Quantification of mineral weathering rates in sulfidic mine tailings under water-saturated conditions

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Abstract
Tailings are a fine-grained waste product produced during the metal recovery process. Tailings consist mostly of different silicates but also sulfides (e.g. pyrite), since 100 % metal recovery is not possible. Freshly processed tailings are deposited in large impoundments. If the mine tailings in the impoundments are exposed to water and oxygen, the sulfides will oxidize and release acidity and metals such as Fe, Cu, Zn, and Pb. The sulfide mineral oxidation reactions are catalyzed by sulfur and iron oxidizing bacteria (principally *Acidithiobacillus ferrooxidans*) that oxidize ferrous iron to ferric iron, which then oxidizes pyrite. When the leachate produced by this process discharges from the impoundment, it is called acid mine drainage, which may lead to the pollution of adjacent streams and lakes.

The intention with this thesis is to investigate and quantify mineral weathering processes and element release rates occurring in water-saturated and soil-covered sulfidic mine tailings. The study was performed in different batch and column experiments in room temperature and in the laboratory. The batch experiments were conducted for ca. three months and investigated: a) microbial and abiotic sulfide oxidation in freshly processed tailings under oxic conditions at pH 2-3 and pH 8, b) microbial oxidation of pure pyrite grains at pH 2-3 under different oxygen concentrations ranging from anoxic to oxic conditions. The column experiments, consisting of unoxidized tailings in water-saturated columns, were conducted for up to three years. In these experiments, an oxygen-saturated solution was continually pumped into the column inlet, and investigated: a) differences in oxidation rates between tailings of two different grain sizes, b) factors affecting element discharge rates, acid neutralization, and sulfide oxidation, c) the effect of ions released in a soil cover on release rates in the tailings.

Sulfide oxidation processes within the batch experiments were limited by surface kinetics. The microbial oxidation of pure pyrite at atmospheric conditions produced the most rapid rate, while the microbial oxidation of pure pyrite at anoxic conditions was slower by 1.8 orders of magnitude. Microbial and abiotic oxidation of pyrite in freshly-processed tailings resulted in pyrite oxidation rates that were intermediate between these two extremes. The results from the microbial experiments with pure pyrite indicated a positive correlation between the concentration of dissolved oxygen, ferric iron and bacterial cells (at a total cell concentration > 10^6 cells/mL and a dissolved oxygen concentration ≥ 13.2 µM), which implies an interdependence of these factors. The results from these batch experiments support the indirect mechanism for microbial oxidation by the ferric oxidation pathway. Pyrite oxidation rates estimated from the batch experiments may be comparable with oxidation rates in the unsaturated zone and at the groundwater table in a tailings impoundment.

Acid neutralization reactions in the column experiments resulted in the release of base cations to the column leachate. Calcite was the most important neutralizing mineral despite that it was only present in minor amounts in the tailings. It was confirmed that acidity forced the calcite dissolution. Element release rates in the column experiments were controlled by the availability of dissolved oxygen, which was a function of the water flow rate into the column. These column experiments also showed that the results are comparable with results from field studies, justifying the use of column experiments to study processes within tailings impoundments.
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List of papers appended to the thesis:


IV. Malmström, M.E., Gleisner, M. and Herbert, R.B., 2004. Element discharge from sulfidic mine tailings at limited oxygen availability. (manuscript)

V. Gleisner, M. and Herbert, R., 2004. Evaluation of the influence of soil cover leachate on weathering in sulfide-rich tailings. (manuscript)

I performed all the microbiological cultivations and inoculations, all the sampling in the laboratory, and also many of the analytical analyses (e.g. particle size distribution, pH, redox potential, spectrophotometry, AAS, TRS, XRD, ESEM-EDAX), while the rest of the analytical analyses (e.g. ICP, IC, BET, optical microscopy) were performed by accredited laboratories or by persons with much experience in using these methods. The geochemical modeling presented in this thesis was primarily performed by my co-authors. I am responsible for the design and maintenance of all the experiments, and for their sampling during the course of the experiments. The interpretations of most of the results were made in collaboration with my co-author(s).

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Magdalena Gleisner
1 INTRODUCTION

Sweden has a long mining history that extends for more than 1000 years into the past. Famous mines include the Falu Copper Mine, the Sala Silver Mine and the Bersbo Copper mine. Falu Copper Mine was already in operation during the 9th century, and it was the largest copper-producing mine in the world during the 17th and 18th century. Sala Silver Mine was operated from the 15th century until the 20th century, and was during the 19th century the largest copper producer in Sweden (Allard et al., 1991).

Today, the mines in the Boliden area, Aitik, Garpenberg and Kiruna are the leading metal producers in Sweden, and Sweden is the leading metal producer within EU. More than 40 million tons of ore were processed during 2003 (Boliden, 2004; SveMin 2004), and 20 million tons of ore were processed during the 9th century, and it was the largest silver producer in Sweden (Allard et al., 1991).

1.1 Environmental problems associated with mining activities

There are various environmental problems that may be associated with mining, such as surface water acidification and the discharge of heavy metals to surface and groundwater. These problems are due to the fact that mine waste often contains different sulfide minerals containing iron and heavy metals, where pyrite is the predominant sulfide mineral. Tailings (grain size < 1 mm) are highly reactive if sulfidic, since they have a much greater surface area and greater air accessibility compared to unmined ores. The tailings are generally mixed with process water and discharged as slurry in large tailings dams, and these deposits become complex hydrogeological environments where weathering reactions occur (Nordstrom and Alpers, 1999; Younger et al., 2002).

Pyrite and the other sulfide minerals within the tailings will oxidize upon exposure to water and atmospheric oxygen or ferric iron, and generate an acidic (generally pH 2-4) and toxic metal-rich leachate (see later sections for details). The sulfide mineral oxidation rates are faster in the upper zones of the waste deposits, where oxygen diffusion through the material is rapid, since this zone often is only partly water-saturated. In addition, sulfide oxidation reactions in mine wastes are usually catalyzed by bacterial activity, which further increase the release of reaction products in the leachate. Large amounts of mine waste may therefore result in leachate generation over long periods of time. When this acidic metal-rich leachate reaches rivers and lakes it can lead to serious water pollution problems known as Acid Mine Drainage (AMD). It is common that the bottoms of AMD-affected rivers and lakes are covered with precipitates of thick rust-colored crusts of iron (oxy)hydroxides, due to the high iron concentration present (Ash et al., 1951; Martin and Mills, 1976; Nordstrom and Alpers, 1999).

Many metals are essential for biota and organisms (e.g. Na, K, Mg, Ca, Fe, Co, Ni, Cu and Zn), while some metals are directly toxic (e.g. As, Pb, Cd and Cr). Some metals are toxic when present as a free cation (e.g. Cu\(^{2+}\)), while less toxic or non-toxic when present as organocomplexes. Toxic metals are easily transported into the organisms by the nutrient assimilation system, where the metabolic binding sites for the essential metals are not specific for these. This implies that the essential metals can be competitively displaced by toxic metals, which are taken up by the metabolic system, and poison the organism. However, the essential metals are also toxic when present in increased concentrations, and this is why AMD affects biota and organisms negatively (Nriagu and Pacyna, 1988; Stumm and Morgan, 1996). One example is elevated concentrations of iron, which can attack the tissues in organisms by peroxidation of lipids. This causes release of hydroxyl free radicals, which can attack proteins, especially those in intestines, and finally cause death (Younger et al., 2002).

Old untreated tailings deposits are a larger threat to the environment compared to tailings deposits in use. This is because the groundwater level within active tailings deposits is usually very close to the deposit surface, while the groundwater level in old deposit lies often far below the ground surface, so that it is easier for oxygen to diffuse deep down. This, together with a high bacterial activity catalyzing the oxidation reactions, causes increased oxidation rates and an elevated release of AMD, which may severely affect the surrounding area. Some Swedish examples are the old mine waste deposits in the Kristineberg and Bersbo areas, where the adjacent streams have been heavily polluted. Today, the deposits in these two areas are remediated with water or soil covers, but since changes within these complex systems are very slow, acidic and metal-rich leachate is still released (see later sections for details regarding Kristineberg) (Allard et al., 1991; Naturvårdsverket, 1993).

1.2 The MiMi program

The MiMi (Mitigation of the Environmental Impact from Mining Waste) program was funded during the period 1998-2003 by the Swedish Foundation for Strategic Environmental Research (MISTRA). The MiMi program was a Swedish multidisciplinary research program, and consisted of researchers and PhD students from six universities, two consultant firms and the mining companies Boliden and LKAB. The overall goal of the MiMi program was to devise methods for the safe disposal of mining waste and for the reliable prediction of their function over very long periods of time. The field site chosen was the Kristineberg mining area in northern Sweden. The final phase of the MiMi program consisted of a Performance Assessment of the soil cover and water cover methods for the prevention and control of sulfide oxidation in mine tailings (Högland and Herbert, 2004).

The MiMi program consisted of seven main projects, where this thesis is part of the subproject Sulphide weathering and the quantification of the effect of remedial activities and the role of bacteria (within the main project Near Field – Methods and tools for optimized soil covers; MiMi, 2002). One of the objectives of the subproject was to quantify the effects of limited oxygen intrusion on mineral weathering reactions, and to study the effects of
limited oxygen availability on the generation of acid mine drainage. The results presented in this thesis have been produced as an activity within the MiMi research program.

1.3 Thesis objectives and structure

The objective with this thesis is to investigate and quantify the sulfide mineral weathering processes and element release rates that occur in water-saturated and soil covered tailings from northern Sweden. The oxidative weathering of pyrite and other sulfide minerals is the primary focus of this work, although the acidic dissolution of aluminosilicates is also considered. This study has been performed as a number of laboratory experiments on pure pyrite and on sulfide-rich mine tailings under different conditions, such as oxygen availability, tailings composition, grain size and in the presence of bacteria. These parameters were chosen since their variation has probably the greatest impact on mineral weathering rates within the same deposit. The reason for performing this study was that the influence of several of these parameters in sulfide-rich tailings has not been properly investigated before. Consequently, this study is important, since the acidic and toxic leachate from tailings deposits is today a large environmental problem that must be solved.

During the period when the studies presented in this thesis were performed, a number of important questions were considered with regard to mineral weathering in sulfide-rich tailings deposits. Since tailings material consists of many different minerals, it was important to quantify the weathering rates for the sulfide minerals under conditions relevant for the interior of the tailings deposit focused on in this study (i.e. Impoundment 1, Kristineberg). The deposit is covered by glacial till, and the availability of dissolved oxygen inside is usually reduced due to water-saturation and the diffusion resistance of the cover material. Hence, there was also a need to determine the oxygen concentrations below the cover, and how the weathering processes were affected by these oxygen levels. The infiltrating water percolates through a till layer where it becomes enriched in ions, and one question was thus to investigate if this enrichment affects the weathering rates. Further, there are also grain size variations in the tailings throughout the deposit, and it was important to find out if these alter the elemental release rates and weathering rates. Finally there are sulfur and iron oxidizing bacteria in the deposit, and it was important to confirm if and how they affected the observed weathering rates at different oxygen concentrations.

These questions are considered in the thesis and in the five appended papers, where the different laboratory experiments are described in detail. In the following two sections of the thesis called “Skellefte Ore District” and “Physical and Biogeochemical Processes in Impoundment 1”, the bedrock, field area, ore treatment, and the most important processes that occur with pure minerals and within a sulfide-rich deposit are described in detail. Knowledge of these factors helps in understanding the different processes within the performed laboratory experiments, and also makes it easier to interpret the true processes in the field. After these two detailed sections, the performed laboratory studies are briefly summarized and the discussion and conclusions are presented. The results and conclusions of the studies presented in this thesis will hopefully be taken into account during tailings reclamation activities in the future. It is intended that the results are to be used by other researchers when, for example, comparing microbial oxidation of pure sulfide grains with the naturally-occurring oxidation processes inside tailings deposits.

2 Skellefte Ore District

2.1 Description of area and bedrock

Kristineberg and Boliden are two mines situated at each end of the 100 km wide Skellefte ore district, which is located in northern Sweden (65°N 19°E), approximately 650 km north of Stockholm (Figure 1). Geologically, the Skellefte district is an Early Proterozoic, 1.90 to 1.87 Ga (Svecofennian) felsic magmatic region of low to medium metamorphic grade in the Baltic Shield. As discussed in Allen et al. (1997), the Skellefte district consists of volcanic, sedimentary and intrusive rocks, and is characterized by abundant moderately to strongly deformed, gray, diagnostically and hydrothermally altered, marine volcanic rocks. Throughout the Skellefte district there is a simple first-order regional stratigraphy consisting of a thick volcanic unit (Skellefte Group), which hosts over 85 pyritic base metal deposits. This is overlain by mainly sedimentary successions. The Skellefte Group is defined as the lowest stratigraphic unit dominated by juvenile volcanioclastic rocks, porphyritic intrusions, and lavas. It contains most of the massive sulfide ores and has an extremely variable internal stratigraphy. Intercalated sedimentary rocks are included in the group and comprise gray to black mudstone, volcanioclastic siltstone, sandstone and breccia-conglomerate, volcanioclastic rocks with a lime matrix in the center of the district, and rare limestone. The Skellefte Group is subdivided into ten geologic domains (e.g. Kristineberg, Maurilden, Boliden) according to the differences in the style, composition, economic viability, and host rocks of the ores (Allen et al., 1997).

