Sulphide-Rich Tailings Remediated by Soil Cover

Evaluation of cover efficiency and tailings geochemistry, Kristineberg, northern Sweden

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Errata


p. 18, Eq. 17:

\[ D_{\text{eff}} = 3.98 \times 10^{-7} \left[ \frac{(\theta - \theta_{w}) - 0.05}{0.95} \right]^{1.7} T^{1.5} \]

should be

\[ D_{\text{eff}} = 3.98 \times 10^{-9} \left[ \frac{(\theta - \theta_{w}) - 0.05}{0.95} \right]^{1.7} T^{1.5} \]

correspondingly Figure 6 at page 19, illustrating this equation be reduced 100 times.

p. 34, Figure 12:

Unit for the element Mg should be mg/l instead of µg/l

Article II, p. 219, Figure 7:

For As fraction B and C have the same colour. Fraction C should be in black colour.

Article III, p.8, Figure 3 (continued):

Unit for the element Mg should be mg/l instead of µg/l

Article IV, p. 60, Figure 1 (caption):

Figure 1 Kristineberg mining area and Impoundment 1. Square indicates location for field installations and the sampling area for the sealing layer. Enlargement is presented in Figure 2.

Should be

Figure 1 Kristineberg mining area and Impoundment 1. Square indicates location for field installations and the sampling area for the sealing layer.
Abstract

The efficiency of soil cover as a method of remediation of sulphide-rich tailings has been studied at an impoundment at the Kristineberg mine, Northern Sweden. Two variations of soil cover were used in the remediation. The major part of the impoundment was covered with a 1.0 m layer of till where the groundwater table was shallow. In combination with the removal of the water dividing ditches surrounding the impoundment, saturation of the tailings as well as the till cover was achieved. In areas with a deeper groundwater it was not possible to saturate the tailings by means of this method. Instead, a sealing layer consisting of a 0.3 m compacted clayey till, acting as an oxygen diffusion barrier, situated underneath a 1.5 m protective cover was used. Field studies at the impoundment cover pore-water extraction and solid-sample collection at five locations. Solid tailings were subject to sequential extractions in the laboratory. Open groundwater pipes for measuring groundwater levels as well as BAT® groundwater pipes for geochemical sampling of the groundwater were installed over the entire impoundment. At a location in the area with the sealing layer, tension lysimeters were installed in a profile in the vadose zone down to the unoxidised tailings. Nearby, one oxygen diffusion lysimeter and one water infiltration lysimeter were installed below 1.5, 1.0, and 0.3 m of protective till cover, respectively. The sealing layer has been investigated in the laboratory with respect to its susceptibility to the effects of freezing and thawing. The solid samples from the tailings revealed that in some areas, the sulphide oxidation prior to the remediation had been intense. In other areas, with a shallower pre-remediation groundwater table, the oxidation seemed to have ceased upon reaching it. In the area with water-saturated tailings, increased pore water concentrations around and below the oxidation zone were visible, due to release of secondarily retained elements. Elements with peaks at this level were As, Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn. However, compared with pre-remediation data the concentrations are generally lowered, indicating that sulphide oxidation has slowed down. Sequential extraction of the solid tailings samples showed that a large part of the elements below the oxidation front, in the secondary enrichment layer, are relatively mobile and are released within the adsorbed, or the amorphous iron (oxy)hydroxide fractions. This was the case for elements such as Fe, As, Ba, Cd, Co, Cr, Cu, Ni, and Zn. The continuous measurements performed in the groundwater pipes show that elements released by raising the groundwater table are transported out of the impoundment, and that the overall water quality is constantly improving due to the inflow of uncontaminated groundwater from the adjacent hill slope. A model for the water transport has been developed and prediction of the future behaviour of the impoundment is proposed. The tension lysimeter measurements show that infiltrating water cause remobilisation and diffusing oxygen still causes some oxidation. However, most of these metals are retained again prior to reaching the groundwater table. The mass flow caused by this mobilisation is very small compared to that of the laterally flowing groundwater. Mobilised elements are Fe, S, Si, Al, Cd, Co, Hg, Mg, Mn, Mo, Ni, Pb, and Zn. The freeze/thaw laboratory experiments stress that the compaction degree is very important for achieving a hydraulic conductivity low enough for the requirements of a sealing layer. If a high enough compaction degree is obtained, the corresponding hydraulic conductivity is very low, approximately $5 \times 10^{-10}$ m/s with the clayey till used at the study site. The freeze/thaw experiments also revealed that when properly compacted the clayey till is sensitive to frost penetration, leading to an increase of hydraulic conductivity, up to $10^{-8}$ m/s. Oxygen diffusion measurements indicate that the effective diffusion through the sealing layer is low for all three different protective till-cover thicknesses, and so is the water infiltration. However, during the field measurements, no frost penetration into the sealing layer was monitored. Based on the oxygen diffusion coefficients measured simple shrinking core models predicted a decrease in oxidation rate of about 2-3 orders of magnitude. During summer 2002 the area with 0.3 m of protective cover was desiccated and the oxygen diffusion coefficient increased one order of magnitude. Thus, it is necessary to prevent the sealing layer from drought as well as from freezing. The oxygen diffusion measurements also indicate a low oxygen transport during winter and late autumn. At the moment the function for the test area with 1.5 m of cover is satisfactory and should remain so if not subject to frost and/or desiccation. The effects by frost penetration in field scale on the sealing layers efficiency as an oxygen barrier is still uncertain since no frost actions in the sealing layer has occurred.

Key words: Geochemistry, soil cover, sulphides, tailings, freeze, thaw, pore water, vadose water, groundwater, oxygen diffusion, water infiltration
List of papers

This thesis consists of the following seven papers, henceforth referred to by their Roman numerals.


*During my postgraduate studies the following papers has also been written. However, these papers are not included in my doctoral thesis.*


1 Introduction

Mining has a rich tradition in Sweden. Several mines were started as early as the Viking era, or the early Middle Ages, and continued to be mined into modern times. Well-known examples are the Falu copper mine, the Sala silver mine and the Bersbo mine. The revenues from these and numerous other mining operations, mainly from the Bergslagen area (Figure 1) in south-central Sweden, made it possible for Sweden to become an important political and trading power in northern Europe and the Baltic region during the 17th and 18th centuries. Know-how and technological advances arrived with skilled labour from abroad; mining experience as well as metal refinement was brought in by Germans. Metal refinement was also brought in by the Walloons (mainly from the county Liège in today’s Belgium), who helped the mining and metallurgical areas of Sweden to develop into quite diversified communities although many of the workers returned to their homeland areas when their contracts were fulfilled. As few as 900 of the Walloons stayed in Sweden (Immigrant-institutet, http://www.immi.se/alfa/v.htm, accessible 2002-11-11). Partly because of the increased demand for labour, due to the increased metal production, Finnish immigrants were resettled in the scarcely populated areas of Värmland and Dalarna in Bergslagen. In the traditional mining area of Bergslagen, mining supported and/or initiated other industrial developments which are still important today; for example suppliers of mining equipment like Sandvik, Atlas Copco, and Svedala. Around the Falu copper mine, associated industries such as production of sulphuric acid, nitric acid (once forest products were no longer used in the mining process), vitriol, red paint pigment, acetic acid as well as tanneries and sausage production arose, and mining companies like Stora Kopparberg also developed interests in forestry and paper mills after ceasing to use the forests in their ore production. Though no longer as important, as it once was, mining for iron oxide ore as well as sulphide ores containing valuable metals such as copper, lead, zinc, silver, and gold is still a major primary industry, especially in northern Sweden. Refinement and high-end metal products have continued to be important in Bergslagen and the surroundings. Memories of a past when mining was one of the most important sources of income are evidenced by the presence of mine and metal refining museums as well as old industrial remnants related to mining and metal production at locations such as Falun, Långbens gruvby, Lesjöfors museum, Nordmark gruvby, Hornkullen, and Lòa. Old and unremediated mining waste deposits are also reminiscent of this era.

A problem associated with these remnants from older mining activities as well as from today’s sulphide-rich tailings or sulphide containing waste rock is that, if left unremediated, generation of acid mine drainage (AMD) or acid rock drainage (ARD) might be initiated. The terms AMD and ARD refer to the same phenomenon; their use is essentially dependent on traditions in the locations where they occur. From here on, the term AMD will be used. AMD formation is due to the presence of oxygen and moisture within the waste. If deposited above ground and left unsaturated, the presence of oxygen and a suitable amount of water will induce oxidation of the sulphides, and metal-rich acidic drainage water will be produced. However, there are certain remediation means that could be utilized to slow down the processes generating the AMD. The commonly used remediation methodologies are soil cover (Swanson and Wilson, 1997) and water cover (Feasby et al., 1997; Gustafsson, 1997). Both aim at reducing the oxygen availability for the waste rock and tailings. To investigate the suitability of these methods as well as to produce more detailed knowledge about the key processes occurring, the MiMi (Mitigation of the Environmental Impact from Mining Waste) project, funded by the Swedish Foundation for Strategic Environmental Research (MISTRA), was initiated in 1998. It is a joint effort by six universities, two firms of consultants and the two mining companies Boliden and LKAB. The field site for the project is the Kristineberg
mine, in Northern Sweden. The present thesis is part of the MiMi subproject *Design of soil covers for long-term performance*, which began in 1998 at the Kristineberg mine. The aim of this study is to investigate the efficiency of soil cover remediation, and to quantify its capability, in the long run, to decrease acid mine drainage from sulphide-rich tailings impoundments to a level which is not harmful to the local environment.

The term used in this thesis with regard to the layer with low hydraulic conductivity commonly used as part of soil cover remediation will be “sealing layer” to comply with the terminology of the MiMi Performance Assessment group. However, when a soil is used as the sealing layer, another term that is appropriate and perhaps more illustrative is “barrier soil”. Both are recognized as adequate names but as for the AMD/ARD issue, the choice is largely dependant on tradition.

![Historical and current mining areas, including known sulphide mineralizations in Sweden.](image-url)

**Figure 1.** Historical and current mining areas, including known sulphide mineralizations in Sweden.
2 Scope of the thesis

The thesis covers the remediation of sulphide-rich tailings by soil covering. The focus is on geochemical processes occurring in the remediated tailings as identified through studies of their solid composition, as well as of pore water and groundwater geochemistry. Also, the function of the soil cover itself and its efficiency in acting as a barrier against oxygen diffusion and water infiltration have been studied. These studies have been conducted with field investigations and laboratory set-ups, for testing material sampled at the field site. The main objectives of these studies have been to improve the existing knowledge of the function of soil covers and to accommodate more secure predictions of the future efficiency of applying soil cover remediation.

3 Review of mining waste research

3.1 Swedish mining waste research

Interest in researching remediation technology for sulphide-rich mine wastes has increased during recent decades. One reason why Sweden tries to remain at the forefront of mine waste research, for some specific types of mine related waste, is that Sweden is one of the major metal mining countries in Europe. Annually 20-27 Mt (million tonnes) of waste rock and 20-22 Mt of tailings from sulphide and iron ore mines are produced and deposited (SWRC, 1998). The different kinds of mining waste produced per year thus amount to more than half of the total industrial waste produced annually in Sweden (by weight), or about ten times the total municipal waste produced every year (by weight) (SWRC, 1998). The amount of mining waste produced has increased almost every year, although the number of mines in production has decreased. Totally over the years, more than 300 Mt tailings and 200 Mt waste rock from sulphide ore mines have been deposited in Sweden (SWRC, 1998).

The first Swedish scientific research conducted on sulphide mining waste were initiated in the 1970s by Jacks (1976) as well as by Qvarfort (1979) and Karlqvist & Qvarfort (1980). The Swedish Environmental Protection Agency (SEPA) initiated a research programme during the years 1983-1988 called “Gruvindustrins restproduktupplag”, in English “Waste deposits from the mining industry” (SEPA, 1993). The purpose of the programme was to develop models for decreasing the heavy metal drainage and AMD production at the waste sites. Modelling was performed to evaluate the effects different dry cover methods could have on metal transport. At the old Bersbo mine site, a full-scale remediation project was performed in the late 1980s using several different types of dry covers (Lundgren, 1993). The incorporating of experiences from projects conducted abroad (mainly in Canada) led to a new initiative for conducting research within this field. The financier of this new strategic research programme, which was run during the years 1994-1996, was the Swedish Waste Research Council (AFR). A large number of research reports were produced within this project (e.g. Eriksson et al., 1994; Gärd et al., 1994; Eriksson, 1996; Håkansson, 1996; Strömberg, 1997; Bergström, 1997; Öhlander et al., 1997; Lövgren and Sjöberg, 1997; and Granhagen, 1998). A need for more research regarding water cover and different polishing techniques was identified as was the need for continued research on dry covers, since knowledge of the processes affecting the cover and the geochemical conditions below the soil cover was still relatively unsatisfactory. After the closure of the AFR-programme, a new project application “Mitigation of the environmental impact from mining waste”, abbreviated MiMi, was initiated in cooperation with the Swedish mining companies LKAB and Boliden. The programme was to be funded by the Swedish Foundation for Strategic Environmental Research (MISTRA).
3.1.1 Gruvindustrins restproduktupplag

Within the programme “Gruvindustrins restproduktupplag” a research plan was produced by the Swedish Geotechnical Institute (SGI), which aimed at quickly producing a methodology to avoid AMD formation from sulphide-rich mining waste (SEPA, 1993). The need for a design technology was deemed acute. It was also realised early on that remediation of the mining waste deposits would be a costly affair. A cheap technology was needed, as was a priority list of the objects. The programme was initiated in 1983. One of the keystones for the programme was the assumption that different types of remediation actions were needed for present as well as for future mining objects. The focus was on cover research (SWRC, 1993). After the completion of the programme, it was concluded that applying a cover was suitable; both on old, already oxidized and on fresh, unoxidized waste (SWRC, 1993). At that time, comparable research had also been initiated in Australia and Canada, and it was advised that the results in these countries and others where to be continually examined (SWRC, 1993). Another important conclusion was that there was a need to verify the results obtained through the programme in a full-scale project. The full scale project would investigate several questions that were hard to investigate in a smaller scale, or to scale up from a smaller scale. Such questions were: How long will oxidation products from the period prior to the remediation continue to leach from a remediated site where oxidation has ceased. What happens if cut-off ditches are introduced around a waste site? Which effects will root penetration through the sealing layer have? Which thicknesses of protective covers and sealing layer would be the most efficient?

3.1.1.1 Bersbo

The pilot project chosen was the old Bersbo mine, just outside the town of Åtvidaberg in southern Sweden. At this site, copper mining is known to have started in the 15th century, but it may also have started as early as the 13th century. The area was mined until the early 20th century (Karlqvist and Qvarfort, 1980; Collin, 1998). The waste mainly consisted of stones of various size dumped in heaps. The two main deposits were covered during 1988-89 (Collin, 1998). The Steffenburg deposit was covered by 0.5 m of compacted clay under 2 m of till. At the Storgruve deposit, another cover type consisting of 0.25 m Cefyll mixed with macadam was used instead of compacted clay. Also the Cefyll was covered by 2 m of till. The outcome of remediation has been studied and several parameters measured.

- Geochemistry of drainage water
- Lateral runoff from the covered deposit
- Water percolation from the covers
- Groundwater levels in the covered waste and in the covers
- Oxygen transfer through the covers
- Oxygen concentration in the mine-waste pore gas

The measured parameters have been evaluated by among others Lundgren (1993, 1997, and 2001). Prior to remediation Bersbo had been quite thoroughly investigated by, for example Håkansson et al. (1989), Karlsson et al. (1988), Allard et al. (1987), Brandt et al. (1987), Lundholm and Andersson (1985). Collin (1998) used the results to evaluate the modelling methodology used to predict the efficiency of soil covers for mine waste deposits. The total database from Bersbo sums up to about 40,000 data points and it is one of the more extensive bodies of material in Sweden for monitoring the remediation of mine waste (SWRC, 1993). At Bersbo geophysical methods were also used to measure the integrity of the sealing layers (Bergström, 1997). The results showed that the cefyll layer was too rigid to withstand settlements within the waste and that the clay was more plastic and could cope with the
inevitable movements in a better way (Bergström, 1997). The somewhat successful methodology incorporating sealing layers and a protective till cover showed that it was to be a promising tool/methodology in the work with mining waste remediation.

![Figure 2. Soil cover designs at Bersbo and Ranstad.](image)

**3.1.1.2 Ranstad**

Following the remediation of Bersbo, the open pit and the leached uranium waste at Ranstad just outside of Skövde, southwestern Sweden was remediated (Börjesson et al., 2001; Börjesson, 2002). The uranium was recovered by sulphuric acid leaching of the alum shale host rock. The alum shale contained about 12 wt. % pyrite and had a rather high concentration of several metals and metalloids such as As, Cu, Ni, V, and Zn (Börjesson et al., 2001). Subsequent to the atmospheric exposure, the oxidation started. The remediation of the area was initiated in 1990. The tailings were covered by a 0.2 m thick, low-permeable (K< 5x10⁻⁹ m/s) layer of clay-mixed till, a 0.2 m drainage layer of crushed limestone and a 1.4 m protective cover of till on top of the drainage layer. Uppermost on the protective cover a 0.2 m layer of topsoil was applied (Börjesson et al., 2001). In addition to the cover remediation, a chemical treatment plant was build to treat the collected drainage water from the ditches collecting the diffuse flow. The covering of the tailings led to a large decrease in most metals in the collected drainage water as well as an increased pH almost instantly as the remediation was completed (Börjesson et al., 2001). The decrease has continued since then, although at a slower rate. However, the volume of leachate water is greater than estimated. It is assumed that it will continue to remain at this high level for a long time to come. Currently, ongoing research is aimed at ways of minimizing the amount of leachate requiring treatment as well as the use alternative methods for treating the formed leachate (Börjesson, 2002). Since 1992, surface water samples have been collected each week from a number of locations such as the drainage ditches surrounding the impoundment. The open pit has been transformed into a lake and its evolution is monitored. Groundwater pipes were installed in the tailings area 1994 and they are sampled once a year (Börjesson et al., 2001). Seven oxygen diffusion lysimeters were installed and are measured with regard to both diffusing oxygen as well as infiltrating water.

Also at Ranstad, Bergström (1997) used geophysical methods to investigate the soil cover remediation. The results showed that at the time of the measurements the sealing layer was homogeneous and free from any increased fracture density.
3.1.2 Other locations in Sweden

Other mining areas in Sweden where research has been performed during the early 1990s include the Laver mine in northern Sweden. Laver is not remediated, which enabled the researchers to study and understand the reactions occurring in an unremediated tailings impoundment. The results from the studies at Laver have been presented by Ljungberg (1999), Ljungberg and Öhlander (1996 and 2001), Holmström et al. (1999a and 1999b), and Öhlander et al. (2001). During 2001, a follow-up study was carried out to control whether the predictions done almost ten years earlier were correct. Now these data are being evaluated at the division of Applied Geology, Luleå University of Technology. At the Stekenjokk mine, remediated by a water cover, unoxidised tailings with a high sulphide and carbonate mineral content were investigated. The research aimed at investigating the geochemical interaction between subaqueous tailings and the waterbody, and the results were presented by Öhlander et al. (1997), Holmström and Öhlander (1999a and 1999b), Holmström et al. (2000), Öhlander and Holmström (2000), and most recently Eriksson et al. (2001). These investigations provided knowledge about the reactions occurring in water-covered tailings which had not been subject to oxidation prior to the remediation, and it also showed how efficient water cover (or subaqueous disposal) could be, if favourable conditions prevail.

In the old mining area of Bergslagen a number of investigations have been performed on mining waste sites. Among others are the investigations at Galgerberget, Falun, by Stockholm University (Granhagen, 1998) on a cover containing a mix of fly ash and biosludge. Lin (Uppsala University) (Lin and Qvarfort, 1996a; Lin and Qvarfort, 1996b; Lin, 1997a; Lin, 1997b; Lin and Herbert, 1997a; Lin and Herbert, 1997b) mainly investigated a waste rock dump, a mill-tailings impoundment and a sulphuric acid industry waste dump in Falun. Herbert (Uppsala University) also worked with the waste rock dump but mainly with the contaminated groundwater flow (1994, 1995, 1996, 1997a, and 1997b). Strömberg (1997) at the Royal Institute of Technology (KTH) in Stockholm investigated the weathering kinetics of sulphidic waste rock in the Aitik mine. Other KTH studies at the Aitik mine site have been performed by among others Eriksson (1996), who studied the waste rock piles and the effects of different kinds of remediation solutions on the formation of AMD.

Research on the effects caused by old mining waste has been performed by others besides the universities. A project group named Dalälvsdelegationen (the Dalälven Delegation) was formed in 1988 by the Swedish government to put together a plan for reducing the metals transported by the river Dalälven, draining the Bergslagen mining district, within ten years. A subgroup investigated the mine waste deposits within the Dalälven catchment. The results were presented in a report (Lundgren and Hartlén, 1990) and a concluding project report from the main group was issued in 1991 (Lineström, 1991).

3.1.3 MiMi

MiMi is the acronym for the current programme in Sweden solely aimed at mining waste research and its remediation (MiMi, 2001). It stands for “Mitigation of the environmental impact from mining waste”. Funding for the research is provided by the Swedish Foundation for Strategic Environmental Research (MISTRA) and it is coordinated together with the Swedish mining companies Boliden and LKAB. The programme started in 1998 and is to continue to the 31st of December 2003. However, this does not mean the end of large-scale mine waste research in Sweden. Another programme “Georange” has already started (http://www.georange.nu/eng/, accessible 2002-11-11). This programme is devoted to developing exploration geology as well as continuing the research to obtain improved mine waste remediation technologies.
In the programme plan for MiMi, one of the more important conclusions for the future was that if Sweden is to continue to be one of the most important mining countries in Europe, it also has to have state-of-the-art remediation knowledge (MiMi, 2001). The knowledge is of importance to enable the northern part of this country (where most of the mining takes place) to continue with its mining activities whilst at the same time ensuring the preservation of one of the last wilderness areas in Europe (MiMi, 2001). The overall goal of the MiMi programme is thus to devise methods for the safe disposal of mining waste and for the reliable prediction of their function over very long periods of time (MiMi, 2001). The programme consists of six different projects, each studying a specific remediation method. Results are to be synthesized by an operative scientific advisory panel appointed to work with the performance assessment methodology. The different project areas are as follows; Soil-covered tailings, water-covered tailings, biogeochemical barriers, co-disposal technique, wetlands as metal traps, and surface water systems (Figure 3). For the sub-project, Design of soil covers for long term performance within the project “Near Field - Methods and Tools for Optimised Soil Covers,” the goal is to formulate requirements for physical integrity of constructed barriers over time.

![MiMi programme organisation](image)

**Figure 3.** MiMi programme organisation.

For the entire MiMi project, one common field site was chosen. The general idea was that this would facilitate coordination, and collaboration between scientists with different specialities would be better if they were working at the same location. Thus, the whole group of researchers could utilize experiences drawn by one researcher. Sampling campaigns could also be coordinated, so that several different kinds of samples could be obtained at one single occasion. The chosen field site was the Kristineberg mine site in Västerbotten, located in northern Sweden (Figure 4). This location was selected since water-covered tailings, soil-covered tailings, and a combination of both (water-saturated soil-covered tailings) were present at the site.
3.2 Related research

Conducting research on mining waste and its remediation can be coupled to other research areas such as landfill-cover research, and the remediation of other industrial wastes/waste deposits, since some of the methodology in designing the cover as well as the potential problems are the same or similar. Research on waste products from other industries could also prove to be important for certain remediation strategies such as applying sawmill waste (Reardon and Poscente, 1984; Yanful et al., 2000a; Yanful et al., 2000b) and pulp and paper residue from the paper mill industry (Cabral et al., 2000; Chtaini et al., 2001) or mixing tailings with fly ash (Stouraiti et al., 2002). Another method could be the use of sludge and green manure to improve the physical characteristics of tailings (Harris and Megharaj, 2001). Other investigations applying materials rich in organic matter (such as municipal sludge) to deplete the oxygen diffusion were performed by Granhagen (1998) and Peppas et al. (2000), but peat, lime-stabilized sewage sludge and municipal solid waste (Elliott et al., 1997) have also been tested. These solutions can in general only be cost-effective if the product is available close to the mine site to be remediated. Success in mitigating the formation of AMD due to sulphide oxidation using the different methods has varied. However, a possible problem could arise due to the soluble organic compounds formed that could infiltrate into the tailings, e.g. Ribet et al. (1995) investigated the organic cover remediation methodology with regard to its potential for metal release by reductive dissolution of weathered mine tailings.

Different passive polishing methods for groundwater remediation can also be connected to mining waste research due to the lower operating costs compared to traditional pump and treat systems. This is especially the case if the oxidation is ongoing and thus forming AMD but deemed to minor to require a remediation, or if the water table as a measure of the remediation at the site is saturating the secondary enrichment layer and the oxidation zone which lead to a dissolution of secondary minerals previously retained. Such passive treatment methods are the engineered wetlands or the permeable reactive barriers. The permeable
reactive barrier is placed in the path of the migrating plume of contaminated groundwater and
the reactive barrier is usually presumed to work for years or even up to decades without
maintenance. Thus the composition of the material inside is crucial. The material inside the
barrier is chosen on case to case bases since the required geochemical reactions inside the
barrier differ. These reactions can be adsorption, precipitation, reductive precipitation (e.g.
from sulphate to sulphide), or biologically mediated transformations using organic carbon as
the energy source. The formed residues are withheld inside the barrier, but the barrier must
yet continue to be permeable and functional as long as deemed needed. Groundwater
remediation using permeable reactive walls have been tested at laboratory, pilot, and full scale
at several locations over the past years. Descriptions for some of the methodologies adapted
when using the permeable reactive walls are presented in, among others; Puls et al. (1999),
Ludwig et al. (2002), and Benner et al. (2002). A summary of the contaminants possible to
treat and some examples on its use is presented in Blowes et al. (2000).

3.3 International research

The Norwegian and the Finnish EPA organizations had been involved in the Swedish
programme of the 1980s, Gruvindistrins restproduktupplag. On its own the Norwegian
organisation NIVA investigated the water-cover remediation technique and the composition
drainage water from mining waste quite thoroughly. Experiences from its 25 years of
investigations were presented in Iversen and Arnesen (1993). In Canada, the most well known
research was conducted by the Mine Environment Neutral Drainage (MEND) programme
during the years 1989-1997. It then continued for another three years with MEND2000.
Within the MEND programme dry covers as well as subaqueous disposal were evaluated and
the conclusion was that dry covers may be effective, but also that they may be expensive to
construct (Feasby et al., 1997). It was also concluded that water covers and underwater
disposal is to be considered as the best prevention technology for unoxidised sulphide-bearing
waste (Feasby et al., 1997).

Early Australian work was performed in the late 1970s and beginning of the 1980s on the
Rum Jungle uranium mine waste. These investigations included temperature and oxygen
measurements in a waste rock dump and studies of the water quality at the site. Later on, the
efficiency of the remediation was investigated (Harries and Ritchie, 1981; Harries and
Ritchie, 1983; Harries and Ritchie, 1985; Harries and Ritchie, 1987; Harries and Ritchie,
1988). A subsidiary branch from ANSTO was formed, Sulphide Solutions, based on the
experiences gained from these and other investigations.

Not only the mining industry working with the production of base metals from sulphide mines
is a target of concern about the environmental effects caused by the oxidation of sulphides.
The coal mining industry’s spoil heaps (as well as the coal itself) can contain increased
concentrations of mainly pyrite; although generally not as high as in sulphide-bearing metal
mine waste. As early as 1960 the state of Ohio issued a report entitled “Acid Mine Drainage
Manual” aimed, in particular, at targeting the important coal mining industry of the state. This
manual stated that residual spoils or gob, containing sulphides, should be subject to good
housekeeping in order to minimize the acid production associated with mining operations
(Brant and Moulton, 1960). The manual states “Gob piles may be covered with sealing
materials such as clay and then the seal protected from erosion until vegetation is established.
Such procedures may in some cases eliminate acid formation entirely”. Other means of
reducing AMD from the spoil heaps were also mentioned in the technical manual issued.
These recommendations included liming of the drainage water, sealing old mine shafts from
atmospheric oxygen by concrete plugs and flooding, or by limiting the air exchange with
masonry walls but allowing the drainage water to be collected using a water trap construction.
Microbiological treatments were also suggested for continued research, in combination with the addition of an organic source such as sewage, sawdust or natural gas for reducing sulphate to hydrogen sulphide. If iron was to be present in the water and not already precipitated it was further suggested as adequate for forming ferrous sulphide to reduce the acidity of the water. This manual represents one of the earliest attempts to abate the AMD problem in an effort to ensure that an important industry continues to be profitable, though not at the expense of the environment.

