leaching temperature.
- The stirrer speed and the liquid/solid ratio were the most critical factors in the maximization of W recovery, with an increase in the stirrer speed having a positive effect while the liquid/solid ratio had a negative effect.
- The maximum W recovery (91.2%) was attained at the highest stirrer speed (410 rpm), low liquid/solid ratio (0.8), long digestion time (6 hours), and low leaching temperature (60°C).
- With the mechanical activation of scheelite resulting from the simultaneous grinding and leaching, a low leaching temperature (60°C) was attainable.
• For low W grade material, such as the historical tailings used in this study, optimizing the liquid/solid ratio is critical for maintaining substantial fluidity in the digestion mixture.
• For subsequent W recovery optimization, the dilution of NaOH solution in the washing stage and the duration of washing would be other factors to optimize.
• The energy conservation factor would be optimized by considering a slight reduction in the digestion time factor.


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Paper V
Geometallurgical study of historical tungsten tailings for reprocessing – The Yxsjöberg case

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ABSTRACT

The geometallurgical concept has mainly been applied to primary ore deposits, starting from ore characterization to the economic optimization of the mining operation. However, as primary ore resources are becoming depleted and lower in grade, alternative sources need to be explored and a question of adaptability of the geometallurgical approach to the secondary resource repositories arises.

The particle size distribution, chemical and mineralogical compositions of the Smaltjärnen historical tungsten tailings from physical separation in Yxsjöberg, Sweden were studied using drill core samples collected from different locations within the tailings repository in order to assess the amenability of the tailings to reprocessing. The tailings are dominated by the –600 to +149 µm particle size fraction. This fraction contains most of the elements of interest (W, Cu, S, Sn, Zn, Be, Bi and F) hosted by scheelite, chalcopyrite, pyrrhotite, cassiterite, danalite (both Zn and Be), bismuthinite and fluorite, respectively. The particle size distribution and mineralogical composition vary across the repository, suggesting a possible existence of geometallurgical domains, which require further assessment to evaluate metallurgical performance.

Keywords: Historical tailings, Tungsten, Scheelite, Geometallurgy, Characterization, Mineralogy, Reprocessing

1. Introduction

In-situ tonnage, grade and recovery estimation based on some metallurgical test work have been the traditional approach to evaluating primary ore deposits (Tayebi-Khorami et al., 2019). However, an understanding of ore properties relevant to successful processing requires a cross-disciplinary approach involving both geology and mineral processing (geometallurgy). This approach enhances resource knowledge from the processing perspective hence lowering operational risk related to ore deposit unknown variation (Lund and Lamberg, 2014). The geometallurgical approach also improves the prediction of mining waste (waste rock and tailings) composition hence appropriate waste management measures can be determined at the inception of the mining operation to attain improved environmental outcomes and circular economy aspirations (Tayebi-Khorami et al., 2019). The geometallurgical concept has mainly been used to characterize primary ores and optimize economic
performance of the mining operation. However, as primary ore resources are becoming depleted and lower in grade, alternative sources need to be explored and there is thus need for the application of geometallurgical approach to secondary ore resources.

A prefeasibility study of reprocessing historical tailings (HT) requires characterization and determination of the presence of geometallurgical domains within the tailings, using appropriate sampling (Lund and Lamberg, 2014). In this study, these steps are simplified and arranged by order of execution: (1) Sample selection, (2) Mineralogical/chemical/physical characterization, (3) Metallurgical test work, and (4) Domain definition (Lishchuk et al., 2020).

The structure and characteristics of a tailings repository is determined by a number of factors, including depositional environment, discharge (spigoting) point, the method of slurry entry into the impoundment, discharge rate, the density of the discharged slurry, particle size and mineralogical composition (Lottermoser, 2010). The visible effects of these factors is stratification including graded and cross bedding of the tailings. Coarser and heavier particles tend to settle near the discharge point while the finer and lighter particles settle further away. Therefore, if certain minerals occur in a particular particle size, they may segregate and accumulate in particular locations of the repository (Lottermoser, 2010). This is an important factor common with most HT repository.

Based on the depositional environment, HT repositories can be subdivided into different geometallurgical units/domains or ore types with similar set of textural and compositional properties and hence metallurgical performance (Lotter, 2011). Different geometallurgical and/or process mineralogical approaches have been used to reprocess tailings or process ores (Brough et al., 2013; Evans et al., 2011; Lotter et al., 2018, 2013; Tungpalan et al., 2015b; Whiteman et al., 2016).