Kristineberg area is located in the western part of the Skellefte ore district, and consists of ore-bearing volcanic rocks overlain by sedimentary rocks. These have been folded, regionally metamorphosed and intruded by two different granitoids (Vivallo and Willdén, 1988). The ore deposits are built up of pyrite-rich massive sulfides and Cu-rich disseminated ores. They are found within a stratigraphic unit consisting of mainly felsic volcanics and redeposited volcanioclastic rocks, where the largest deposit is the Kristineberg ore body. The sulfide mineralogy of the ores consists of pyrite, pyrrhotite, sphalerite, chalcopryte and galena. The ore deposits are stratabound and also affected by deformation and metamorphism. Underlying the ores are volcanic rocks altered into quartz-sericite rocks and chlorite schists, where the chlorite-rich zone is close to the ore (Vivallo and Willdén, 1988).

2.2 Meteorological conditions

The annual mean temperature in the Kristineberg mining area is 0.7 °C, with 5 months with an average air temperature below 0°C, and the average annual precipitation is 660-670 mm/year (Malmström et al.,
The major part of the precipitation is in the form of snow, which accumulates until the snowmelt in April-May.

2.3 Mining history in the Kristineberg mining area

In 1918, a large Zn-Cu ore body was discovered in Kristineberg, and the mining activities there started in 1940, when the Kristineberg mine and the ore concentrator opened. Many different ores from about ten mines situated in the western part of the Skellefte ore district have been processed at the ore concentrator, such that the impoundments contain a mixture of tailings from different sources. Over the years, five large tailings impoundments (Impoundments 1, 1B, 2, 3 and 4) were constructed in the Kristineberg mining area. Impoundment 1 and 2 were already filled up in the early 1950s, followed by Impoundment 3 and finally Impoundment 4, which did not receive mill tailings after 1991. Impoundment 1B was constructed to be used as an intermediate storage deposit for low grade pyrite and pyrrhotite. In 1991, the Kristineberg ore concentrator closed, and the five tailings impoundments were remediated after closure using a number of techniques, including liming, flooding, raising the groundwater table, and installing a soil cover (Carlsson et al., 2003; Lindvall et al., 1999).

Today mining is performed at four localities within the Skellefte ore district (Kristineberg, Renström, Petiknäs and Maurliden), while about 25 mines are closed, such as the world-famous Boliden gold mine. The Kristineberg mine is still active, with 500,000 tons of ore mined there every year, which is more than a third of all the ore processed at the mill in Boliden (Boliden Mineral AB, 2004). The ores in Kristineberg may be divided into the following subspecies: pyrite ore with a low content of copper (often below 1%); copper-pyrite ore, which is a pyritic ore with chalcopyrite (Cu above 1%); quartzitic ore, which is a sericite-quartz schist or chlorite-quartz schist with a pronounced impregnation of chalcopyrite and pyrite; and zinc ore, which is composed chiefly of pyrite and sphalerite (du Rietz, 1953). The Kristineberg mine is also the deepest in Sweden, currently reaching a depth of 1170 meters below the ground level. Since the closure of the Kristineberg ore concentrator in 1991 all mined ores from the Skellefte ore district are processed at the Boliden ore concentrator (Boliden Mineral AB, 2004).

Figure 1. Impoundment 1 (larger deposit) and 1B (smaller deposit) in Kristineberg, northern Sweden (Corrège, 2001).
2.4 Ore processing at the Boliden ore concentrator

During the metal recovery process at the ore concentrator, the mined ores acquire special properties that have an effect on the weathering reactions occurring in the deposits, and are studied in the MiMi program. Briefly the mined ore is processed mechanically and chemically in several steps, which finally results in (1) a product that is enriched in desirable metals (i.e. copper, gold, lead, silver and zinc), and (2) mill tailings.

Accurately described, the ores are coarsely crushed at the mine site, before transport to the Boliden ore concentrator. After entering the concentrator, the ore is finely ground to separate the mineral grains from each other, and then mixed in several steps together with process water to improve the metal recovery process. In the first mixing step, the pH is increased to 11-12 by adding buffering chemicals (e.g. slaked lime), which is necessary for the extraction of the metals from the ground ores, and also to prevent the growth of acidophilic microorganisms. The next mixing step includes selective flotation for each metal, where the particles are floated stepwise in foam, consisting of e.g. xanthates, frothing agents and a bactericide. Xanthates act as flotation agents and raise the metal recovery yields. A bactericide is used to prevent the growth of microorganisms in the process water (Y. Andersson, Boliden Mineral AB – personal communication, 1999; Boliden Mineral AB, 2004).

After this separation procedure the mineral grains are dried and filtered. The residue from the metal recovery process is called tailings, and consists mostly of silicate minerals but also of sulfide minerals, since a metal recovery of 100% is not possible. The tailings are divided into two fractions, where the total average grain size is 50 (±45) μm. The finer fraction (same material as used in Paper I) is thereafter deposited in the large tailings pond Gillervatnet in the Boliden area, while the coarser fraction is thereafter deposited in the large tailings pond resulting in vertical and horizontal variability in the tailings. These variations are related to the distance from the tailings discharge pipe where the tailings were discharged as slurry; the coarser grains sedimented closer to the pipe, while the finer grains sedimented further away. However, the discharge pipe was moved on numerous occasions, resulting in vertical and horizontal variability in the tailings composition. Nevertheless, the deposit declines downwards southeast, implying a larger amount of fine-grained tailings in that area (Höglund and Herbert, 2004).

The total thickness of the tailings deposit ranges from a few meters up to approximately 11 m, with an average thickness of 6 to 8 m. During periods of active deposition, tailings are usually maintained close to water-saturation because of the large volumes of water required for discharging the slurry. However, when Impoundment 1 was no longer in use, the water level started to decline, and an unsaturated zone was created in the upper layers of the tailings. In the impoundment, the depth to the groundwater table varied during the year, and also between the different areas of the impoundment, from 0.5 meters to 2.5 meters below the ground surface (Axelsson et al., 1991). Because the tailings were unsaturated at the ground surface, oxygen could diffuse into the impoundment and oxidize sulfides, and an oxidized zone started to develop at the surface of the deposit. With time, the oxidized zone increased in depth; the thickness of the oxidized zone is directly related to the depth to the groundwater table. This resulted in an oxidized zone of ca. 0.1 meters in the southwest area, which increases in thickness towards the northeast, where the oxidized zone is about 1.15 meters thick (Holmström et al., 2001).

Sulfide oxidation in Impoundment 1 was thus allowed to proceed uninhibited for about 45 years (early 1950s–1996). In 1996 the deposit was remediated by raising the groundwater table and installing a soil cover, with the intention to minimize oxygen diffusion and water infiltration into the tailings. Prior to the soil cover installation, 10 kg/m² lime was spread all over the deposit. Half of the deposit was remediated by filling ditches along the edge of the impoundment, which resulted in an increase in the groundwater level (see Figure 1). In the area affected by a raised groundwater table, the deposit was covered with single layer cover consisting of 1 m unspecified glacial till. Since the vertical hydraulic conductivity (Kv) of the till (3 x 10⁻⁶ m/s) and the tailings (3 x 10⁻⁷ m/s) are rather similar (Höglund and Herbert, 2004), the groundwater rose into the soil cover, and the tailings became permanently water-saturated. In some parts the groundwater even reaches the ground surface. Finally, to reduce the erosion of the soil cover, the surface was seeded with grass (Lindvall et al., 1999; Carlsson et al., 2003).

In the other half of the deposit where the depth to groundwater was greater, a double layer cover was installed, consisting of a sealing layer (0.3 m compacted glacial till, well graded, with a high clay content of 8%, Kv = 1 x 10⁻⁹ m/s; (Lindvall et al., 1999)) overlain by a protective cover (1.5 m unspecified till; Figure 1). Before remediation, the groundwater table was situated a few meters down, implying that a sealing layer was necessary to inhibit oxygen entry, since there was no possibility of raising the groundwater table in this area. The sealing layer is compact and prevents the percolation of water to the underlying tailings. When applying the sealing layer, a second groundwater table is created on top of this. The protective cover prevents the erosion of the sealing layer and functions as a water storage layer, maintaining the sealing layer at water-saturation (Lindvall et al., 1999; Carlsson et al., 2003).
Table 1
Mineral content in unoxidized tailings from Impoundment 1, Kristineberg, in decreasing order of abundance, based on calculations using average chemical composition from 73 samples (Holmström et al. 2001).

<table>
<thead>
<tr>
<th>Sulfide mineral content</th>
<th>Wt. % c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe₁₋ₓS</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
</tr>
</tbody>
</table>

Most common transparent minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAlSi₃O₈</td>
</tr>
<tr>
<td>Mg-chlorite</td>
<td>(Fe,Mg,Al)₆(Si,Al)₄O₁₀(OH)₈</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>NaAlSi₃O₈ - CaAl₂Si₂O₆</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₃(AlSi₃)O₁₀(OH)₂</td>
</tr>
<tr>
<td>Amphiboles-Pyroxenes</td>
<td>(X,Y,Z)₇₋₈(Al,Si)₂Si₆O₂₂(OH)₂</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,Fe)₃AlSi₃O₁₀(OH)₂</td>
</tr>
</tbody>
</table>

Non-sulfide minerals occurring in minor amounts

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illmenite</td>
<td>FeTiO₃</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₂O₄</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
</tr>
<tr>
<td>Titanite</td>
<td>CaTiSiO₅</td>
</tr>
<tr>
<td>Epidote</td>
<td>Ca₃(Al,Fe)₃(SiO₄)₃(OH)</td>
</tr>
<tr>
<td>Sericite</td>
<td>KAl₃(AlSi₃)O₁₀(OH)₂</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca₅(PO₄)₃(OH,F,Cl)</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
</tbody>
</table>

a X=Ca,Na,Pb,K; Y=Fe(II),Li,Mg,Mn(II); Z=Fe(III),Cr(III),Al,Ti
b X=Ca,Na,Zn,Li; Y=Cr,Al,Fe(III),Ti,V
c Mineral content is only reported for the sulfides. Based on the calculations it is assumed that all Fe-sulfides are in form of pyrite, and Cu, Zn, Pb and As are in form of sphalerite, chalcopyrite, galena and covellite.

3 PHYSICAL AND BIOGEOCHEMICAL PROCESSES IN IMPOUNDMENT 1

The tailings deposit environment is a complex system of coupled physical and biogeochemical processes which can be divided into primary processes (e.g. water infiltration, water-saturation, oxygen diffusion, sulfide oxidation) and secondary processes (e.g. microbial activity, secondary precipitates, complexation, surface runoff; see Figure 2). In the following section, the most important processes in Impoundment 1 are discussed.

3.1 Water infiltration and oxygen diffusion into tailings

Both oxygen and water are required for the continual oxidation of sulfide minerals. If only oxygen is available, the minerals will still oxidize, but the oxidation products will not be transported away from the sulfides, since water is necessary to dissolve and transport the oxidation products. Oxygen also supports the production of ferric iron, which is another oxidant of sulfide minerals (discussed in detail in section 3.2.2). If there is no oxygen supply, sulfide oxidation reactions will be prevented.

3.1.1 Percolation, groundwater table and groundwater flux – Kristineberg case

The water flux in to the tailings is derived from precipitation (rain and snow) and in-flow of ground- and surface water. In Kristineberg ~50 % of the precipitation evaporates and does not infiltrate into the deposit (Axelsson et al., 1986). Some of the precipitation is also lost in form of surface runoff, while the remaining part (~15 %; ca. 100 mm/year, see below) percolates down through the unsaturated zone, and finally reaches the groundwater table (Höglund and Herbert, 2004). The groundwater influx to Impoundment 1 enters primarily from the hillslope to the southwest with a general flow direction towards the northeast. A total of 685,000 m³ groundwater is estimated to enter yearly (Corrège, 2001).