4 Weathering, a process governing the environmental setting

The oxidation and weathering of rocks and their minerals are important processes governing the local, regional and the global environment. It is believed that during the last 4,000 million years, weathering has decreased the temperature at the Earth’s surface by 30-45°C (Schwartzman and Volk, 1991). This temperature decrease has been brought about through consumption of CO$_2$ during the weathering of silicates; lowered concentrations have enabled larger heat flows to radiate out of the atmosphere since CO$_2$ is a greenhouse gas. The release of weathered elements is the grindstone that forms life; essential biochemical elements is released from the minerals as well as macro and micronutrients that is utilized to create and sustain life and the build-up of organic carbon in bodies and plants (Schlesinger, 1991; White and Brantley, 1995). It is also a process that if changed, can alter the natural environment and cause harm to a variety of species. Due to its importance to the context of environmental change, the weathering of silicate minerals and rocks has been investigated extensively. Among others researching the processes caused by chemical weathering are Oxburgh et al. (1994), Malmström (1996), Öhlander et al. (1996), Walther (1996), Chen and Brantley (1997), Gout et al. (1997), Nesbitt and Markovics (1997), Land (1998), Strandh (1999), and Land et al. (1999). Physical erosion of the rocks and soils is also caused by freezing/thawing, water and sudden temperature changes. If unnecessary deterioration of a construction such as a soil cover is to be prevented, it is important to bear these actions in mind when planning.

4.1 Chemical oxidation of sulphides

The problem that is mainly associated with sulphide-rich mining waste is AMD formation due to the chemical oxidation of the sulphides. This process has been intensively studied by among others Singer and Stumm (1970), Steger and Desjardins (1978), Taylor et al. (1984), Moses et al. (1987), Moses and Herman (1991), Ahonen and Tuovinen (1992), Elberling et al. (1993), Elberling et al. (1994), Nakamura et al. (1994), Nicholson and Sharer (1994), and Thomas et al. (1998).

The two most common Fe-sulphides are pyrite and pyrrhotite. Pyrite is the most abundant sulphide mineral in the earth’s crust, and as most sulphides it is formed when metal-bearing fluids (magmatic, hydrothermal or meteoric) precipitate Fe when entering a reducing environment. It can also be found in sediments as a secondary formed mineral, authigenic pyrite, which has been produced due to utilization of dissolved sulphate by bacteria to metabolize organic matter. As the sulphate reduction becomes a dominant oxidative process, large amounts of hydrogen sulphide are produced, which through reactions with reduced iron, via a complex pathway, produce a variety of metastable iron-sulphide minerals and thermodynamically stable pyrite (Morse, 1994). This is for instance common along the Bothnian Bay in Sweden (Mácsik, 1999) and in other locations around the world as well, such as Australia (Blunden and Indraratna, 2001) where coastal floodplain deposits can be found. This type of sediment is commonly referred to as acid sulphate soil. Both pyrite and pyrrhotite are often major components in complex sulphide ores, mined for their valuable
metal content. Typical metal-bearing sulphide minerals are chalcopyrite (CuFeS$_2$), sphalerite (ZnS) and galena (PbS). In the waste forming from sulphide ores the two Fe-sulphide minerals are often abundant and enriched due to the removal of the ore minerals. These minerals can be used in the production of sulphuric acid; however, use for this purpose depends on the cost for the alternative raw materials available, such as primary sulphur. The crushed and ground sulphide particles, usually in the size-range of silt to fine sand, expose a larger surface area to volume ratio compared to natural conditions. This enables a rapid oxidation of the sulphides if the environmental conditions permit oxygen and water to reach the sulphide. When these Fe-sulphides are oxidised, dissolved Fe$^{2+}$, SO$_4^{2-}$ and H$^+$ are formed. Under most conditions, pyrrhotite is considered the more easily oxidised mineral of the two (Nicholson and Sharer, 1994). Some intermediate phases of sulphur can form during oxidation. Oxidation is a complex process involving several steps. The oxidation of pyrite and pyrrhotite is commonly described by the reactions given in equation 1 and 2.

$$2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 2\text{Fe}^{2+} + 4\text{H}^+ + 4\text{SO}_4^{2-}$$ \hspace{1cm} (1)

$$\text{Fe}_{1+x}\text{S} + \frac{4-x}{2}\text{O}_2 + x\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + (1-x)\text{Fe}^{2+} + 2x\text{H}^+$$ \hspace{1cm} (2)

where $x = 0-0.125$

The Fe$^{2+}$ formed and released may oxidise further and generate additional acid through the equations 3 and 4.

$$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O}$$ \hspace{1cm} (3)

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+$$ \hspace{1cm} (4)

Fe remains in the reduced ferrous (Fe(II)) state for quite some time, if the solution remains acid (pH≤4) (Nordstrom et al., 1978). Reaction 3 is a slow process and is considered the rate-determining step in the formation of AMD (Singer and Stumm, 1970). The reaction proceeds so slowly under acid conditions that acid mine waters would not commonly occur were it not for acidophilic Fe-oxidising bacteria such as Acidithiobacillus ferrooxidans (Nordstrom et al., 1978) and other related species. It has been reported that the bacteria can speed up the rate of Fe$^{2+}$ oxidation several times. Bacterial oxidation is fastest at a pH of around 2-3 and dominates in substantially acidic waters (Banks et al., 1997). Bacterial oxidation may even occur at low temperatures. Ahonen and Tuuvenen (1989) found that oxidation occurred at 4°C, but at a very slow rate, Ebenå et al. (2001) reported non-negligible activity of Acidithiobacillus ferrooxidans at a temperature of 4°C for a strain isolated from the Kristineberg mining area. Elberling et al. (2000) reported that the Acidithiobacillus ferrooxidans had been found in tailings at the Nanisivik mine, Baffin Island, located in an area subject to permafrost. Although at a reduced rate, the bacteria showed that they were able to survive and adapt to the environment and were responsible for about a third of the ongoing oxidation. The ferric iron (Fe(III)) is itself a very strong oxidant which may oxidise pyrite and pyrrhotite (in absence of oxygen). This can be described by the following reaction steps illustrated in equation 5 and 6.

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$ \hspace{1cm} (5)

$$\text{Fe}_{1-x} + (8-2x)\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow (9-3x)\text{Fe}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+$$ \hspace{1cm} (6)

Oxidation of other sulphides may also release metals and sulphate, although no acid is formed.
in the primary step. The sulphide minerals sphalerite, galena and chalcopyrite might oxidise congruently, as written in equation 7 to 9.

\[
\begin{align*}
    \text{ZnS} + 2\text{O}_2 & \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \quad (7) \\
    \text{PbS} + 2\text{O}_2 & \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \quad (8) \\
    \text{CuFeS}_2 + 4\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{SO}_4^{2-} \quad (9)
\end{align*}
\]

To form acid, these cations have to be hydrolysed, which only occurs at a relatively high pH (Stumm and Morgan, 1996). In mine waste environments, these high pH levels are not normally encountered. However, for sulphides such as chalcopyrite the released ferrous iron (Fe(II)) may be oxidised to ferric iron (Fe(III)) and then form Fe-hydroxide, according to reactions 3 and 4 and thus produce acid. In the presence of Fe(III) in acid conditions (pH~2) the predominant oxidation reactions for these minerals (Eq. 10-12), according to Rimstidt et al. (1994), are:

\[
\begin{align*}
    \text{ZnS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightarrow 8\text{H}^+ + \text{SO}_4^{2-} + \text{Zn}^{2+} + 8\text{Fe}^{2+} \quad (10) \\
    \text{PbS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightarrow 8\text{H}^+ + \text{SO}_4^{2-} + \text{Pb}^{2+} + 8\text{Fe}^{2+} \quad (11) \\
    \text{CuFeS}_2 + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} & \rightarrow \text{Cu}^{2+} + 17\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (12)
\end{align*}
\]

5 Introduction to remediation

Although the environmental impacts from mining occur at all stages of the life cycle of a mine; starting with exploration, over the creation of open pits or underground mines, the formation of waste rock dumps and during the processing of the ore, the major long-term effect is considered to be from the tailings impoundments or the waste rock heaps (Morin and Hutt, 1996). In general, the current practice is to construct water-retaining dams to prevent oxidation of the sulphides by keeping the tailings water saturated by decreasing the seepage loss. However, past practice was in general to keep the water level low and to use a spigotting location at the perimeter of the dam, the coarse, more permeable, material was retained in the up-gradient near-dam area and the water table thus kept low (Robertson, 1994).

The most convenient solution to avoid the problem with remediation of the tailings is to use it as a backfill in the mines. Each year about 2 Mt of tailings is backfilled in Sweden (so-called “cut-and-fill mining”), which also is the approximate capacity at the moment (SWRC, 1998). Normally, the fraction used as a backfill material is the coarser fraction of the tailings. The remaining part has to be deposited somewhere, and the most common methodology is to pump it dispersed in water, typically at a solid content of 20-40% by weight, into a natural valley surrounded by valley slopes. It should contain surface drainage systems (ditches) and a downstream dyke. The dyke is usually constructed of an earth-fill material that can be found close to the mine site. However, tailings impoundments and dykes can be constructed in numerous ways depending on the local geography surrounding the mine-site and legislation demands. To prevent oxidation and, in most cases, the production of acid mine drainage (AMD) following the closure of an impoundment, the waste has to be remediated.

The target during remediation has to be to keep the release from the deposit and the rest of the mining area as close as possible to the local background level, and to do this for a period of time in the range of thousands of years, if possible. This low level of AMD release should ideally take place without any additional measures after the finished remediation following the closure of the site. Generally, two solutions are considered for remediating a tailings impoundment. One is to dewater the deposit and add a cap consisting of a low-permeable
material and a protective cover. The other option is underwater disposal (Feasby et al., 1997). The use of underwater disposal, in general, requires a more advanced methodology to ensure the physical stability of the dam unless natural features such as a lake can be used. Earthquakes or other soil movements are more likely to induce liquefaction in a water-covered tailings impoundment than in a dewatered tailings impoundment. A failure after finished remediation probably causes less environmental impact in a dewatered and covered tailings impoundment than in a water-covered tailings impoundment. The tailings dams and their covers are also subject to slow deterioration due to chemical weathering and physical forces such as erosion, frost and vegetation but also due to effects from animals. It is thus logical to investigate and use materials that have shown persistence towards these actions. Materials known to be effective are natural materials, such as soils that have evidently been in place in natural surroundings since the previous ice age, which occurred some 7000-15000 years ago in Sweden depending on the investigated location (Lundqvist, 1986). Nevertheless, prior to considering the use of one material rather than another, whether naturally occurring soils or manufactured like waste products such as certain ashes or enhanced materials by the addition of bentonite (e.g. bentonite enriched sand, BES) or polymeric additives, it has to be carefully investigated with regard to its durability against chemical and physical weathering, since its purpose is to decrease the availability of oxygen for the sulphide-rich waste for a long period of time. Comparing the diffusion capacity of oxygen in air (worst case prior to remediation) and water, the diffusion constant in water is about four orders of magnitude lower. This low diffusion constant in water, or a water saturated soil cover, is the explanation for how the AMD generating processes can be slowed down so efficiently due to the remediation.

5.1 Soil cover

Soil covers are in some contexts referred to as dry covers, which is a somewhat misleading description since the idea of adding the soil cover is to ensure a near-saturated condition in the soil or in a part of the cover to minimize the oxygen transport into the waste. Soil covers can be constructed in various ways and have been investigated at laboratory, pilot, and full scale at many instances by, just mentioning a few; Yanful (1993), Woyshner and Yanful (1995), Swanson et al. (1997), O’Kane et al. (1998), Yanful et al. (1999), Simms and Yanful (1999), and Lundgren (1997 and 2001).

In general, tailings deposits have no bottom liner, so the process water and the possible oxidation products might be transported as a plume with the groundwater out of the impoundment. Some materials present at the sites prior to the mine waste deposition, such as peat, could be compressed if situated underneath the tailings impoundment, and thus act as a filter due to a high capacity to bind S and heavy metals (Salminen and Sipilä, 1996). An installation of permeable reactive barriers as previously described is also a possible mean to abate the groundwater contamination. A relatively large part of the various oxidation products can be shown to be retained as secondary minerals or adsorbed to surfaces of mineral grains, mainly within the vadose zone of the impoundment, prior to being transported out of the impoundment (Blowes and Jambor, 1990; Al et al., 1997; McGregor et al., 1998; McGregor et al., 1998b; Holmström et al., 1999; Ljungberg and Öhlander, 2001; Johnson et al., 2000; Holmström et al., 2001; Dold and Fontboté, 2001). If the impoundment at this stage becomes water covered or the tailings water saturated due to a raised groundwater level, it is likely that the secondarily retained products will be dissolved and at a later stage transported out of the impoundment (Holmström et al., 1999, Corregé et al., 2001). After this washout event the remediation should work properly and protect the waste from further oxidation, provided continued water saturation conditions prevail.
The simplest soil cover is to just add some unspecified soil material, as in example A (Figure 5). According to estimations presented in “Gruavfall från sulfidmalmsbrytning – metaller och sult vatten på drift” (SEPA, 1993), 1.0 to 1.5 m of till cover is likely to decrease the oxidation rate by 80-90%. To enhance the performance of the cover a number of actions can be taken. The disadvantage of just adding a single unspecified soil layer on top of the waste is that the volume of infiltrating water is just slightly reduced (~10%), the metal leachate forming might still be too high as the estimated decrease in oxidation rate in combination with the high infiltration in a single soil layer often is insufficient.

Figure 5 Four different soil-cover designs.
The concept for designing a more advanced soil cover includes a compacted sealing layer with low hydraulic conductivity such as clay or clayey till (where larger stones have been removed) as in example B. Applying this type of cover was estimated (SEPA, 1993) to reduce the oxidation by >99% if 0.5 m of compacted clay and 1.5 m of protective till was applied on top of the waste. Water infiltration was to be reduced by >95% and the amount of metals transported out of the impoundment with the leachate was estimated to be reduced by >99.8%. A drainage layer on top of the sealing layer (Example C) further reduces the infiltration as the hydraulic gradient is kept lower but this trend to increase the transport of oxygen into the tailings as the water content in the cover is reduced. A coarse layer between the sealing layer and the tailings (Example D) may act as a capillary break which prevents dewatering by capillary transport downwards. If the low hydraulic conductivity layer is dewatered there is an increased risk for cracks followed by an increased transport of oxygen. To prevent mixing of the coarser materials and the finer, surrounding material, a geotextile is usually installed in between. This however, has implications for the long term function as the durability of a synthetic material in the time perspective of thousands of years can be questioned. If the geotextile fails due to ageing or mechanical settlement the layers are likely to be mixed and the function of the drainage layer decreased or completely prevented. To prevent erosion of the protective till cover on top of the layer with low hydraulic conductivity a vegetation layer is applied to the protective cover. Important questions are whether the roots of the local species, likely to inhabit the remediated impoundment at some point in the future, will penetrate the low permeable layer, and how thick the protective cover has to be to prevent this, and frost/thaw effects causing cracks and the formation of macropores leading to an increased hydraulic conductivity. After the protective cover has been applied, grass is usually selected for preventing erosion of the protective cover.

The protective cover normally serves one or more of the following functions (from Koerner & Daniel, 1997):

- to store water that has infiltrated into the cover until it is later removed by evapotranspiration;
- to physically separate the underlying drainage and barrier layer components and buried waste from burrowing animals and plant roots;
- to minimize the possibility of human intrusion into the contaminated material;
- to protect underlying layers from excessive wetting/drying (which could cause cracking of fine-grained soils);
- to protect underlying layers in the surface barrier from freezing (which could cause frost heave of underlying soils or cracking of fine-grained soils).

Adding a drainage layer might be desirable for three reasons (from Koerner & Daniel, 1997):

- to reduce the head of water on the barrier layer, thus minimizing infiltration;
- to drain the overlying protection layer, thereby increasing its water storage capacity;
- to reduce and control pore water pressures in the cover soil, and thus improve slope stability.

For the first of these points above it is important to understand that adding a drainage layer can also have a deleterious effect if the drainage layer dries the overlying soil to the point where vegetation fails to thrive. For remediation of mining waste this also has the implication of decreasing the efficiency of the sealing layer, acting as an oxygen diffusion barrier, since the water saturation is decreased. Often, the last reason of the above listed is the most
important. If the cover soil becomes saturated and the water table rises to the surface of the cover system, the factor of safety against a slope failure is reduced to about half the level of that of an unsaturated cover (Koerner & Daniel, 1997). Instead of the conventional low-permeable layer a relatively recent invention could be used; the capillary barrier concept. The idea behind the capillary barrier is that a layer of fine-textured soil is applied to a coarse-textured soil. If these layers are in equilibrium, and there is no water movement between the two layers, they will have the same soil water potential. For any given soil water potential the coarser textured soil will tend to have a much lower water content (drier) than the fine-textured soil. The hydraulic conductivity of unsaturated soils decreases exponentially with decreasing water content, because water flow paths through thin films are extremely tortuous. Dry gravel is thus, theoretically, much less permeable to water than moist sand. The finer textured soil layer will retain most of the moisture and the coarser will serve as a barrier to water percolation due to its dryness. However, there are at least two concerns with capillary barriers:

- the fine-textured soil must not be allowed to migrate over time into the coarser soil;
- after extremely high precipitation (relatively speaking) it may cease to function, temporarily, as the coarse-textured soil becomes moist, losing its water-impeding capability.

To solve the first of the two problems above a geotextile could be used. As for the second problem no convenient solution has been proposed. As previously noted the long term sustainability of synthetic geotextiles is still a matter of uncertainty. The capillary barrier concept has been investigated by among others Rasmuson and Eriksson (1987) and Nicholson et al. (1989). However, according to Morris and Stormont (1997) capillary barriers are not as effective as conventional compacted clay barriers in the hydraulic isolation of waste deposits in climates with moderate to high precipitation. Their principal use is rather in arid or semi-arid environments where the combined effect of evaporation, transpiration, and lateral drainage exceeds the infiltration from precipitation, and thereby maintains a sufficient capillary tension in the upper layer, so that breakthroughs of water into the coarser layer do not occur (Stormont and Anderson, 1999).

### 5.2 Estimating the efficiency of a soil cover

The design incorporating the sealing layer concept is based on the maintenance of a high degree of saturation in the compacted soil layer, thereby decreasing the oxygen diffusion and water infiltration into the waste. As can be seen in Figure 6 the water saturation (defined as $S = \theta_w/\theta$ where $\theta_w$ and $\theta$ is the volume of the water per unit volume of soil and the total volume of the pores, respectively) for a sealing layer has to be about 85-90% or higher to provide an effective diffusion coefficient low enough in the gaseous phase for the porosity chosen in the example. As shown by the figure the effective diffusion coefficient decreases rapidly at high water saturation levels. This implies that the diffusive gaseous flux is becoming less important and that its effective diffusive flux ($D_{eff}$) can even become lower than $D_{eff}$ for water, 2.1x10^{-9} m²/s (CRC Handbook of Chemistry and Physics, 1981). This implies that although the transport of dissolved oxygen in pore water is very small, the relative importance for pore water transport increases at high saturation levels in the soil. The model simulating the sealing layer is based on the Millington-Shearer semi-empirical equation, which is a simple and well-known model for non-aggregated soils, to estimate the effective diffusion coefficient. This model has in many applications provided a reasonable fit to experimental data over a wide range of $\theta_w$ (Collin and Rasmuson, 1988). The function can be written as in equation 13 (Millington and Shearer, 1971):
\[ D_{\text{eff}} = D_0 \left(1 - \frac{\theta_w}{\theta}\right)^2 \left(\theta - \theta_w\right)^{2x} \]  

(13)

and \( x \) are obtained by the solution of
\[ \left(\theta - \theta_w\right)^{2x} + \left[1 - \left(\theta - \theta_w\right)\right]^x = 1 \]  

(14)

where the value of \( x \) is a weak function of the water content.

Equation 14 can not be solved analytically but Schaefer (1997) proposed that it could be expressed as:
\[ D_{\text{eff}} = D_0 \left(1 - \frac{\theta}{\theta}\right)^m \left(\theta\right)^n \]  

(15)

where
\[ m = 10/3 \text{ and } n = 4/3 \text{ for } (\theta - \theta_w) \geq 0.2 \]
\[ m = 16/5 \text{ and } n = 6/5 \text{ for } (\theta - \theta_w) < 0.2 \]
\[ D_0 = 1.78 \times 10^{-5} \text{ m}^2/\text{s} \]
\[ \theta = \text{porosity (volume of pores per unit volume of soil)} \]
\[ \theta_w = \text{volume of the water per unit volume of soil} \]

In the analytical approximation of the Millington and Shearer model the porosity 0.22 was chosen, which is a probable level for a compacted clayey till. Werner (2000) compared the numerical solution (Eq. 13 by using Eq. 14) with the analytical approximation (Eq. 15) and obtained good correlation.

In David and Nicholson (1995), a function for estimating the effective diffusion coefficient for oxygen into tailings (partly dependent on the degree of saturation) was presented (Eq. 16). It is included in Figure 6 as well.
\[ D_{\text{eff}} = \tau D_o^\theta (1 - S)^\alpha + \frac{\tau D_o^\theta}{H} \]  

(16)

where
\[ D_{\text{eff}} = \text{effective diffusion coefficient (m}^2/\text{s)} \]
\[ \alpha, \tau = \text{fitting parameters calculated from laboratory column data of tailings from Quirke mine Ontario (} \alpha = 3.27, \tau = 0.27 \]
\[ D_o^\theta = \text{coefficient for free diffusion in air (} 1.78 \times 10^{-5} \text{ m}^2/\text{s)} \]
\[ D_o^\theta = \text{coefficient for diffusion of oxygen in water (} 2.1 \times 10^{-9} \text{ m}^2/\text{s)} \]
\[ S = \frac{\theta_w}{\theta} \]
\[ H = \text{modified dimensionless Henry’s constant (} 26.32 \text{ at } 10 \degree \text{C)} \]

However, in Figure 6 also a semi-empirical equation presented by Stuparyk (1995), based on the work of Reardon and Moddle (1985), for the effective diffusion into tailings is shown (Eq. 17).
\[ D_{\text{eff}} = 3.98 \times 10^{-7} \left[\frac{((\theta - \theta_w) - 0.05)}{0.95}\right]^{1.7} T^{1.5} \]  

(17)

where
\[ D_{\text{eff}} = \text{effective diffusion coefficient (m}^2/\text{s)} \]
\[ \theta = \text{porosity} \]
\[ \theta_w = \text{volume of the water per unit volume of soil} \]
\[ T = \text{temperature (K)} \]
For both functions representing the tailings (Eq. 16 and 17), a temperature of 10°C was applied. As can be seen, the variation in the effective diffusion coefficient between the two tailings models is relatively large. It is thus necessary to investigate the tailings at each site so that an adapted function for the effective diffusion coefficient can be applied. Functions for cover materials and tailings can be adopted and utilized in modelling prior to the remediation to calculate the effectiveness of a potential cover at different degrees of water saturation (Collin and Rasmuson, 1988; Werner, 2000). From the figure it is apparent that the effective diffusion coefficient is lower in the Millington-Shearer model at each calculated saturation value compared to the tailings models (although compared to David and Nicholson the difference must be considered as negligible). This illustrates that applying a soil cover is also an effective remediation method also when tailings are partly saturated. Due to the compaction of the sealing layer, it is likely to achieve a lower porosity and retain water more easily and thus a lower value for $D_{eff}$ in a compacted sealing layer than in the more permeable tailings is achieved. It also illustrates that to prevent the sealing layer from drying, root penetration, and freeze/thaw actions creating cracks or macropores is of great importance, since such defects will induce a higher value for $D_{eff}$.

![Figure 6. $D_{eff}$ for various functions. Note the log$_{10}$ scale on the vertical axis.](image)

To be able to calculate the flux of oxygen per unit time and unit area through the sealing layer by diffusion, simply knowing the $D_{eff}$ value for the layer is not enough; in most circumstances the gradient over the barrier also has to be known. If using an oxygen diffusion lysimeter installed underneath a sealing layer to estimate the effective diffusion coefficient, the following equations are appropriate. Models for diffusion are based on Fick’s first law:

$$F = -D \frac{dc}{dz}$$

(18)
which are transformed into

\[ F = -D_{\text{eff}} \left( \frac{\Delta c}{\Delta z} \right) \]  

(19)

where \( D_{\text{eff}} \) is an experimentally determined effective value of \( D \).

The \( \Delta c \) corresponds to the difference in concentration of, in this case, oxygen and the \( \Delta z \) is the distance between the two points of oxygen measurements. Although the transport over the chosen boundary is random, the net flow is from the higher concentration to the lower until they are equilibrated at which time the net flow is zero. However, in a sulphide-rich tailings or organic rich environment oxygen is consumed and the net flow therefore rarely reaches equilibrium. Using Fick’s first law to calculate the flux through a porous layer (such as a soil) requires the user to presume approximate steady-state diffusion for the period. Cussler (1984) showed that an approximate expression for \( D \) could be obtained if combined with mass-balances for two well-stirred volumes, separated by the porous soil layer. If the lysimeter volume is \( V_V \) and has a cross-section area \( A \), the oxygen flux into the lysimeter is illustrated by equation 20.

\[ F_{lm} = \left( \frac{V_V}{A} \right) \frac{dC_{lm}}{dt} \]  

(20)

Here \( F_{lm} \) mean “Flow in lysimeter” and \( C_{lm} \) correspondingly means “Concentration in lysimeter”.

For approximate steady-state conditions, the flux through the soil layer (Eq. 19) equals the flux indicated by the change in concentration in the lysimeter (Eq. 20). Hence,

\[ -D_{\text{eff}} \left( \frac{\Delta c}{\Delta z} \right) = \left( \frac{V_V}{A} \right) \frac{dC_{lm}}{dt} \]  

(21)

where \( \Delta c = C_{lm} - C_0 \)  

(22)

then rearranging (Eq. 21) using (Eq. 22)

\[ - \frac{D_{\text{eff}} A}{\Delta z V_V} (C_{lm} - C_0) = \frac{dC_{lm}}{dt} \]  

(23)

and introducing \( \beta = \frac{D_{\text{eff}} A}{\Delta z V_V} \)

(24)

gives the expression in equation 24.

\[ - \beta (C_{lm} - C_0) = \frac{dC_{lm}}{dt} \]  

(25)
This (Eq. 24) is a separable differential equation and can be integrated, using the initial condition with zero oxygen concentration in the lysimeter immediately after flushing the system with N₂ gas at \( t=0 \) when \( C_{lm}(0)= 0 \), i.e.

\[
\int_{0}^{t} \beta dt = \int_{0}^{C_{lm}} \frac{dC_{lm}}{C_{lm} - C_{0}}
\]

then it is possible to obtain

\[
C_{lm}(t) = C_{0}[1 - \exp(-\beta t)]
\]  \hspace{1cm} (27)

where \( C_{0} \) is the atmospheric oxygen, if rearranging to obtain \( D_{ef} \) the equation is

\[
D_{ef} = \ln\left(\frac{C_{0}}{C_{0} - C_{lm}(t)}\right) \frac{V_{f} \Delta z}{At}
\]  \hspace{1cm} (28)

once \( D_{ef} \) is determined \( F \) can be calculated using equation 19.

Utilizing these functions (Eq. 13-28), based on sound assumptions for the site, whether from field investigations or laboratory estimations, makes calculation of the amount of sulphides that may be oxidised due to the oxygen transport possible and the efficiency of the cover can be determined. The derived equations can also be adjusted with regard to infiltrating water. However, normally the volume of the infiltrating water is small compared to the pore volume of the lysimeter and can be neglected.

To check the validity of the assumed steady-state diffusive flux through the soil layer, the time to reach steady-state, \( t_{ss} \) (Eq. 29) can be estimated (Crank, 1979).

\[
t_{ss} = \frac{0.45(\Delta z)^2}{D_{air}}
\]  \hspace{1cm} (29)

Where \( D_{air} \) is the oxygen diffusion coefficient in the soil gas. Using an estimated value of \( 1.8 \times 10^{-5} \text{ m}^2/\text{s} = 1.6 \text{ m}^2/\text{d} \) (CRC Handbook of Chemistry and Physics, 1981) and a soil cover thickness (\( \Delta z \)) of 1.5 m, a time to reach steady-state conditions of about 0.7 days is calculated. Hence, the approximation seems to be appropriate.