A historical tailings repository may have several geometallurgical domains depending on type of primary ore, processing methods that generated the tailings, method of deposition of the tailings into the impoundments, and the weathering history of the tailings. This may result in tailings reprocessing flowsheets and metallurgical performances being different from those of primary ores from which the tailings were produced. Moreover, the amount of valuable minerals in HT depends mainly on the initial beneficiation methods employed and their processing efficiencies. Geometallurgical studies are thus essential in understanding the variability in the tailings repository and determining the feasibility of reprocessing the tailings (Tungpalan et al., 2015a; Whiteman et al., 2016). Using this integrated approach allows for a better understanding of characteristics and metallurgical performance of the tailings (Tungpalan et al., 2015a).

The above approach has been used in the ERA-MIN project REMinE (Improve Resource Efficiency and Minimize Environmental Footprint) dealing with historical mine wastes; Smaltjärnen historical tungsten ore tailings repository in Yxsjöberg, Sweden, the Cabeço do Pião tailings dam in Portugal (Figueiredo et al., 2018), and the Sasca Montana tailings management facility in Romania.
(Filcenco-Olteanu et al., 2017). The Yxsjöberg case has two tailings repositories namely Smaltjärnen and Morkulltjämen of which the former is the focus of this study.

Tungsten (W), copper (Cu), fluorine (F), sulphur (S), tin (Sn), zinc (Zn), beryllium (Be) and bismuth (Bi) are the elements of high concentration in the Smaltjärnen HT (Hällström et al., 2018), and are all among the EU critical raw materials with high economic importance and supply risk. Although four of these elements (Cu, S, Sn and Zn) are not classified as critical raw materials by the EU, they have high economic importance (Commission, 2017), emphasizing the importance of studying this HT ore repository. Preliminary mineralogical and geochemical studies of the tailings revealed that scheelite, chalcopyrite, fluorite, pyrrhotite, cassiterite, danalite and bismuthinite are the main minerals hosting W, Cu, F, S, Sn, Zn, Be and Bi, respectively, with Zn and Be both contained in danalite (Hällström et al., 2018).

The objective of this study is to investigate the amenability of the Smaltjärnen HT to reprocessing using the tailings storage facility (TSF) characterization in the proposed methodology (Mulenshi et al., 2019). The first two steps of the geometallurgical program: (1) Sample selection and (2) Mineralogical/chemical/physical characterization are applied to the Smaltjärnen TSF in order to define its structure in the selected locations and understand the effect of the depositional environment.

2. Materials and Methods

The steps and methods proposed for reprocessing the tailings are given in Fig.1. The methodology is divided into three main steps namely TSF characterization, metallurgical test work, and process design and analysis. Each of these steps has defined tasks, which may in turn have further sub-steps and associated tasks e.g. characterization of tailings is a task in the TSF characterization step. In this study, the focus is on TSF characterization and hence the tasks and methods involved in the first step will be expanded upon.

![Fig.1. Methodology proposed for the reprocessing of the Smaltjärnen HT (Mulenshi et al., 2019).](image-url)
2.1. The Yxsjöberg mine

One of the most important tungsten mining areas in northern Europe was Bergslagen in central Sweden where the Yxsjöberg historical tungsten ore tailings repositories (Smaltjärnen and Morkulltjämen) are located. The latter repository has tailings deposited from 1969 to 1989 (Höglund et al., 2004). The tailings in the Smaltjärnen repository were produced from the ore that was mined at the Yxsjö Mines, while it was in operation from 1935 to 1963, with the average ore grade of 0.3-0.4 wt.% WO$_3$, 0.2 wt.% Cu and 5-6 wt.% fluorite (Hübner, 1971; Rothelius, 1957). The exploited minerals were scheelite for W, chalcopyrite for Cu and Fluorite. The tailings repository is estimated to have about 2.2 million tons of tailings and covers an area of 26 hectares, with elemental concentrations of 1-2 wt.% S, 0.02-0.2 wt.% Cu, 0.02-0.3 wt.% W, 0.02-0.04 wt.% Sn and 0.02-0.03 wt.% Be (Höglund et al., 2004). The scheelite grain size in the ore was 0.2-4.0 mm and 90 wt.% of the ore was liberated at 0.4 mm particle size (Rothelius, 1957). The concentrate recoveries were 50-70 wt.% for scheelite, 50 wt.% for fluorite and 25 wt.% for chalcopyrite meaning that a considerable amount of these valuable minerals ended up in the tailings (Rothelius, 1957). The Yxsjö processing plant had three main sections namely gravity separation, magnetic separation, and flotation, from which tailings were generated and discharged onto the Smaltjärnen TSF (Fig.2).