In the northeast area of Impoundment 1, where a double layer soil cover has been installed, the rate of percolation through the soil cover is limited by the vertical hydraulic conductivity of the sealing layer (Kᵥ = 1 x 10⁻⁹ m/s). For this Kᵥ value, and assuming a water-saturated sealing layer and that the pore water pressure is in equilibrium with the atmosphere at the base of sealing layer, the annual recharge to the tailings would be 32 mm/year. In general, a conservative value of 100 mm/year
is assumed for vertical percolation through such sealing layers (Höglund and Herbert, 2004). However, field infiltration lysimeter studies in Kristineberg have indicated a percolation rate through the sealing layer of ~4 mm/year (Carlsson et al., 2003). This low percolation rate is probably due to the fact that the test area used for this study was a bit more compact relative to the ordinary sealing layer, resulting in a $K_z$ value of ~5 x 10^{-10} m/s (Carlsson and Elander, 2001).

3.1.2 Oxygen levels and diffusion

Oxygen can be transported into the tailings deposit by three mechanisms: (1) advective transport with water that contains oxygen, (2) free or forced air convection through the top layer of the tailings deposit and (3) diffusion in the gaseous and aqueous phases through pores in the tailings material (Werner, 2000). The last mechanism is the dominant mechanism for transporting the atmospheric oxygen from the surface of the tailings to the depth where the oxidation takes place (Jaynes et al., 1984; Nicholson et al., 1989; Pantelis and Ritchie, 1991; Yanful, 1993). The oxygen diffusion mechanism in either gas or water phase may be treated as one-dimensional, and can then be approximated by Fick’s First Law:

$$F_{O_2}(t) = -\theta_a D_{eff} \frac{\partial C(t)}{\partial z} \quad (1)$$

where $F_{O_2}(t)$ is the mass flux of oxygen (mass flux per unit area per unit time), $\theta_a$ is air-filled porosity (volume per volume), $D_{eff}$ is the effective diffusion coefficient (for air = 1.8 x 10^{-5} m² s⁻¹; for water = 2.2 x 10^{-11} m² s⁻¹), $C(t)$ is concentration at time $t$ (mass per volume) and $z$ is depth within the soil or tailings mass (length). In tailings $D_{eff}$ is a function of the diffusion coefficient for oxygen in air and a factor that depends on the percentage of gas-filled pores (related to the volumetric moisture content) and a tortuosity factor characteristic of the soil. The air-filled porosity, $\theta_a$, can be related to the degree of saturation, $S_r$, where $\theta_t$ is the total porosity, according to Equation 2 (Elberling et al., 1993; Yanful, 1993).

$$\theta_a = \theta_t (1 - S_r) \quad (2)$$

The oxygen diffusion rate in the unsaturated zone is high, relative to the saturated zone, since the oxygen diffusion rate is 10 000 times faster in air than in water (Yanful, 1993). Therefore, in the unsaturated zone, the sulfide oxidation rate may be relatively rapid, since the potential availability of both water and oxygen is large. Below the groundwater table, oxygen diffusion is heavily reduced, and the oxygen content will be limited to its solubility in water, which results in that sulfide oxidation should occur slowly below the groundwater table.

![Diagram](image_url)

Figure 2. Major physical, chemical and biological processes in a soil covered tailings deposit (modified from MiMi, 2003).
Impoundment 1 was uncovered until 1996, and oxygen could easily diffuse into the deposit. However, the oxygen concentration inside varies depending on the degree of water-saturation, temperature, the rate of water infiltration and the rate of oxygen consumption. Elberling et al. (1993) conducted field studies on uncovered unsaturated tailings deposits in Canada. They reported that the pore gas oxygen concentration decreased from atmospheric concentrations (20.9 vol-%) to less than 5 vol-% within the upper 60 cm of the impoundments. This showed that oxygen gradients exist in unsaturated tailings. At water-saturated conditions, i.e. below the groundwater table, the oxygen concentration decreased from atmospheric concentrations to less than 5 vol-% within the upper 60 cm of the impoundments. This showed that oxygen gradients exist in unsaturated tailings. At water-saturated conditions, i.e. below the groundwater table, the oxygen concentration limited to the solubility of oxygen in water, or 258 µM at 25°C (i.e. 20.9 vol-%). In general, however, the dissolved oxygen (DO) levels are very low in saturated tailings deposits.

After the remediation of Impoundment 1 in 1996 the tailings were water-saturated in the southwest area closest to the hill slope (see Figure 1). Field investigations from this site (Figure 1; close to pipe D) showed that the DO level in the pore water was ~3 µM already a few centimeters below the protective till cover (Herbert and Gleisner, 2004). This confirms that the DO level in the saturated zone today is very low, that DO is rapidly consumed, and that sulfide oxidation is most likely very low in this area. Calculations made before remediation showed that the annual oxygen intrusion through the sealing layer would be about 0.06 mol/m² (Lindgren and Pers, 1995). Lindvall et al. (1999) measured the DO levels below the sealing layer in the northeastern area, and reported that they were close to zero. Werner et al. (2001) investigated the oxygen levels in the unsaturated zone below the sealing layer more thoroughly (Figure 1; around P7). They reported average oxygen levels of 1.10 vol-% at a depth of 1.8 m below the surface (1.5 m protective cover + 0.3 m sealing layer). The annual oxygen flux through the sealing layer was on the order of 0.4 mol/m². However, they concluded that remediation of tailings impoundments using dry cover can lead to small oxygen and water fluxes during dry periods, since the low permeability sealing layer may dry out and let oxygen and water pass through. This may lead to continued sulfide oxidation below the dry cover, even though the oxidation rate after remediation most likely is much slower than before remediation.

### 3.2 Abiotic pyrite oxidation

#### 3.2.1 Pyrite oxidation with oxygen as oxidant

Pyrite is the most abundant sulfide mineral in ores from the Skellefte ore district, with arsenopyrite, chalcopyrite, covellite, galena, pyrrhotite and sphalerite occurring in lesser abundance (Table 1). It can be inferred that pyrite oxidation is probably responsible for iron release and acidification of surface water in the mining area. Sulfide oxidation depends on a wide variety of factors, including water accessibility, oxygen concentration, ferric iron concentration, acidity, microbial population and temperature. Many studies have been conducted on pyrite oxidation, and recently two reviews have been presented by Nordstrom and Southam (1997) and Nordstrom and Alpers (1999).

The pyrite molecule has valence bands that are derived only from orbitals of the metal atoms, and cannot be attacked by protons, i.e. it is acid-insoluble (Luther, 1987; Rohwerder et al., 2003). The overall reaction for pyrite oxidation in water with access to DO is often written according to Equation 3, where ferric hydroxide, sulfate and 4 protons are produced. In Equation 3 there are 14 electrons transferred for the oxidation of disulfide. However, electron transfers of only 1 or 2 electrons are possible, which means that this reaction in reality will be divided into at least 15 steps with many intermediate products. This equation does not either consider geochemical mechanisms or rates, the fact that ferric hydroxide is an idealized phase, and that ferrous iron oxidizes very slowly in acidic conditions (unless the redox potential is very high, i.e. in the presence of DO and bacteria). Pyrite oxidation in water with access to DO may also be written according to Equation 4, where ferrous iron, sulfate and 2 protons are produced. This reaction will also be divided into many steps, resulting in different intermediate sulfur phases and side reactions, where for example elemental sulfur or sulfoxyanions, such as thiosulfate and sulfite, are formed. However, sulfoxyanions are rarely detected in natural waters, since they are a good source of energy for sulfur oxidizing bacteria (Nordstrom and Alpers, 1999).

\[
\begin{align*}
\text{FeS}_2 + 3.75 \text{O}_2 + 3.5 \text{H}_2\text{O} &\rightarrow \text{Fe(OH)}_3 + 2 \text{H}_2\text{SO}_4 \quad (3) \\
\text{FeS}_2 + 3.5 \text{O}_2 + \text{H}_2\text{O} &\rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (4)
\end{align*}
\]

The DO concentration controls the iron release rate, and when the DO level is limited the pyrite oxidation rate will be reduced, e.g. in the saturated zone of Impoundment 1. Equation 4 can be used for calculating the possible iron release when the DO concentration (moles/liter), DO flux (moles/time) and water infiltration rate is known.

The stoichiometric dissolution of pyrite (reaction 5) will result in the release of two moles of sulfate per mole of ferrous iron. However, Descostes et al. (2004) found that abiotic pyrite dissolution by DO in HCl or HClO₄ (at pH 2-3) was nonstoichiometric, where one mole of pyrite released 1.6 moles of sulfate and 0.4 moles of elemental sulfur were precipitated. This is also confirmed by Sasaki (1994), who studied pyrite oxidation by DO at abiotic conditions in HCl or H₂SO₄ (initial pH = 2.0). He found that Fe was preferentially leached to the solution ([Fe₅/Fe₆]<2), and S was accumulated on the pyrite surfaces.

#### 3.2.2 Pyrite oxidation with ferric iron as oxidant

At low pH, ferric iron may be the major oxidant of pyrite (Equation 5), since it interacts with reactive surface sites more effectively than DO (McKibben and Barnes, 1986; Nordstrom and Alpers, 1999). Singer and Stumm (1970) found that oxidation of pyrite by ferric iron can be carried out both in the presence and in the absence of DO. Ferric iron is moreover a strong oxidant for all types of reduced sulfur species, which is apparent since sulfoxyanions do not accumulate in intermediate steps when ferric iron is present (Moses et al., 1987).
FeS₂ + 14 Fe³⁺ + 8 H₂O → 15 Fe²⁺ + 2 SO₄²⁻ + 16 H⁺ (5)

The rate-limiting step in the oxidative dissolution of pyrite by ferric iron is considered to be the oxidation of ferrous iron by DO to regenerate ferric iron, at low and circumneutral pH values (Equation 6) (Singer and Stumm, 1970; Moses and Herman, 1991).

Fe²⁺ + 0.25 O₂ + H⁺ → Fe³⁺ + 0.5 H₂O (6)

At circumneutral pH values, ferrous iron will be rapidly oxidized to ferric iron by DO (Rimstidt et al., 1994). However, if ferrous iron is present, it may accumulate on the pyrite surface and block the surface reaction sites (Moses and Herman, 1991).

3.2.3 Valid abiotic pyrite oxidation rate laws
Several studies have been performed to investigate pyrite oxidation rates at abiotic conditions, where the rate laws presented by Williamson and Rimstidt (1994), applicable over a wide range of solution compositions, are commonly used today. They determined one important rate law for pyrite oxidation by DO, valid for a pH interval of 2-10 (Equation 7), and two important rate laws for pyrite oxidation by ferric iron; in the pH interval 0.5-3.0 in oxygen-free (N₂-purged) solutions (Equation 8), and at presence of DO (Equation 9). They also showed that pyrite oxidation by ferric iron reduction is correlated with the redox potential in the solution, and that there is a pH-dependence in Equation 7 and 8.

\[
R = 10^{-8.19} \left[ \frac{[O_2]}{[H^+]} \right]^{0.50} [\text{mol m}^{-2} \text{s}^{-1}] (7)
\]

\[
R = 10^{-8.58} \left[ \frac{[Fe^{3+}]}{[Fe^{2+}]} \right]^{0.30} \left[ \frac{[O_2]}{[H^+]} \right]^{0.47} [\text{mol m}^{-2} \text{s}^{-1}] (8)
\]

\[
R = 10^{-6.07} \left[ \frac{[Fe^{3+}]}{[Fe^{2+}]} \right]^{0.93} [\text{mol m}^{-2} \text{s}^{-1}] (9)
\]

The rate of the pyrite oxidation reaction is faster by a factor of 3-100 when the oxidant is ferric iron instead of DO (McKibben and Barnes, 1986; Edwards et al., 1999; Nordstrom and Alpers, 1999). Williamson and Rimstidt (1994) also concluded that the reaction rate for pyrite oxidation by ferric iron reduction is enhanced by the presence of DO when the availability of ferric iron is high (Equation 9).

3.2.4 The effect of temperature on weathering rates
During the summertime in Kristineberg, the mean temperature in air rises to approximately 12°C, while it is around -20°C during wintertime (Axelsson et al., 1986). The temperatures in the interior of the deposits are however not the same as the temperatures outside. Ahonen and Tuovinen (1989) reported that the temperature in tailings deposits could differ from below freezing to up to 50°C or even higher. Ebenå (2003) reported that the temperature one meter below the soil cover in Impoundment 1 varies between 2 and 10°C over the year.