Other actions that may affect the flux of oxygen, in excess to diffusion, are convective movements of oxygen driven by thermal gradients, barometric variations and advective transport due to constant wind conditions at the site (Ritchie, 1994; Morin and Hutt, 1997). However, in remediated tailings impoundments the main transport of oxygen is usually considered to be by diffusion (Magnusson and Rasmuson, 1983; Collin and Rasmuson, 1988) even though, occasionally barometric variations have been demonstrated to have an important influence (Lundgren, 2001). For other types of waste such as waste rock convective movements are of greater importance (Harries and Ritchie, 1981) although, at some waste rock deposits such as Aitik, diffusion is regarded as the main process transporting oxygen (Strömberg, 1997). Advection is generally less important due to the fact that wind directions persist for hours, whereas the thermal gradient for convection could persist over years (Ritchie, 1994).
The other important purpose of installing a sealing layer is to reduce the flux of water into the waste, which will limit the leachate formation in the waste deposit. The main source of water entering the waste is precipitation, which will be stored seasonally as snow or in foliage. Nevertheless, a part of it is likely to infiltrate into the protective cover and part of it will form surface runoff. Some water will evaporate and the rest will be transported downward by gravitational forces. However, the soil tends to retain water by capillary action. Water can also be withdrawn from the soil due to transpiration by plant roots. When transported downwards, further infiltration will be slowed down by the sealing layer, thus forming a perched groundwater table on its surface (Figure 7). This water might also be subject to lateral run-off on top of the sealing layer. If perched, this water head can be used in a simplistic model to calculate the flow of water through the sealing layer, using Darcy’s law, as written in equation 30.

\[
q = k \frac{\Delta h}{I} A = k \frac{H + D}{D} A
\]

Figure 7. Saturated water infiltration using Darcy’s law.

According to equation 30; D represents the thickness of the layer (I) whereas H is the depth of perched water table and thus the head of water on top of the sealing layer. The pressure difference, (\(\Delta h\)) is correspondingly “H+D” since saturated conditions in the sealing layer are presumed (but unsaturated in the underlying tailings). Then A is the square unit area of the sealing layer, and k is the hydraulic conductivity of the material. When performing calculations for the “worst-case” water infiltration through a sealing layer it is usually considered to be fully saturated, since the hydraulic conductivity of soils increases with increasing degree of saturation (Koerner and Daniel, 1997). In other disciplines such as soil mechanics, the coefficient k, is named permeability. However, generally the term hydraulic conductivity is considered as a more appropriate name for the coefficient, and this term will be used hereafter. The absolute permeability of a soil is not a true material constant since it is affected by temperature. Thus, the absolute permeability is related to the hydraulic conductivity (Eq. 31).

\[
K = \frac{k \eta_w}{\rho_w g}
\]

where
\[k = \text{hydraulic conductivity}\]
\[\rho_w = \text{density of water (t/m}^3\text{)}\]
\[\eta_w = \text{dynamic viscosity (Pa s)}\]
\[g = \text{gravity (m/s}^2\text{)}\]
\[K = \text{absolute permeability (m}^2\text{)}\]
By minimizing the leachate production the transport out of the impoundment of dissolved oxidation products can be minimized. The amount of water infiltrating through the cover can be measured by collection in lysimeters. The size and construction of a lysimeter may vary, but in principle, the lysimeter is a relatively large container with a known surface area to which a drainage pipe is attached. Either the bottom of the lysimeter, or the lysimeter itself, has a slight angle, so that the collected infiltration water can be transported to the drainage pipe. The amount of infiltrated water is measured and a value of the annual infiltration can thereby be calculated (e.g. as m³/m², a). If correlated to the conditions at the site prior to the remediation, it is possible to calculate the efficiency with which the cover prevents the infiltration of water. The amount of oxygen transported by the infiltrating water can also be calculated, since the solubility of oxygen in water is known. Generally, gaseous diffusion is the dominant mechanism for diffusion in unsaturated porous soils and the diffusion of oxygen in water or oxygen transported dissolved in infiltrating water is considered less important (Nicholson et al., 1989).

5.3 Other barrier materials

Non-natural sealing/barrier materials or materials that are unavailable in the vicinity of the waste location can also be utilized as a cover material with comparable or perhaps even better performance for preventing oxygen diffusion and water infiltration. Examples of such materials are cefyll (concrete mixed with fly ash), bentonite enriched sand (BES) or BES with polymeric additives (to improve the properties), synthetic geomembranes, and geosynthetic clay liners (Oweis and Khera, 1998). These materials have been used as, or could be used as, a sealing layer on top of mine waste as well as on common landfills and other industrial waste. For most of these materials, the same precautions have to be taken to avoid drying and/or freezing of the sealing layer which might cause the formation of cracks and/or macropores. However, for some of these materials, knowledge about the long-term integrity of the material when they are applied on top of waste could also be a matter of concern. Such concerns may be the resistance to settling or the decomposition of polymers. It is in general presumed that the sensitivity to settlements is comparable for most materials but the long term sustainability with regard to polymeric decomposition is a subject for uncertainty. Organic covers have been designed in some instances with the idea of consuming the diffusing oxygen before it reaches the waste (Reardon and Poscente, 1984; Elliott et al., 1997; Granhagen, 1998; Cabral et al., 2000; Peppas et al., 2000; Yanful et al., 2000a; Yanful et al., 2000b; Chtaini et al., 2001; Harris and Megharaj, 2001; Stouraiti et al., 2002). Depending on the material used and the design, success has varied.

6 Site description

The Kristineberg mining area is located in the western part of the Skellefte ore district, approximately 175 km south-west of Luleå (Figure 4 and 8). The approximately 1.9 Ga old ore-bearing volcanic rocks are overlain by sedimentary rocks. The metamorphosed volcanic and sedimentary rocks display a marked foliation and extensive sericitization (Vivallo and Willdén, 1988). Pyrite-rich sulphide ores are intercalated within a stratigraphic unit mainly consisting of basic volcanics and redeposited volcano-clastic rocks (Willđén, 1986). For further description of the area and its geology and ores, see Gavelin (1943), Du Rietz (1951), Gavelin and Kulling (1955), and Grip (1973). The largest ore body in the area is the Kristineberg Zn-Cu deposit, which was discovered in 1918. It was not until 1940 that Boliden Mineral AB started mining activities and mining is still in progress. Other mines close to the Kristineberg mine are the Kimheden, Hornträsk, Rävliden and Rävildmyn mines, all of which are closed and remediated. The annual precipitation in the area varies between 400-800 mm/a (Axelsson et al., 1991) and the annual mean temperature is 0.7°C (Axelsson et al., 1986). In
general, the impoundment is snow-covered between late October/early November and late April/early May (Axelsson et al., 1986). The vegetation consists mainly of coniferous forest, but some deciduous forest is also present in the area. Boglands are common. The major soil type in the area is podzol weathered till (Granlund and Wennerholm, 1935; Granlund, 1943). Five tailings impoundments are located within the Kristineberg mining area. As many as 10 different ores from the western part of the Skellefte field mining district were processed in the dressing plant until its closure in 1990. The impoundments thus contain a mixture of several different kinds of tailings.

**Figure 8. Impoundment 1, Kristineberg mining area.**

In this thesis Impoundment 1 was investigated (Figure 8). It is the oldest within the mining area. It has a surface area of about 0.10 km² and until the early 1950s, it was used for tailings.
disposal (Boliden Mineral AB, 1995). The tailings discharge was located along the southern hill slope. Pre-remediation characterisation of the geochemistry and hydrogeology of the impoundment was carried out by Qvarfort (1983, 1989), Axelsson et al. (1986), Ekstav and Qvarfort (1989) and Axelsson et al. (1991) (see also compilation in Malmström et al., 1999). In the years 1976 and 1978 attempts were made to sow grass seed. In 1996 the impoundment was remediated by till covering (Lindvall et al., 1999). The intention was to use 1 m of unspecified till as a protective layer in areas with a shallow groundwater table; the purpose was to saturate the tailings to prevent further oxidation. In other areas with a deeper groundwater table where saturation was not considered possible, 1.5 m of till was applied above a 0.3 m sealing layer to prevent oxygen and water transport into the tailings. The sealing layer consists of a compacted clayey till. After remediation, the groundwater table is shallow in the area in which saturation of the tailings was part of the remediation. In some areas it even reaches the surface. Prior to the application of the till cover, 10 kg/m² of lime was added on top of the tailings. The impoundment is located in a valley and underlain by peat and till. The thickness of the tailings ranges from a few metres up to approximately 11 m. The average thickness is between 6 and 8 m. Impoundment 1 is located in the uppermost part of the valley and the drainage water from the impoundment is mainly transported downstream into Impoundments 2 to 4.

7 Methodology

7.1 Tailings, pore water, groundwater, and vadose water sample collection

The tailings were sampled at five locations in Impoundment 1 using a drill rig (rotary drill). The tailings were divided in 20 cm samples, except for the first 2 m, where the sample length was 10 cm. The tailings were transferred to plastic (polyethylene) bags. From some of the sampled tailings, pore water was extracted. Precautions were taken to avoid premature oxidation of the pore water samples. All samples used for pore water extraction were transferred to double plastic bags (polyethylene) within a few minutes after retrieval. Both plastic bags were filled with Ar-gas. All pore water was extracted within a few hours after drilling using an Ar-gas filled glove box. The material used for pore water extraction was taken from the inner core of the samples and extracted using a portable Masterflex® vacuum pump and acid-washed Millipore® 47 mm filter holders. The pore water was filtered through 0.22 µm Millipore® filters.

Groundwater was collected using the BAT® system (Torstensson and Petsonk, 1988). A vial made of Duran® was evacuated and refilled with argon several times to obtain an expected remaining volume of oxygen ranging between 0.1 and 0.01%. When vacuum was obtained the vial and a double-ended needle were mounted on the sampling device and lowered down through the groundwater pipe. One end of the needle penetrates the membrane on the vial and the other penetrated a rubber membrane on the BAT® filter tip. Water entered the vial due to the pressure gradient. Before using the obtained water the volume in the filter tip was renewed at least two times. The groundwater was filtered using a portable Masterflex® vacuum pump and acid-washed Millipore® 47 mm filter holders. The groundwater was filtered through 0.22 µm Millipore® filters.

To obtain vadose soil and tailings water cylindrical tension lysimeters (Prenart equipment ApS., Fredriksberg, Denmark) were installed. The tension lysimeters were installed horizontally or at a low angle at six depths in the vadose zone from a trench. To obtain the vadose water, a vacuum pump was used and the water was collected in HDPE bottles. The
Vadose water was filtered using a portable Masterflex® vacuum pump and acid-washed Millipore® 47 mm filter holders. The water was filtered through 0.22 µm Millipore® filters. In some instances, unfiltered samples were also analysed.

All equipment used for sampling of water has been acid-washed in 5% HNO₃.

The groundwater levels have been measured regularly in 29 piezometers across the impoundment using an electronic probe. Some of these piezometers were already installed in the 1980s during the pre-remediation measurements, and some were installed by Boliden as part of the control programme. However, most of them were installed recently as part of the MiMi programme and are open two inch groundwater pipes with a 0.8 m screen section in the bottom part.

### 7.2 Cover samples

The sealing layer and the protective till samples were collected at Impoundment 1 both when the tension lysimeters were installed and when drilling were performed. A larger sample of the sealing layer was collected during the installation of the oxygen diffusion and water infiltration lysimeters. The samples were collected at the till quarry close to Rävlidmyran, one of the former mines in the area, situated a few kilometres away from Impoundment 1.

### 7.3 Sequential extraction

Some tailings samples from the drilling were chosen after the chemical composition of the solid samples was investigated, to be subject to sequential extractions following a slightly modified methodology based upon the methodology derived by Hall et al. (1996a, 1996b). The purpose was to more securely define the forms in which the metals are present at different depths in the impoundment; for example in the oxidised layer, in the unoxidised but secondarily enriched layer just below the oxidation front, and in the unoxidised tailings at greater depth. The samples were dried at 50°C and sieved. The fraction <63 µm fraction was used. The sequential extraction steps as defined by the methodology are adsorbed/exchangeable/carbonates, labile organics, Amorphous Fe- and Mn- oxyhydroxides, Crystalline Fe-oxides, sulphides and organic matter and a residual fraction.

### 7.4 In-situ analysis of water

#### 7.4.1 All water samples

Redox and pH were measured with a Metrohm® Pt-electrode and a Metrohm® combined pH electrode. The pH electrode was calibrated using two Titrisol® pH 4 and 7 buffers. The redox electrode was checked using two Ag/AgCl Reagecon® standards (124 mV and 358 mV). All redox values were adjusted to the standard hydrogen electrode. The conductivity was measured with a Hanna® conductivity meter.

#### 7.4.2 Groundwater

Alkalinity was determined by titration with a decimolar Titrisol® HCl solution, using a portable Hach® digital titrator. All measurements were taken within a few minutes after the opening of each sample. The water left in the bottle was then divided into three subsamples for the analyses performed in laboratories: one for anion analyses (currently chloride, sulphate and nitrate), one for metals and main elements, and one for dissolved organic content. The water samples for anion analyses were filtered directly into plastic bottles and placed in a refrigerator immediately. The water samples for analysis of main elements and metals were
also filtered directly in acid-washed 60 ml Azlon HDPE bottles and they were acidified with 1% redistilled suprapur HNO₃. The water samples for organic content were filtered using a metal filter-holder and a glass container through Whatman® glass fibre filters (0.7 µm pore size and ø 47mm) burnt before use at 450°C for 24h. The water was then poured into Falcon® plastic tubes acidified with 1% 2M HCl and placed in the refrigerator immediately. Blank analysis using the same methodology with milli-Q water instead of groundwater verified that the conditions of manipulation and analyses were satisfactory, with less than 2% average relative error on all pipes and elements.

7.4.3 Pore and vadose water

After being filtered through 0.22 µm Millipore® filters and placed in acid-washed 120 ml HDPE bottles the samples for analysis of main elements and metals were acidified with 1% redistilled HNO₃ prior to analysis. Samples for anion analysis were also filtered in plastic bottles and immediately placed in a refrigerator.

7.5 Oxygen diffusion and water infiltration measurements

Oxygen diffusion was measured in three separate oxygen diffusion lysimeters made of stainless steel with the cross-section area 1.6x1.6 m² and a height of 0.2 m. These lysimeters were installed in the tailings horizontally. A schematic outline is presented in Figure 9. The oxygen diffusion lysimeter is installed in contact with the sealing layer, supported by high quality concrete. Bentonite was added to the flat upper surface of the concrete to improve the sealing for minimizing oxygen diffusion from the lysimeter to the surrounding tailings. The water infiltration lysimeter is installed about 0.5 m down in the tailings. The test areas has a sealing layer of 0.3 m consisting of compacted clayey till, except for one area with only 0.3 m of protective cover over a 0.5 m sealing layer. For the other two test areas the protective cover is 1.5 and 1.0 m, respectively.

![Figure 9. Oxygen diffusion and water infiltration installation.](image_url)
7.6 Geophysics

As previously mentioned geophysical investigations of soil covers at tailings impoundments have been performed at the Ranstad and Bersbo sites. Within the MiMi, a joint project aiming at investigating mainly Impoundment 1 at the Kristineberg mining area has been conducted in collaboration with the Division of Applied Geophysics at Luleå University of Technology. The investigation aimed at checking the state of the sealing layer and thickness of the protective cover by using ground penetrating radar (GPR) but also investigating the waste by resistivity mapping (soundings and pseudosections), induced polarisation mapping and sounding (IP), the self-potential method (SP), and topographic surveys. Results of the investigations have been presented by Bérubé (2002). In general, the GPR and the resistivity methods provided the best data concerning subsurface conditions and in particular the resistivity pseudo sections combined with inversion modelling. The SP measurements provided good results at parts of the investigated area and the IP method provided questionable results.

8 Standards and analytical methodology

The samples of solid tailings and till were digested following the procedure described by Burman et al., (1978). Tailings samples were fused with LiBO₂ at 1000°C and the beads thus formed were dissolved in 0.7 M suprapur HNO₃. The major elements and Ba, Be, La, Mo, Nb, Sc, Sn, Sr, V, W, Y, and Zr were analysed by ICP-AES (ARL 3560 B). For analysis of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, S, and Zn tailings samples were digested in 7 M suprapur HNO₃ in Teflon bombs and heated in a microwave oven. The solutions were then centrifuged, diluted and finally analysed by ICP-AES (ARL 3560 B) and ICP-MS (VG Elemental Plasma Quad).

The pore waters, and the groundwater were acidified with 1% suprapur HNO₃ prior to analysis and then analysed for Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, and Zn using high resolution ICP-SMS (Finnigan MAT ELEMENT). Hg was measured using atomic fluorescence (PS Analytical). Ca, K, Mg, Na, S, Si, and Sr were analysed by ICP-AES (ARL 3560 B).

All vadose water samples were acidified using 1% suprapur HNO₃ and analysed for Ca, Fe, K, Mg, Na, Si, and S with ICP-AES. High resolution ICP-MS (ICP-SMS) was used for the analysis of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sr, and Zn. Hg was analysed with atomic fluorescence (PS Analytical).

The sequential extraction samples were acidified with 1% suprapur HNO₃ prior to analysis and then analysed. Concentrations of Ca, Fe, K, Mg, Na, S, Si, Al, Cu, Mn, and Zn in the sequential extraction solutions were determined with ICP-AES (ARL 3560 B), and As, Ba, Cd, Co, Cr, Mo, Ni, Pb, and Sr with ICP-SMS (Finnigan MAT ELEMENT). Hg was determined with atomic fluorescence (PS Analytical). Analyses of the solid residual for the elements Si, Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, Ba, Be, Cr, La, Mn, Nb, Sc, Sn, Sr, V, W, Y, Zn, and Zr were performed with ICP-AES (ARL 3560 B), and Cd, Co, Cu, Hg, Ni, and Pb with ICP-QMS (VG Elemental Plasma Quad).

The accuracy and precision of the analyses have been checked by analysing reference materials. For solid tailings, the reference materials used were GBW 10, SARM-1, DRN and GSR 6. The pore water and the sequential extraction samples were checked using synthetic quality check standards (Ödman et al., 1999). The instrumental precision determined as ±1 std. deviation for three to four runs on the same sample was generally better than 1% for the
major elements and 10% for the trace elements when analysing solid tailings. For the water samples, the precision was generally better than 5%.

9 Summary of Results

The choice of the Kristineberg mine as the common field site for MiMi presented both advantages and disadvantages. For field work, especially when working with soil cover remediation, the site had a few drawbacks. It was already remediated, which meant that to do installations and field investigations beneath the soil cover, the cover had inevitably to be removed and replaced. The results obtained cannot, therefore, be directly interpreted as comparable to the impoundment as a whole since different equipment was used to manufacture the sealing layer depending on the scale. Heavy equipment was originally used to produce the sealing layer at the impoundment but smaller equipment (vibratory plate compactor units) where used when replacing a removed part of the cover. This could result in discrepancies, and it also has to be assumed that any extrapolation to the impoundment as a whole from test area data should be performed with the utmost care and attention.

9.1 Paper I

Paper 1, showing the results of the investigations of solid tailings and pore water composition, demonstrates that the oxidation depths from prior to the remediation varied. Oxidation depths between 0.1 and 1.15 m were measured and the differences probably depend on the position of the groundwater table prior to the remediation. The purpose of the investigation was to characterize the mineralogy of the tailings, the chemical composition of tailings and pore water, and to try to track the processes occurring in the impoundment prior to the remediation as well as to measure the initial effects of the performed remediation, about two years after completion of the cover. Below the oxidation front an enrichment zone was found in the solid tailings for several elements including Cu. In this zone, elements released by oxidation prior to the remediation were secondarily retained. The solid Cu concentration in this zone can be as high as 4450 ppm Cu, compared to the average for the entire unoxidised impoundment at 956 ppm. Transformation of various sulphide minerals such as pyrrhotite, chalcopyrite, galena and pyrite into covellite is a possible explanation for the high Cu concentration. Adsorption of Cu onto different mineral surfaces is another. Using Zr to approximate the total mass that disappeared from the oxidised zone shows that almost 43 wt.% has disappeared.

Pore water was sampled at the part of the impoundment where the water table was raised. Here the raised water table saturated the tailings including the enrichment zone and the oxidised layer. pH is about 5.5 at most depths in the impoundment, except in and around the oxidation front where it decreases to values as low as 3.8. The elements released in the highest amounts during the pre-remediation oxidation were Fe and S from pyrite oxidation, and Ca and Mg from carbonate and silicate (mainly chlorite) buffering. Higher pore water concentrations of these elements at depth indicate that the source, pyrite oxidation and buffering reactions, has slowed down. The high concentrations at depth are caused by vertical downward transport of pre-remediation oxidation products not easily secondarily retained in the tailings below the oxidation front. Around the former oxidation front where pH is low, Si, Al, As, Cd, Co, Cu, Pb, and Zn have their highest concentration. These elements were secondarily retained below the oxidation front during pre-remediation weathering. When the groundwater table is raised as part of the remediation, they are released and pore water concentrations increase. There is a potential risk that these elements will be flushed out from the impoundment. The results suggest that the remediation has achieved the goal of reducing sulphide oxidation, but that there is a release of old oxidation products.
Figure 10. Dissolved pore water concentration vs. depth in Profile 4.

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<th>Profile 4</th>
<th>Ca (mg/l)</th>
<th>Fe (mg/l)</th>
<th>Mn (µg/l)</th>
<th>Mg (mg/l)</th>
<th>S (mg/l)</th>
<th>As (µg/l)</th>
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<th>Cu (µg/l)</th>
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<td>Depth (cm)</td>
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<td>800</td>
<td>400</td>
<td>0</td>
<td>Overlying till</td>
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In Paper 2, solid tailings samples from the sampling campaign described in Paper 1 were subjected to sequential extractions. The purpose was to investigate the form in which several elements, such as As and Cu, are secondarily enriched just below the former oxidation front. The purpose was also to show how the elements are associated at different depths in the impoundment. The chosen methodology involved a five-step sequential extraction and the residual fraction. The first four steps (A-D) are presumed to dissolve various secondary fractions, the fifth (E) mainly sulphides and in the residual fraction silicates were presumed to remain. The samples subjected to sequential extractions were sieved, and the fraction passing through a 63 µm sieve was chosen for the extraction. Obviously, the sieving of the sample affects the comparison between the solid tailings concentration of various elements, from Paper 1, and the total extracted amount from the sieved sample. In general, the finer particles contained more sulphides but less silicate than the bulk tailings samples did.

In the oxidised tailings the sulphide fraction still dominates for several elements, such as Fe, S, Cd, Co, Cu, Hg, and Zn. Averages for these elements in the oxidised zone range from 55.7 (Hg) up to 82.2 wt.% (Co), although the concentrations are severely depleted compared to the unoxidised tailings. Most likely the oxidation products were transported downwards in the impoundment during the oxidation stages and partly retained below the oxidation front, as previously described in Paper 1. Some fractions of the oxidation products were, however, retained in the oxidised layer. According to the extractions the major secondary phase for elements in the oxidised zone varies for the different elements. As examples, for Pb, the major fraction was the Fe-oxyhydroxide, and for Co, it was the most easily dissolved fraction, the adsorbed/exchangeable/carbonate fraction.

Below the oxidation front, in the enrichment layer, the amount of sulphides in the tailings sharply increases. In general, this reveals an even more pronounced association to the sulphide extraction for most of the elements. The part extracted from the sulphide fraction for these elements in the unoxidised tailings is on average between 55.8 (Cu) and 93.1 wt.% (S). Copper is further enriched in the sulphide fraction for the sample situated in the enrichment layer, together with As, Cd, Ni, S, Fe, and Zn. The accumulated amounts from the sequential extractions exhibit minor peaks for the elements As, Ni, Fe and S at this level, whereas the solid tailings analyses do not. This is most likely because the fraction <63 µm was used. Thus a higher percentage of sulphides were used in the extractions compared to the total content analysis of the tailings. Evaluating the fraction abundance at the secondary enrichment level, it is possible to conclude that the sum of the secondary fractions extracted is equal in size to that of the sulphide extraction step for As and Ni. The elements Cd, Fe and Zn are largely associated with the sulphide extraction step (76-79 wt.%). Nevertheless, the amount associated with the adsorbed/exchangeable/carbonate fraction might be up to 19 wt.% (Cd and Zn). This still represents a considerable part of the total amount extracted at this level. Copper is also mainly associated with the sulphide extraction step (69 wt.%), but 16.4 wt.% is associated with the extraction steps releasing the secondary fractions. The 16.4 wt.% represent more than the total content (as mg) in some of the deeper, unoxidised tailings. The peak for the sulphide extraction step evident at this level probably corresponds to the formation of covellite, as has been verified from thin sections around this level in the impoundment, but a large part is also retained at this level as secondary precipitation products retained in extraction steps releasing the secondary fractions. This increase in extraction steps releasing the secondary fractions for the samples below the oxidation front corresponds to the peaks in pore water concentrations. Thus, elements retained below the oxidation front are presumed to have become mobile after the rise of the groundwater table, mainly from fractions corresponding to extraction steps releasing the secondary fractions. The results show
that there is a large potential for release of previously retained elements in and below the oxidation front in oxidised and unremediated tailings, if remediated by water saturation.

Figure 11. Sequential extractions for solid tailings from Profile 4.
9.3 Paper III

Paper 3 deals with the infiltrating water entering the oxidised zone through the sealing layer applied to the part of Impoundment 1 where it was not possible to achieve water saturation of the tailings. The water infiltrating through the protective cover and the sealing layer has low concentrations of most elements and a pH of just above 4 when entering the oxidised zone of the tailings. When percolating into the oxidised tailings and the upper part of the unoxidised tailings, pH decreases and conductivity increases due to the remobilization of secondarily retained oxidation products as well as from the continued oxidation caused by diffusing oxygen and the dissolved oxygen transported in the infiltrating water.

The amount of water infiltrating through the sealing layer is low, compared with the pre-remediation conditions, approximately $4 \times 10^{-3} \text{ m}^3/\text{m}^2$, a. Water infiltration can roughly be estimated to have decreased by 98% compared to the pre-remediation level. The dissolved secondary products originate from both the oxidised tailings and the unoxidised secondary enrichment zone dating back to the time prior to the remediation, and from ongoing oxidation due to the diffusion of oxygen. No distinction has been made in this paper between dissolved secondary oxidation products and the present oxidation products. The total mass of contaminants transported within the vadose zone of the impoundment is low due to the limited water transport, although the concentrations can be high. The dissolved elements are to a large part retained again between the lysimeter just below the oxidation front, installed at a depth of 200 cm, and the deepest lysimeter in the profile, roughly half a meter below the oxidation front. Between the deepest lysimeter and the groundwater table, it is likely that the concentration decreases even further. In the part of the impoundment covered by a sealing layer, the dissolved elements released by infiltrating water or mobilised due to the ongoing oxidation thus re-precipitate, co-precipitate, or adsorb on primary mineral surfaces further down before reaching the groundwater table. The concentration of the elements in the groundwater in the areas covered by a sealing layer is not caused by the processes occurring in the overlying tailings vadose zone but by groundwater flow from the part of the impoundment with a simple till cover and water saturation of the tailings. A much smaller part of the precipitation is prevented from groundwater formation in the area where water saturation was chosen as the remediation method compared to the areas with a sealing layer. In addition, water from the southwestern hill slope is transported into the tailings impoundment. The inflowing water from the hill slope also flows to the areas with the sealing layer, which in general are the outflow areas of the impoundment. As an example, the horizontal groundwater flow rate at the tension lysimeter installation site is approximately 30-90 m$^3$/m$^2$, a rate which is substantially higher than the measured infiltration rate of $\sim 4 \times 10^{-3}$ m$^3$/m$^2$. The water infiltrating and the oxygen diffusing through the sealing layer and entering the vadose zone of the tailings is thus much less important for the local groundwater composition than laterally flowing groundwater.
Figure 12. Behaviour for some elements in the vadose zone underneath the sealing layer. Observe the log_{10} scale on the x axis for the elements Al, Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn.
Figure 12. cont
9.4 Paper IV

The groundwater composition and its evolution over time in Impoundment 1 are evaluated in Paper 4.