**Fig.2.** Simplified flowsheet of the Yxsjö processing plant from which the HT were generated and then randomly discharged into the Smaltjärnen TSF. The aerial photo of the repository was taken in 1963 just before the processing plant stopped being in operation (Hübner, 1971; Rothelius, 1957; Survey, 1963).
2.2. Sampling and sample preparation

The Smaltjärnen TSF was sampled by collecting drill core samples from nine different locations as shown in Fig.3. The red dots represent the drill core sampling locations and the numbering of the sampling locations was based on the sequence of sampling in each sampling campaign. The first four locations were distinguished by _1 and _2 meaning 1_1 was in the first campaign while 1_2 was in the second campaign. In the first campaign, a Cobra hand drill was used with an open gauge steel tube (40 mm diameter and 1 m length) for sample holding. In the second campaign, a percussion drill rig from Envix Nord AB was used, which used plexiglass tubes (40 mm diameter and 1.2 m length each tube) for sample holding. The sample locations were selected based on visual (color and granulometry) variations of the tailings, and proximity to discharge points. Sample location 1_2 is close to sample location P4 referred to in the geochemical characterization of these historical tailings (Hällström et al., 2018).

In the Cabeço do Pião case of Portugal, a regular rectangular mesh grid sampling method was used to determine the sampling points (Figueiredo et al., 2019). However, in this study, the sampling points may be considered to have been randomly picked in the selected sampling locations (areas). A summary of information about the sampling locations is given in Table 1, with locations 1_1, 1_2 and 6 being the focus in this paper.

Each drill core was subdivided, vertically, into layers based on color and granulometry. This approach was taken in order to have a clear understanding of layers represented in each drill core. The layers represent variations in mineralogy and process parameters during the production.

![Fig.3. Drill core sampling locations on the Smaltjärnen TSF represented by red dots that are connected by white arrows for direction order of interpolated longitudinal section views. The yellow squares show two discharge points, and the yellow lines show the repository limit.](image-url)
Table 1. Information of sampling locations.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Sampling Points GPS Coordinates [DMS (degrees, minutes, seconds)]</th>
<th>Altitude with tailings (m)</th>
<th>Number of drill holes</th>
<th>Drill hole depth (m)</th>
<th>Number of drill cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_1</td>
<td>60°02'30.0&quot;N 14°46'15.7&quot;E</td>
<td>307</td>
<td>1</td>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
<td>2_1</td>
<td>60°02'24.7&quot;N 14°46'31.9&quot;E</td>
<td>309</td>
<td>1</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>1_2</td>
<td>60°02'30.4&quot;N 14°46'31.2&quot;E</td>
<td>306</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>2_2</td>
<td>60°02'26.9&quot;N 14°46'34.4&quot;E</td>
<td>314</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>60°02'31.9&quot;N 14°46'16.5&quot;E</td>
<td>291</td>
<td>1</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>60°02'26.8&quot;N 14°46'26.5&quot;E</td>
<td>305</td>
<td>1</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>60°02'24.2&quot;N 14°46'29.6&quot;E</td>
<td>305</td>
<td>2</td>
<td>4.8</td>
<td>8</td>
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<tr>
<td>6</td>
<td>60°02'33.6&quot;N 14°46'30.8&quot;E</td>
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<td>1</td>
<td>2.2</td>
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<tr>
<td>7</td>
<td>60°02'34.5&quot;N 14°46'29.7&quot;E</td>
<td>315</td>
<td>2</td>
<td>2.4</td>
<td>4</td>
</tr>
</tbody>
</table>

The thickness of each observed compacted layer was measured using a measuring tape, to have its approximate thickness in the tailings repository. The number of layers observed in sampling locations 1_1, 1_2 and 6 were 10, 11 and 3, respectively, with sampling location 1_2 having the longest drill core of approximately 5 meters. Based on the location of the two discharge points, observed southward flow of tailings into the Smaltjärnen Lake (Fig.3), and applying the altitude information (Table 1) to the drill cores vertical profiles, two interpolated longitudinal section views of the repository were constructed as shown in Fig.4. Each colour above the ‘Altitude without tailings’ represents a tailings layer in the repository and its compacted thickness.

Fig.4. Interpolated longitudinal section views of the repository shows the depositional environment and the tailings thickness variation on the TSF: Left – direction order 7, 6, 1_2, 2_2 and 2_1; Right – direction order 3, 1_1, 4 and 5.