The prevailing temperature within the deposit is a very important factor for the weathering processes, including pyrite oxidation and other weathering reactions (see below). The effect of temperature on reaction rate is expressed in the Arrhenius equation:

\[ k = Ae^{-\frac{E_a}{RT}} \] (10)

where \( k \) is the reaction rate, \( A \) (the pre-exponential factor) is regarded as an empirical constant in complex systems, \( E_a \) is the activation energy, \( R \) is the gas constant and \( T \) is the absolute temperature (Drever, 1997). When the mineral weathering rate is high, heat is generated. For example, oxidation of pyrite by DO at 20-30°C and pH 2-4, generates 56.9 ±7.5 kJ/mole. This results in temperature increases, which can affect the rate for bacterial activity, and also the chemical reaction rates (Goodman et al., 1981; McKibben and Barnes, 1986).

3.2.5 The effect of grain surface-area and -structure on weathering rates
The available surface area of granular material such as tailings is inversely proportional to the grain diameter, implying that smaller grains have a larger surface area. In addition, there is a linear relationship between the mineral surface area and pyrite oxidation rate, resulting in that smaller grains show a higher oxidation rate (Nicholson, 1994). Strömberg and Banwart (1999a) investigated the physical scale of waste rock that significantly contributed to acidity and alkalinity generation. They concluded that the fraction of fine material (< 0.25 mm) within waste rock presumably has a much larger influence on the weathering rates than the size distribution of the remaining larger particles.

Since the grain size distribution of the tailings within Impoundment 1 varies (as discussed above), this implies that the weathering properties vary in different parts of the deposit. Thus, the larger fraction of fine-grained material located towards the southeast in Impoundment 1 should show higher weathering rates relative to the coarse-grained material located to the northwest.

In addition to grain size variations, there are also intergranular variations, with high excess energy sites in the surface textures of the mineral grains. These sites consist of grain edges and corners, defects, solid and fluid inclusion pits, cleavages and fractures, and function as surface areas where the oxidation processes are centered (McKibben and Barnes, 1986). Moreover, the intergranular variations within the tailings may also increase the weathering rates, especially in the southeast part of Impoundment 1 where the mineral surface area is greater.

3.3 Oxidation of other sulfide minerals
Other sulfide minerals in Impoundment 1 are arsenopyrite, chalcopyrite, covellite, galena, pyrrhotite and sphalerite (Table 1). The molecular structures of these sulfide minerals are different from pyrite, since they have valence bands derived from both the metal and sulfide orbitals.
This implies that these minerals can be dissolved by non-oxidative proton attack (Schippers and Sand, 1999; Rohwerder et al., 2003), which may be important at anoxic and dysoxic conditions in the interior of the deposit, since ferrous iron may then be released (e.g. from chalcopyrite and pyrrhotite).

The sulfide minerals other than pyrite can also be oxidized by DO, but most of these reactions are not acid producing (Equation 11-13). However, when e.g. arsenopyrite and chalcopyrite are instead oxidized by ferric iron, these minerals are acid producing (Equation 14-15).

\[
\begin{align*}
\text{CuFeS}_2 + 4 \text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{SO}_4^{2-} \quad (11) \\
\text{PbS} + 2 \text{O}_2 & \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \quad (12) \\
\text{ZnS} + 2 \text{O}_2 & \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \quad (13) \\
\text{FeAsS} + 13 \text{Fe}^{3+} + 8 \text{H}_2\text{O} & \rightarrow 14 \text{Fe}^{2+} + \text{SO}_4^{2-} + 13 \text{H}^+ + \text{H}_3\text{AsO}_4 \quad (14) \\
\text{CuFeS}_2 + 16 \text{Fe}^{3+} + 8 \text{H}_2\text{O} & \rightarrow \text{Cu}^{2+} + 17 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (15)
\end{align*}
\]

Nicholson (1994) reported about the oxidation processes for pyrrhotite (Equation 16). Pyrrhotite has the formula Fe_{1-x}S, where \(x\) varies from 0.125 (FeS) to 0 (FeS). Fe_{2}S_{3} is the iron-deficient end-member. Compared with pyrite, the iron-deficiency in the crystal structure of pyrrhotite may affect the oxidation processes. Nicholson (1994) showed that the oxidation rates of pyrrhotite are 20 to 100 times more rapid than those of pyrite. This implies that pyrrhotite may play an important role in acid production from oxidation of sulfide-rich tailings, and increase the potential for environmental impact.

\[
\text{Fe}_{1-x}\text{S} + (2-0.5x) \text{O}_2 + x \text{H}_2\text{O} \rightarrow (1-x) \text{Fe}^{2+} + \text{SO}_4^{2-} + 2x \text{H}^+ \quad (16)
\]

Jambor (1994) reported a general sequence of the oxidizing tendencies for the important sulfide minerals in tailings, which goes from readily attacked to increasingly resistant:

pyrrhotite > galena-sphalerite > pyrite-arsenopyrite > chalcopyrite

The high resistance of chalcopyrite to weathering depends on that the grains often are encapsulated in silicate grains in tailings, and thereby may escape from the dissolution processes (Jambor, 1994).

### 3.4 Microbiology in acid mine environments

In all natural ecosystems (e.g. mines, lakes, deep sea, soil, food, inside animals) there is an abundant activity of organisms, which catalyze chemical and biological reactions to obtain energy. All organisms on Earth are divided in Bacteria, Archaea and Eukarya, with bacteria being relevant for this thesis. Furthermore, organisms are also classified according to their ability to obtain energy in chemolithotrophs (oxidize inorganic compounds; i.e. many bacteria), chemoorganotrophs (oxidize organic compounds; i.e. animals, protists, fungi and some bacteria) and phototrophs (use light; i.e. green plants and some bacteria). Finally, the last classification divides them in two groups depending on their ability to obtain carbon, according to: autotrophs (transform carbon dioxide to organic carbon) and heterotrophs (mineralize organic carbon to inorganic carbon) (Ledin and Pedersen, 1996; Madigan et al., 2000).

In acid mine waters, the most prevailing bacteria are chemolithotrophic acidophiles. Most of these are autotrophs, such as the sulfur and iron oxidizer *Acidithiobacillus ferrooxidans*, the sulfur oxidizers *At. thiooxidans* and *At. albertensis* and the iron oxidizer *Leptospirillum ferrooxidans*. There are also heterotrophes in minor amounts, such as *Ferromicrobium acidophilus* and *Acidiphilium* species (Johnson, 1998; Kelly and Wood, 2000). However, only a minor fraction of all bacteria species have been able to be cultivated in laboratory (Amann et al., 1995). This implies that the named species mentioned above might not be the most important in reality. To investigate the in situ-distribution of known species, PCR-based techniques such as denaturing gradient gel electrophoresis (DGGE) and fluorescent in situ hybridization (FISH) are used. DGGE gives only an indication of the diversity of the in situ-bacterial population, while FISH gives quantitative results, where DNA probes are hybridized to extract DNA for microbial community analyses (Bond and Banfield, 2001; Ebenä et al., 2003).

#### 3.4.1 Description of the sulfur and iron oxidizer *Acidithiobacillus ferrooxidans*

The most well-know bacteria in acid mine waters are of the acidophilic species *Acidithiobacillus ferrooxidans*, formerly *Thiobacillus ferrooxidans* (Kelly and Wood, 2000), which are Gram-negative, rod-shaped, autotrophs and obligate chemolithotrophs. For their growth, the optimum pH levels are 2.0-3.5, but they can survive from 0.5 up to 5.5 (Goodman et al., 1981; Ledin and Pedersen, 1996). They obtain energy from the oxidation of ferrous iron and elemental or reduced sulfur compounds (e.g. metal sulfides), using DO as the electron acceptor under oxidizing conditions (Equation 3), and thus catalyze the oxidation of iron and sulfide minerals. They are mesophilic and their optimum growth temperature is in the range of 25-35°C, where the upper limit is about 42°C, and the lower range is not yet well-defined for this species (Ahonen and Tuovinen, 1989). However, Ebenä et al. (2001) isolated a strain of *At. ferrooxidans* obtained from Impoundment 1 in Kristineberg, and showed that the optimal temperature for this strain was approximately 15°C, even though it survives at temperatures close to the freezing point.

*At. ferrooxidans* are also facultative anaerobes, and thus have an alternative mechanism to obtain energy under oxygen limitation or at extremely low pH (< 1.3), where they have been shown to use ferric iron as the electron acceptor (Equation 5) (Brock and Gustafson, 1976; Hutchins et al., 1986; Johnson and McGinness, 1991; Sand, 1989). This implies that partial elimination of oxygen is not critical for their ability to oxidize pyrite, such as in the interior of the tailings impoundments (Singer...
and Stumm, 1970), where the environment is anoxic ([DO] < 3.13 µM, 25°C) or dysoxic ([DO] = 3.13-21.9 µM, 25°C; Raiswell and Berner, 1985).

### 3.4.2 Pyrite oxidation by bacterial mediation

Singer and Stumm (1970) showed that the oxidation rate of free ferrous iron (Equation 5) in acid mine water increased by a factor larger than 10^6 in the presence of iron oxidizing bacteria relative to abiotic conditions. Olson (1991) presented an interlaboratory comparison, which showed that the rate of pyrite oxidation by DO (pH 2, 28°C, [DO] = 241 µM) (Equation 4) increased with a factor of 34 in the presence of *At. ferrooxidans*. This large difference between microbial oxidation of pyrite or free ferrous iron depends on that free ferrous iron is easy available for the cell through the membrane. However, pyrite is a solid substrate on that free ferrous iron is easy available for the cell to be assimilated. The mechanism for bacterial dissolution of pyrite is discussed below.

Microbial pyrite oxidation is described to occur directly or indirectly (Silverman, 1967). The direct mechanism occurs with bacterial cells attached to the grains, where the cells use DO as the electron acceptor and biologically oxidize sulfur or iron by an enzyme system, according to Equation 4. In the indirect mechanism, the cells oxidize soluble ferrous iron to ferric iron (Equation 6), which chemically degrades pyrite (Broek and Gustafson, 1976; Ehrlich, 1981; Edwards et al., 1999). Yu et al. (2001) showed that the direct mechanism dominated during the bacterial adaptation period (i.e. lag phase), and both mechanisms are important during the most rapid bacterial growth stage (i.e. log phase). However, it is generally concluded that the indirect mechanism is the most likely mechanism (e.g. Sand et al., 2001; Rohwerder et al., 2003). Sand et al. (2001) showed that the most probable model for the indirect mechanism is where the primary ferric iron is complexed to bacterial extracellular polymeric substances. This ferric iron oxidizes the pyrite through chemical attack on the crystal lattice, with thiosulfate being the main intermediate product (Equation 17 and 18).

\[
\begin{align*}
\text{FeS}_2 + 2 \text{Fe}^{3+} + 3 \text{H}_2\text{O} &\rightarrow \text{S}_2\text{O}_3^{2-} + 7 \text{Fe}^{2+} + 6 \text{H}^+ \quad (17) \\
\text{S}_2\text{O}_3^{2-} + 8 \text{Fe}^{3+} + 5 \text{H}_2\text{O} &\rightarrow \text{SO}_4^{2-} + 8 \text{Fe}^{2+} + 10 \text{H}^+ \quad (18)
\end{align*}
\]

Although Sand et al. (2001) indicated that this oxidation mechanism operates indirectly via ferric iron, bacteria are actually attached to the mineral surfaces. Rodriguez et al. (2003) concluded that pyrite oxidation is initiated by direct mechanisms (Equation 4) during the initial stage, since all cells initially adhere to the pyrite surfaces. They also concluded that the indirect mechanisms (Equation 6) are dominating thereafter, because a majority of the cells linearly leave the grain surfaces to be planktonic in the solution.

Very few studies have quantitatively addressed the effect of low oxygen partial pressure on microbial pyrite oxidation. Myerson (1981) reported that the growth of *At. ferrooxidans* in the presence of pyrite was inhibited at [DO] < 12.9 µM at 25°C. Field investigations of sulfidic waste rock dumps confirm that pyrite oxidation by *At. ferrooxidans* occurs at anoxic conditions (Goodman et al., 1983). Still, there is a lack of an experimentally-determined relationship between DO concentration and the microbial pyrite oxidation. Rate laws for microbial pyrite oxidation are not found in the literature, as they are for abiotic pyrite oxidation (cf. Williamson and Rimstidt, 1994) and microbial ferrous iron oxidation (Pesic et al., 1989; Kirby et al., 1999).

### 3.4.3 Bacterial community in sulfide-rich tailings

In freshly processed tailings the pH level is alkaline, because of liming, and the tailings often contain a bactericide. However, after some time the bactericide concentration is depleted, because of natural leaching by water percolation through the deposit, and microorganisms will start to grow. At these relatively high pH levels, sulfide oxidizers such as *Thiobacillus neapolitanus*, *T. thioparus* and *T. denitrificans* may be present (Ledin and Pedersen, 1996). These bacteria initiate the sulfide oxidation reactions, and with time the pore water will become more acidified due to acidity released. Acidophilic sulfur and iron oxidizers will then start to grow and catalyze the oxidation reaction further, producing even more acidity.