![Location of the groundwater pipes at Impoundment 1 and 1B. In this study Impoundment 1 was investigated (the northern impoundment).](image)

The results show that the groundwater composition varies considerably in the impoundment, even under the same type of cover. In the area remediated by the saturated till cover average pH is in general lower than in the area with the compacted clayey till layer. Concentrations of elements such as Fe and Zn are generally much higher in the water-saturated area. The pH increases generally while the redox generally decreases across Impoundment 1, where some areas show quicker changes than others.
The reactions producing the acid waters and the dissolution of metals and metalloids seem to have slowed down. A model for the future behaviour of Impoundment 1 is proposed, which is based on the assumption that in the area with the raised groundwater table, secondarily retained elements below the oxidation front became mobilised when water saturated. Thus, increased metal concentrations are found at this level. Then, following this remobilisation, a washout was initiated due to the inflow of clean groundwater from the southwestern hill slope.
Figure 15. Illustration of the washout peak for a mobile element under the prevailing conditions and compared with Fe in pipe F and J.

The chosen remediation method thus enabled the formation of a plume of dissolved oxidation products, which are to be transported out of the impoundment. The prediction from the model is that a general decrease in the dissolved amounts should be observed over the entire impoundment within 3 to 4 years. The water infiltrating through the dry cover does not lead to an important release of elements to the groundwater. Different elements exhibit different transport behaviour; Cu, Cd, and Pb seem to have decreased drastically due to the remediation. Some elements like Fe, S and Mg continue to migrate downwards in the impoundment from the oxidised zone. It seems, however, that the horizontal transport is much more important than the vertical. A special behaviour is visible for Zn; which is rather immobile during the winter but mobile during the summer.

9.5 Paper V

In Paper 5 the susceptibility of frost/thaw actions on the clayey till used as the sealing layer at Impoundment 1 were investigated by cyclic freezing and thawing of compacted samples in the laboratory.

Figure 16. Particle size distributions for the collected sealing layer material used in the freezng and thawing investigation. Shaded area indicates the sample spread for the clayey till in the pre-remediation investigation.
Four samples were compacted to the level that was measured in field as a part of the control programme (~96% of modified Proctor). In all four samples, void ratio and porosity changes could be traced under the eight cycles of freeze/thaw. Although these changes were measurable, the change in hydraulic conductivity for all samples except one (C) may be considered negligible. For most of the samples, the void ratio and porosity decreased during the final cycles. This could indicate that a normalisation/stabilisation within the samples occurs with regard to freeze/thaw effects. However, the hydraulic conductivity was high compared to the pre-remediation investigation results (when suitable sealing layer soils were sought), during all stages of the freeze/thaw investigation (>2x10^{-8} m/s). The expected initial level for the compacted samples was in the range of 10^{-9} m/s instead of the much higher measured hydraulic conductivity. It was presumed that the same soil, if compacted to a higher degree and thus having a lower porosity and a correspondingly lowered hydraulic conductivity, would show a much higher sensibility to freezing and thawing. Therefore, a second series with two samples compacted to a higher degree (~100% of modified Proctor) and at slightly higher water content was performed. These samples had a much lower initial hydraulic conductivity compared to the first series, 3.5-7x10^{-10} m/s. The results obtained after repeated freeze/thaw make the assumption of increased sensibility probable, since the increase in hydraulic conductivity for both samples after four cycles of freeze/thaw is about 25 times. The hydraulic conductivity was now of the same magnitude as the initial values for the first series, about 10^{-8} m/s.

**Figure 17.** The set-up of the permeameters during the freeze/thaw investigation.
When the results are compared it is evident that the hydraulic conductivity for a clayey till can vary within a wide range depending on relatively small differences in compaction since the same equipment was used in both investigations. The results from this investigation confirm that a suitable low hydraulic conductivity can be obtained by using a clayey till as sealing layer in a soil cover remediation, but also that the (well-known) importance of appropriate investigations of the material prior to remediation and appropriate construction requirements and control are what will finally determine the efficiency of the sealing layer. Based on the hydraulic conductivity measurements, it can be concluded that the clayey till is sensitive to freeze/thaw effects that change the hydraulic conductivity if the sealing layer has been properly compacted.

**Figure 18.** Hydraulic conductivity change during the freeze/thaw investigation. Note the log\(_{10}\) scale on the vertical axis.
9.6 Paper VI

Paper 6 presents results from the oxygen diffusion and water infiltration lysimeters 1.5 years after the installation at Impoundment 1. The oxygen diffusion results from 1999-2000 indicate that the effective diffusion coefficient \(D\) of the soil cover is low. The model-fitted values of \(D\), and the associated diffusive oxygen flux varied approximately one order of magnitude between different periods. For instance, one oxygen lysimeter with a total soil cover thickness of 1.8 m had a \(D\) of \(3 \times 10^{-4} \text{ m}^2\text{d}^{-1}\) during the early summer of 2000, and about \(5 \times 10^{-5} \text{ m}^2\text{d}^{-1}\) during early autumn the same year. However, the amount of available data was not sufficient to allow any general conclusions regarding the seasonal characteristics. The results obtained at this stage did not show any consistency between the total soil cover thickness and its performance as an oxygen barrier. Groundwater wells installed at the top of the sealing layer (in the protective cover) indicate that a periodic accumulation of water within the soil cover was occurring. This perched water table results in small oxygen fluxes and is thus reducing the oxygen-driven oxidation in the tailings. However, during extended periods with drought, the water retention characteristics of the clayey till used as the sealing layer as well as the depth to the groundwater table may be critical to the efficiency of the cover as an oxygen barrier. Evaluation of water lysimeter data indicates that only a small fraction of the precipitation infiltrates into the part of the impoundment remediated by the more advanced soil cover incorporating a sealing layer. This results in a low groundwater recharge within this part of the impoundment. If the water fluxes through the sealing layer are low for an entire impoundment, its groundwater table fluctuations might prove crucial to the contaminant recharge into the groundwater. Observation of groundwater variations in the soil cover and in the tailings may thus provide key components to the monitoring of a soil cover remediation performance. The results in this study show that soil cover remediated tailings can decrease the oxygen and water availability to a very large extent, and thus significantly reduce the contaminant discharge to the surroundings, provided that the sealing layer used is well compacted and has a low hydraulic conductivity. Since the precipitation during the investigated period was larger than normal, it was necessary to continue the studies of the sensitivity of the soil cover effects due to variations in the hydrological conditions. Long-term monitoring of the groundwater table and the oxygen concentrations at the impoundment is thus necessary to gain a better understanding of the overall remediation effects on the generation and transport of contaminants within the deposit.

9.7 Paper VII

For Paper 7, the same installations as for Paper 6 were utilized. However, additional measurements were incorporated and the evaluation extended. Measurements indicate that the effective diffusive coefficient is low. The use of simple shrinking core models indicate a decrease in oxidation rate of 2-3 orders of magnitude due to the remediation actions (Figure 19). The test area with 1.0 m of cover exhibit a ten times higher effective diffusive coefficient \(D_{\text{eff}}\) than the areas with 1.5 and 0.3 m of protective cover for most of the periods since installation. The reason for this is still unknown. However, measurements from the summer 2002 showed that the cover protected by 0.3 m of protective cover was sensitive for desiccation; the precipitation was lower than previous years and \(D_{\text{eff}}\) for this area increased by one order of magnitude up to the level of the area with 1.0 m of protective cover. The area with 1.5 m of cover seemed unaffected at the same level as earlier.

In Figure 19, \(D_{\text{Average}}\) is used in the calculations. These values are calculated as follows; positive diffusion coefficients for the period from June 2000 to May 2002 have been averaged together, and the two summer values from 2002 have been averaged together. \(D_{\text{eff}}\) for the tailings (without any cover) is estimated from field data from the site.
Oxygen concentrations in the protective cover are at times very low (Figure 20). This results in diffusion of oxygen from the lysimeters to the protective cover. The absolute value of the negative effective diffusion coefficient calculated is of the same order as the positive one. Therefore, this is interpreted as that there actually is a net diffusion out of the lysimeter and not due to leakage. The major oxygen diffusion period seems to be from May to September, with small fluxes occurring from late autumn until spring. This implies that the oxygen diffusion into the tailings is very low during the winter.

Periodically a perched water table is present in the protective cover, mainly during snowmelt and late autumn during the intense rains. This perched water table is an effective hinder for oxygen diffusion although it never lasts long due to lateral run-off. As could be expected the oxygen concentration in the protective cover is low during periods with high water content (Figure 20). Thus the perched water table is an effective mean to minimize the oxygen diffusion into the tailings. However, keeping a perched groundwater table increases the infiltration rate and thus the formation of drainage water.
Since the climate probably will be warmer in the future with shorter and milder winters, the design demands for the protective cover might have to be changed from preventing frost penetration into the sealing layer to instead be designed to provide enough retained water available for evapotranspiration, to prevent desiccation of the sealing layer. A dry sealing layer is much less efficient, as was shown by the 0.3 m area, in the summer 2002. It still remains to see whether the damage formed during the dry summer 2002 was irreparable. Frost penetration of the sealing layer has not yet occurred, and the effects in field scale of frost actions on cover efficiency are still uncertain. Since the 1.5 m cover area was unaffected by the dry conditions, it seems as if this cover was thick enough to sustain the dry conditions. It is likely that this thickness of the protective cover is the most appropriate of the three since it will prevent both rather dry conditions as well as freezing of the sealing layer during most winters.

**Figure 20.** Comparison between perched water table and oxygen concentrations.
10 Conclusions

From the results it is obvious that prior to the remediation oxidation was intense in some areas with a deeper groundwater table; in other areas where a shallower groundwater table was present oxidation seem to have stopped prior to the remediation. Similar to what has been found in several other investigations, a secondary enrichment underneath the oxidation front of metals and metalloids during the ongoing oxidation were formed. Upon water saturating the tailings as part of the remediation strategy, this secondary enrichment was dissolved and a peak in pore water concentration was detected. Major elements such as Fe and S increased in concentration with depth, indicating a downward transport of oxidation products not retained in the secondary enrichment zone. A similar behaviour is visible for the cations Ca and Mg, present in the buffering carbonate and different silicate (mainly chlorite) minerals. This indicates that the remediation was successful in decreasing the oxidation rate. Inflow of unpolluted groundwater from the nearby south-western hill slope leads to the formation of a plume, which is gradually transported out of the impoundment leading to decreased concentration of metals and metalloids around the former oxidation front. The proposed model indicated a visible decrease in groundwater concentrations in about 3 to 4 years all over the impoundment. This is provided that the water saturation of the tailings remains. Thus the water saturation methodology, incorporating a simple soil cover can be deemed as effective provided that actions are taken to take care of the initial was-out that will likely occur if the tailings are previously oxidised. To ensure saturated conditions also under drought is crucial to keep further sulphide oxidation at a low rate.

For the area remediated by the sealing layer methodology the measured oxygen diffusion rates have been low, indicating a decreased oxidation of about 2-3 orders of magnitude. However, according to the freezing/thawing experiments in the laboratory the sensitivity for well compacted samples, having a low initial hydraulic conductivity and corresponding low porosity, is high. With an increased hydraulic conductivity the effective diffusion coefficient is increased and the efficiency of the sealing layer decreased. Frost penetrations of the sealing layer in the field have not been detected so the increases in oxygen diffusion caused by frost actions in field scale are still unknown. However, drought occurred during the summer 2002, and for the sealing layer protected by 0.3 m of till the increase in the effective oxygen diffusion coefficient was one order of magnitude. This induces a higher oxidation rate in the tailings underneath due to the increased availability of oxygen (a higher flux of oxygen through the sealing layer). For the protective cover thicknesses of 1.0 m and 1.5 m no change was detected. This imply that although, considering the probable climatic change as proposed for the next century, the protective cover thicknesses should not be reduced (due to the presumed decreased frost penetration) since the risk for desiccation during summer caused by the important relation between precipitation and evapotranspiration might increase. There is also the matter of root penetration to take into consideration. However, the concluding remark for the sealing layer area is that it is currently efficient in decreasing oxygen diffusion and water infiltration and is likely to continue like this until severely affected by frost or desiccation.

To remediate tailings impoundments by water saturation of soil covered tailings or by the application of composite cover with a sealing layer both are viable methods to prevent and decrease the oxidation rates in tailings. However, remediation should preferably be performed prior to initiation of sulphide oxidation, thereby the measures required to mitigate migrating oxidation products by passive or active treatment methods can be minimized. With a composite cover the decrease in oxygen availability is probably lower, but choosing this remediation strategy will not form the plume transported in the water saturated tailings if water saturating a previously oxidised tailings impoundment.
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Geochemical investigations of sulfide-bearing tailings at Kristineberg, northern Sweden, a few years after remediation

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Abstract

In the Kristineberg mining area in northern Sweden, massive, pyrite-rich Zn–Cu ores are intercalated in ca. 1.9 Ga volcano-sedimentary rocks. Investigations of a tailings impoundment remediated by means of both till coverage and raising the groundwater table have been undertaken. The aim of the study was to characterise the tailings with respect to mineralogy, the chemical composition of both the tailings and the pore water, and to try to identify the significant reactions that may have occurred before and after remediation. It was found that the oxidation front had reached down to depths of between approximately 0.1 and 1.15 m before remediation. The oxidation of sulfides has produced high concentrations of some metals in the pore water; up to 26, 16, 4.1, 2.7 and 82 mg/l have been measured for Al, Mn, Fe and Zn, respectively. Concentrations of metals such as Cd, Co, Cu, Ni and Pb are lower, with average concentrations of 18.4, 83.8, 45, 79.6 and 451 μg/l, respectively. Higher concentrations of major elements such as Ca, Fe, Mn, Mg and S have been measured at depth in pore water than at shallower levels. This is probably caused by flush out of elements after remediation and vertical transport from the upper parts before remediation. The pH is relatively high, approximately 5.5 at most depths in the tailings, except in and around the former oxidation zone where it is lower, and where the highest dissolved concentrations of elements such as As, Cd, Co, Cu, Pb and Zn occur. This is probably due to the release of metals secondarily retained below the oxidation front prior to the remediation. Since the groundwater table is raised, the groundwater reaches the retained metals, which leads to desorption of metals and dissolution of secondary minerals. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mine tailings; Remediation; Sulfide oxidation; Geochemistry
1. Introduction

Acid drainage from mining waste has been recognised as an environmental problem for some time. Complex biological, geochemical and physical processes determine the mobilisation and dispersion of contaminants from untreated mining waste, as well as from remediated waste deposits. This in turn has an impact on the surrounding environment. A thorough characterisation of the waste in question is necessary to understand the problem of acid mine drainage, to predict future problems and to find efficient remediation methods. Covering the waste with soil or water are two common methods of remediation. In northern Sweden, till deposited from the glacial ice between 8000 and 10 000 years ago is commonly used as a soil cover. Both unremediated tailings and tailings remediated with dry and water cover have been studied and characterised earlier by, e.g. Boorman and Watson (1976), Blowes and Jambor (1990), Fraser and Robertson (1994), Pedersen et al. (1994, 1997), Holmström and Öhlander (1999), Holmström et al. (1999, 2000). Studies of tailings remediated by a combination of both methods, however, are few.

The field studies within the Swedish Mitigation of the Environmental Impact from Mining Waste (MiMi) programme, which will continue for several years, started in 1998 at a chosen field site, the Kristineberg mine, named after a small village. The aim of the programme is to evaluate existing remediation methods, and, if possible, to improve them, but also to try to find new, efficient and cost-effective remediation methods to solve the environmental problems related to mining and the disposal of mining wastes.

In this study, sulfide-bearing tailings left without any cover for almost 50 years at the Kristineberg mine have been studied 2 years after remediation. The impoundment has been remediated by a combination of covering the waste with till, and by raising the groundwater table. The aim of this study was to characterise the tailings mineralogy, the chemical composition of both the tailings and pore waters, and to identify important reactions that may have occurred before and after the remediation.

2. Area description

The Kristineberg mining area is located in the western part of the Skellefte district in northern Sweden, approximately 175 km south-west of Luleå and consists of ca. 1.9 Ga ore-bearing volcanic rocks overlain by sedimentary rocks (Fig. 1). The metamorphosed volcanic and sedimentary rocks display a marked foliation and extensive sericitization (Vivallo and Willdén, 1988). Pyrite-rich massive sulfide ores are intercalated within a stratigraphic unit, consisting of mainly basic volcanics and redeposited volcano-clastic rocks (Willdén, 1986). For further descriptions of the geology of the area and the ores, see Du Rietz (1951), Gavelin (1943), Gavelin and Kulling (1955) and Grip (1973).

The largest ore body in the area is the Kristineberg Zn–Cu deposit, which was discovered as early as 1918. Mining began in 1940 by Boliden Mineral AB, and is still in progress. Other mines close to the Kristineberg mine are the Kimheden, Hornträsk, Rävlden and Rävldmyr mines, all of which are closed and remediated. The annual precipitation in the area varies between 400 and 800 mm/year (Axelsson et al., 1991a). A large part of the precipitation is in the form of snow, which accumulates during winter until the snowmelt season in late April/early May. The vegetation consists mostly of coniferous forest, but some deciduous forest occurs. Boglands are common. The major soil type in the area is podzol weathered till (Granlund, 1943; Granlund and Wennerholm, 1935).

Five tailings impoundments are located within the Kristineberg mining area (Fig. 1). Many different ores from the western part of the Skellefte-field mining district have been processed at the processing plant, and the impoundments contain a mixture of different tailings. Impoundment 1, the oldest impoundment within the mining area, has been investigated in this study. The impoundment is situated in a small valley and is underlain by peat and till. It was used until the early 1950s and has an area of approximately 0.10 km² (Boliden Mineral AB, 1995), and the tailings was discharged along the southern hill slope. Pre-remediation characterisation of the geochem-
istry and hydrogeology of the impoundment was carried out by Qvarfort (1983), Axelsson et al. (1986), Ekstav and Qvarfort (1989) and Axelsson et al. (1991a,b) (see also compilation in Malmström et al., in press).

In 1976 and 1978, attempts were made to seed grass on the impoundment. The impoundment was finally remediated in 1996 by a combination of raising the groundwater table, where this was possible, by sealing of intercepting and draining ditches, and dry cover application on the remaining regions of the impoundment. For a detailed description, see Lindvall et al. (1999). The intention was to apply 1 m of unspecified till as a protective layer in areas with a shallow groundwater table, and in other areas, to apply 1.5 m of unspecified till as a protective layer on top a 0.3-m thick sealing layer of clay till. The thickness of the till cover ranges from 0.85 up to almost 1.8 m; the thickness of the whole impoundment ranges from a few up to approximately 11 m, with an average thickness of 6–8 m. The groundwater table is shallow, reaching the surface in some parts of the impoundment, and the impoundment is now almost completely covered by grass.

3. Methodology

3.1. Sampling

Sampling of solid tailings and pore water was
performed in 1998. Five profiles were drilled in Impoundment 1 using a drill-rig (Fig. 1). The profiles were spread across the impoundment. All profiles extended down to the underlying peat/till. The drill cores were split into 20-cm subsamples, which were placed in polyethylene plastic bags immediately, or within a few min. A total of 127 samples of solid tailings and till were selected for analysis. Pore water was extracted from two of the drill cores from both the saturated and unsaturated zones. A total of 54 samples of pore water were extracted and analysed. Precautions were taken to avoid premature oxidation of the pore water samples. All samples used for pore water extraction were transferred to double plastic bags (polyethylene) within a few minutes after retrieval. Both plastic bags were filled with Ar gas. All pore water samples were extracted within a few hours after the drilling, using an Ar gas-filled glove box. The material used for pore water extraction was taken from the inner core of the samples stored in the plastic bags. Approximately 5–20 ml of water was extracted from each sample. The pore water was extracted using a portable Millipore* vacuum pump and Millipore* 47 mm filter holders with 0.22 μm Millipore* membrane filters. The pore water was collected in acid-washed 60-ml Azlon* HDPE bottles. The filters were acid-washed for 3 days using 5% HOAc. All other equipment was acid-washed in 5% HNO₃ prior to use, and washed in 0.1 M HCl between samples in the field in order to avoid contamination.

Redox and pH were measured with a Metrohm* Pt electrode and a Metrohm* combined pH electrode in the extracted pore water. The pH electrode was calibrated using two Titrisol* pH 4 and 7 buffers. The redox electrode was checked using two Ag/AgCl Reagecon* standards (124 and 358 mV). All redox values have been adjusted to the standard hydrogen electrode.

3.2. Mineralogical examinations

A total of 35 polished, thin sections were made from the tailings sampled and studied by optical microscopy, and XRD analyses were undertaken on 10 samples. The XRD measurements were performed with a TUR M62 diffractometer (step width, 0.02°; accumulation time, 2s/step) using CoKα radiation over a 2θ range from 2–42°.

3.3. Analysis

The samples of solid tailings were digested following the procedure described by Burman et al. (1978). Tailings samples were fused with LiBO₂ at 1000°C, and the beads thus formed were dissolved in 0.7 M suprapur* HNO₃. The major elements and Ba, Be, La, Mo, Nb, Sc, Sn, Sr, V, W, Y and Zr were analysed by ICP-AES (ARL 3560 B). For analysis of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, S and Zn, tailings samples were digested in 7 M suprapur* HNO₃ in Teflon bombs and heated in a microwave oven. The solutions were then centrifuged, diluted and finally analysed by ICP-AES (ARL 3560 B) and ICP-MS (VG Elemental Plasma Quad). The pore waters were acidified with 1% suprapur* HNO₃ prior to analysis and then analysed for Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb and Zn using high resolution ICP-SMS (Finnigan MAT ELEMENT). Hg was measured using atomic fluorescence (PS Analytical). Ca, K, Mg, Na, S, Si and Sr were analysed by ICP-AES (ARL 3560 B). Due to the small amount of pore water, no anion analyses were carried out.

The accuracy and precision of the analyses were checked by analysing reference materials. For solid tailings, the reference materials used were GBW 10, SARM-1, DRN and GSR 6. The pore water was checked using synthetic quality check standards (see Ödman et al., 1999). The instrumental precision, determined as ±1 S.D., for three to four runs on the same sample was generally better than 1% for the major elements and 10% for the trace elements when analysing solid tailings. For the pore waters, the precision was generally better than 5%.

4. Results

4.1. Chemical composition of the tailings

The average chemical composition of the solid
tailings is summarised in Table 1, with a subdivision between the tailings that were oxidised before remediation and unoxidised tailings. The unoxidised tailings contain high concentrations of metals and metalloids, with average values of 183 ppm As, 21.5 ppm Cd, 56.4 ppm Co, 956 ppm Cu, 463 ppm Pb, 14.4% S and 8861 ppm Zn, whereas the oxidised tailings contain much lower concentrations; 36.2 ppm As, 1.47 ppm Cd, 7.77 ppm Co, 159 ppm Cu, 454 ppm Pb, 1.81% S and 559 ppm Zn. The concentrations of Si, Al, Ca, K, Na, Ti (all expressed as oxides), Ba, Cr, Sr and Zr, elements which exist mainly in different silicates, are especially higher in the oxidised zone. The depth of the oxidised zone formed before remediation ranges from approximately 0.1 m (Profile 3) up to approximately 1.15 m (Profile 6), based on the chemical composition and field observations during drilling.

The concentration profiles of different elements vs. depth in the tailings material generally show relatively constant trends with depth in unoxidised tailings in all profiles, despite fluctuations between individual points. This is shown in Figs. 2–5, which show concentration profiles from Profiles 4 and 6. The fluctuations in the profiles are not surprising, considering that tailings are affected by sedimentary processes, such as graded bedding due to grain size and weight differences of different minerals, during deposition. Tailings from several different mines have also been deposited in Impoundment 1. However, distinct peaks are discernible for some metals. For example, Cu concentration peaks are found in most profiles below the pre-remediation oxidation front.

The chemical composition of the overlying till used as cover material during remediation is very different from that of the tailings. The till is richer in Al, Zr, Sr, Ca, Ba, Ti, Si, Na and K, and has a lower content of heavy metals than the underlying tailings (Figs. 2–5). The thickness of the overlying till is estimated to be approximately 1 m in all profiles, based on field observations and the chemical composition, with the exception of Profile 7, where the thickness is approximately 1.5 m. In most cases, the drilling reached the underlying till, which is also rich in Al, K, Zr, Ti, Si, Na and Sr (Fig. 4). In Profile 3, the underlying till was situated approximately 6 m below the impoundment surface, in Profile 5 approximately 9 m and in Profile 6 approximately 11 m. The underlying till was not sampled in Profiles 4 and 7.

### 4.2. Mineralogy

Based on chemical composition, the sulfide mineral content of the unoxidised tailings ranges from 10 to 30%, totally dominated by pyrite, and

---

**Table 1** Average composition of oxidised and unoxidised tailings at Kristineberg, impoundment 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Unoxidised tailings (73 samples) [wt. % ± S.D.]</th>
<th>Oxidised tailings (12 samples) [wt. % ± S.D.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.8 ± 6.7</td>
<td>63.1 ± 7.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.35 ± 1.50</td>
<td>11.4 ± 1.47</td>
</tr>
<tr>
<td>CaO</td>
<td>1.01 ± 0.49</td>
<td>1.24 ± 0.74</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>24.0 ± 5.0</td>
<td>8.45 ± 5.59</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.81 ± 0.40</td>
<td>1.88 ± 0.97</td>
</tr>
<tr>
<td>MgO</td>
<td>7.73 ± 1.46</td>
<td>6.65 ± 3.52</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.12 ± 0.02</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.46 ± 0.35</td>
<td>1.46 ± 0.88</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07 ± 0.02</td>
<td>0.08 ± 0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.30 ± 0.06</td>
<td>0.45 ± 0.07</td>
</tr>
<tr>
<td>S</td>
<td>14.4 ± 4.7</td>
<td>1.81 ± 2.79</td>
</tr>
<tr>
<td>LOI</td>
<td>12.4 ± 2.6</td>
<td>5.03 ± 3.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Unoxidised tailings [ppm ± S.D.]</th>
<th>Oxidised tailings [ppm ± S.D.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>183 ± 157</td>
<td>36.2 ± 28.9</td>
</tr>
<tr>
<td>Ba</td>
<td>281 ± 79</td>
<td>481 ± 193</td>
</tr>
<tr>
<td>Be</td>
<td>0.84 ± 0.15</td>
<td>1.06 ± 0.37</td>
</tr>
<tr>
<td>Cd</td>
<td>21.5 ± 12.5</td>
<td>1.47 ± 2.39</td>
</tr>
<tr>
<td>Co</td>
<td>56.4 ± 21.3</td>
<td>7.77 ± 9.18</td>
</tr>
<tr>
<td>Cr</td>
<td>46.2 ± 13.3</td>
<td>60.7 ± 19.9</td>
</tr>
<tr>
<td>Cu</td>
<td>956 ± 316</td>
<td>159 ± 132</td>
</tr>
<tr>
<td>Hg</td>
<td>2.42 ± 1.17</td>
<td>0.94 ± 0.52</td>
</tr>
<tr>
<td>La</td>
<td>22.4 ± 5.3</td>
<td>25.7 ± 5.5</td>
</tr>
<tr>
<td>Mo</td>
<td>24.0 ± 6.7</td>
<td>17.7 ± 11.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.95 ± 2.58</td>
<td>4.52 ± 3.35</td>
</tr>
<tr>
<td>Pb</td>
<td>463 ± 283</td>
<td>454 ± 318</td>
</tr>
<tr>
<td>Sc</td>
<td>5.90 ± 1.38</td>
<td>7.46 ± 1.10</td>
</tr>
<tr>
<td>Sr</td>
<td>40.1 ± 21.0</td>
<td>90.5 ± 51.8</td>
</tr>
<tr>
<td>V</td>
<td>26.9 ± 8.1</td>
<td>34.3 ± 8.9</td>
</tr>
<tr>
<td>Y</td>
<td>17.6 ± 3.1</td>
<td>21.2 ± 3.3</td>
</tr>
<tr>
<td>Zn</td>
<td>8861 ± 4744</td>
<td>559 ± 919</td>
</tr>
<tr>
<td>Zr</td>
<td>117 ± 41</td>
<td>205 ± 78</td>
</tr>
</tbody>
</table>

*Samples affected by secondary enrichment are excluded. All major elements except S are expressed as oxides.*
the tailings are not economic to reclaim. The most common sulfide minerals observed in the thin sections, in decreasing order of occurrence, are pyrite (FeS₂), pyrrhotite (Fe₁₋₃S), sphalerite (ZnS), chalcopyrite (CuFeS₂), galena (PbS) and covellite (CuS). Pyrite is by far the most abundant sulfide mineral. Arsenopyrite (FeAsS) occurs in small amounts. Based on the average chemical composition in Table 1, the wt.% of the different sulfides can be calculated. The results show that approximately 26% of the unoxidised tailings consist of pyrite (as pyrite was more abundant than pyrrhotite, it has been assumed that all iron sulfide is in the form of FeS₂, which may lead to a slight underestimation of the iron sulfide content). According to such calculations, the tailings also consist of 1.3% sphalerite, 0.28% chalcopyrite, 0.05% galena and 0.04% arsenopyrite. The content of the minor sulfides may be overestimated, as all Cu, Zn, Pb and As have been assumed to

Fig. 2. Profiles showing the concentrations of Al, Ca, Fe, Mg, Mn, Si and Ti (expressed as oxides) vs. depth in solid tailings in Profile 4.
Fig. 3. Profiles showing the concentrations of As, Cd, Co, Cu, Ni, Pb, S and Zn vs. depth in solid tailings in Profile 4.
occur in the form of these metal sulfides. Fe-oxyhydroxides also occur, but these may have precipitated due to evaporation of pore water after sampling, forming so-called tertiary minerals (Jambor, 1994). Gypsum occurs as massive euhedral grains, some of which also appear to be of tertiary origin.