From the depositional environment observed in the two longitudinal section views, the three locations used in this study provide a good representation of the deposit in discharge direction and orthogonal to that of tailings near discharge points (locations 1_1 and 6), and lower-level areas where larger volumes of tailings flow from surrounding higher-level areas and accumulate in several layers (location 1_2).
In order to further characterize the tailings samples physically (moisture content, texture and particle size distribution), chemically (elemental composition), and mineralogically, the samples were dried in air at 105 °C for 48 hours, with sample weighing done before and after drying for moisture content determination. The dried samples were then split into sub-samples using a riffle splitter. Replicate dry samples of approximately 150 grams each representing the tailings layers in a particular drill core were sieved using a RO-TAP® Sieve Shaker model RX-29 with five sieves to obtain six size fractions (>1190 μm, −1190 to +600 μm, −600 to +297 μm, −297 to +149 μm, −149 to +75 μm and <75 μm).

2.3. Characterization of drill core samples

In the TSF characterization step, characterization of drill core samples is an essential task done in a sequence of steps and methods (Fig.5).

![Diagram of characterization steps](image)

Fig.5. Drill core samples characterization sequence of steps and methods (Mulenshi et al., 2019).

3. Results and discussion

From the defined tasks of TSF characterization in Fig.1, it is observed that except for the sequential characterization of tailings, results from the other tasks are mostly in the ‘Materials and Methods’ section of this study. Therefore, in this section, the results of the sub-steps and associated tasks in the characterization of tailings as presented.

In order to appreciate the particle size variation in the three selected locations of the repository, the determined D_{80} values for the layers of the drill cores were plotted against the depth as shown in Fig.6 (left). It was observed that particles in drill core 1_1 are generally coarser than those in drill cores 1_2 and 6. Based on the principle of particles segregation and settling in the TSF, drill cores 1_1 and 6 were sampled near the spigotting points and hence they, generally, contain coarser particles than drill core 1_2, which is further away from both outlets, and at a lower altitude (Fig.3 and Fig.4) (Lottermoser, 2010).
The variation in particle size distribution across the tailings repository indicates the presence of geometallurgical domains, which may have different metallurgical performances (Lotter, 2011) as well as affect the choice of reprocessing methods. For instance, in location 1_1, further grinding may be required as the minerals of interest may be locked up in the coarse particles. PSD curves for the three drill cores were determined using all the layers in each drill core. In all drill cores the dominating particle size fractions were –600 to +300 µm and –300 to +149 µm as can be seen in Fig.6 (right). Drill cores 1_2 and 6 had more fines (–75 µm) than drill core 1_1. This variation in particle size is indicative of varying process parameters such as grinding size and/or changes in the mineralogy during the production period of 1936 to 1963.

Based on the chemical analysis, the main oxides were SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$ while W, Cu, S, Sn, Zn, Be and Bi were the main elements. The weighted average concentrations in each layer was calculated from the elemental concentrations in the particle size fractions, and subsequently for the entire drill core. Except for drill core 1_1, all elements were high in particle size fractions –600 to +297 µm and –297 to +149 µm. Therefore, for purposes of reprocessing these HT, mineral liberation analysis (MLA) needs to be carried out.

Elemental concentrations and mass distributions also vary with depth and across the repository (Fig.7). The highest WO$_3$ concentration was observed in drill core 1_1 as shown in Fig.7 (left). Sulphur depletion due to oxidation was expected in this TSF, with the depletion decreasing from top to bottom, due to the long storage period. However, besides oxidation, sulphur variations may also be attributed to mineralogical changes during production, and a detailed analysis of the sulphur depletion trend on location 1_2 is given in our earlier publication (Mulenshi et al., 2019). As was the case for WO$_3$, the highest S concentration was between 88 and 153 cm depth. These highest S concentrations were 1.89, 1.85 and 3.05 % in the drill cores 1_1, 1_2 and 6, respectively. Chemical composition variability in different locations of the Smaltjärnen TSF would have an effect on the concentrate
grades and recoveries. Subsequently, process and product optimization practices such as process parameter variation and blending of tailings before reprocessing would be necessary.

![Graph showing WO₃ concentrations and mass distributions in the three drill cores.](image)

**Fig. 7.** WO₃ concentrations (left) and mass distributions (right) in the three drill cores.

Table 2 summarizes the weighted average elemental concentrations in the three drill cores. Drill core 1_1 has higher concentrations of WO₃, Cu, Sn, Zn, Be and Bi than drill cores 1_2 and 6, and drill core 6 has the highest S concentration. Taking the average WO₃ and Cu concentration in these three tailings locations to be 0.15 % and 0.11 %, respectively, and applying them to the estimated 2.2 million tons of tailings in this repository gives approximately 3300 tons of WO₃ and 2512 tons of Cu.