Ebenâ et al. (2003) investigated the microbial communities in pore water samples from Impoundment 1, Kristineberg, by MPN-dilution and PCR-screening. They found iron- and sulfur oxidizing-bacteria (*At. ferrooxidans* were in majority among these) in hot-spots throughout the deposit, even at anoxic or dysoxic locations below the groundwater table. These findings are in agreement with Wielinga et al. (1999), who also found hot-spots with high bacterial concentration, high diversity and high activity in anoxic zones. This shows that the microbial community and processes in a tailings deposit are far more complex than simple, strictly-controlled laboratory experiments. This also implies that oxygen has not been completely excluded from the impoundment as a result of covering, and that the installation of covers will not totally inhibit the pyrite oxidation processes.

### 3.5 Pyrite oxidation in Impoundment 1

Carlsson et al. (2003) reported that the average pyrite content in Impoundment 1 is ~20 % in unoxidized tailings and ~1-2 % in oxidized tailings. They also analyzed the pore water (e.g. pH, S and Fe) in the till cover, the unsaturated zone and the saturated zone near P7 and well O (see Figure 1). Their results are presented in Figure 3, which illustrates the different oxidation zones in a tailings impoundment profile. It is evident that dissolved S increases with depth in the protective layer, while pH and dissolved Fe are rather stable. The pyrite oxidation reaction front is situated in the unsaturated zone, just below the border between oxidized and unoxidized tailings where pyrite, water and DO are available. At the oxidation front there is a lack of pH-buffering minerals (see discussion below), and the lowest pH levels and highest sulfate and ferrous iron concentrations are found here. Below the oxidation front, the enrichment zone is found. In this zone pH-buffering minerals increase the pH level, resulting in decreased solubility and precipitation for many elements. Finally, below the groundwater table, all DO has been
consumed and conditions are strictly anoxic, sulfate and ferrous iron concentrations decrease and eventually stabilize (Fe $\sim$ 7.5 mM; S $\sim$ 20 mM), and pH reaches circum-neutral levels again. It is evident that sulfide oxidation is an on-going process in Impoundment 1, at least in some regions, since the pore water samples reported in Carlsson et al. (2003) were collected three years after the installation of the sealing layer.

In the base case used in MiMi’s Performance Assessment (Höglund and Herbert, 2004), the oxygen intrusion rate through the sealing layer is assigned a conservative value of 1 mol/m$^2$/year. In combination with an infiltration rate of 100 mm/year, this would result in pore water concentrations of 3 mM ferrous iron and 6 mM sulfate. These predictions are lower than actual concentrations at the oxidation front analyzed by Carlsson et al. (2003), and imply that it is difficult to predict the accurate oxygen concentrations below the sealing layer.

3.6 Acid neutralizing processes in Impoundment 1

In a tailings impoundment environment, processes that buffer the pH by consuming protons are important, since these processes may thus reduce the acid mine drainage.

3.6.1 Alkalinity and acidity

The buffer capacity of an aqueous system is defined as the alkalinity (Equation 19) or acidity (Equation 20), which controls the pH. The net alkalinity or acidity depends on the relative rates of mineral dissolution, which produces or consumes acidity. The alkalinity is defined as the acid neutralizing capacity in solution with respect to the CO$_2$-H$_2$O titration end point, at about pH 5.4 (Stumm and Morgan, 1996; Drever, 1997; Strömberg and Banwart, 1999b). In acid water the alkalinity is negative, i.e. [H$^+$] $>$ [HCO$_3^-$]. Acidity includes aluminum and ferric iron as well (Drever, 1997).

\[
alcalinity = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (19)
\]

\[
\text{Acidity} = [\text{H}^+] - [\text{HCO}_3^-] + 3[\text{Fe}^{3+}] + 2[\text{Fe(OH)}^{2+}] + [\text{Fe(OH)}_2^+] + 3[\text{Al}^{3+}] + 2[\text{Al(OH)}_2^+] + [\text{Al(OH)}_3^-] \quad (20)
\]

Acidity may also be present in a latent form as ferrous iron, which is expressed first when DO is available. In this case, ferrous iron may oxidize to ferric iron (Equation 5), which further hydrolyzes and finally precipitates as ferric iron oxyhydroxide and releases protons.

3.6.2 Weathering of pH-buffering minerals

The net alkalinity or acidity in a tailings deposit system depends on ion exchange, on the protonation of mineral surface sites, and on mineral dissolution and alteration reactions. Ion exchange and surface protonation are fast reactions and have limited buffering capacity. Mineral dissolution and alteration reactions are slower and have a much larger buffer capacity, and are thus dominant and the most important in the system. Dissolution of non-sulfide minerals may buffer pH by consuming protons, and important pH-buffering minerals in Impoundment 1 are calcite, chlorite, amphibole, plagioclase and K-feldspar (Höglund and Herbert, 2004). In Impoundment 1, K-feldspar, Mg-chlorite, plagioclase and amphiboles-pyroxenes are most common, while calcite is only present in trace amounts (Table 1).

Calcite dissolution (Equation 21) consumes protons at a rate that is faster than pyrite oxidation by DO (Equation 4) by three orders of magnitude (Höglund and Herbert, 2004).
CaCO₃ + 2 H⁺ → Ca²⁺ + CO₂ + H₂O  

However, since calcite only is present in minor amounts in Impoundment 1 (Table 1) and is quickly depleted, the neutralization potential of Mg-chlorite, plagioclase, and K-feldspar is more important. Weathering rates for plagioclase and K-feldspar are two orders of magnitude slower than pyrite oxidation, and Mg-chlorite is three orders of magnitude slower than pyrite oxidation (Younger et al., 2002; Salmon and Malmström, 2004).

Mg-chlorite is strongly pH-buffering, and is probably the mineral which has the main responsibility for acid neutralization in Impoundment 1, since one molecule of Mg-chlorite consumes 16 protons when it is acidentally dissolved (Equation 22). In an ideal closed system, the acidic dissolution of Mg-chlorite increases the pH level to almost neutral or slightly basic pH (Höglund and Herbert, 2004).

Mg₄FeAlSi₃AlO₁₀(OH)₈ + 16 H⁺ → 4 Mg²⁺ + Fe²⁺ + 2 Al³⁺ + 3 SiO₂ + 12 H₂O  

(22)

Plagioclase and K-feldspar are slightly weaker pH-buffering minerals compared to chlorite. Dissolution of plagioclase (Na/Ca-feldspar with variable composition) may consume one or more protons, depending of the formula of the mineral. One example is given in Equation 23, where the plagioclase adesine is acidically dissolved by consuming 5.8 protons. Dissolution of K-feldspar is similar to plagioclase. Stoichiometric dissolution of K-feldspar in a closed aquatic system releases alkalinity, while under open acidic conditions, one K-feldspar molecule consumes one proton and is then transformed to monosilicic acid, for example kaolinite (Equation 24) (McBride, 1994).

Na₀.₄₅Ca₀.₄₅Al₂₅₅Si₂₅₅O₈ + 5.8 H⁺ → 0.55 Na⁺ + 0.45 Ca²⁺ + 1.45 Al³⁺ + 2.55 SiO₂ + 2.9 H₂O  

(23)

KAlSi₃O₈ + H⁺ + 4.5 H₂O → 0.5 Al₂Si₂O₅(OH)₄ + 2 Si(OH)₄ + K⁺  

(24)

Due to the different dissolution rates for the pH-buffering reactions discussed above, several reaction fronts will develop at various depths in tailings deposits, and these fronts will move downwards. At the sulfide oxidation front (located where pyrite, DO and water is available) metals and acidity are released, and these are transported downwards in the deposit. The calcite dissolution front is located deeper down, is very distinct, and moves downwards faster compared to the sulfide oxidation front, due to the faster dissolution rate for calcite relative to pyrite. The front for e.g. Mg-chlorite and K-feldspar moves rather slowly and is not as distinct as the sulfide oxidation front, due to the slower dissolution rates for these minerals relative to pyrite. Field studies at Impoundment 1 show that Mg and Al are depleted in the weathered zone, due to chlorite dissolution (Höglund and Herbert, 2004). These field studies together with theoretical estimates show that about 50-75 % of the acidity produced from sulfide oxidation is neutralized by Mg-chlorite dissolution (Höglund and Herbert, 2004). MiMi’s Performance Assessment (Höglund and Herbert, 2004) has shown that it is not possible for all acidity (including latent acidity) to be neutralized before it exits the deposit, and thus the mine drainage is acidic.

3.6.3 Precipitation and sorption of metals

In the mine tailings leachate, there are high concentrations of different ions, and some will precipitate to form secondary minerals at saturation, in the presence of DO and/or at increased pH. Common secondary precipitates are for example ferrihydrite (FeO[OH], α-FeOOH), goethite (α-FeOOH), gypsum (CaSO₄ x 2H₂O), jarosite (K,Na,H₂O[Fe₃(OH)₆(SO₄)₂]), schwertmannite (Fe₃O₉(OH)₆(SO₄)₂) and anglesite (PbSO₄) (Gleisner and Herbert, 2002; Jönsson, 2003).

The specific surface areas of secondary iron oxides and hydroxides are rather large. Their surface sites are negative and consist of hydroxyl groups, which are pH-dependent (i.e. increased negativity with increasing pH). These sites interact with ions in the solute, and contribute to acid-base reactions, ion exchange and formation of surface complexes. This implies that metal cations in the leachate strongly adsorb to the precipitates, and are depleted when pH is increased. Metal ions in the leachate may also be depleted by complexation to organic matter, which is present in low concentrations (Drever, 1997; Jönsson, 2003).

4 SUMMARY OF THE PAPERS

In this section the performed laboratory experiments (presented in Paper I-V appended to the thesis) are briefly summarized. The materials, methods and results in these studies are thoroughly presented and discussed in the appended papers.

4.1 Paper I

The aim with this paper was to investigate the abiotic and microbial sulfide oxidation rates under oxic conditions in freshly processed pyrite-rich tailings (obtained from the tailings mill in Boliden, northern Sweden). A comparison of oxidation rates was performed for pyrite under a) abiotic-alkaline, b) abiotic-acidic, and c) microbial-acidic conditions. These respective rates can be related to pyrite oxidation in a) newly deposited tailings, b) the same tailings after the acid neutralization potential is consumed, and c) tailings after an acidophilic bacterial population has been established. Sulfides present in this tailings material were pyrite (32.4 wt.%), sphalerite (0.79 wt.%), arsenopyrite (0.64 wt.%), galena (0.21 wt.%), and chalcopyrite (0.18 wt.%). The original pH in the fresh tailings slurry was 10-12, due to chemical treatment during the recovery process at the mill.

Three batch experiments were performed in duplicate at room temperature in Erlenmeyer flasks placed on a rotary shaker under oxic conditions for three months. Tailings and distilled water were added (tailings mass/total mass of 1:10) to each flask. For the microbial study, an active mixed acidophilic culture originating from an acidic pond in Kristineberg, was cultivated on a modified 9K
nutrient medium, and then inoculated to the microbial flasks. Conditions in the solutions were: a) untreated, b) acidified, and c) acidified-inoculated. The leachate in the batch experiments was sampled and analyzed weekly for pH, redox potential, sulfate and metals.

Speciation modeling of the leachate composition during the experimental period was performed with Visual MINTEQ (Gustavsson, 1999), a Windows™-based version of MINTEQA2 (Allison et al., 1991), to predict the potential precipitation of secondary minerals in the solutions. This indicated that all batch solutions were originally greatly supersaturated with the iron oxides ferrhydrite, lepidocrocite, and goethite. For the unacidified abiotic experiment, these conditions persist throughout the remainder of the experiment. Upon acidification, mineral equilibria in the acidic abiotic and microbial experiments shift, resulting in that both ferrhydrite and gypsum are in equilibrium in solution. At the end of the batch run, the more soluble ferrhydrite becomes increasingly undersaturated in the microbial experiments, while the less soluble Fe oxides lepidocrocite and goethite approach equilibrium.

Pyrite oxidation rates (presented in Table 2) were estimated based on the sulfur release rates to the solutions. As expected, microbial oxidation displayed the most rapid rates, followed by abiotic oxidation in acid environments and finally by abiotic oxidation in untreated tailings. Because of the potential precipitation of gypsum in the batch solutions, these oxidation rates are considered minimum values.