In the oxidised tailings the sulfide content is generally low. The most common sulfide minerals in the oxidised tailings, in decreasing order of occurrence, are pyrite, chalcopyrite, pyrrhotite, sphalerite and galena. Pyrrhotite has been shown in other investigations to be more easily oxidised than the other sulfide minerals (Nicholson and Sharer, 1994; Blowes et al., 1998). Fe-oxyhydroxides are common, occurring as individual grains, aggregates and coatings on the silicate minerals. The pyrite content in the oxidised zone is approximated as 3.3% (again assuming that all iron sulfide is in the form of pyrite), 0.08% is sphalerite, 0.05% chalcopyrite, 0.05% galena and 0.008% arsenopyrite. These results are based on
Fig. 5. Profiles showing the concentrations of As, Cd, Co, Cu, Ni, Pb, S and Zn vs. depth in solid tailings in Profile 6.
the average composition shown in Table 1 and, as mentioned above, may overestimate the minor sulfide content.

The most common types of gangue minerals in both types of tailings are quartz (SiO₂), K-feldspar (KAlSi₃O₈), Mg-chlorite [e.g. (Fe,Mg, Al)₃(Si,Al)₂O₁₀(OH)₈], talc [Mg₃Si₄O₁₀(OH)₂], plagioclase (NaAlSi₃O₈–CaAl₂Si₂O₈), muscovite [KAl₃(AlSi₃)O₁₀(OH)₂], amphiboles/pyroxenes [amphiboles: (X,Y, Z)₃₋₇(Si,Al)₂O₅(OH)₂, where X = Ca, Na, Pb, K; Y = Fe(II), Li, Mg, Mn(II); Z = Fe(III), Cr(III), Al, Ti; pyroxenes: XY(Al, Si),O₆, where X = Ca, Na, Zn, Li; Y = Cr, Al, Fe(III), Ti, V] and biotite [K(Mg,Fe)₃ AlSi₃O₁₀(OH)₂]. Ilmenite (FeTiO₃), magnetite (Fe₃O₄), hematite (Fe₂O₃), titanite (CaTiSiO₄), epidote [Ca₃(Al,Fe)₃(SiO₄)₃(OH)], sericite [KAl₃(AlSi₃)O₁₀(OH)₂], zircon (ZrSiO₄), apatite [Ca₅(PO₄)₃(OH,F,Cl)] and calcite (CaCO₃) also occur, but in minor amounts. A summary of the XRD analyses of the tailings is shown in Table 2.

### 4.3. Pore water in the tailings

Pore water samples were taken from Profiles 4 and 6. The material from all depths from both profiles was saturated with water, except for the upper 2–3 m in Profile 6. The trend in pore water pH is similar for both profiles, with relatively constant pH of approximately 5.5 at depth (Fig. 6). The pH is somewhat higher in the till cover in Profile 4, between 6 and 6.8. Below the till cover, the pH decreases to 4.6–4.8 in the upper part of the impoundment, including the depths at which the pre-remediation oxidation zone occurs, then increases again to values of approximately 5.5–6 below this zone. The pH close to the surface of the impoundment is lower in Profile 6, with values of approximately 3.8–4.6 in the uppermost 4.3 m, where the pre-remediation oxidation front and the till cover are situated. Below this depth, the pH rises to between 5 and 6. The redox potential displays a similar trend in both profiles (Fig. 6), although redox values are somewhat higher in Profile 4 than in Profile 6. Both profiles show increasing redox potential with depth, with values ranging from approximately 150 to 550 mV.

The total element concentration in the pore water is lower in the uppermost tailings (Fig. 6). This is the case for both profiles. Elements such as Mn, Ni, Cr, Si, S, Mg, Fe and Ca in Profile 4 all show high, or the highest, concentrations below approximately 6 m. In Profile 6 this is true for Sr, Mn, S, Mg and Fe, but here the concentrations increase below 2.5 m (Figs. 7 and 8). The dominating metals in the tailings pore water are Fe, S, Ca, Mg, Zn, Al, Si and Mn (Figs. 7 and 8). The heavy metal concentrations are generally much lower at greater depths in the tailings, e.g. for Cd, Co, Cu, Ni and Pb.

### Table 2

Summary of the relative abundance of minerals identified by XRD analysis

<table>
<thead>
<tr>
<th>Profile number</th>
<th>Depth (cm)</th>
<th>Description</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Chlorite</th>
<th>Pyrite</th>
<th>Muscovite</th>
<th>Talc</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>80–90</td>
<td>Till/ox</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>120–130</td>
<td>Ox</td>
<td>+ + +</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>140–150</td>
<td>Ox/unox</td>
<td>+</td>
<td>+</td>
<td>+ + +</td>
<td>+</td>
<td>+ + +</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>200–240</td>
<td>Unox</td>
<td>+ + +</td>
<td>+</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>320–340</td>
<td>Unox</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>480–500</td>
<td>Unox</td>
<td>+ + +</td>
<td>+</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>720–740</td>
<td>Unox</td>
<td>+</td>
<td>+ + +</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>160–170</td>
<td>Unox</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>280–300</td>
<td>Unox</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>200–220</td>
<td>Ox/unox</td>
<td>+ + +</td>
<td>+ + +</td>
<td>+ + +</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* + + + + , very common mineral; + + + , common mineral; + + , minor mineral; and + , trace mineral.

*a*bTill/ox is a sample from the boundary between the till cover and the oxidised zone, ox denotes oxidised tailings, unox are samples with unoxidised tailings and ox/unox is a sample from the boundary between the oxidised and unoxidised zones.
In both profiles, elements such as Sr, Pb, Mo, Mn, Co, Cd, As, Si (Profile 4) and Zn, Pb, Ni, Mo, Na, Cu, Cr, Co, Cd, As, Al and Si (Profile 6) show maximum, or close to maximum, concentrations around the former oxidation zone situated at approx. 1.35–1.45 m in Profile 4 and 2.1 m in Profile 6, or approximately within 2–3 m below it (Figs. 7 and 8).

4.4. S.I. calculations

Using pore water data, saturation indices (S.I.) of various minerals were calculated using the geochemical equilibrium model PHREEQC (Parkhurst, 1995) with the MINTEQ database (Allison et al., 1991). While thermodynamic calculations cannot confirm whether or not a mineral is actually present, they can indicate, for example, whether the mineral in question would have a tendency to precipitate, or if present, dissolve. In these calculations the total S analyses from the pore waters have been converted to sulfate, due to the lack of anion analyses. Although this is not entirely correct, it may be a reasonable approximation. Saturation indices for carbonate minerals are not reported, as carbon concentrations were not determined.

The results showed that secondary sulfates such as gypsum (CaSO$_4$·2H$_2$O), anglesite (PbSO$_4$), barite (BaSO$_4$) and different kinds of jarosite [KFe$_3$(SO$_4$)$_2$(OH)$_6$ and NaFe$_3$(SO$_4$)$_2$(OH)$_6$] may be at solubility equilibrium with aqueous concentrations of elements such as Ca, S, Pb, Ba, K and Na at some depths. Pore waters in both profiles were close to solubility equilibrium with gypsum at most depths in the unoxidised tailings, whereas pore waters in the tailings were oversaturated with respect to barite. Pore waters were largely undersaturated with respect to anglesite at most depths, other than a few modelled points, where pore waters were close to equilibrium with this mineral. All other secondary Cu or other metal-containing sulfates, as well as Mn-oxyhydroxides and Mn-oxides, were found to be undersaturated.

Pore waters in Profile 4 were oversaturated with respect to all jarosites (H-, K- and Na-jarosite), Fe-oxyhydroxides and Fe-oxides, and even
Fig. 7. Profiles showing the concentrations of Ca, Fe, Mn, Mg, S, Si, Al, As, Cd, Co, Cu, Ni, Pb and Zn vs. depth in the pore water in profile 4.
Fig. 8. Profiles showing the concentrations of Ca, Fe, Mn, Mg, S, Si, Al, As, Cd, Co, Cu, Ni, Pb and Zn vs. depth in the pore water in Profile 6.
with respect to Fe(OH)$_{3}$, other than at a single point in the pre-remediation oxidising zone (Fig. 9). This is an unusual result, considering the highly insoluble nature of Fe(OH)$_{3}$ and the fast precipitation kinetics of this secondary mineral, particularly at the relatively high pH values and iron concentrations measured. This may indicate, for example, that the measured redox potential does not reflect the Fe(II)/Fe(III) redox pair.

Pore waters were oversaturated with respect to goethite, hematite and lepidocrocite throughout Profile 6; however, pore waters were undersaturated with respect to Fe(OH)$_{3}$ to a depth of 4 m. Below 4 m, Fe(OH)$_{3}$ was close to solubility equilibrium with pore waters (Fig. 9).

5. Discussion

5.1. Mass depletion and element mobility

From Table 1, it is evident that the concentrations of the sulfide-bound elements Fe, As, Cd, Co, Cu, S and Zn are much lower in the oxidised zone compared with the unoxidised. On the other hand, elements such as Si, K, Na and Ti show higher concentrations in the oxidised zone. This is due to losses of sulfide minerals during weathering, which increases the proportion of silicate minerals.

It is possible to determine the gains or losses during weathering by comparing the average elemental composition of the oxidised zone with that of the unoxidised zone. In the calculations shown here, it is assumed that Zr is an immobile element and occurs in minerals resistant to weathering. Almost all of the total Zr content in most silicic rocks occurs as the mineral zircon, ZrSiO$_4$ (Watson and Harrison, 1983), which is resistant to low-temperature weathering (Nickel, 1973). This is illustrated in Fig. 10 by plotting the average composition of the oxidised zone versus that of the unoxidised zone. The elements that fall below the line from the origin to the Zr point have, to various extents, been lost during weathering. All elements, except Na, K and Sr, have been de-
Fig. 10. Diagram to illustrate the method used to calculate the mass changes. All elements that fall below the Zr-line have decreased in concentration during the weathering and vice versa. Note that some elements have been scaled.

completed. Mixing of tailings and the till cover in some samples may be the cause of the apparent enrichment of Na, K and Sr. The mass change in the oxidised zone can be calculated with the following equation:

$$\text{Mass change} \% = \left( \frac{C_{Zr}^{\text{un}}}{C_{Zr}^{\text{o}}} - 1 \right) \times 100$$  \hspace{1cm} (1)

where $C_{Zr}^{\text{o}}$ is the concentration of Zr in the oxidised zone and $C_{Zr}^{\text{un}}$ is that in the unoxidised zone. The results show that the mass change in the oxidised zone is 42.8% compared with the unoxidised zone. This result suggests that almost half of the original material in the oxidised zone has weathered and been transported away from the oxidising zone.

If Zr is assumed to be immobile, the relative change in concentration between the oxidised and unoxidised zones can be calculated for all the elements with Eq. (2) (modified from Grant, 1986; Öhlander et al., 1989, 1991; Land, 1998).

$$\text{Mass change} \% = \left( \frac{C_i^{\text{o}}}{C_i^{\text{un}}} \right) \times \left( \frac{C_{Zr}^{\text{un}}}{C_{Zr}^{\text{o}}} - 1 \right) \times 100$$  \hspace{1cm} (2)

where $C_i^{\text{o}}$ is the concentration of element $i$ in the oxidised zone, and $C_i^{\text{un}}$ that in the unoxidised zone.

It can be estimated from Eq. (2) that As, Cd, Co, Cu, Ni, Pb, S, Zn and Fe have decreased by 88.7, 96.1, 92.1, 90.5, 56.6, 43.8, 92.8, 96.4 and 79.8%, respectively. From these calculations, the following order of mobility for different metals can be set up for the solid tailings: Zn > Cd > S > Co > Cu > As > Fe > Ni > Pb.

The mobility of these metals subsequent to release by sulfide oxidation is controlled by precipitation–dissolution reactions, co-precipitation reactions, solid–solution substitutions and adsorption–desorption reactions (Blowes and Jambor, 1990). The order of mobility calculated for the tailings at Kristineberg indicates that Zn is a very mobile ion. This has also been shown by Johnson and Thornton (1987), Kooner (1993) and Paulson (1997). Sphalerite is also considered to be relatively easily oxidised (Jambor, 1994). Cd generally follows Zn, since their ion sizes are similar (Brehler, 1978). Cd is therefore a common trace element in sphalerite. S has also been shown to be relatively mobile in mine-waste environments (Ljungberg and Öhlander, 1996), but S in the form of sulfate can also be controlled by reactions with, e.g. Fe-oxyhydroxides (Karltun, 1995), such as adsorption and co-precipitation. Fe generally precipitates as different oxides, oxyhydroxides or hydroxysulfates (Fig. 9), and is therefore less mobile. The Ni$^{2+}$ ion is similar in size to Fe$^{2+}$. This is one reason why Ni is common as a trace component in Fe minerals, such as pyrrhotite (Fleischer, 1955). In the mine-waste environment, Ni may, in part, be controlled by the same reactions controlling Fe. Cu is known to be relatively immobile compared to, for example, Zn (Kooner, 1993). Cu can take part in solid–solution substitutions, such as the transformation of pyrrhotite into covellite (Blowes and Jambor, 1990; Holmström et al., 1999). As is considered to be less mobile in acidic environments (Bowell, 1994), whereas Pb is less mobile, as it often forms anglesite, which is relatively insoluble (Williams, 1990). Jambor (1994) mentions that the general sequence of ‘readily attacked’ to ‘increasingly resistant’ minerals is pyrrhotite > galena–sphalerite >
pyrite–arsenopyrite > chalcopyrite > magnetite, but it is also evident that the mobility of elements varies, depending upon how easily they are transported away from the source minerals after being released by sulfide oxidation.

5.2. Cu enrichment zone

Below the former oxidation front there is a zone in which enrichment of Cu occurs in the solid phase, as shown in Figs. 3, 5 and 11. The thickness of this zone ranges from 0.1–0.2 up to almost 0.8–0.9 m in Profile 5. Holmström et al. (1999) found a similar Cu enrichment zone with a thickness of approximately 1 m in the tailings at the Laver Cu mine, in northern Sweden. The Cu enrichment is evident in all drilled profiles, except in Profile 7, which is situated farthest away from the old spigotting location. The solid-phase Cu concentration rises to a maximum of 4450 ppm Cu (Profile 5) compared with the average value of 956 ppm Cu for unoxidised tailings. No other metal shows this distinct enrichment, and the Cu enrichment is not followed by an enrichment of S or Fe (Fig. 11). The enrichment is thus not due to increasing chalcopyrite content, but is instead probably caused by formation of covellite, via transformation of pyrrhotite, chalcopyrite, galena and pyrite. Secondary covellite has been identified in thin sections. An example of secondary covellite is shown in Fig. 12. Similar reactions have been described by, for example, Boorman and Watson (1976), Blowes and Jambor (1990), Blowes et al. (1992) and Holmström et al. (1999). Further immobilisation of Cu may occur, due to adsorption on mineral surfaces and co-precipitation with precipitating oxyhydroxides (e.g. Holmström et al., 1999).

5.3. Underlying till

The solid heavy-metal concentrations are rather high at the levels of the sampled profiles at which the underlying till was reached (Profiles 3, 5 and
indicating that at least the uppermost part of the underlying till has been affected by the tailings and the acid mine drainage. The concentrations can be as high as 69 ppm As, 894 ppm Cu, 392 ppm Pb, 10.8% S and 5950 ppm Zn (Profile 6) in the underlying till. It is possible that the uppermost part of the underlying till contains sulfides originating from the tailings, and that leachate waters have penetrated into the till to unknown depths. In addition, metals may have adsorbed onto mineral surfaces, or precipitated in the till as secondary minerals. Groundwater sampled 1.3 m below the tailings also contains high metal concentrations, with average concentrations of 5.7 g/l Fe, 4.4 g/l S, 612 mg/l Mg and 0.3 mg/l Zn (Holmström, unpublished data), indicating that the groundwater in the till is contaminated. These concentrations can be compared with results from uncontaminated groundwater in northern Sweden (Land, 1998), in which concentrations such as 0.041–0.098 mg/l Fe, 0.774–0.779 mg/l S, and 0.676–0.770 mg/l Mg were found. The geochemical modelling with pore water from Profile 6 also indicated oversaturation with respect to some secondary minerals, such as goethite, gypsum and K-jarosite, in the uppermost part of the underlying till, as in the rest of the tailings below the till cover (Fig. 9).

5.4. Processes affecting the pore water

The concentrations of Fe and S are very high in the pore waters in both profiles. Profile 4 has maximum concentrations of up to 4.1 g/l Fe and 2.7 g/l S, and profile 6 has maximum concentrations of 2.1 g/l Fe and 1.7 g/l S. The Zn concentrations are also very high: up to 82 mg/l Zn in Profile 4 and 53 mg/l in Profile 6. The Mg, Al and Si concentrations are also high compared with, for instance, the concentrations in soil water in natural till (Land, 1998). The maximum concentrations are 276 mg/l Mg, 14.4 mg/l Al and 34 mg/l Si in profile 4 and 236 mg/l Mg, 26.2 mg/l Al and 26.9 mg/l Si in Profile 6. This indicates that the oxidation of sulfides prior to remediation was intense, and that buffering reactions with different silicates were important.

Pre-remediation pH measurements in Impoundment 1 (slurry pH) carried out by Qvarfort (1987) in the beginning of the 1980s showed that the pH was low, between 2.6 and 3.8, with the exception of one extreme value of 7.3, in the upper 2 m of the impoundment, where the oxidation front was situated. Humidity cells tests (British Columbia Acid Mine Drainage Task Force, 1989) performed (Holmström, unpublished data) on samples from Impoundment 1 after remediation gave pH values in leachates that ranged from 2.3 up to 2.7 in oxidised tailings, comparable to the values found by Qvarfort 1987, and from 3.7 to 4.6 in unoxidised tailings. These low pH values suggest that the pH in the oxidised zone prior to remediation was low enough to make buffering reactions with different silicates important. They also indicate that the pH values were higher in the unoxidised zone. Silicate minerals provide the bulk of the buffering capacity when hydroxide minerals have been consumed and no longer buffer (pH < 3.5) (Blowes and Ptacek, 1994).

The trend in pH of the pore water with depth is similar for both Profiles 4 and 6. A rather constant pH is found at depth, but with a somewhat higher pH in the till cover in Profile 4, of approximately 6–6.8. This is probably due to the liming during remediation. The dissolved Ca content is also somewhat higher in the till cover in Profile 4 than in Profile 6.

The dominating elements in the tailings pore
Fig. 13. Diagram showing pore water concentrations from profiles 4 and 6 to illustrate that pyrite oxidation, presumably buffered by chlorite dissolution, has been intense in the tailings.

water are Fe, S, Ca, Mg, Zn, Al, Si and Mn. In Profile 6 the concentrations of some of these elements correlate reasonably well with pH. \( R^2 = 59.8\% \) for pH–Mg, 43.2\% for pH–Fe and 62.5\% for pH–S. This is not the case for Profile 4, where the correlations are \( R^2 = -2.7\% \) for pH–Mg, \(-3.5\% \) for pH–Fe and \(-2.4\% \) for pH–S. The correlation between Fe and Mg is good for both profiles \( (R^2 = 96.7\% \) for profile 4 and 83.8\% for Profile 6), indicating that pyrite oxidation has probably been buffered mostly by dissolution of Mg-bearing silicates in the tailings, where chlorite is especially common (Fig. 13). The total molar concentrations correlate well with pH through the entire profile in Profile 6 \( (R^2 = 58.9\% \) ), but not in Profile 4 \( (R^2 = -2.8\% \) ). Considering only the upper 3 m of Profile 4, the correlation is better \( (R^2 = 60.8\% \) ). These results indicate that pH, to some extent, controls the element concentrations in the tailings, especially in the upper parts of the impoundment.

The total element concentration of the pore water is now lower in the uppermost tailings in both profiles, possibly indicating an outwash zone (Fig. 6). Elements, such as Mn, Ni, Si, S, Mg, Fe and Ca in Profile 4, all show high, or highest, concentrations below approximately 6 m. In Profile 6, this is true for Sr, Mn, S, Mg and Fe, but here the concentrations are higher below 2.5 m. Ekstav and Qvarfort (1989) found indications that this was not the case prior to remediation, and concluded that there were no major differences between shallow and deep groundwater. The differences between the data presented by Ekstav and Qvarfort (1989) (Table 3) and the present data may be explained, at least partly, by outwash of elements after remediation. This possible ‘outwash zone’ seems to be deeper in Profile 4 than in Profile 6.

A possible explanation for the outwash zone in Profile 4 being deeper than that of Profile 6 is that the groundwater table was very shallow in the north-western part of the impoundment, even before remediation. The strong oxidation of sul-
Table 3


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average ± S.D. (201 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.88 ± 0.37</td>
</tr>
<tr>
<td>[mg/l]</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>297 ± 124</td>
</tr>
<tr>
<td>Fe</td>
<td>3906 ± 1270</td>
</tr>
<tr>
<td>Mg</td>
<td>277 ± 119</td>
</tr>
<tr>
<td>Na</td>
<td>6.56 ± 0.68</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>8620 ± 3174</td>
</tr>
<tr>
<td>Cd</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05 ± 0.03</td>
</tr>
<tr>
<td>Cu</td>
<td>2.5 ± 1.67</td>
</tr>
<tr>
<td>Pb</td>
<td>1.39 ± 0.57</td>
</tr>
<tr>
<td>Zn</td>
<td>333 ± 197</td>
</tr>
</tbody>
</table>

The oxidation front reached the groundwater table, which, according to the results from the drillings, was as shallow as 0.5 m below the tailings surface in Profile 4, before remediation. Because the oxidation was the source of increased concentrations of Fe, S and other elements, as well as of elements such as Ca and Mg released by buffering reactions, the concentrations have decreased in the uppermost part of the tailings since the oxidation stopped. In the south-eastern parts of Impoundment 1, where Profile 6 is located, the oxidation was still active when the till cover was applied. After till cover emplacement, the oxidation slowed down, perhaps ceased, and oxidation and weathering products have been gradually flushed out by precipitation water and mixing and dilution with groundwater flowing in from the till areas to the north-west of the impoundment. Since a much shorter period of time has elapsed since the cessation of oxidation in the south-eastern part of the impoundment than in the north-western part, the outwash zone is shallower in Profile 6 than in Profile 4.

Although the total molar concentration is higher at depths below 5–6 m (Fig. 6), the heavy metal concentrations are in general much lower at greater depths in the tailings. This is the case for Cd, Co, Cu, Ni, Pb and Zn for Profile 6, and also for Profile 4, except for Ni and Zn. This is probably an effect of the higher pH at greater depth, which ranges from approximately 5 to almost 6 in both profiles. The concentrations of these elements are probably controlled by adsorption/desorption reactions. Heavy metals are considered to be more sensitive to changes in pH compared with major cations such as Mg and Ca, and heavy metals are also more likely to be adsorbed onto different hydrous metal oxides (e.g. Kinniburgh and Jackson, 1981; Kinniburgh et al., 1976). Adsorption of major elements is only important at higher pH, above 6.5. In particular, Ca, Mg and S are rather mobile under the pH conditions prevailing today, and before remediation. These metals have been transported by vertical flow from the zone of oxidation down to deeper levels prior to remediation, which was also suggested and reported by Ekstav and Qvarfort (1989). The high concentration of the major ions below 6 m (Profile 4) and 2.5 m (Profile 6) may be remnants and a reflection of the older type of contaminated water.

In both profiles, elements such as Al, As, Co, Cd, Cu, Pb, Si (Profile 4) and Al, As, Cd, Co, Cu, Ni, Pb, Si and Zn (Profile 6) show maximum, or close to maximum, concentrations close to the former oxidation front, situated at ca. 1.35 m in Profile 4 and at ca. 2.1 m in Profile 6, or within a few m below. These maxima correlate rather well with the depths at which pH is lowest in both profiles. Before remediation and during oxidation of the tailings, metals were released in the oxidation zone and at the oxidation front. Surface adsorption and precipitation is more pronounced at high pH. pH usually increases below the oxidation front in tailings, in which hardpans composed of secondary minerals may also form (Boorman and Watson, 1976; McSweeney and Madison, 1988; Blowes and Jambor, 1990; Blowes et al., 1992). The humidity cells tests performed also indicated that pH is higher in unoxidised tailings at Kristineberg compared with oxidised tailings (Holmström, unpublished data). The released metals were probably transported downwards and precipitated as secondary minerals, or were adsorbed onto different particle surfaces when the pH increased below the oxidation zone.
from Hall et al. (1996) have been performed with material from Profile 4 (Carlsson et al., in preparation). The results show that adsorption is important for metals such as Cd, Co, Cu, Ni and Zn, especially below the oxidation front.

The groundwater table was raised by approximately 0.5 m, even more in some areas, during remediation. Possible explanations for the high metal concentrations below or close to the former oxidation zone may thus be desorption of metals or dissolution of secondary minerals due to the raised groundwater table used as a remediation method. The groundwater table reached the old oxidation zone, where pH is still low today, thereby promoting desorption of metals and dissolution of secondary minerals.

6. Conclusions

Oxidation and weathering of tailings Impoundment 1 at Kristineberg appear to have been intense before the impoundment was remediated. The oxidation front had penetrated down to depths of approximately 0.1–1.15 m before remediation, with a downward movement at a maximum rate of 2.6 cm/year. Below the oxidation front there is an enrichment zone, in which Cu is immobilised. The solid Cu concentration in this zone can be as high as 4450 ppm Cu, compared to the average of 956 ppm Cu in unoxidised tailings. Transformation of pyrrhotite, chalcopyrite, galena and pyrite into covellite is a possible explanation. Adsorption of Cu onto different mineral surfaces is another possible explanation.

Assuming that Zr is immobile during weathering, it can be approximated that almost 43% of the total mass has disappeared in the oxidised zone during weathering and oxidation. The As, Cd, Cu, Ni, Pb, S and Fe concentrations have decreased by 88.7, 96.1, 90.5, 56.6, 43.8, 92.8 and 79.8%, respectively, giving an order of mobility of Zn > Cd > S > Co > Cu > As > Fe > Ni > Pb for the solid tailings.

It is probable that sulfide oxidation ceased after remediation. Higher dissolved concentrations of the major elements Ca, Fe, Mn, Mg and S are measured at depth in the tailings. This could be due to flush out of elements in the upper part of the tailings after remediation, and vertical transport from the upper parts before and after remediation. Metals and metalloids, such as Si, Al, As, Cd, Co, Cu, Pb and Zn, show maximum concentrations around the former oxidation zone and a few m below. The pH is rather high at most depths in the tailings, except in and around the former oxidation zone, where the highest heavy metal concentrations are generally measured. Desorption of metals after remediation is probably occurring as a result of raising the groundwater table.