**Table 2.** Weighted average elemental concentrations in the three drill cores.

<table>
<thead>
<tr>
<th>Samples</th>
<th>WO₃ (%)</th>
<th>Cu (ppm)</th>
<th>S (%)</th>
<th>Sn (ppm)</th>
<th>Zn (ppm)</th>
<th>Be (ppm)</th>
<th>Bi (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drill core 1_1</td>
<td>0.20</td>
<td>1418</td>
<td>1.32</td>
<td>602</td>
<td>319</td>
<td>282</td>
<td>538</td>
</tr>
<tr>
<td>Drill core 1_2</td>
<td>0.12</td>
<td>981</td>
<td>1.33</td>
<td>558</td>
<td>251</td>
<td>241</td>
<td>368</td>
</tr>
<tr>
<td>Drill core 6</td>
<td>0.13</td>
<td>1026</td>
<td>1.73</td>
<td>517</td>
<td>275</td>
<td>223</td>
<td>435</td>
</tr>
</tbody>
</table>

Using X-ray Diffraction (XRD), several mineral phases were identified in the four layers (1_2-1, 1_2-4, 1_2-8 and 1_2-9) of drill core 1_2. Pyrrhotite and calcite were not present in the upper layer of drill core 1_2 (layer 1_2-1) due to weathering. The acid produced by the oxidation of pyrrhotite was neutralized by calcite and hence the depletion of the two minerals in the surficial layer (Hällström et al., 2018). Based on optical microscopy, scheelite occurred as both fine and coarse mineral grains. Its grains in the tailings fine fraction (<75 um) were liberated whereas those in the coarse fraction were not. In the primary skarn ore, the fairly coarse-grained scheelite was associated with the pyroxene skarn characterized by xenomorphic hedenbergite (normally >200 µm) while the fine-grained scheelite was associated with the amphibole skarn mainly consisting of hornblende (Siirak et al., 1978).

Using SEM-EDS, more mineralogical studies were conducted on drill core layers 1_2-4 and 1_2-9. BSE images of samples showing mineral phases and analytical spots (spectra) are shown in Fig.8. Using element-to-mineral conversion (EMC) in HSC chemistry software and knowledge of minerals known to be present in the tailings, the minerals were identified based on the chemical composition of each spectrum. Other minerals identified include hedenbergite, albite, actinolite,
andradite, quartz, bismuthinite, chalcopyrite, magnetite, pyrite, pyrrhotite and sphalerite. The host minerals for elements of interest in the tailings (W, Cu, S, Sn, Zn, Be, Bi and F) are scheelite, chalcopyrite, pyrrhotite, cassiterite, danalite (both Zn and Be), bismuthinite and fluorite, respectively.

4. Conclusions

In this study, TSF characterization was investigated as a prerequisite to reprocessing of the Smaltjärnen HT. Using the two steps of the geometallurgical program (1) sample selection and (2) mineralogical/chemical/physical characterization, the structure of the Smaltjärnen TSF and effect of the depositional environment was determined. With the findings of this study, a re-mining plan for the repository is possible, and in the subsequent steps (metallurgical test work, and process design and analysis) of reprocessing the Smaltjärnen HT, informed decisions that would enhance process and product optimization can be made. The following are the findings and conclusions:

- The coarser particle size fraction (–600 to +149 μm) has the highest concentration and volume of most elements of interest. In this particle size range, scheelite was both fine and coarse grained, liberated and non-liberated, meaning that mineral liberation analysis would be essential for reprocessing of these tailings. This being a consistent observation in the locations under study shows a possible underlying processing issue in the Yxsjöberg beneficiation processes.

- In all locations, elements of interest in the tailings are W, Cu, S, Sn, Zn, Be, Bi and F, and they are contained mainly in scheelite, chalcopyrite, pyrrhotite, cassiterite, danalite (both Zn and Be), bismuthinite and fluorite, respectively. The average WO₃ and Cu concentrations in the sampled locations are 0.15 % and 0.11 %, respectively, and applying them to the estimated 2.2 million tons of tailings in this repository gives approximately 3300 tons of WO₃ and 2512 tons of Cu.

- In addition to possible processing issues and minor mineralogical changes during production,
the depositional environment leads to variations in particle size distribution and mineralogical composition across the repository. These variations are indications of the presence of possible geometallurgical domains within this repository and hence the need for subsequent metallurgical testing to assess the effect on metallurgical performances.

- Based on the above characterization results, beneficiation options for reprocessing the Smältjärnen historical ore tailings include froth flotation, magnetic separation and gravity separation as demonstrated in our earlier publication (Mulenshi et al., 2019).

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