The release rates for copper and zinc from chalcopyrite and sphalerite in the acid experiments were also investigated. These rates were normalized to the metal concentration in the tailings, and then compared to the release rate for iron from pyrite. These normalized results indicated that metal release decreased in the order Cu > Zn > Fe, demonstrating that pyrite is more resistant to oxidation than sphalerite and chalcopyrite, which is in agreement with Scharer et al. (1994). However, the comparison of these normalized sulfide mineral oxidation rates must be considered with some caution, since it is likely that the sulfides contain impurities, and that the precipitation of iron oxides would result in an underestimation of Fe release. The release rates obtained for Cu, Fe and Zn in the two acidic experiments suggest that chalcopyrite, pyrite, and sphalerite oxidation is controlled by both pH and microbial catalysis. Using the obtained release rates, chalcopyrite and sphalerite oxidation rates were estimated. Chalcopyrite and sphalerite oxidation rates were greater by a factor of 1.5 and 2, respectively, in the microbial experiment relative to the acidic-abiotic experiment. Pyrite oxidation rate was greater by more than one order of magnitude in the microbial experiment compared to the acidic abiotic experiment. These results suggest that pyrite is more resistant to acidic abiotic oxidation than to microbial oxidation, while a significant fraction of sphalerite and chalcopyrite were oxidized in the acid-abiotic solutions.

4.2 Paper II

This study investigates the effect of the oxygen partial pressure on oxidation of pure pyrite in the presence of the sulfur and iron oxidizer Acidithiobacillus ferrooxidans. This study is important, since very few studies have quantitatively addressed the effect of low oxygen partial pressure on microbial pyrite oxidation. Hence, there was a need to determine microbial pyrite oxidation rates over a range of DO concentrations under controlled conditions. In order to improve the understanding of the relationship between microbial pyrite oxidation rates, DO, and ferric iron concentrations, pyrite oxidation rates at various concentrations of DO were examined.

Five different batch experiments were performed in duplicate at room temperature for 75 days under various DO levels (≤ 0.006, 13.2, 64.8, 129, 273 µM) in Nalgene bottles. The reactors contained pure pyrite grains (particle size 63-250 µm) and a modified 9K nutrient medium at pH 3. The reactors were inoculated with an active pure strain of At. ferrooxidans. All solutions were frequently sampled and analyzed for sulfur, total iron, Fe(II), pH, redox potential and microbial activity.

In order to determine if specific solid phases were in equilibrium with the reactor solutions, as an indication of possible precipitation and solid phase control of solute concentrations, the saturation indices of various secondary precipitates were investigated with the geochemical model PHREEQC2 (Version 2.6 from 2002; Parkhurst and Appelo, 1999), in conjunction with the PHREEQC database to assess the potential precipitation of secondary minerals in the columns. These calculations indicate that a number of mineral phases approach equilibrium (i.e. saturation index ~0) in the various reactor solutions, during the experimental period. Goethite is close to saturation in many of the solutions at the start of the experiment, while lepidocrocite is the only phase that is close to equilibrium at the end of the experiments. Lepidocrocite may control iron solubility at low DO concentration (≤ 13.2 µM); in the other experiments, lepidocrocite is supersaturated and may be precipitating. Potassium jarosite (KFe₃(SO₄)₂(OH)₆) is supersaturated at higher DO concentrations (64.8-273 µM), and strengite (FePO₄ · 2H₂O) is supersaturated in all solutions; both these phases may be precipitating when supersaturated. Regardless of the equilibrium iron phase, these results indicate that iron should be precipitating from the reactor solutions and will be controlling Fe solubility in the experiments.

The results from the bacterial enumeration of the planktonic cells in the reactor solution showed that the cell concentration in all the experiments generally increased with increasing DO content. Bacterial concentration at [DO] = 273 µM was one order of magnitude greater (≥10⁶ cells/mL) compared with experiments at [DO] ≤ 129 µM (≥10⁵ cells/mL).

Pyrite oxidation rates from all experiments (presented in Table 2) showed positive correlation with DO, Fe(III) and bacterial concentration. The microbial oxidation rates determined in this study were significantly slower than rates presented by Olson (1991). This is probably the result of different physical and geochemical conditions between the two studies. In particular, the final pH values of the solutions from the Olson study were lower by about one pH unit than in this present study, which led to much higher total Fe concentrations in the study by Olson (1991). At low pH (< 2), most of the total iron will be present as Fe(III). Therefore, the significantly greater
Table 2
Estimated sulfide mineral oxidation rates from the studies in Paper I-III and V presented in the thesis. The standard deviations given originate from average values derived from duplicate experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_{FeS2}$ - abiotic (mol m$^{-2}$ s$^{-1}$) ($\times 10^{-10}$)</th>
<th>$R_{FeS2}$ - microbial (mol m$^{-2}$ s$^{-1}$) ($\times 10^{-10}$)</th>
<th>$R_{Fe1-xS}$ - abiotic (mol m$^{-2}$ s$^{-1}$) ($\times 10^{-10}$)</th>
<th>$R_{ZnS}$ - abiotic (mol m$^{-2}$ s$^{-1}$) ($\times 10^{-10}$)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh tailings</td>
<td>0.36 (±0.03)$^a$</td>
<td></td>
<td></td>
<td></td>
<td>[DO]=273µM pH = 8</td>
</tr>
<tr>
<td>Fresh tailings</td>
<td>0.59 (±0.03)$^a$</td>
<td>2.4 (±0.2)$^a$</td>
<td></td>
<td></td>
<td>[DO]=273µM pH = 2-3</td>
</tr>
<tr>
<td>Pure pyrite</td>
<td></td>
<td>7.0 (±2.8)$^a$</td>
<td></td>
<td></td>
<td>[DO]=273µM pH = 2.5</td>
</tr>
<tr>
<td>Pure pyrite</td>
<td></td>
<td>3.1 (±1.4)$^b$</td>
<td></td>
<td></td>
<td>[DO]=129µM pH = 2.6</td>
</tr>
<tr>
<td>Pure pyrite</td>
<td></td>
<td>2.6 (±0.5)$^b$</td>
<td></td>
<td></td>
<td>[DO]=64.8µM pH = 2.6</td>
</tr>
<tr>
<td>Pure pyrite</td>
<td></td>
<td>0.19$^b$</td>
<td></td>
<td></td>
<td>[DO]=13.2µM pH = 2.6</td>
</tr>
<tr>
<td>Pure pyrite</td>
<td></td>
<td>0.099 (±0.112)$^b$</td>
<td></td>
<td></td>
<td>[DO]≤0.006µM pH = 2.8</td>
</tr>
<tr>
<td>Old unoxidized tailings, coarse$^c$</td>
<td>0.0023$^d,e$</td>
<td></td>
<td>0.023$^d,f$</td>
<td>0.12$^d$</td>
<td>coarse-grained anoxic pH ~ 5</td>
</tr>
<tr>
<td>Old unoxidized tailings, fine$^c$</td>
<td>0.00085$^d,e$</td>
<td></td>
<td>0.0030$^d,f$</td>
<td>0.0082$^d$</td>
<td>fine-grained anoxic pH ~ 4</td>
</tr>
<tr>
<td>Old unoxidized tailings, coarse$^c$</td>
<td>0.0026$^g,e$</td>
<td></td>
<td>0.027$^g,f$</td>
<td>0.00081$^g$</td>
<td>coarse-grained anoxic pH ~ 5</td>
</tr>
</tbody>
</table>

$^a$ Rates from batch study with freshly processed Boliden tailings (Paper I).
$^b$ Rates derived from batch study with pure pyrite grains (Paper II).
$^c$ Oxidation rates derived from column experiments are limited by the DO level and the flow rate.
$^d$ Rates derived from column study with Kristineberg tailings (Paper III). The estimated rates are not strictly abiotic, since the presence of acidophilic bacteria was also confirmed in the tailings and in the leachage.
$^e$ Assumption: all released sulfate from the Kristineberg tailings originates from pyrite (Paper III).
$^f$ Assumption: all released sulfate from the Kristineberg tailings originates from pyrrhotite (Paper III).
$^g$ Rates derived from column study with Kristineberg tailings (Paper V). The estimated rates are not strictly abiotic, since the presence of acidophilic bacteria was also confirmed in the tailings and in the leachage.

Fe(III) concentration at lower pH in the study by Olson (1991) is likely the major factor responsible for the much higher oxidation rates in that study.

The results from this study show that bacterial concentration is dependent on the availability of DO at all DO concentrations (i.e. [DO] ≤ 273 µM), but other studies have shown that pyrite oxidation is independent of bacterial concentration at levels above ~10^6 cells/mL. The results obtained in this study support the indirect mechanism of microbial pyrite oxidation at presence of DO, where At. ferrooxidans oxidizes ferrous iron to ferric iron, which then oxidizes pyrite.

4.3 Paper III

The study in Paper III focuses on the 11 first months of a ~33 month laboratory experiment. Results from the full period are presented and discussed in Paper IV. The study in Paper III was performed to simulate oxygen-limited conditions in water-saturated tailings, following the installation of a soil cover. Investigations of variations in sulfide oxidation behavior between two 50-year-old unweathered sulfidic tailings from the interior of the same deposit (the soil covered Impoundment 1, in Kristineberg, northern Sweden) were performed.

Tailings used in the experiments were collected from two different sites from the unsaturated zone of the deposit, right below the oxidized zone. The materials were of two different grain sizes (coarse-grained: 0.02-0.6 mm, and fine-grained: 0.0015-0.06 mm) and with slightly different mineralogical composition. Sulfide minerals present were (reported for the coarse-grained and fine-grained tailings, respectively): pyrite (16.7 and 22.1 vol.%), pyrrhotite (3.25 and 0.30 vol.%), sphalerite (1.4 and 0.05 vol.%), chalcopyrite (0.70 and 0.53 vol.%), galena (0.10 and 0 vol.%), and arsenopyrite (0.10 and 0 vol.%).

The experiment was performed at room temperature under 11 months in two water-saturated columns, where air-saturated distilled water was pumped into the bottom of the columns, and leachate discharging from the top. The leachate was sampled at the column outlet, and samples for
Speciation modeling of the leachate composition during the leaching period was performed with PHREEQC. Geochemical calculations indicated that the leachate from the coarse tailings was relatively close to saturation with respect to ferrihydrite and gibbsite (Al(OH)₃). The leachate from the fine tailings was close to saturation with respect to chalcedony (SiO₂) during the entire experimental period, while ferrihydrite was close to saturation until day 250, when the solution became unsaturated with respect to ferrihydrite (data not shown). This is in agreement with the geochemical modeling of groundwater samples from Kristineberg (Holmström et al., 2001), suggesting that ferrihydrite may be present and interact with the aqueous solution in the unoxidized tailings in Impoundment 1, Kristineberg.

Although the major sulfide mineral in the tailings was pyrite (ideal S:Fe molar ratio of 2.0), the S:Fe molar ratio in the leachates over the eleven months was between 1.0-1.5. This observed molar ratio is in agreement with previous field data and laboratory experiments using tailings from the site. This indicates either that pyrrhotite is the main iron sulfide undergoing oxidation in the experiments, or, alternatively that the S:Fe molar ratio in the leachate is determined by pyrite weathering in conjunction with other processes releasing iron or immobilizing sulfate. Indeed, speciation modeling of the leachates indicates that ferrihydrite was close to saturation, suggesting that a ferric oxyhydroxide may have dissolved/precipitated during the experimental period, thereby affecting the S:Fe molar ratio. The S:Fe molar ratio may also have been affected by the observed element concentrations in the leachates, since they still were declining slightly at the end of the 11 months, i.e. steady-state was not fully achieved. Further, the S:Fe molar ratio may also have been affected by washout of ions present in the tailings pore water prior to the start of the experiments.

In this study, the release of sulfate, iron, and zinc is tentatively attributed to sulfide oxidation at the end of the experiments. The results indicate that sulfide oxidation continues in a tailings deposit where the oxygen availability is decreased, even though the rates are low. Pyrite and pyrrhotite (as an alternative) oxidation rates obtained (derived from surface area normalized release rates) from the two column experiments during “steady-state” in the coarse and fine tailings, respectively, are presented in Table 2. The sphalerite oxidation rates (Table 2) were found to be low compared with the pyrrhotite oxidation rate but higher than pyrite oxidation rates.

The presence of a mixed acidophilic bacterial culture in the tailings and the leachate (containing the sulfur and iron oxidizers, e.g. Acidithiobacillus ferrooxidans), was also confirmed by both cultivation and optical microscopy at the end of the experimental period. This implies that the obtained oxidation rates are not strictly abiotic.