This study shows that remobilisation of elements from secondary minerals formed during oxidation prior to the remediation, as well as by desorption, is probably occurring in the tailings at Kristineberg. This seems to be a consequence of the higher groundwater table. To be able to fully understand and characterise the processes occurring in an impoundment remediated with both a till cover and a raised groundwater table, the development of the water quality within the tailings in the longer perspective must be studied by prolonged groundwater sampling. A more thorough understanding of the hydrology is also needed. Such studies are in progress. At Kristineberg, there is a water-covered downstream impoundment, where the pH is increased by liming, which functions as a trap for metals released from the upstream impoundments, including Impoundment 1 studied here (Lindvall et al., 1999). However, in other cases where the groundwater table is raised as part of the remediation, release of metals from their secondary retention after oxidation may be a problem. The results of this study illustrate that the best situation is when sulfide-rich waste is never allowed in direct contact with the atmosphere or oxides, and when such waste is remediated unoxidised.

Acknowledgements

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Carlsson E., Thunberg J., Öhlander B., and Holmström H.
Sequential extraction of sulfide-rich tailings remediated by the application of till cover, Kristineberg mine, northern Sweden

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Abstract

A sequential extraction has been carried out on sulfide-rich mine tailings. The purpose was to investigate how elements released by oxidation are secondarily retained in the tailings and the possible consequences of the remediation. After investigating the solid tailings, seven samples were chosen for sequential extractions. Two samples were oxidised, situated just above the oxidation front; two samples from just below the former oxidation front with increased concentrations of several elements; two unoxidised samples were from an intermediate depth, and the deepest sample was from the tailings–peat boundary at the bottom of the impoundment. Five phases were extracted: adsorbed/exchangeable/carbonate; labile organics; amorphous Fe-oxyhydroxides/Mn-oxides; crystalline Fe-oxides; and organics/sulfides. The addition from dried porewater to the extracted fractions has been calculated and considered as minor. In the oxidised tailings, the sulfide fraction still dominates for elements such as Fe, S, Cd, Co, Cu, Hg and Zn, although the concentrations are low compared to the unoxidised tailings. Generally, the second most important fraction is the adsorbed/exchangeable/carbonate fraction. Below the oxidation front, the sulfide content of the tailings sharply increases. In the secondary enrichment zone, the total element concentrations increase compared with the deeper unoxidised samples, mainly due to secondary retention. For some elements, secondary retention is greater than the total amount extracted for the deeper unoxidised samples. In the secondary enrichment zone the adsorbed/exchangeable/carbonate fraction represents approximately 20 wt.% or more for Cd, Co, Mn, Ni and Zn. The amorphous iron oxyhydroxide or the crystalline iron oxide fractions are less important at this level, although for As, Ba and Cu the amorphous iron oxyhydroxide fraction represents up to 20 wt.%. At the lower border of the enrichment zone, the total concentration for most metals is lower, but the importance of the adsorbed/exchangeable/carbonate fraction is further enhanced for Cd, Cu, Ni and Zn. These elements have 35–60 wt.% of the total amount from this fraction. For As, Cd, Cu, Ni and Pb, the secondary fractions extracted (extractions A–D) represent between 60 and 80 wt.% of the total content. At greater depth in the impoundment the relative importance of the adsorbed/exchangeable/carbonate fraction decreases, whilst the importance of amorphous iron oxyhydroxide and crystalline iron oxide fractions increases. The adsorbed/exchangeable/carbonate fraction is the most easily remobilised fraction.

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A raised groundwater table previously situated below the enrichment zone may result in the release of secondarily retained metals.

Keywords: Sulfide-rich tailings; Sequential extraction; Heavy metals

1. Introduction

Acid mine drainage from sulfide mine tailings is recognised as an important pollutant. Complex relationships between biological, chemical and hydrological factors control the dispersion of contaminating effluents from untreated as well as remediated waste deposits. To be able to understand key processes for designing efficient remediation methods, thorough investigations of the waste are of fundamental importance. Studies of the mines at Laver (Ljungberg, 1999; Holmström, 2000) and Kristineberg (Holmström et al., 2001) in northern Sweden showed that a large part of the metals released by sulfide oxidation is secondarily retained in the tailings below the oxidation front. Adsorption to mineral surfaces was found to be a key process, as well as secondary mineral formation. The sulfide-rich tailings at Kristineberg were left without any cover for almost 50 years and were remediated in 1996 by the application of till cover. The tailings impoundments were remediated by a combination of till coverage and raising the groundwater table. Holmström et al. (2001) have studied the mineralogy and chemistry of the solid fraction, as well as the composition of the porewater. The aim of this investigation was to characterise the fractions in which the elements that have been analysed occur. This characterisation was performed by the use of sequential extractions, with the various steps slightly modified from Hall et al. (1996a,b) and optimised for extractant selectivity and efficiency for secondary Fe-oxyhydroxides. Since it was presumed that a large amount of the elements analysed would be present in this fraction, especially close to the previous oxidation zone, this method was preferred in the sequential extractions. An understanding of how various elements occur at different depths is important for the understanding of the present state of the impoundment. It could also prove to be a useful tool for predicting future conditions in the impoundment. Single or sequential extractions as a method for determining the occurrence of trace and major elements in soils and sediments have been used in many studies with different purposes during the years. The sequential extraction technique derived by Tessier et al. (1979) was used by Fanfani et al. (1997) to study weathering of mine tailings. Although the results confirmed the general alteration modalities observed in the area through mineral studies, the development of a new method was proposed. Non-sequential extraction experiments were used by McGregor et al. (1998) to investigate the constituents within shallow, weathered tailings in the vadose zone. The extracted fractions were defined as water-soluble, acid-leachable and reducible, based on the work of Ribet et al. (1995). The results showed that large parts of the retained elements in the oxidised zone could be released by acid-leaching or reducing conditions. When working with sequential extractions, it is important to stress that the extractions are operationally defined. There is no such thing as an extractant that is completely selective and efficient. Redistribution of leached elements from one phase to another does occur in various proportions during extraction. As a consequence, a wide array of single and sequential extractions has been proposed.

2. Area description

The Kristineberg mining area is located in the western part of the Skellefte ore district, approximately 175 km south-west of Luleå (Fig. 1). The approximately 1.9-Ga-old ore-bearing volcanic rocks are overlain by metasedimentary rocks. The metamorphosed volcanic and sedimentary rocks display marked foliation and extensive sericitisation (Vivallo and Willdén, 1988). Pyrite-rich sulfide ores are intercalated within a stratigraphic unit.
Fig. 1. Map showing the location of the Kristineberg mining area and Impoundments 1 and 1B with sampling locations.

mainly consisting of basic volcanics and redeposited volcano-clastic rocks (Willden, 1986). For further description of the area and its geology and ores, see Du Rietz (1951), Gavelin (1943), Gavelin and Kulling (1955) and Grip (1973). The largest ore body in the area is the Kristineberg Zn–Cu deposit, which was discovered in 1918. It was not until 1940 that mining activities were started by Boliden Mineral AB, and mining is still in progress. Other mines close to the Kristineberg mine are the Kimheden, Hornträsk, Rävldiden and Rävldmyr mines, all of which were closed and remediated. The annual precipitation in the area varies between 400 and 800 mm/year (Axelsson et al., 1991) and the annual mean temperature is 0.7 °C (Axelsson et al., 1986). In general, the impoundment is snow-covered between late October/early November and late April/early May (Axelsson et al., 1986). Snow melt mostly occurs during April/May. The vegetation mainly consists of coniferous forest, but some deciduous forests also occur. Boglands are common. The major soil type in the area is podzol weathered till (Granlund and Wennerholm, 1935; Granlund, 1943). Five tailing impoundments are located within the Kristineberg mining area. As many as 10 different ores from the western part of the Skellefte field mining district were processed in the processing plant, and
thus the impoundments contain a mix of several different kinds of tailings. In this study, Impoundment 1 was investigated (Fig. 1). It is the oldest within the mining area. It has a surface area of approximately 0.10 km² and was used for disposal of tailings until the early 1950s (Boliden Mineral AB, 1995). The tailings discharge was located along the southern hill slope. In 1976 and 1978, attempts were made to sow grass. In 1996 the impoundment was remediated by the application of till cover and raising the groundwater table, after which grass was sown (Lindvall et al., 1999). The intention was to use 1 m of unspecified till as a protective layer in areas with a shallow groundwater table. In other areas with a deeper groundwater table, 1.5 m of till was placed above a 0.3-m sealing layer. The sealing layer consists of a compacted clayey till. Prior to the application of the till cover, 10 kg/m² of lime was added to the top of the tailings. After remediation, the groundwater table has become shallow in parts of the impoundment due to the fact that upstream ditches are refilled. In some parts of the impoundment, it reaches the surface. The impoundment is located in a valley and underlain by peat and till. The thickness of the tailings ranges from a few to approximately 11 m. The average thickness is between 6 and 8 m. The oxidation zone reaches a depth of approximately 50 cm in the tailings at the sampling location.

3. Materials and methods

3.1. Sampling

The tailings were sampled in October 1998. The impoundment was sampled with a drill rig (rotary drill) and the tailings were divided in 20-cm samples, except for the first 2 m, for which the sample length was 10 cm. From the sampled tailings, porewater was extracted. Precautions were taken to avoid premature oxidation of the porewater samples. All samples used for porewater extraction were transferred to double polyethylene bags within a few minutes after retrieval. Both plastic bags were filled with Ar gas. All porewater was extracted within a few hours after the drilling using an Ar-gas-filled glove box. The material used for porewater extraction was taken from the inner core of the samples stored in the plastic bags. Approximately 5–20 ml of water was extracted from each sample. The pore water was extracted using a portable Millipore® vacuum pump and Millipore® 47-mm filter holders with 0.22-µm Millipore® membrane filters. The porewater was collected in acid-washed 60-ml Azlon® HDPE bottles. The filters were acid-washed for 3 days using 5% acetic acid (HOAc). All other equipment was acid-washed in 5% HNO₃ prior to use and washed in 0.1 M HCl between samples in the field in order to avoid contamination. Redox and pH were measured with a Metrohm® Pt electrode and a Metrohm® combined pH electrode in the extracted porewater. The pH electrode was calibrated using two Titrisol® pH 4 and 7 buffers. The redox electrode was checked using two Ag/AgCl Reagecon standards (124 and 358 mV). All redox values have been adjusted to the standard hydrogen electrode. Both solid tailings and porewater were analysed. A total of five profiles were drilled in Impoundment 1 (drill profiles 3–7, Fig. 1). Sampling occurred from the surface down to the underlying material. A total of 54 porewater extractions were analysed, together with 119 samples of the solid material. Mineralogical studies on the material were also performed. A total of 35 thin sections from the impoundment have been evaluated. Samples were impregnated with resin before sectioning. Thin sections were studied by optical microscopy and X-ray diffraction (XRD) analysis was performed on 10 samples. The XRD measurements were performed with a TUR M62 diffractometer (0.02° step, accumulation time 2 s/step) using CoKα radiation over a 20 range from 2° to 42°. The samples used for the sequential extraction were from drill profile 4 (Figs. 1 and 2) and selections were based on porewater and solid tailings analyses. Samples chosen for the sequential extraction were dried at 50 °C and sieved, and the particle size fraction <63 µm was used. This size was chosen, since it was assumed that using the same particle size fraction would give comparable results from the different samples. It is evident from the
fieldwork, as well as from laboratory studies of the particle size distribution, that graded bedding occurs in the tailings. The coarser particles were in general visually identified as different kinds of silicates, indicating mainly sulfide minerals in the finer fractions. A total of seven samples from profile 4 were collected for sequential extractions (Fig. 2). Two samples are from the oxidised zone of the tailings, 135 (sample 121) and 145 cm (sample 122) below the till surface. One sample was taken just at the border of the oxidised zone, 155 cm (sample 123) down in the impoundment, and another at an intermediate depth of 185 cm (sample 126). Three samples were collected from the lower part of the impoundment. Two of them were taken at a depth 770 (sample 156) and 790 cm (sample 157), while the last one (sample 164) was located at the peat–tailings boundary at a depth of 932 cm. This sample contained some peat. All values given are the centre depth for the samples used in the sequential extraction.

3.2. Description of the tailings and the porewater

In drill profile 4, the oxidation zone extends 0.5 m down in the tailings. This conclusion is based on the chemical analyses. No significant differences with regard to colour between oxidised and unoxidised tailings were found in profile 4. Generally, the colour was grey in the oxidised layer and dark grey in the unoxidised; in some samples in the oxidised zone a slight greenish tone was also discernible. Probably the water saturation of the oxidised layer, due to the remediation method,
dissolved the precipitated iron hydroxides visible prior to remediation. In areas where the more advanced till cover was used, reddish iron-precipitates are still present (Carlsson et al., in press). The water ratio of the tailings was investigated and found to vary between 0.13 and 0.32, with an average of 0.20 (40 samples). No relation between water ratio and depth was found. Compact density was measured on 11 unoxidised samples from different depths. It was found to vary between 3.02 and 3.53 t/m³. Using the compact density and water ratio values, the undisturbed porosity for the samples was calculated. It varies between 0.35 and 0.46. Particle size distributions for sample 128 (depth 220 cm) and 155 (depth 750 cm) from profile 4 in the tailings are presented in Fig. 3. Visual inspection during the sieving analyses revealed that the coarser particles generally consist of quartz and feldspar grains. Average concentrations of unoxidised tailings based on 73 samples and of oxidised tailings based on 12 samples are presented in Table 1. The material from all depths from profile 4 was saturated with water. The trend in porewater pH shows a relatively constant pH, approximately 5.5, at greater depths (Fig. 4). The pH is somewhat higher in the till cover in Profile 4, approximately 6–6.8. Below the till cover, the pH decreases to 4.6–4.8 in the upper part of the impoundment, including the depths at which the pre-remediation oxidation zone is thought to exist, then increases again to values of approximately 5.5–6 below this zone. There is a trend of decreasing redox potential with depth, with values ranging from approximately 200 to 540 mV. The total element concentration in the porewater is lower in the uppermost tailings. The predominant metals in

![Fig. 3. Particle size distribution for sample 128 (220 cm depth) and sample 155 (750 cm depth).](image-url)
the tailings porewater are Fe, S, Ca, Mg, Zn, Al, Si and Mn. The heavy metal concentrations are generally much lower deeper down in the tailings, e.g. for Cd, Co, Cu, Ni and Pb. Pre-remediation pH measurements in Impoundment 1 (slurry pH) by Qvarfort (1987) in the early 1980s showed that the pH was low, between 2.6 and 3.8, with the exception of one extreme value of 7.3, in the upper 2 m of the impoundment, where the oxidation front was situated. These low pH values suggest that the pH in the oxidised zone prior to remediation was low enough, making buffering reactions with different silicates important. They also indicate that the pH values were higher in the unoxidised zone. Silicate minerals provide the bulk of the buffering capacity when hydroxide minerals have been consumed and no longer buffer (pH < 3.5) (Blowes and Ptacek, 1994).

### 3.3. Mineralogy

In the unoxidised tailings, the sulfide mineral content ranges from 10 to more than 30%. The most common sulfide minerals identified by studies of thin sections are, in decreasing order: pyrite, pyrrhotite, sphalerite, chalcopyrite, galena and covellite. Pyrite is by far the most common sulfide mineral. Some of the Fe-hydroxides identified in the tailings were formed by the evaporation of porewater after sampling, so-called tertiary minerals (Jambor, 1994). Gypsum occurs as massive euhedral grains, and some of them also appear to be of tertiary origin. In the oxidised tailings, the sulfide content is generally approximately 1–2%. The most common sulfide minerals are, in decreasing order: pyrite, chalcopyrite, pyrrhotite, sphalerite and galena. The most common types of gangue minerals in both types of tailings are quartz, K-feldspar, Mg-chlorite, talc, plagioclase, muscovite, amphiboles, pyroxenes and biotite. Illmenite, magnetite, hematite, titanite, epidote, sericite, zircon, apatite and calcite also occur, but in minor amounts.

### 3.4. Sequential extraction

The sequential extraction procedure used in this study was slightly modified from Hall et al. (1996a,b) and is briefly outlined as follows. The extraction steps dissolve the following fractions: extraction A, adsorbed/exchangeable/carbonate; extraction B, labile organics (e.g. humic and fulvic substances); extraction C, amorphous iron oxyhydroxides and manganese oxides; extraction D, crystalline iron oxides (e.g. goethite, hematite, magnetite); and extraction E, organics (e.g. humic and fulvic substances more refractory than those in extraction B) and sulfides.

#### 3.4.1. Extraction A

(1) To 1 g of dried and sieved sample in a centrifuge tube, 10 ml of 1.0 M CH₃COONa at
pH 5 was added. The centrifuge tube was placed in a shaker for 6 h and then centrifuged for 15 min at 3000 rev./min. (2) The supernatant was decanted into a test-tube. (3) Steps 1 and 2 were repeated. (4) The residue was rinsed with 5 ml of H$_2$O and centrifuged, and the supernatant was added to the test-tube. Step 4 was carried out twice.

3.4.2. Extraction B
(5) To the residue from step 4, 50 ml of 0.1 M Na$_3$P$_2$O$_7$ was added, and the centrifuge tube was placed in a shaker for 1 h and then centrifuged. (6) The supernatant was decanted into a new test-tube. (7) Steps 5 and 6 were repeated. (8) The residue was rinsed with 5 ml of H$_2$O and centrifuged, and the supernatant was added to the test-tube. Step 8 was carried out twice.

3.4.3. Extraction C
(9) To the residue from step 8, 10 ml of 0.25 M NH$_2$OH·HCl in 0.10 M HCl was added. The centrifuge tube was placed in a water bath at 60 °C for 2 h and then centrifuged. (10) The supernatant was decanted into a test-tube. (11) Steps 9 and 10 were repeated. (12) The residue was rinsed with 5 ml of H$_2$O and centrifuged, and supernatant was added to the test-tube. Step 12 was carried out twice.

3.4.4. Extraction D
(13) To the residue from step 12, 15 ml of 1.0 M NH$_2$OH·HCl in 25% CH$_3$COOH was added. The centrifuge tube was placed in a water bath at 90 °C for 3 h and then centrifuged. (14) The supernatant was decanted into a test-tube. (15) Steps 13 and 14 were repeated, with the exception that the heating was restricted to 1.5 h. (16) The residue was rinsed with 5 ml of 25% CH$_3$COOH and centrifuged, and supernatant was added to the test-tube. Step 16 was carried out twice.

3.4.5. Extraction E
(17) To the residue from step 16, 750 mg of KClO$_3$ and 5 ml of 12 M HCl were added. The centrifuge tube was vortexed and a further 10 ml of HCl was added. After 30 min, 15 ml of H$_2$O was added and the tube was then centrifuged. The supernatant was decanted into a test-tube. (18) To the residue, 10 ml of 4 M HNO$_3$ was added. The centrifuge tube was placed in a water bath at 90 °C for 20 min and then centrifuged. The supernatant was decanted into a test-tube. (19) The residue was rinsed with 5 ml of H$_2$O and centrifuged, and supernatant was added to the test-tube. Step 19 was carried out twice.

3.5. Standards and analytical methodology
The samples of solid tailings were digested following the procedure described by Burman et
al. (1978). Tailings samples were fused with LiBO$_2$ at 1000 °C and the beads thus formed were dissolved in 0.7 M Suprapur HNO$_3$. The major elements and Ba, Be, La, Mo, Nb, Sc, Sn, Sr, V, W, Y and Zr were analysed by ICP-AES (ARL 3560 B). For analysis of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, S and Zn, tailings samples were digested in 7 M Suprapur HNO$_3$ in Teflon bombs and heated in a microwave oven. The solutions were then centrifuged, diluted and finally analysed by ICP-AES (ARL 3560 B) and ICP-MS (VG Elemental Plasma Quad). The porewater samples were acidified with 1% Suprapur HNO$_3$ prior to analysis and then analysed for Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn using high-resolution ICP-SMS (Finnigan Mat Element). Hg was measured using atomic fluorescence (PS Analytical). Ca, K, Mg, Na, S, Si and Sr were analysed by ICP-AES (ARL 3560 B). Due to the small amount of porewater, no anion analyses were carried out. The sequential extraction samples were acidified with 1% Suprapur HNO$_3$ prior to analysis and then analysed. Concentrations of Ca, Fe, K, Mg, Na, S, Si, Al, Cu, Mn and Zn in the sequential extraction solutions were determined with ICP-AES (ARL 3560 B), and As, Ba, Cd, Co, Cr, Mo, Ni, Pb and Sr with ICP-SMS (Finnigan Mat Element). Hg was determined with atomic fluorescence (PS Analytical). Analyses of the solid residual for the elements Si, Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, Ba, Be, Cr, La, Mo, Nb, Sc, Sn, Sr, V, W, Y, Zn and Zr were performed with ICP-AES (ARL 3560 B), and Cd, Co, Cu, Hg, Ni and Pb with ICP-QMS (VG Elemental Plasma Quad). The accuracy and precision of the analyses were checked by analysing reference materials. For solid tailings, the reference materials used were GBW 10, SARM-1, DRN and GSR 6. The porewater and sequential extraction samples were checked using synthetic quality check standards (see Ödman et al., 1999). The instrumental precision determined as $\pm 1 \times$ S.D. for three–four runs on the same sample was generally better than 1% for the major elements and 10% for the trace elements when analysing solid tailings. For the porewater samples, the precision was generally better than 5%. The analytical precision ($1 \sigma, n=4$ for ICP-AES and $n=3$ for ICP-SMS) for the elements analysed in all sequential extraction samples on average was 0.37% in extraction A, 0.72% in extraction B, 0.07% in extraction C, 0.01% in extraction D, 0.15% in extraction E and 3.39% in the residuals. Average procedural blanks for the elements Ca, Fe, Mg, S, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn in extraction A was 4.8%, in extraction B, 46.7%, in C, 5.0%, in D, 17.0%, and in E, 7.7% of the extracted amount from the samples. The elements with a generally high percentage in the total procedural blanks were Ca, Ba, and Ni. The elements Cd, Co, Cr, and Mn had a high percentage in the total procedural blanks for the two oxidised samples, 121 and 122. The high percentage rates depend on low concentrations in the extractions, sometimes with concentration levels below the detection limit. Concentrations below the detection limit have been interpreted in the calculations as half the detection level. In particular, extraction B showed many results below the detection limit.

3.6. Leaching selectivity and efficiency

Since the tailings were sampled below the groundwater table, porewater within the samples has dried, which might affect the results. This may be of concern, particularly with respect to the adsorbed/exchangeable/carbonate fraction (sequential extraction step A), since the dried porewater is likely to be released by the first extraction step. Calculations checking the relevance for this concern based on the porewater analysis and the water ratios measured for the tailings were performed (Table 2). Based on the water ratio, the porewater available to dry for 1 g of solid tailings has been calculated. The contribution calculated for the porewater is controlled against the amount extracted in sequential extraction step A. Results are presented in Table 2. The results show that, in extraction step A, the average contribution of the various elements from dried porewater to the extraction step A is 5.7%. The contribution for each element is <10%, except for two samples for Ca (samples 122 and 156) and Fe (samples 156 and 164), and one sample each for Pb (122) and Sr (126) (Table 2). Sample 164 was compared to porewater extracted from sample
Table 2
Calculated contributions from dried pore water in extraction step A

| Contribution of total from pore water (wt.%) | 4:122 A | 4:126 A | 4:156 A | 4:164 A
<table>
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<tr>
<td>Mg</td>
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<td>1.89</td>
<td>5.82</td>
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</tr>
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<td>0.23</td>
<td>0.32</td>
<td>6.2</td>
<td>3.63</td>
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<tr>
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<td>0.06</td>
<td>0.149</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>0.07</td>
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<td>0.000</td>
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<tr>
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<tr>
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*Sample 4:164 is compared with pore water from sample 4:163.*

and might partially explain the extremely high contribution from porewater, according to the calculations almost twice the extracted amount. On the other hand, Al, Cd, Co, Cr, Cu, Ni and Zn have a calculated porewater contribution to this extraction step of <1% (Table 2). Transfer of leached elements from one extraction to another does not seem to be of concern, since the variation in concentration between the different steps for the elements is relatively large. Another important question is whether the extraction steps in this method extract the expected fractions for the sulfide-rich tailings. The sequential extraction procedure employed was optimised for extractant selectivity and efficiency for secondary Fe-oxyhydroxides. This is important, since it is presumed that adsorption of trace elements onto this fraction plays an important role in retaining mobilised elements in the impoundment. One way to control the accuracy of the method for at least one of the steps is to calculate the correlation between Fe and S in extraction step E, which is considered to dissolve sulfides. The mineralogical results show that the most common sulfide in the tailings is pyrite (Holmström et al., 2001), FeS2. Recalculating the extracted amount of Fe and S to mmol, a correlation was derived (Fig. 5) that is extremely high (>0.99), and the linear fit gives the resulting formula FeS1.89. This is very close to the ideal formula for pyrite, and strengthens the assumption that sulfides (mainly pyrite) are extracted in this particular step. The sequential extraction methodology was successfully used earlier by Land et al. (1999) on extracting elements retained by secondary Fe-oxyhydroxides in till. Presumably, there should be no different behaviour in extractant selectivity when applying the methodology to other materials, such as tailings.

4. Results

The differences between the element concentrations analysed in the solid samples and the sum of the sequential extractions are, for 26 out of 95 analyses, within 25% of the total concentration analysed of the solid extraction in samples 121–156 (for which total analysis was performed) (Table 3), although the sieving procedure was applied. The total amount extracted (including the residuals) of elements mainly present in silicates...
Table 3
Comparison with solid tailings analyses

<table>
<thead>
<tr>
<th></th>
<th>4:121 vs.</th>
<th>4:122 vs.</th>
<th>4:123 vs.</th>
<th>4:126 vs.</th>
<th>4:156 vs.</th>
<th>4:157 vs.</th>
<th>4:157 vs.</th>
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<td>101.4</td>
<td>139.6</td>
<td>160</td>
<td>600.5</td>
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</table>

Calculated as: \((\text{total extracted/solid tailings content}) \times 100\), which gives an equal amount if the result is 100. Values above 100 indicate higher concentrations in the extraction samples and below 100 indicate depletion in the extraction samples compared to total tailings concentration.

(Al, Ca, Mg, Mn, Si, Ba and Cr) generally sums up to less than the solid total concentration. The elements that are present in sulfide minerals (Fe, As, Cd, Co, Cu, Hg, Mo, Ni, S and Zn) are enriched compared to the solid total concentration results. This is explained by the fact that the material analysed for the solid total concentration and the material used in the extractions are not exactly the same, although they are from the same sample. The particle size \(<63 \text{ \(\mu\)m} \) was selected in the sequential extraction samples, whereas bulk samples were used for the analysis of total content. The preferential particle size for the sulfides is thus smaller, as previously noted, compared to the silicates. The comparisons of the total amount extracted and composition of the tailings were performed between samples from the same depth. Exceptions are samples 157 and 164, which were compared with the closest sample analysed above and below. These two samples were not included in the comparison above, but the general conclusion with respect to decreased concentration of silicate elements and increased concentration of elements present in the sulfides also seems to be valid for these two samples. Total concentrations were not analysed in these two samples. The reason for this was a lack of material from some of the depths where samples for thin section, solid extraction analysis and porewater were taken. The closest sample with sufficient material was, therefore, chosen for the sequential extractions.

4.1. Oxidised zone

In the oxidised zone, most elements are strongly depleted. This is especially true for elements associated to different kinds of sulfides (Table 1, Figs. 6–8).

4.1.1. Major elements

For Ca, Al, Mg, Mn and Si in the oxidised zone, the major source is the residual; between 87.5 \% and 98.7 \% is from that fraction. Nevertheless, for Ca, 11.9 \% was extracted in the adsorbed/exchangeable/carbonate step. The residual mainly consists of silicates. The main contrib-
Fig. 6. Major elements fraction association expressed as mg/g or µg/g.
Fig. 7. Minor elements fraction association expressed as $\mu$g/g.
Fig. 8. Solid tailings and accumulated sequential extractions for drill profile 4.

The major contributors of Fe in the oxidised zone are the sulfide fraction (59.1 wt.%) and S (80.7 wt.%) in the oxidised zone. Although the sulfide content in the two oxidised samples is depleted, the sulfide content in samples 121 and 122 is 4.4 and 13 wt.%, respectively. For the uppermost oxidised sample, the content of Fe in the residual is the same as for the content in the sulfide extraction step, at 44 wt.%. The second largest contributor of Fe is the residual, with 28.6 wt.%, and third most important is adsorbed/exchangeable/carbonate extraction, at 8.6 wt.%. For S, the other major contributor to the total content is the adsorbed/exchangeable/carbonate fraction at 18.3 wt.%. 

4.1.2. Trace elements

In the oxidised zone, the amounts of elements present in sulfide minerals are severely depleted.
(Table 1, Figs. 6–8) compared with the deeper, unoxidised tailings. For Cd, Co, Cu, Zn and Ni (sample 122), the major extraction in this zone is still the sulfide fraction. The wt.% derived from this fraction varies between slightly more than 20 (Ni, sample 121) and 92 wt.% (Cd, sample 121). The part not accounted for by sulfides is generally derived from the adsorbed/exchangeable/carbonate fraction (Cd, Co, Cu, Zn and to some extent Ni). The part present in this fraction varies between 3.1 (Cu, sample 121) and 43.6 wt.% (Zn, sample 122). Amorphous iron oxyhydroxides seem to be important retainers for Ni in both samples from the oxidised zone (23.9 and 12.7 wt.%, respectively), as well as for Cu in the deeper sample from this zone (sample 122), in which 12.4 wt.% is retained. Crystalline iron oxides are also an important retainer for Ni in this sample (11.3 wt.%). Pb is retained with amorphous iron oxyhydroxides in both samples from the oxidised zone (48.1 and 18.7 wt.%), as well as with crystalline iron oxides (34.8 and 55.1 wt.%), and only a minor amount associated to the sulfide extraction step is still present (11.6 and 10.7 wt.%). Mo is mainly present in the residual (61.5 and 65.1 wt.%), with the remaining amount extracted almost solely in the sulfide extraction (35.3 and 31.0 wt.%). Cr is almost only present in the residual (94.0 and 94.5 wt.%). The same is true for Ba (89.3 and 75.5 wt.%), except for a minor part present in the amorphous iron oxyhydroxide fraction (6.9 and 16.9 wt.%). For both samples, crystalline iron oxides are also of minor importance (3.1 and 6.4 wt.%). Arsenic, as a general rule, is mainly found in the crystalline iron oxide fraction (67.1 and 33.0 wt.%), except for the deeper oxidised sample, where the sulfide fraction is slightly higher (35.5 wt.%). For the uppermost sample, only 11.9 wt.% was extracted in the sulfide fraction. The adsorbed/exchangeable/carbonate fraction represented 10.3 and 10.0 wt.%, respectively, in both samples, and amorphous iron oxyhydroxides also contained a larger amount of As (7.9 and 16.5 wt.%). Sr was also present to the greatest degree in the residual in both samples (87.6 and 84.6 wt.%) and the second most important fraction was the crystalline iron oxides (5.6 and 5.4 wt.%).

4.2. Unoxidised zone

In the uppermost part of the unoxidised zone, several elements exhibit secondary enrichment zones (Holmström et al., 2001). Elements such as Cd, Cu and Zn exhibit a well-defined enrichment zone (Fig. 7).

4.2.1. Major elements

Ca, Al, Mg, Mn and Si are for the most part, as was the case in the oxidised zone, present in the residual fraction. An average between 67.2 (Mn) and 96.5 wt.% (Si) occurs in the residual fraction. Ca is also represented in the adsorbed/exchangeable/carbonate fraction (~8.3 wt.%), as well as in the amorphous iron oxyhydroxide fraction (~10.0 wt.%). Al on average has 5.8 wt.% from the amorphous iron oxyhydroxide fraction and 5.4 from the sulfide fraction. The second largest average extraction for Mg is the sulfide fraction step, at 4.2 wt.%. All other fractions for Mg represent < 2 wt.%. Mn has 10.9 wt.%, on average, extracted in the adsorbed/exchangeable/carbonate fraction and 13.8 wt.% from the sulfide fraction. For Si the average of all fractions, except for the residual and the amorphous iron oxyhydroxide fraction that account for 1.2 wt.%, represent less than 1 wt.%. Fe extracted as, on average, 80.4 wt.% in the sulfide fraction and 9.9 wt.% from the residual. On average, 4.9 wt.% was extracted for Fe in the amorphous iron oxyhydroxide extraction; 2.1 wt.% was extracted in the adsorbed/exchangeable/carbonate fraction, as well as in the crystalline iron oxide fraction. S is mainly extracted from the adsorbed/exchangeable/carbonate fraction (average 8.1 wt.%) and the sulfide fraction (average 90.6 wt.%).

4.2.2. Trace elements

The sample situated closest to the oxidation front exhibited increased concentrations of the trace elements Cd, Cu (and to a smaller extent in the second sequential extraction sample below the oxidation front) and Zn. Between 68.8 and 76.4 wt.% was released in the sulfide extraction step for these elements. For Cd and Zn, 19.0 and 18.6 wt.%, respectively, is from the adsorbed/exchangeable/carbonate fraction, whereas for Cu only 5.0
wt.% was released with that fraction. On the other hand, 8.0 wt.% Cu was extracted with the amorphous iron oxyhydroxide fraction. The remaining part of these three elements mainly belongs to the residual, ranging from 4.1 to 14.8 wt.%. Elements exhibiting possible enrichment in both the uppermost and the second uppermost unoxidised sample are As and Ni, as well as the earlier mentioned Cu. Ni is extracted from the same fractions in these samples as the previously described enriched trace elements. Most important are the adsorbed/exchangeable/carbonate (average 44.1 wt.%) and the sulfide fractions (average 37.2 wt.%). Arsenic was extracted from amorphous iron oxyhydroxides (~22.15 wt.%) and sulfides (~35.15 wt.%) in both samples, but in the uppermost unoxidised sample the residual contained a large amount of As (35.7 wt.%). In the deeper enriched sample the crystalline iron oxyhydroxides accounted for 23.4 wt.% and the soluble organic fraction 14.5 wt.%. Below the enrichment zone (samples 156, 157 and 164) Cd, Ni, Pb and Zn are to an extent associated with the adsorbed/exchangeable/carbonate fraction. On average 36.6, 43.0, 19.0 and 29.4 wt.%, respectively, of these elements was released in this extraction step. Especially for Pb the variation is large, ranging from 0.2 to 36.5 wt.%. The other important fraction is the sulfide extraction step (except for Pb), representing 49.3, 37.63, 7.57 and 59.1 wt.%, respectively, on average. For Pb the important contributors are amorphous iron oxyhydroxides (~59.5 wt.%) and the crystalline iron oxyhydroxides (~12.9 wt.%). For Cu the adsorbed/exchangeable/carbonate fraction represents, on average, 17.6 wt.% and the amorphous iron oxyhydroxides, 12.5 wt.%. These two fractions are the most important if the sulfide fraction is not considered. The Cu extracted from the sulfide fraction, on average, in the unoxidised zone represents 55.8 wt.% of the total Cu content.

5. Discussion

During the 40 years of oxidation taking place in the upper, unsaturated part of the impoundment, the oxidation products were transported downwards dissolved in porewater originating from percolating rain. The pH in the oxidised zone was low and only a minor fraction of the oxidation products were retained. Adsorption onto primary minerals and the formation of secondary minerals, such as covellite and iron hydroxides, and co-precipitation with these below the oxidation front have been shown to be important scavenger mechanisms retaining the oxidation products before the percolating water reached the groundwater table (Holmström et al. 2001). After remediation, the raised groundwater table released some of the retained secondary products. This is shown in the porewater profiles for drill profile 4 (Fig. 9) for the elements As, Cd, Cu and Zn. In the oxidised zone, elements associated with sulfides are evidently depleted (e.g. As, Cd, Co, Cu, Ni and Zn); nevertheless, the elements Cd, Co, Cu and Zn (and S) are still mainly associated with the sulfide fraction in the sequential extraction. This is mainly due to the low-pH environment prior to remediation, which prevents the oxidation products from being retained in the oxidation zone. Below the oxidation zone the pH increased and the elements were retained, thus forming a secondary enrichment zone, especially evident for Cu in the solid tailings analyses. In the oxidised zone the retained amounts (fraction A–D) are smaller compared to the amount in the unoxidised tailings. In general, element association with the adsorbed/exchangeable/carbonate fraction is weakened by transition from the oxidised to the unoxidised tailings. Elements such as Ca, Fe, Al, As, Cr, Cu and Mn exhibit increased amounts in the amorphous iron oxyhydroxide and/or crystalline iron oxide fractions in the unoxidised tailings, and decreased concentrations in the adsorbed/exchangeable/carbonate fraction. Pb shows the opposite behaviour, and in general only a minor amount of total Pb is present in the sulfide extraction step, which most likely shows that only a small fraction of the Pb originates in sulfides. It is also possible to conclude that the total amount of the elements retained in extraction steps A–D differ between the oxidised and unoxidised tailings. Generally, there is a larger accumulation of the elements in extraction steps A–D in the unoxidised tailings. Exceptions are Mg, S, Hg, Mo and Pb, for which the oxidised tailings retained a larger amount, although the difference is minor for most elements. Elements
with a larger amount retained in fractions A–D in the unoxidised tailings are Ca, Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Sr and Zn. This indicates transport of mobilised elements from the oxidised, uppermost part of the impoundment. These elements are thus not retained in the upper part but, subsequent to oxidation, are transported downwards with percolating water into the unoxidised tailings, where they are partly retained in various ways, such as by adsorption on mineral surfaces and/or by the formation of secondary minerals.

As can be observed from the analyses of total content in the solid samples, the peak in concentration for Cu has been interpreted as a result of secondary enrichment (sample 123 at a depth of 155 cm, Fig. 7) immediately below the oxidation front (Holmström et al., 2001). According to the extractions, the major part of Cu is from the sulfide fraction, accounting for almost 69 wt.%. Of the extractions consisting of secondary phases, adsorbed/exchangeable/carbonate accounts for 5 wt.% and the amorphous iron oxyhydroxide frac-
tion for 8 wt.%. Studies of thin sections reveal that, at a depth of 200–240 cm in drill profile 4, secondarily formed covellite is present (Holmström et al. 2001). No thin sections were available from a depth of 155 cm. From drill profile 5 in the impoundment, thin sections level with sample 123, at a depth of 160–170 cm, show the formation of covellite, as well as at 190–200 cm. The solid tailings concentration of Cu in profile 5 between depths of 145 and 230 cm varies between 2230 and 4450 ppm. The average concentration of Cu in the unoxidised tailings is 960 ppm (Table 1). Thus, the secondary enrichment zone for Cu might have been formed by the formation of covellite, CuS (cf. Boorman and Watson, 1976; Blowes and Jambor, 1990; Lin and Qvarfort, 1996; McGregor et al., 1998; Holmström et al., 2001), due to transformation of pyrrhotite, chalcopyrite, galena, and pyrite. The other fractions thought to be important scavengers, such as the adsorbed/exchangeable/carbonate fraction and the amorphous and crystalline iron oxyhydroxide fractions, are thus of minor importance for retaining Cu, although values of 16.3 wt.% (1332 μg) in sample 123 and 66.8 wt.% in sample 126 (1465.7 ppm) were found for fractions A–D. This concentration of secondary retained Cu is at the level of or higher than the total concentration for some of the deeper samples. It is possible that even larger amounts of Cu prior to remediation had been retained with the adsorbed/exchangeable/carbonate fraction, as well as with the amorphous and crystalline iron oxyhydroxide fractions. After raising the groundwater table, these fractions dissolve, resulting in the peak for dissolved Cu in the porewater at this level. According to Fig. 6, presenting the total extracted amounts, Cd, Zn and possibly As also exhibit peaks for sample 123 in the sequential extraction. Cd and Zn show generally good correlation with the total content analysed, but at the level of the peak, as was the case for Cu, a substantially larger amount has been extracted compared to the total content. The reason for the increased concentration at this level, which is not present at greater depth, is probably that the particle size was chosen for the sequential extractions. Dissolved elements are more likely to adsorb onto finer particles. As can be observed from the pattern of fraction abundance, both Cd and Zn exhibit the same behaviour. Some 19 wt.% was extracted from the adsorbed/exchangeable/carbonate fraction, slightly more than 76 wt.% from the sulfide fraction and approximately 4 wt.% from the residual. The adsorbed/exchangeable/carbonate fraction for Cd (61.8 ppm) at this level represents more than the total extracted amount in the deeper, unoxidised samples. As for Cd, the adsorbed/exchangeable/carbonate extraction step for Zn (21 690 ppm) is greater than the total amount extracted from the deeper, unoxidised samples. For As, sample 123 has 31.1 wt.% (212.5 ppm) of total As content in extraction steps A–D. In sample 126, this has increased to 61.8 wt.% (380.1 ppm). This shows how important this fraction could be for retaining certain elements within the impoundment. Unfortunately, this fraction is easily dissolved and might thus, during changed environmental conditions, such as lowered pH and/or redox potential, release large amounts to the surroundings, as was shown by the porewater profiles. This increase in extraction steps A–D for the samples below the oxidation front corresponds to the peaks in porewater concentrations, and thus the elements retained below the oxidation front are presumed to have become mobile after the rise in the groundwater table.

6. Conclusions

Several elements, such as As and Cu, have been secondarily enriched just below the former oxidation front. After remediation of the impoundment, the raised groundwater table has partly dissolved this enrichment, resulting in increased porewater concentrations at this level. The most important secondary phase for Pb in the impoundment is amorphous iron oxyhydroxides and, to a smaller extent, the crystalline iron oxides. This is the case also for Ba and Cr. The elements Ni, Cd, Co, Mn, S and Zn are almost entirely retained within the adsorbed/exchangeable/carbonate fraction. Arsenic is retained in the crystalline iron oxides fraction and, to lesser extent, in the amorphous iron oxyhydroxide fraction. Fe is mixed between adsorbed/exchangeable/carbonate and the amorphous iron oxyhydroxide fractions (although the amounts are
small as a percentage). In addition, Ca, Cu and partly Ni exhibit this fraction-association behaviour. Sr has a larger affinity for the amorphous iron oxyhydroxide fraction. In the impoundment, the adsorbed/exchangeable/carbonate fraction generally exhibits the highest percentage for retention of mobilised elements, followed by amorphous iron oxyhydroxides and the crystalline iron oxides.

In the oxidised tailings the sulfide fraction still dominates for several elements, such as Fe, S, Cd, Co, Cu, Hg and Zn. Averages for these elements in the oxidised zone range from 55.7% (Hg) up to 82.2 wt.% (Co), although the concentrations are severely depleted compared to the unoxidised tailings. Below the oxidation front the amount of sulfides in the tailings sharply increases, generally resulting in an even more pronounced association with the sulfide fraction for most of these elements. The part extracted from the sulfide fraction for these elements in the unoxidised tailings is between 55.8% (Cu) and 93.1 wt.% (S). Cu is also enriched in the sulfide fraction for sample 123, together with (As), Cd, (Ni), (S), (Fe) and Zn. The accumulated amounts from the sequential extractions exhibit minor peaks for the elements As, Ni, Fe and S, whereas the solid tailings analyses do not. Evaluating the fraction abundance, it is possible to conclude that the sum of the secondary fractions A–D is equal in size to that of the sulfide extraction step for As and Ni. The elements Cd, Fe and Zn are largely associated with the sulfide extraction step (76–79 wt.%), but the amount associated with the adsorbed/exchangeable/carbonate fraction might be up to 19 wt.% (Cd and Zn). Thus, this still represents a considerable part of the total amount extracted at this level. Cu is also mainly associated with the sulfide extraction step (69 wt.%), but 16.4 wt.% is associated with extraction steps A–D. This represents more than the total content (as µg) in some of the deeper, unoxidised tailings. The peak evident at this level probably corresponds to the formation of covellite, as has been verified from thin sections around this level in the impoundment, but a large part is also retained at this level as secondary precipitation products retained in extraction steps A–D. This increase in extraction steps A–D for the samples below the oxidation front corresponds to the peaks in porewater concentrations, and thus the elements retained below the oxidation front are presumed to have become mobile after the rise in the groundwater table.

Acknowledgments

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Geochemistry of the infiltrating water in the vadose zone of a remediated tailings impoundment, Kristineberg mine, northern Sweden.

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Geochemistry of the infiltrating water in the vadose zone of a remediated tailings impoundment, Kristineberg mine, northern Sweden.

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Abstract

At the remediated tailings Impoundment 1 at Kristineberg, Northern Sweden, installations of tension lysimeters were performed in the protective cover (10, 50, and 100 cm), in the oxidised tailings (150 cm), in the unoxidised secondarily enriched tailings (200 cm) and in the unoxidised tailings (260 cm). The lysimeters in the till protective cover contained relatively low concentrations of most elements. After infiltration through the sealing layer, consisting of 0.3 m compacted clayey till, pH decreased and conductivity, together with the concentrations of several major and trace elements, increased significantly. In the lysimeters installed in the tailings at depths of 150 and 200 cm average pH decreased to 3.4 at 150 cm and 3.2 at 200 and average conductivity increased to 2.9 mS/cm. Elements such as Al, Cd, Co, Fe, Mn, Mo, Ni, Pb, S, Si and Zn had the highest concentrations in the lysimeter at 200 cm depth. Examples of concentration averages for this lysimeter are Cd 600 µg/L, Fe 1500 mg/L, Mn 11 mg/L, Ni 1.06 µg/L, S 1800 mg/L, and Zn 190 mg/L. Between the depths of 200 and 260 cm the concentration of most elements decreased. The increase between the lysimeters at the depths of 150 and 200 cm can be explained by remobilization of secondarily retained oxidation products as well as from the continued oxidation. The decrease between the second and the third lysimeters is interpreted as co-precipitation with different Fe oxyhydroxides as well as adsorption onto secondarily formed minerals and primary mineral surfaces. Calculations of saturation indices indicate that several different hydroxides might precipitate at this level. This retention takes place mainly due to the increase in pH. The pH increases from 3.2 up to 4–4.4 in this depth interval. Between the deepest lysimeter and the groundwater table, the element concentrations probably decrease even further. pH increases to 5–6.5 in the groundwater. Most of the pre-remediation oxidation products that are secondarily retained above or below the oxidation front and are released by the small amount of infiltrating water together with the present oxidation products are retained again during continued transport downwards. If the depth to the groundwater table is large enough, most of the metals released by the infiltrating water and the diffusing O₂ do not reach the groundwater.

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1. Introduction

Acid mine drainage from sulphide-rich mine tailings is recognised as an important pollutant. Complex relationships between biological, chemical and hydrological factors control the dispersion of contaminants from untreated as well as remediated waste deposits. To understand the main processes is of fundamental importance for efficient remediation of tailings and for avoiding future problems. Both unremediated tailings and tailings remediated by different methods have been studied and characterised over the past 30a (e.g. Boorman and

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Watson, 1976; Blowes and Jambor 1990; Fraser and Robertson, 1994; Pedersen et al., 1994, 1997; Holmström, 2000).

The sulphide-rich tailings in the so-called Impoundment 1 at Kristineberg in northern Sweden were left without any cover for almost 50 a. The impoundment was remediated in 1996 by a combination of covering the tailings with a protection layer of till, and by raising the groundwater table so that the tailings and the overlying till over a part of Impoundment 1 were saturated (Lindvall et al., 1999). In areas with a deeper groundwater table a more advanced till cover was used. This method consists of a sealing layer of compacted clayey till with a thickness of 0.3 m and above that a 1.5 m thick protective cover of unspecified till. In these areas, the groundwater table is located at about a depth of 2 m in the tailings, thus about 4 m below the till surface. This is the area in which this investigation has taken place. The mineralogy and the chemistry of the solid tailings fraction as well as the composition of the pore water have been characterised by Holmström et al. (2001), who found that raising the groundwater table resulted in release of metals secondarily retained below the oxidation front prior to the remediation. Sequential extractions on the tailings from different depths were performed by Carlsson et al. (2002). It was found that below the oxidation front, a large proportion of the total concentration of several metals was present in the adsorbed/exchangeable/carbonate fraction. The aim of this investigation is to characterise the geochemistry of the water infiltrating into the tailings of Impoundment 1, where the more advanced remediation technique was used, and to study the efficiency of applying till cover on oxidised tailings. It was also of interest to study if the secondarily retained elements were remobilized by the infiltrating water. The sampling was performed with 3 lysimeters (Prenart Equipment ApS, Denmark) installed in the vadose zone of the tailings, above the present groundwater table, but beneath the sealing layer and the protective cover, and with 3 additional lysimeters installed in the protective layer. The tailings groundwater has also been sampled at the location of the lysimeter installation with a BAT* groundwater pipe (Torstensson and Petsonk, 1988).

2. Area description

The Kristineberg mining area is located in the western part of the Skellefte ore district, approximately 175 km SW of Luleå (Fig. 1). The approximately 1.9 Ga old ore-bearing volcanic rocks are overlain by sedimentary rocks. The metamorphosed volcanic and sedimentary rocks display a marked foliation and extensive sericitization (Vivallo and Willdén, 1988). Pyrite-rich sulphide ores are intercalated within a stratigraphic unit mainly consisting of basic volcanics and redeposited volcano-clastic rocks (Willdén, 1986). For further description of the area and its geology and ores, see Du Rietz (1951), Gavelin (1943), Gavelin and Kulling (1955) and Grip (1973).

The largest orebody in the area is the Kristineberg Zn–Cu deposit, which was discovered in 1918. It was not until 1940 that Boliden Mineral AB started mining activities and mining is still in progress. Other mines close to the Kristineberg mine are the Kimheden, Horntråsk, Räviden and Rävidmyr mines, all of which are closed and remediated. The annual precipitation in the area varies between 400 and 800 mm/a (Axelsson et al., 1991) and the annual mean temperature is 0.7 °C (Axelsson et al., 1986). The vegetation consists mainly of coniferous forest, but some deciduous forest is also present in the area. Boglands are common. The major soil type in the area is podzol weathered till (Granlund and Wennnerholm, 1935; Granlund, 1943). Five tailings impoundments are located within the Kristineberg mining area. As many as 10 different ores from the western part of the Skellefte field mining district were processed in the processing plant, and thus the impoundments contain a mix of several different kinds of tailings. In this study Impoundment 1 was investigated (Fig. 1). It is the oldest within the mining area. It has a surface area of about 0.10 km² and until the early 1950s, it was used for tailings disposal (Boliden Mineral AB, 1995). The tailings discharge was located along the southern hillslope. In the years 1976 and 1978 attempts were made to sow grass seed. In 1996 the impoundment was remediated by till covering, raising the groundwater table and seeding with grass (Lindvall et al., 1999). After the remediation, the groundwater table is shallow in some parts of the impoundment. In these parts, it reaches the till surface. The intention was to use 1 m of unspecified till as a protective layer in areas with a shallow groundwater table. In other areas 1.5 m of till was applied above a 0.3 m sealing layer. The sealing layer consists of a compacted clayey till. Prior to the application of the till cover 10 kg/m² of lime was added onto of the tailings. A few years after remediation the impoundment is now almost completely covered by grass. The impoundment is located in a valley and underlain by peat and till. The thickness of the tailings ranges from a few metres up to approximately 11 m. The average thickness is between 6 and 8 m. The oxidation zone reaches about 50 cm depth in the tailings at the sampled location. After the application of till cover the upper part of the oxidised zone is approximately 150 cm below the surface.

3. Materials and methods

3.1. Sampling

Soil and tailings water were collected with cylindrical tension lysimeters (length = 95 mm, outer diameter = 21
mm) made of PTFE (Polytetrafluoroethylene) mixed with glass and with a pore size of 2 μm (Prenart equipment ApS, Fredriksberg, Denmark). Before installation the PTFE cups and tubing were flushed with 1 L of 1.0 M HCl and then rinsed with 4 L of deionized water. The PTFE cups were installed horizontally or at a low angle at 6 depths from a trench in November 1998. The distance from the trench to the lysimeters was about 1 m, horizontal distance, and a rod was used to make the hole prior to the installation. In the protective layer, the installation depths were 10, 50 and 100 cm. In the tailings, one lysimeter was installed close to the sealing layer, at a depth of 150 cm below the protective till surface. Another lysimeter was installed at 200 cm whilst the deepest lysimeter was installed at 260 cm depth. A slurry of silica flour and deionized water was used to ensure good capillary contact between the cups and the tailings. The lysimeters were installed at the upstream side of the trench. Following the installation the trench was refilled by the original material and the sealing layer was restored by using bentonite. When applying the till cover a small amount of tailings was accidentally mixed into it, some minor amounts were also left on top of the protective till. The lysimeters were connected to a tension-controlled vacuum pump in such a way that the difference between the vacuum and the soil tension was held constant (−100 kPa). For two days following installation in October 1998, the tailings water was purged and discarded. Sampling was initiated in May 1999, after the thawing period. Sampling then roughly continued on a monthly basis until late October 1999. Samples were filtered using 0.22 μm Millipore filters. On some occasions, unfiltered samples were also analysed. There was no significant deviation between filtered and unfiltered element concentrations.

Redox and pH were measured with a Metrohm® Pt-electrode and a Metrohm® combined pH-electrode. The pH-electrode was calibrated using two Titrisol® pH 4 and 7 buffers. The redox electrode was checked using two Ag/AgCl Reagecon® standards (124 mV and 358 mV). All redox values were adjusted to the standard H-electrode.
3.2. Description of the tailings and the installation

In the area of the installation, the oxidation zone extends 0.3–0.5 m in the tailings, based on visual inspection during excavations. Generally the colour in the oxidised zone is red-yellow and at some levels a slightly greenish tone is discernible. Reddish coloured tailings were also interlayered in what seemed to be unoxidised tailings in the lower part of the oxidised zone. During tailings disposal the spigotting location for the tailings was positioned in the opposite (north-western) end of the impoundment. It is probable that the installation area was at times dry during the tailings discharge, which could have resulted in oxidation of the tailings during the use of the impoundment. The oxidised tailings was from time to time covered with fresh tailings resulting in the layered structure. Average chemical compositions of the unoxidised tailings based on 73 samples and of the oxidised based on 12 samples are presented in Table 1. The area of the installation has been remediated with a qualified 0.3 m thick sealing layer of compacted clayey till. Above this layer a 1.5 m thick protective layer of unspecified till has been applied. The installation area is situated close to a slope and the protective till cover is approximately 1.2 m thick. A tentative outline of the installation is presented in Fig. 2. The level of the groundwater table is monitored with a 5-cm polyethylene well and the chemical composition of the groundwater is sampled with a BAT* ground-water pipe installed at a depth of 6 m. The groundwater level is relatively stable at 4–5 m below the protective till surface, thus approximately 1.5–2.5 m below the deepest lysimeter (Fig. 2).

3.3. Mineralogy

In the unoxidised tailings, the sulphide mineral content ranges from 10 to more than 30%. The most common sulphide minerals are, in decreasing order, pyrite, chalcopyrite, sphalerite, chalcopryite, galena, and covellite. Pyrite is by far the most common sulphide mineral. Some of the Fe-hydroxides identified in the tailings were formed by evaporation of pore water after sampling, so-called tertiary minerals (Jambor, 1994). Gypsum occurs as massive euhedral grains, some of which also appear to be of tertiary origin.

In the oxidised tailings, the sulphide content is generally around 1–2%. The most common sulphide minerals are, in decreasing order, pyrite, chalcopryite, pyrrhotite, sphalerite, and galena.

The most common gangue minerals in both types of tailings are quartz, K-feldspar, Mg-chlorite, talc, plagioclase, muscovite, amphiboles/pyroxenes and biotite. Illmenite, magnetite, hematite, titanite, epidote, sericite, zirkon, apatite, and calcite also occur, but in minor amounts.

3.4. Standards and analytical methodology

All water samples were acidified using 1% suprapure HNO3 and analysed for Ca, Fe, K, Mg, Na, Si, and S with ICP-AES. High resolution ICP-MS was used for the analysis of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sr, and Zn. Mercury was analysed with atomic fluorescence. The lysimeter water was checked using synthetic quality check standards (Ödman et al., 1999). The instrument precision was determined by 3 to 4 runs on the sample material, as ±1 S.D. deviation. Generally, the deviation was better than 1.2% for major elements and 1.9% for trace elements.
4. Results

The lysimeters were sampled on 9 occasions from May to October. It was not possible to extract water from every lysimeter on every occasion due to the limited amount of water available. The lysimeter installed at 10 cm was sampled 8 times, the one at 50 cm was sampled 6 times and the deepest till lysimeter 7 times. In the tailings the lysimeter at 150 cm was sampled on all 9 occasions and the intermediate at 200 cm was sampled 4 times. The deepest lysimeter at 260 cm was sampled 7 times.