This study shows that pyrite-rich tailings from two sampling sites in the same deposit show different weathering behavior, and that the primary difference can be attributed to differences in mineral composition and grain surface area between the materials. Heterogeneity in physical properties will also influence the water flow and the transport of DO and oxidation products. It is thus concluded, based on column experiments, that heterogeneity of tailings will result in zones with different oxidation rates, related to their physical and chemical properties.

These rates reflect oxidation under oxygen-limited conditions at water-saturation, which is the aim with the installation of a soil cover on tailings deposits. Since the concentrations in the leachate from the columns were still declining at the end of this first 11 months of experiment, these estimated rates represent upper limits of the sulfide mineral oxidation rates at the given conditions.

4.4 Paper IV

The study in Paper IV was performed during ~33 months, and is an extended study (regarding both experimental time and modeling) of exactly the same experiment performed in Paper III, where the early leachate compositions from the same pair of columns were evaluated after ~11 months. Paper III and Paper IV are both presented in the thesis in order to illustrate the necessity of performing long-time column experiments to obtain steady-state (i.e. stable element concentrations in the leachate over a long time), and thus the true element release rates that may reflect the conditions in field.

The experiment was performed with water-saturated, unoxidized sulfidic tailings (from Impoundment 1, Kristineberg) of two different grain sizes in two columns at reduced oxygen availability. The aims with this study were to: determine the element discharge rates, address the congruency of heavy metal release, investigate the pH-buffering, and address the effect of the Fe(III) oxidation pathway on the element discharge rates.

The tailings materials and columns used are the same pair as presented in Paper III. The air-saturated inlet solution was continually pumped through both columns for a total of ~33 months. After ~11 months the distilled inlet water to the coarse-grained column was changed to an air-saturated ferric iron solution for the rest of the experimental period. The inlet fluid to the fine-grained column consisted of distilled water throughout the entire experimental period. In order to investigate the processes that control element release, the flow rate was increased by one order of magnitude in the fine-grained column during the last seven months of the experiment. Sampling and analyzing procedures were exactly the same as reported in Paper III.

Speciation modeling of the leachate composition during the leaching period was performed with PHREEQC. This indicated that none of the minerals, which may potentially control element concentrations in AMD environments (Nordstrom and Alpers, 1999), were consistently close to equilibrium with the aqueous phase, with exception for possibly a SiO₂-phase. Mass-balance over the columns, using the leachate composition and measured water flow rate, indicated that less than 1% of the sulfides and even less of the aluminosilicates and (hydr)oxides had been depleted during the experiment.

To investigate the water residence time within the columns, a non-reactive tracer test was performed, and this showed that the water flow was heterogeneous. Inside the columns, there were presumably preferential flow paths and/or stagnant pore water zones, a portion of which could
have originated during the column preparation before the start of the experiments. However, previous studies (Berglund et al., 2003; Malmström et al., 2004) have also indicated flow heterogeneity in tailings deposits, because the release of the contaminants in the leachate have been affected and decreased strongly.

During the first and second year of the experimental period the element concentrations in the leachates declined slowly, indicating temporary geochemical processes (e.g. dissolution of secondary minerals) and/or washout of pore waters containing high elemental concentrations from stagnant pore water zones. Steady-state was not achieved until after approximately two to three years of experimental period, and this implies that a long period of time is necessary before the effect of remediation by soil cover is apparent in the groundwater quality inside the deposit, and also in the discharge from the deposit.

Comparisons between these column experiments and reported field studies from Impoundment 1 (Werner et al., 2001; Carlsson, 2002; Carlsson et al., 2003) show that the sulfate and base cation release rates in the columns generally are faster by one order of magnitude relative to estimated release rates at the oxidation front in field. However, since the DO entrance rate to the columns was faster by one order of magnitude relative to the ingress rate in the field, this would explain the higher sulfate release rate in the column experiments. A consequently greater acidity production in the column experiments leads to a greater cation release rate in the columns. Nevertheless, release rates in the column experiments and in the field are similar within a factor a ten; hence, the weathering processes occurring in the columns experiments are comparable with the processes occurring inside Impoundment 1.

Investigations of the element release rates in the column leachates showed at steady-state that sulfate, iron and zinc originated from the congruent oxidation of pyrite and sphalerite by the incoming oxidants, while arsenic, copper and lead were partly retained in the material. This retention occurred over a distance of only ~20 cm in the columns (see Paper IV for details), and also under shorter water residence times than those estimated for the interior of a tailings deposit. These results imply that substantial retention of elements is also likely in the field. Further, among the pH-buffering elements in the leachate, calcium was dominating, principally due to calcite dissolution. The base cations sodium, potassium and magnesium were released by the dissolution of aluminosilicates, and these reactions were presumably controlled by chemical kinetics. The pH level in the column leachates was ca. 4.5-5 and the acidity was low, which seemed to be a function of the water flow rate and oxygen ingress rate. The release of base cations was forced by the acidity production rate, while pH levels and water residence times were less important.

4.5 Paper V

The laboratory study in Paper V was similar to the column studies in Paper III-IV. The intention with this study was to evaluate if the composition of the pore water percolating through the soil cover on Impoundment 1, in Kristineberg, could have any influence on the element release rates in the tailings. The hypothesis was that Fe, Al, and Mn could be released to the water percolating through the soil, and that Fe(III) and Al(III) would hydrolyze in solution, while Mn(IV) could precipitate, thus adding acidity to the input solution (Drever 1997; Höglund and Herbert, 2004). Further, the dissolution rate of pH-buffering minerals (Equation 21-24) may be elevated and base cation concentrations may be higher, due to the increased acidity. Finally, Fe(III) may also enhance pyrite oxidation via the ferric iron pathway (Equation 5).

This hypothesis was tested in a ~24 month column experiment, where distilled water was enriched in solutes by passing a column filled with soil cover material, and then air-saturated prior to entering a column filled with water-saturated sulfidic tailings (tailings from the same original sample as the coarse tailings used in Papers III-IV). The leachate was sampled at the outlet of the tailings column, and samples for pH, redox potential, anion and cation analyses were collected frequently. To study the soil cover-effect, this experiment was compared with a previous column experiment (Paper III; coarse tailings column), where air-saturated distilled water directly entered the water-saturated tailings column.

The results of the experiment showed that the concentrations of some elements (primarily Si, Al, Fe and Mn) in the ion-enriched inlet water increased greatly during the experimental period, while others stayed constant. This implies that these elements are mobilized from the glacial till and released to the percolating water, which infiltrates through the tailings. A maximum concentration of only 15 µM total iron was measured in the soil leachate. Even if all this iron occurred as ferric iron, this concentration is very small compared to the DO concentration (i.e. 268.5 µM at 22.5°C), and hence would contribute very little to the rate of pyrite oxidation by ferric iron reduction. However, Al(III), Fe(III) and Mn(IV) (the latter two produced by the oxidation of Fe(II) and Mn(II), respectively) may have hydrolyzed or precipitated, and may thus have increased the solution acidity. Increased acidity implies a higher amount of protons for dissolution of pH-buffering minerals, which then may have released more base cations.

The element concentrations in the tailings leachate showed a similar decreasing trend with time as reported for the comparable column experiment in Paper III, where the inlet water was composed of distilled water instead of ion-enriched water. Generally, surface area-normalized release rates (data shown in Paper V) and sulfide oxidation rates (Table 2) estimated in this study are slightly greater (factor of 1.6 for release rates; factor of 1.1 for pyrite and pyrrhotite oxidation rates) compared to the rates estimated in Paper III. However, since these rates are derived from column experiments, they are thus of minor importance, since they are limited by the oxygen flow into the column. Further, the greater element concentrations in the tailings leachate from this experiment, compared with the previous experiment (Paper III), are most likely due to the oxygen flow rate, which was slightly greater in this ion-enriched experiment relative to the similar experiment with distilled water.

The molar ratio of sulfate to iron in the leachate stabilized after six months at ca. 1.5, and persisted throughout the experimental period. This low ratio shows
either that sulfate has precipitated, or that iron is in excess. Mineral equilibrium calculations performed with PHREEQC did not indicate that any secondary sulfate minerals could be precipitating from the solution at the end of the experiment. However, the calculations showed that ferric hydroxide was either close to saturation or undersaturated at various stages throughout the experiment. This suggests that an iron excess may explain the low S/Fe ratio, with iron concentrations greater than expected for the stoichiometric dissolution of pyrite. The excess iron may be partially derived from pyrrhotite oxidation, since the pyrrhotite content was relatively high, or from the dissolution of iron (oxy)hydroxides that may have formed in the tailings prior to the start of the experiment.

This study shows that remediation of tailings impoundments by soil covers provides slightly enhanced concentrations of ions with the infiltrating water to the tailings. However, most of the ions percolate into the impoundment without any apparent effect on the weathering rates in the tailings material, while a few may slightly increase the acidity. With the results from this study, it is recommended that soil covers should have a low iron content for the best effect of covering tailings deposits.

5 DISCUSSION

5.1 Experimental design

The studies within this thesis have been of two different types: batch and column experiments performed at room temperature in the laboratory. Element release rates and sulfide mineral oxidation rates (Table 2) have been estimated from the experiments, where the oxidation rates are based on the sulfur release rates to the solutions (i.e. from the sulfur moiety of sulfide minerals). There are, however, a number of basic differences in the design of batch and column experiments, which requires that the experimental results should be interpreted in different ways.

In the different batch experiments, which were performed in duplicates, the oxygen concentration in the reactors was maintained at a stable DO concentration ([DO] \( \leq 273 \) µM) through equilibrium with molecular oxygen at a constant partial pressure. All tailings/pyrite grains were water-covered, the solution was constantly circulating within the batch reactors and all the grains were mixed continually. Since the oxygen supply in this case was virtually unrestricted, these conditions imply that the sulfide oxidation processes within the batch experiments were limited only by surface kinetics. Products released from sulfide oxidation reactions in batch experiments were enriched in the solution or precipitated (primarily as Fe-(oxy)hydroxides) on particles or reactor walls. Because of the relatively large availability of molecular oxygen, the element release rates will be rather rapid. That is, chemical kinetics controls the element release rates from sulfides, such that easily-oxidized sulfides (such as pyrrhotite) may be oxidized prior to pyrite. Preferential pyrrhotite oxidation also results in a sulfur to iron molar ratio close to one in the solution, compared with the column experiments where the ratio will be closer to the stoichiometry of pyrite, due to the oxygen-limited conditions (discussed below).

The design of the column experiments results in conditions that are significantly different from the batch experiments. In the column experiments, the tailings were water-saturated and there was a continual supply of air-saturated solution into the bottom of the columns. The DO present in the solution was however consumed rather rapidly after entrance to the column by biogeochemical processes in the tailings material. As a result, most of the interior volume of the columns was anoxic, which also was confirmed in the leachate where a strong dominance of ferrous iron over ferric iron was observed. In the column experiments, the oxygen supply was limited to the rate at which it was supplied with the input solution. Sulfide mineral oxidation by DO or ferric iron occurred where oxygen was available, i.e. close to the inlet. Sulfide oxidation was thus limited by the supply of oxygen, and not by chemical kinetics.

Experiment duration is a critical factor when evaluating the results of column experiments, since stable leachate concentrations may only be attained after several years. This is illustrated in Papers III and IV. The leachate from the column study in Paper III was evaluated after 11 months regarding weathering rates and leaching variations due to different grain-sizes. After 11 months the discharging element concentrations seemed to have stabilized to some extent (Figure 4), and it was confirmed that a smaller grain-size results in greater concentrations of discharging elements. Further, the results suggested that pyrrhotite, due to its softness relative to pyrite, may contribute to a large portion of the iron and sulfur present in the leachate, and that the observed iron to sulfur ratio close to 1.0 also originated from pyrrhotite oxidation. However, this column leaching experiment continued another two years, and subsequent analyses of the leachate showed that steady-state was not achieved until after 2-3 years (Figure 5). The later investigation showed that element release rates derived from column experiments were comparable with rates observed in the field.

The observed slow approach to steady-state in the column studies thus implies that a long period of time is necessary before the effect of remediation by soil cover, i.e. decreasing concentrations of contaminants, is reflected in the groundwater quality inside the deposit, and finally also in the discharge.

5.2 Laboratory and field oxidation rates

Microbial and abiotic pyrite oxidation rates estimated from all batch experiments (freshly processed tailings at [DO] = 273 µM; pure pyrite grains at [DO] \( \leq 273 \) µM) are presented in Table 2. Comparing these rates shows that microbial pyrite oxidation rates of pure pyrite at [DO] = 64.8-273 µM were greater by a factor of 1.1-2.9 relative to microbial pyrite oxidation in fresh tailings, even though the pH level was similar in all microbial reactors. The reason for the faster rates in the pure pyrite experiments, despite only one out of three experiments was at equilibrium with atmospheric oxygen, is most likely due to that the pyrite was first ground prior to the start of the experiments, and then the pyrite grains were ultrasonicated in 95 % ethanol to remove fine adhering particles. This grinding and
cleaning process most likely produced fresh, more reactive surfaces relative to the pyrite present in the fresh tailings that were not treated. Further, the presence of pH-neutralizing minerals in the fresh tailings, such as slaked lime (from the floatation process), calcite and aluminosilicates, may also have buffered the solution and resulted in somewhat less acidity. The lower microbial rates in the experiments with fresh tailings may also reflect the greater uncertainty in these values, since an accurate determination of the pyrite content and available pyrite surface area in the tailings was difficult. However the rate variations between pure pyrite at [DO] = 64.8-273 µM and microbial pyrite oxidation in fresh tailings are within the same order of magnitude, which indicates that buffering processes in the tailings did not exert an overly great influence on microbial pyrite oxidation.

The microbial pyrite oxidation rates in fresh tailings at [DO] = 273 µM are greater by 1.1-1.4 orders of magnitude relative to pure pyrite oxidation at low [DO] (≤ 13.2 µM). Further, microbial pyrite oxidation rates obtained in the fresh tailings are faster by a factor of 4.1-6.7 relative to abiotic pyrite oxidation at pH 2-3 and pH 8 in the same fresh tailings. In addition, the abiotic pyrite oxidation rates obtained at [DO] = 273 µM are faster by a factor of 1.9-6.0 relative to microbial pure pyrite oxidation at [DO] ≤ 13.2 µM. Although the rate variations between the different batch experiments were expected, this shows that pyrite can oxidize microbially where the DO level is strongly reduced, even though the rate is much slower than at oxic conditions. However all microbial rates obtained in this study (Table 2) are slower, when compared to previous studies. For example, the results in the studies by Olson (1991) and Nicholson (1994) show oxidation rates that are faster than the rates from Paper I and II. The reason for the higher rates in other studies probably depends on the lower pH of these studies (pH 2), higher temperatures (ca. 25-30°C), a greater degree of mixing (gyratory shaker at 200 rpm) and greater Fe(III) concentrations.

Microbial pyrite oxidation rates obtained from the pure pyrite experiments at the various DO levels also showed a positive linear correlation with the concentration of DO, ferric iron and cells, which implies that these factors are dependent on each other. This relationship applies for a total cell concentration > 10^6 cells/mL, at [DO] ≥ 13.2 µM. The positive correlation implies that the DO level governs the oxidation rate, since DO oxidizes both pyrite and ferrous iron, and the cell growth is dependent on the DO as electron acceptor for oxidizing ferrous iron. The resulting ferric iron will then oxidize pyrite, and thus the indirect microbial pyrite oxidation is supported in Paper II.

In a field perspective, the microbial pyrite oxidation rates obtained from fresh tailings in batch experiments (Table 2) may be applicable to the oxidation rates derived in the unsaturated zone of the tailings impoundment above the groundwater table, where oxygen, an active bacterial culture and water are available. Since the oxidation rates...
Figure 5. Concentration of elements [mol dm$^{-3}$] in the outflow from the columns as function of time [day]. Grey shaded area indicates period for KCl-tracer test. N.B. Logarithmic scale on the vertical axis. Panels to the left are for the fine tailings, panels to the right are for the coarse tailings. a-b) Fe, Zn, and $\text{SO}_4^{2-}$; c-d) Al, Si, and Mn; e-f) Na, K, Ca, and Mg. (From Paper IV)

for the microbial pure pyrite batch experiments were estimated at DO levels ranging from anoxic to oxic (Table 2), these rates may reflect oxidation at conditions that are probably present in the unsaturated zone and at the groundwater table. Paper II indicates that the pH level and total Fe concentration is important when predicting the pyrite oxidation rates. However, pH levels in the oxidation zone in Impoundment 1 may be $>2$, due to acid consuming processes that also occur. At pH $>2$ much dissolved iron will precipitate, and hence decrease the oxidative capacity of the solution. Papers I and II show that optimal conditions for pyrite oxidation include a low pH, high concentration of ferric iron and presence of DO, as well as the presence of active iron and sulfur oxidizers that catalyze the reactions.

Pyrite oxidation rates (Table 2) in the column experiments were derived from surface-area normalized release rates, which were estimated when the element concentrations in the leachate achieved steady-state. However, steady-state was not reached until after approximately two to three years of experimental period. These estimated pyrite oxidation rates are several orders of magnitude slower than both abiotic and microbial pyrite oxidation rates derived from the batch experiments. The major reason for this is that the oxidation rates in the column experiments are controlled by the supply of molecular oxygen with the inflowing water. Oxygen is rapidly consumed close to the column inlet, such that anoxic conditions prevail through most of the column. This implies that sulfide mineral oxidation is only possible close to the inlet where DO is available. Further, the supply of oxygen is sufficiently slow so that sulfide oxidation rates are limited. Papers III-V have shown that the element release rates are rather slow compared to the batch
experiments, and that iron, zinc and sulfate release rates were controlled by the inflow rate of DO. In addition, Paper IV showed that pyrite and sphalerite oxidized congruently (i.e. sphalerite oxidation produces equal moles of zinc and sulfate) in the presence of DO or ferric iron. In terms of the release of other elements, the column experiments also showed that substantial retention in the tailings is expected of arsenic, copper and lead.

While the column experiments were designed to investigate biogeochemical processes that are expected to occur in the natural environment inside Impoundment 1 in Kristineberg, the derived sulfide oxidation rates from the column experiment (Table 2) do not reflect the true oxidation rates in field since the oxygen ingress rates differ. Furthermore, the derived sulfide oxidation rates are of minor importance, since they are oxygen-limited. Nevertheless, much can be learned about the associated processes of acid production and neutralization with this experimental design (see below).

Comparisons of reported field studies from Impoundment 1 (Werner et al., 2001; Carlsson, 2002; Carlsson et al., 2003) and these column experiments (see Paper IV for details) show that the release rates for sulfate in the columns generally are faster by one order of magnitude relative to estimated release rates at the oxidation front in field. Since the DO entrance rate to the columns was faster by one order of magnitude relative to the entrance rate in the field, this would explain the greater sulfate release rate in the column experiments. However, the release rates in the column experiments and in field are similar within a factor a ten, since the oxygen ingress rates differ by a factor of ten, which implies that the weathering processes occurring in the columns experiments are comparable with the processes in the interior of the deposit.

Additionally, as explained earlier in section 3.2.5, there are also physical factors affecting the element release rates, such as the grain-size variations of the tailings. A smaller grain-size is inversely proportional to a larger surface area, and thus has a larger capacity for oxidation reactions to occur, resulting in higher release rates. This was confirmed in Paper III, where the element concentrations obtained from weathering of fine-grained tailings were greater relative to element concentrations from coarse-grained tailings. Transforming this to field conditions in Impoundment 1, it shows that zones containing finer-grained material located towards the southeast may exhibit greater release rates relative to the coarser-grained material located to the northwest.

Finally, the soil cover on Impoundment 1 may also affect the oxidation processes to some extent, since the percolating water becomes enriched in Fe, Al and Mn, which by hydrolysis provides the solution with acidity. Elevated concentration of ferric iron from the soil cover may also increase the pyrite oxidation rate. It is thus important to use soil material with a low iron content in future remediation activities of mine tailings deposits by soil covering.

5.3 Effect of bacteria on oxidation rates

Since there are anoxic conditions inside the columns, the possibility for sulfur and/or iron oxidizing bacteria to catalyze the sulfide mineral oxidation reactions is also limited. This is due to the fact that they can not oxidize the sulfides faster than DO is added to the system. Since the microbial pyrite oxidation rates in the batch experiments (Paper II) were reduced by 1.8 orders of magnitude when the DO level was changed from oxic to anoxic, a comparison between the batch and column experiments at anoxic conditions show that microbial pyrite oxidation in batch experiments still are faster by 1.6-2.1 orders of magnitude relative to the pyrite oxidation rates derived from column experiments. This difference is probably due to the fact that the oxygen supply under anoxic conditions in the batch experiment was still greater than the oxygen supply in the column experiment. In addition, the microbial conditions were optimal (except for the DO availability) in the batch experiments prior to the start of the experiments, while the tailings in the column experiments were not exposed to a nutrient medium. This implies that the estimated rates in the column experiments can be considered as abiotic, even though the tailings were not sterilized before used in the experiments and bacteria certainly are present. However, it should be noted that there are active sulfur and iron oxidizers present even in anoxic zones below the groundwater level, according to field studies performed in Impoundment 1 (Ebenå et al., 2003).

5.4 Acidity production and consumption

The most important acid consuming processes (described earlier in section 3.6.2) in a tailings deposit are dissolution of pH-buffering minerals, which here are presented in decreasing order of importance: calcite > Mg-chlorite > plagioclase > K-feldspar > other aluminosilicates and micas. In Impoundment 1 calcite is only present in trace amounts (Table 1), which implies that it is depleted quickly, and thus Mg-chlorite should be the dominating pH-neutralizing mineral in the deposit.

The column studies showed that calcium was the dominating base cation in the leachates, and that calcite dissolution, unexpectedly, was the main acidity neutralizing process (70-80%). The calcium release was controlled by proton production. Magnesium, potassium and sodium were released to the leachates from the dissolution of aluminosilicates (primarily Mg-chlorite), and these neutralizing processes were controlled by (bio)geochemical kinetics. Interpretations of the different results from the column experiments showed that the acidity production rate forced the base cation dissolution reactions, which consumed protons in the pH-buffering zone, while pH levels and water residence time were less important. However, the pH levels in the column leachates were ca. 4-5 and the acidity was low, which seemed to be a function of the water flow rate and DO ingress rate. These results thus show that the pH level in the discharge from the Impoundment 1 will be around 4-5, while the pH in the oxidation zone will be slightly lower because of active sulfide oxidation processes.

These results also show that pH-neutralizing processes, especially calcite dissolution, are important in Impoundment 1. When calcite still is present protons may be consumed rapidly. However, when it is depleted, Mg-chlorite will be the most important pH-neutralizing mineral
because of its large quantities and relatively rapid dissolution kinetics compared with other silicates in the impoundment. This indicates that the pH levels in the discharge may decrease slightly when calcite is depleted, on the assumption that the DO availability is low under a soil cover, limiting the proton production from the sulfide oxidation reactions occurring in the tailings. Thereafter, Mg-chlorite is the dominating pH-neutralizing mineral, but it is vital that oxygen availability remains limited if the pH is to remain near neutral levels in the discharge from the deposit.

6 CONCLUSIONS

- Microbial pyrite oxidation rates estimated from the batch experiments may be comparable with microbial pyrite oxidation rates in the unsaturated zone and at the groundwater table in a tailings impoundment, where oxygen, an active bacterial culture and water are available.
- Sulfide oxidation processes in the batch experiments were limited only by surface kinetics and not by oxygen availability.
- The results from the microbial experiments with pure pyrite indicated a positive linear correlation between the concentration of dissolved oxygen, ferric iron and bacterial cells (at a total cell concentration > 10^8 cells/mL and a dissolved oxygen concentration ≥ 13.2 µM), which implies an interdependence of these factors.
- The indirect mechanism for microbial pyrite oxidation by the ferric oxidation pathway was supported by the results from these batch experiments with pure pyrite.
- The results from the column studies verified that a smaller grain-size is inversely proportional to a larger surface area, and thus has a larger capacity for oxidation reactions to occur, resulting in higher release rates.
- Iron, zinc and sulfate release rates in the column experiments were controlled by the supply of oxidants (i.e. dissolved oxygen, ferric iron), which was dependent of the water flow rate into the column.
- The estimated rates in the column experiments can be considered as abiotic, since the microbial activity was reduced, due to the limited availability of oxygen.
- Acid neutralization reactions in the column experiments resulted in the release of base cations to the column leachate. Calcite was the most important pH-buffering mineral, even though it was only present in minor amounts in the tailings. Mg-chlorite, which also has a rather large pH-buffering capacity, will be the most important pH-neutralizing mineral when calcite is depleted, because of its large quantities in the tailings. It was confirmed that acidity forced the calcite dissolution, and aluminosilicate dissolution was controlled by (bio)geochemical kinetics.
- Steady-state element release from the column experiments was not achieved until after 2-3 years, which show that long-term column experiments are important to study the weathering processes within tailings.
- These column experiments also showed that the results are comparable with results from field studies, implying that column experiments can be used to realistically simulate and study processes within tailing impoundments.
- This study also confirms that a long period of time is necessary before the effect of remediation by soil cover is reflected in the groundwater quality in the impoundment.

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