Measurements of pH and conductivity were made if enough water remained to do so after the amount needed for the element analyses had been withdrawn. The pH in the soil cover varies during the sampling season between 4 and 5.5 (Table 2). For the 3 different installation depths pH was 4.5–5 in the 10 cm lysimeter; it increases to about 5.5 at the depth of 50 cm, and at 100 cm it decreased to about 4–4.5. After percolating through the sealing layer pH decreases at 150 cm, in the uppermost part of the oxidised zone, down to 3.2–3.6 (Fig. 3; Table 2). The only sample from a depth of 200 cm with enough water for measuring pH, exhibits a similar pH of about 3.2. In the deepest lysimeter at a depth of 260 cm, pH increases to 4–4.4. In the groundwater, pH varies between 5 and 6.4. For the till cover the conductivity level is about 0.15–0.2 mS/cm at the depth of 10 cm. At 50 cm it increases to 0.2–0.4 mS/cm and at the deepest (100 cm) level the conductivity is 0.2–1.0 mS/cm. The relatively high conductivity of the till material is largely explained by the reconstruction of the protective cover after installation, when some tailings accidentally were mixed with the protective till cover. Also on top of the till cover some residual tailings was left. The conductivity in the tailings water is high in both lysimeters, where it was possible to perform measurements (Fig. 3, Table 2). The limited amount of water extracted at 200 cm was not sufficient to enable conductivity readings. At the depth of 150 cm it varies between 2.6 and 3.5 mS/cm. At 260 cm it is between 2.1 and 2.75 mS/cm. The conductivity of the groundwater is comparable with the lysimeters installed in the tailings at 2.3–3.05 mS/cm.

4.1. Major elements

In the till cover the concentration of dissolved Ca increases with depth. Average concentration (Table 2) increases about 5 times up to 39.5 mg/L; that is still a magnitude lower than the concentration in the uppermost tailings lysimeter. For K, average concentrations in the till increase slightly with depth from 5.7 mg/L up to 12.5 mg/L. This is about the same level as in the tailings. Sodium is fairly constant with depth in the till cover, and varies between 3.4 and 5.5 mg/L. Iron is at a concentration of 2 mg/L in the deepest till lysimeter: this concentration is less than 2% of the lowest Fe concentration in the tailings that is found in the uppermost tailings lysimeter. Average S concentration increases from 6.7 mg/L in the uppermost tailings lysimeter to 65.8 mg/L in the deepest lysimeter. Still, this concentration is much lower than the concentration in the uppermost tailings lysimeter. Si in the till increases from an average of 1.2 mg/L in the uppermost till lysimeter to 15.9 mg/L in the deepest. Compared to the results for the tailings, the Si concentration is 2–3 times
Table 2

Average concentrations for tension lysimeter samples from the protective till cover, tailings and groundwater

<table>
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<th>Conductivity</th>
<th>Ca</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
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<th>Co</th>
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<th>Cu</th>
<th>Hg</th>
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<th>Mo</th>
<th>Ni</th>
<th>Pb</th>
<th>Sr</th>
<th>Zn</th>
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<td>4.71</td>
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<td>1.06</td>
<td>5.73</td>
<td>2.63</td>
<td>4.64</td>
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<td>1.24</td>
<td>490.0</td>
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<td>±S.D.</td>
<td>4.60–4.92</td>
<td></td>
<td>1.36</td>
<td>1.84</td>
<td>0.87</td>
<td>0.56</td>
<td>1.26</td>
<td>0.96</td>
<td>0.41</td>
<td>90.83</td>
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<td>0.07</td>
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<td>2.12</td>
<td>3.99</td>
<td>1.03</td>
<td>14.86</td>
<td>1.74</td>
<td>836.1</td>
<td>–</td>
<td>1.28</td>
<td>35.78</td>
<td></td>
<td>291.00</td>
<td>75.03</td>
<td>–</td>
<td>374.29</td>
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<td>205.80</td>
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<td>836.1</td>
<td>–</td>
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<td>35.78</td>
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<td>291.00</td>
<td>75.03</td>
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<td>46.71</td>
<td>205.80</td>
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<td>±S.D.</td>
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<td>3.99</td>
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<td>0.62</td>
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<td>0.57</td>
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<td>0.255</td>
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<td>15.5</td>
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Note that the number of samples used for average and standard deviation calculations vary between 3 and 7.

b Indicates only one sample above detection limit.

c Indicates samples above detection limit. B.d. indicates below detection limit. Average pH was calculated by recalculating pH to H⁺, also for pH no standard deviation was calculated instead the spread of measured pH is included.
Fig. 3. Tension lysimeter and groundwater concentrations; note the log<sub>10</sub> scale for Al, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Zn.
Fig. 3. (continued)
higher in the uppermost two tailings lysimeters but lower in the deepest.

The relatively high concentrations of dissolved S in till lysimeters compared to the present concentrations of S in the till itself could be explained by the fact that tailings were mixed into the till cover during the refilling of the trench after the installation. Still, the concentration obtained is low compared to the concentrations in the tailings. Table 1 shows till composition, in which the concentrations of S and sulphide associated elements are low.

Calcium exhibits the same concentration interval for the uppermost two lysimeters installed in the tailings, about 370 mg/L. In the deepest lysimeter, Fig. 3, the concentration decreased to less than half of the previous level. Potassium and Na have higher concentrations in the lysimeter located at 150 cm than in the two deeper ones at 200 and 260 cm. Iron, S, and Si exhibit a boomerang-shaped curve resulting in increased concentrations for the lysimeter located at 200 cm compared with the one at 150 cm. For the deepest lysimeter, installed at 260 cm, the concentrations have decreased down to the level of or even lower than the one found in the uppermost lysimeter. The groundwater samples have similar concentrations of Fe, K, Na, and S as the deepest lysimeter. The concentration of Ca in the groundwater is
higher than in the deepest lysimeter, but the concentration of Si is lower.

4.2. Trace elements

For the trace elements in the till cover lysimeters, As is below detection in all samples and the elements Al, Cd, Cu, Mn, Mo, Ni, Sr and Zn increase with depth. The relatively high average concentrations obtained for several of these elements, such as Co (110.5 μg/L), Cr (128.8 μg/L), Cu (152.6 μg/L), Mn (1225 μg/L), Ni (349.3 μg/L), Sr (368.1 μg/L), and Zn (1439.3 μg/L), in the deepest till lysimeter depend on the reconstruction of the till cover, as previously explained, when some tailings may have been mixed with the till. Till analyses rule out the explanation that these concentrations could be caused by the till alone (Table 1).

Iron, S, and Si, the trace elements Al, Cd, Co, Hg, Mg, Mn, Mo, Zn and to some extent Ni and Pb exhibit the boomerang-shaped concentration profile with the highest concentrations in the lysimeter at 200 cm. For Mg, Ni and Pb the decrease in the deepest lysimeter is not as evident as for the other elements. Barium exhibits the opposite behaviour, with the lowest concentration in the lysimeter at 200 cm. Concentrations of Cu and Sr decrease with depth in the tailings. Arsenic has only one sample at 150 cm and none at 200 cm above the detection limit. In the deepest lysimeter the concentration is evidently increased, at all instances of sampling the level is above the detection limit. Chromium shows the same behaviour as As, with highest concentrations in the deepest lysimeter and low concentrations in the other two installed in the tailings. Groundwater concentrations of the elements Al, As, Cd, Co, Cr, Hg, Mg, Mn, Ni, Pb, and Zn are lower or even much lower compared to the deepest lysimeter. The concentration of As is below the detection limit. For Ba and Mo the concentrations are more or less at the same level in the deepest lysimeter and in the groundwater. Copper has higher concentrations in the groundwater than in the deepest lysimeter. This is also the case for Sr, although the difference is minor.

4.3. S.I. calculations

Using pore water data, saturation indices (S.I.) of various minerals were calculated using the geochemical equilibrium model PHREEQC (Parkhurst, 1995) with the MINTEQ database (Allison et al., 1991). While thermodynamic calculations cannot confirm whether or not a mineral is actually present, they can indicate, for example, whether the mineral in question would have a tendency to precipitate, or if present, dissolve. In the calculations the total S analyses from the lysimeters have been converted to SO₄. Although this is not entirely correct, it may be a reasonable approximation. Saturation indices for carbonate minerals are not reported, as alkalinity was not determined. The given conditions for the calculations have been of importance for the outcome. The uncertain parameter has been the pe (redox) level for the lysimeters used in the calculations, since Eh measurements were not performed at the moment the underpressure was released in the sample container but a short while after. To enable better calculations a complementing Eh measurement was performed in August 2001. On this occasion the underpressure was released within a glove box filled with Ar while in the field. These Eh readings and element concentrations were thus utilized in the S.I. calculations mentioned herein. However the differences between the readings were less than 20 mV for the two different methods of measurement. In the case of the groundwater the measurements have been performed immediately after release from the sampling tube. A pe level of 3.7 was used to determine the reported saturation indices for the groundwater. The pe in the vadose zone is higher than for the groundwater. At the level of 150 cm it was calculated to be 9.97 and at 260 cm 7.27. At the level of 200 cm there was insufficient water to perform measurements, thus the pe level at 150 cm was used in the calculations. The charge balance calculations from the S.I. calculations show that the deviation is at most ±5%.

The results showed that in the lysimeter at 150 cm secondary minerals such as different nontronites, K-jarosite, goethite, cuprousferrite and lepidocrocite might be oversaturated. At 200 cm the same minerals exhibited oversaturation as well as H-, and Na-Jaroslites. However, if the pe-level of the deepest lysimeter was used at 200 cm the number of secondary minerals decreased, mainly due to the fact that no jarosites exhibited saturation. In the lysimeter at 260 cm, where the pH is higher, the number of minerals indicated to be oversaturated increased. Also the saturation indices increased for most minerals. At this level the minerals indicated to be oversaturated, in addition to the previously mentioned are alunite, pyrophyllite, kaolinite, Al₂(OH)₆SO₄, maghemite, and diaspore. For the groundwater oversaturated compounds were alunite, barite, Fe(OH)₂Cl₀.₃, goethite (FeOOH), gypsum, and lepidocrocite (FeOOH).

5. Discussion

Because the concentrations of different elements vary with lysimeter depth, it is possible to discuss the element content in the tailings vadose zone as a matter of zonation. The lysimeters are installed at depths of 150, 200, and 260 cm, in the uppermost part of the oxidised zone, just below the border of the oxidation front and in the unoxidised tailings, respectively.
The lysimeter at the 200 cm level contributed almost no water at all after 4 sampling occasions. This may have been due to precipitation on the surface or within the lysimeter pores. The concentrations of Fe and S decreased during the sampling period in this lysimeter (Fig. 4). This is also, to some extent, the case for the elements Al, Co, Mg, Mn, Ni and Pb. This could reflect clogging of the lysimeter by precipitates. In the other lysimeters no such time-dependant trends are visible. However, the S.I. calculations did not indicate that a significantly higher number of secondary minerals were oversaturated at this level. An alternative explanation is precipitation of compounds within the tubing of the lysimeter since the opening of the tube was not sealed from O2 in-between the measurements. The possible precipitation inside the pores of the lysimeter or on the outside of the filter tip could, due to the long exposure period, adsorb other elements and thus function as a filter material. During the sampling period, this lysimeter was also the most difficult to obtain water from. These two observations could depend on the presumed precipitation at this level.

Water from rain percolates downwards in the protective cover. A part of the precipitation evaporates, and some of the infiltrating water is removed by plants. The remaining part is hindered at the sealing layer. Occasionally, even a perched groundwater level above the sealing layer is formed. A minor portion of the water percolates through the sealing layer. Based on field infiltration lysimeter studies at Kristineberg, the average yearly infiltration volume through the sealing layer based on measurements since September 1999 is \(4 \times 10^{-3} \text{ m}^3/\text{m}^2\), a (Carlsson, unpublished data). Compared with the pre-remediation conditions the amount of water entering the tailings has been significantly reduced from about 0.23 m\(^3\)/m\(^2\), a prior to the remediation (Axelsson et al., 1986). A rough estimation based on the available data is that the infiltration has been reduced by \(\sim 98\%\) in the test areas due to the remediation measures. Even if it is likely that these test areas are compacted to a lower hydraulic conductivity than the average for the entire impoundment it should give a hint about the degree of reduction for the infiltrating water. Also the O\(_2\) transport should have been largely decreased since the calculated diffusion coefficient for the cover is low (Werner et al. 2001). In the till cover the element concentrations dissolved in the infiltrating water are relatively low and pH is relatively high, but in the oxidised zone, elements retained after previous oxidation might be released. Also remaining sulphides are likely to be oxidised by the diffusing O\(_2\). Due to the lack of buffering minerals left in the oxidised tailings, pH decreases. A 5-step sequential extraction method, slightly modified from Hall et al. (1996a, b), was used by Carlsson et al. (2002) to investigate the fraction associations at different depths in the tailings from the part of the impoundment where 1.0 m of till was applied and the groundwater table raised. The conclusion from the extractions performed on the tailings was that the adsorbed/exchangeable/carbonate fraction (the most easily extracted step), as well as the amorphous Fe (oxy) hydroxides fraction, is important for retaining elements at or below the former oxidation zone. Elements to a large part (20–60 wt.%) associated with these fractions are Cd, Co, Cu, Ni, and Zn. This association is especially evident just below the former oxidation front, where secondary enrichment has resulted in increased concentration of these elements. The pH is low in the oxidised zone and just below it, resulting in release of the easily soluble secondary products. The water is transported downwards and successively more retained products are dissolved. Entering the enrichment zone and leaving the oxidation zone results in increased pH. The increased pH results in lowered solubility for most of the elements and several elements are retained again.

Fig. 4. Fe and S time dependency in lysimeter 5 (200 cm).
(2000) suggested that pH in a low pH zone (2.1–3.5) close to or above the oxidation front might be controlled by jarosite dissolution and ferrihydrite or goethite precipitation. The lowered concentration of K and increased concentration of Fe make this explanation unlikely at this impoundment. For the next pH-level situated at the location of the 260 cm lysimeter, the concentration of dissolved Al is at the same level as at the 200 cm lysimeter, although higher than in the uppermost lysimeter at 150 cm. This fact does not mean that Al is not released within this pH-interval but rather that the installation depth for the lysimeter might have been too deep to coincide with the peak of dissolved Al. The content of calcite is low and of siderite negligible in the impoundment.

Adsorption onto the precipitating and existing secondary phases probably has a major scavenging effect, especially for trace elements such as Cu$^{2+}$ and Pb$^{2+}$. Copper$^{2+}$ and Pb$^{2+}$ were shown to have a critical pH-interval for adsorption onto Fe- and Al-oxides at a pH of 3–5 (Kinniburgh and Jackson, 1981). Pb often forms anglesite which is relatively insoluble (Williams, 1990). For Zn$^{2+}$, Ni$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ the critical pH-interval is between 5 and 6.5 for adsorption onto Fe- and Al-oxides (Kinniburgh and Jackson, 1981). Cu and Zn were also shown to adsorb onto Fe-hydroxides by Johnson and Thornton (1987). It was also shown by Johnson and Thornton (1987), Kooner (1993), and Paulsen (1997) that Cd is relatively mobile. Cadmium often follows Zn, since their ion sizes are similar (Brehler, 1978). Continuously with increasing depth in the tailings, as pH increases from about 3 up to 4–4.4 in the deepest lysimeter and finally to around pH 6 in the groundwater, mobility decreases and adsorption reactions become increasingly important. As can be seen, the elements Cd, Co, Ni and Zn have a high concentration in all tailings lysimeters although lower in the deepest indicating immobilization with depth. In the groundwater, the level has decreased compared to the levels in the lysimeters. This can probably be explained by the critical pH-interval for adsorption onto Fe- and Al-oxides, since the levels for these elements were about 5–6.5, which is the pH of the groundwater but also dilution contributed to the much higher groundwater flow is a possibility if the groundwater contains lower concentrations than the groundwater forming infiltration. McGregor et al. (1998) found that goethite could act as a sink for Ni and that other sinks detected for heavy metals included jarosite. Al et al. (1997) found that Na, K, Ca, Mg, Al and Ni in low-pH pore water may be controlled by precipitation or co-precipitation in secondary mineral coatings on pyrite grain surfaces. The S.I. calculations indicated that different kinds of hydroxides could precipitate within the unoxidised tailings. The trace element behaviour could thus be controlled by these reactions within the unoxidised tailings.

For Cu the concentration decreases with depth in all lysimeters. Although the groundwater has an even higher pH it contains a higher concentration of Cu. This can be explained by the fact that only a small fraction of the groundwater is from the part of the impoundment in which the investigation is performed and a transport of dissolved Cu and other constituents from other parts of the impoundment is probable. Using Darcy’s law, hydraulic conductivity results from Axelsson et al. (1986) and the present groundwater levels close to the lysimeter installation indicates a flow in the order of 30–90 m$^3$/m$^2$, a which is thus several orders of magnitude larger than the amount of water infiltrating through the sealing layer ($\sim 4 \times 10^{-3}$ m$^3$/m$^2$, a). Lead behaves more like the elements Cd, Co, Ni and Zn. The dissolved element concentrations thus probably decrease by adsorption onto primary, secondary or tertiary formed minerals (re-precipitated dissolved secondary minerals) to a large part. The dissolution of elements secondarily retained below or in the oxidised zone and the following adsorption or re-precipitation at greater depth is the probable cause for the boomerang-shaped concentration curve visible for Al, Cd, Co, Fe, Hg, Mg, Mn, Mo, Ni, Pb, S and Zn (Fig. 3). Fig. 5 shows schematically how this occurs in the impoundment. Most likely, the scavenging of dissolved oxidation products depends on
Fig. 6. Solid tailings analysis from drill profile 7.
pH-changes within the vadose zone, enabling precipitates to form and trace elements to adsorb onto precipitated or precipitating minerals. As was indicated by the S.I. calculations more secondary minerals were likely to precipitate at increased depth in the tailings.

The groundwater entering this part of the impoundment is a mixture of groundwater from different parts of the impoundment where two different tailings remediation techniques were used. The first one is discussed above and the second is performed by raising the groundwater table above the oxidised zone by the application of 1 m of unspecified till. An upstream cut-off ditch was sealed in order to reduce the unsaturated zone within the tailings (Holmström et al., 2001). The latter case, there is a dissolution of the retained but easily remobilized fractions in the enrichment zone (Holmström et al., 2001). The major part of the groundwater present at the sampling point probably originates in the part of the impoundment remediated with 1.0 m of till cover. The element concentrations in the groundwater thus represent a mixture of a smaller amount of water infiltrating through the sealing layer and groundwater transported to the lysimeter location from the area remediated by 1.0 m of till cover.

Just below the oxidation front, the unoxidised tailings buffer the infiltrating water and increase the pH. When this occurs elements from the infiltrating water are immobilized. The elements thus retained might very slowly be transported downwards if the buffering capacity (and thereby the infiltrating water pH) decreases in the enrichment zone. However, this will take a very long time due to the small amounts of water available for releasing the primary oxidation products. The infiltrating water finally reaches the groundwater table located about 4–5 m below the till surface. At this level, the major part of the dissolved elements in the tailings pore water might have been removed, thus entering the groundwater containing lowered concentrations of most elements.

The increased concentration of Ca in the uppermost part of the tailings can be explained by the remediation actions. Prior to the application of the sealing layer, 10 kg/m² of lime was spread over the impoundment. This lime, placed between the sealing layer and the tailings, dissolves as the percolating water is transported through it.

According to the solid tailings analysis from a profile situated close to the lysimeter installation, a peak of Cu is very distinct (Fig. 6). It is also situated very close to the oxidation front. According to investigations by Boorman and Watson (1976), Blowes and Jambor (1990), Blowes et al. (1992), and Holmström et al. (2001) Cu often forms secondary enrichment zones by the formation of covellite by solid-solution substitutions, e.g. the transformation of pyrrhotite, chalcocypirite, galena, and pyrite. Covellite has been verified in the impoundment by investigations of thin sections at the level of the secondary copper enrichment in the tailings (Holmström et al., 2001). It is thus likely that the secondarily enriched Cu can be explained largely by this transformation into secondary covellite. However, according to sequential extractions by Carlsson et al. (2002) the amount of Cu present in an easily dissolved fraction (adsorbed/exchangeable/carbonate) at the level of the secondary enrichment could amount to more than the total content of Cu below the enrichment zone. After the remediation the major retaining process for Cu is probably adsorption onto secondary Fe oxhydroxides and mineral surfaces. Copper, together with the elements Cd, Co and Ni seems to be largely retained at a depth between ~320 and 400 cm below the till surface (Fig. 6). Lead was retained at the depth of 250 cm in this profile whilst Zn has a larger area of accumulation between 350 and 500 cm. At this point the till cover is about 200 cm thick but at the location of the lysimeter installation, the till cover was about 150 cm. If the depth in the tailings of the secondary enrichment zone is equal, the major secondary formation of these elements should be at the depth of ~250–350 cm (~200 cm for Pb and ~300–450 cm for Zn). This is consistent with the findings from the lysimeters, since the concentrations of these elements decrease largely between a depth of 200 and 260 cm in the tailings. An exception is Cu that is higher at the 150 cm level than at 200 cm, which shows that it is efficiently retained prior to the lysimeter at 200 cm. Just below the oxidation front, a possible increased concentration of Al is visible. The increase can be explained by silicate dissolution reactions, chlorite is particularly common.

6. Conclusions

The percolating water entering the oxidised zone through the sealing layer has low dissolved-solids concentrations and a pH of just above 4. When infiltrating the oxidised tailings and the upper part of the unoxidised tailings, pH decreases and conductivity increases due to the remobilization of secondarily retained oxidation products. Also oxidation of sulphide minerals due to O₂ diffusion through the sealing layer takes place. The amount of water infiltrating through the sealing layer is low, compared with the pre-remediation conditions, approximately 4×10⁻³ m³/m²·a. The dissolved secondary products originate from both the oxidised tailings and the unoxidised secondary enrichment zone dating back to the time prior to the remediation together with the present oxidation. The total mass of contaminants transported within the vadose zone of the impoundment is low due to the limited water transport, although the concentrations can be high. In the part of the impoundment covered by a sealing layer, the elements thus released re-precipitate, co-precipitate, and
adsorb on tertiary formation products or onto primary mineral surfaces before reaching the groundwater table. The concentration of the elements in the groundwater in the areas covered by a sealing layer is thus not caused by the processes occurring in the vadose zone. As could be seen from Fig. 3, most elements have lower concentrations in the groundwater than in the tailings unsaturated zone. This is explained by a much larger horizontal groundwater flow than vertical infiltration of water, as well as by retention mechanisms acting on the infiltrating water in the vadose zone of the tailings.

In other parts of the impoundment, covered by 1 m of unspecified till and protected from oxidation by a raised groundwater table, several elements have increased solid concentrations just below the oxidised zone due to the oxidation and retention prior to the remediation. At this level sampled pore water shows increased concentrations, this indicates that secondarily retained elements are released and transported away with the groundwater. Sequential extractions show that the most easily dissolved fraction, the adsorbed/exchangeable/carbonate extraction, is an important provider to the total element concentration just beneath the oxidation front. It is thus the composition of this groundwater that mainly governs the groundwater composition in the areas remediated by a sealing layer and a protective till cover. The water infiltrating and the O$_2$ diffusing through the sealing layer and entering the vadose zone of the tailings are less important for local groundwater composition.

Acknowledgements

This study was financed and supported by the MISTRATA-research programme “Mitigation of the environmental impact from mining waste” (MiMi). The authors would like to thank Milan Vnuk for preparing all figs. and Boliden AB, especially Johan Ljungberg and Manfred Lindvall. We also wish to thank all members of the Division of Applied Geology and all personnel involved in the MiMi-project for constructive and interesting discussions.

References


Geochemical investigations of the groundwater in sulphide-bearing tailings remediated by applying till cover.


Corregé O., Carlsson E., and Öhlander B.
Abstract: At the Kristineberg mine in northern Sweden, sulphide-rich tailings were remediated in 1996 by applying till covers. The sulphides were isolated from the atmosphere to prevent oxidation. This was realized either by covering with unspecified till in combination with a raised groundwater level making the tailings water saturated, or by covering with compacted clayey till overlain by unspecified till (dry cover). During and after 1998, 14 groundwater pipes were installed in the tailings impoundment to study the effects of the remediation. Sampling has been performed on more than 25 occasions during more than two years, and the samples were analysed for major elements and metals, anions, pH, redox and conductivity. The results show that the groundwater characteristics vary considerably in the impoundment, even under the same type of cover. In the tailings with simple till cover and raised groundwater, pH ranges between 3.9 and 6.9, Fe-concentration between 30 and 22,000 mg/L, and Zn-concentration between 3 and 2,700,000 µg/L. The corresponding results for the dry cover show a pH ranging between 5.0 and 7.0, Fe-concentration between 300 and 480 mg/L, and Zn-concentration between 8 and 215 µg/L. The pH is generally increasing and redox is generally decreasing across the studied impoundment, where some areas showed quicker changes than others. The source reactions of the pollution seem to have slowed down. Before the remediation, metals released by sulphide oxidation were partly secondarily retained in the tailings below the oxidation front. Such metals, mainly Fe, S, Mg and Zn, have been remobilised by a first washout as a result of the raised groundwater level. A second washout by the clean groundwater from the western till slope, combined with the slowing down of the acid-producing reactions should lead to significant and general decreases in the observed concentrations within 3 to 4 years.

Introduction

Acid drainage from mining waste has for some time been recognised as an environmental problem. Isolating sulphide-bearing waste by applying soil cover or water cover are two common methods of remediation (Feasby, 1995). In northern Sweden, till deposited from the glacial ice between 8,000 and 10,000 years ago is commonly used as soil cover (e.g., Lindvall et al., 1999). Both unremediated tailings and tailings remediated with dry and water cover have been studied and characterised earlier (for example: Boorman and Watson, 1976; Blowes and Jambor, 1990; Fraser and Robertson, 1994; Pedersen et al., 1994; Pedersen et al., 1997; Holmström and Öhlander, 1999; Holmström et al., 1999; Holmström et al., 2000). Studies of tailings remediated by a combination of both methods, however, are few.

The field studies within the Swedish MiMi-programme (Mitigation of the Environmental Impact from Mining Waste), started in 1998 at the chosen field site, the Kristineberg mine. The aim of the programme is to evaluate existing remediation methods, and, if possible improve them, but also to try to find new, efficient and cost-effective remediation methods to solve the environmental problems related to mining and disposal of mining wastes. In this study, sulphide-bearing tailings left without any cover for almost 50 years at the Kristineberg mine have been studied two years after remediation. The studied impoundment has been remediated by a combination of covering the waste with till, and by raising the groundwater table. The aim of the present study was to characterise the groundwater quality and its variation in the tailings. As reported in other studies dealing with sulphide mine remediation, transport of elements leading to the formation of a plume can be one of the major processes involved (Paulson, 1997; Johnson, 2000).
1 Study area

The Kristineberg mining area is located in the western part of the Skellefteå district in northern Sweden, approximately 175 km southwest of Luleå (see Fig. 1) and consists of 1.9 Ga massive pyrite rich ore bodies intercalated within volcanic rocks and overlain by sedimentary rocks. For further description of the geology of the area and the ores, see Du Rietz (1951), Gavelin (1943), Gavelin and Kulling (1955) and Grip (1973). The largest ore body in the area is the Kristineberg Zn-Cu deposit. Mining started in 1940 and is still in progress.

Figure 1. Location of the study area. The northern Impoundment is referred as Impoundment 1 and the southern one as Impoundment 1B. Impoundment 1 is studied in the present article.

Five tailings impoundments are located within the Kristineberg mining area. Since many different ores from the western part of the Skellefteå field mining district have been processed at the processing plant, the impoundments contain a mixture of different sulphidic tailings. Impoundment 1, the oldest impoundment within the mining area, has been investigated in this study. The impoundment is situated in a small valley and is underlain by peat and till. It was used until the early 1950s and covers approximately 0.10 km\(^2\) (Boliden Mineral AB, 1995). Pre-remediation characterisation of the geochemistry and hydrogeology of the impoundment was carried out by Qvarfort (1983), Axelsson et al. (1986), Ekstav (1989) and Axelsson et al. (1991) (see also compilation in Malmström et al., 1999).

The impoundment was remediated in 1996 by a combination of raising the groundwater table where this was possible, by sealing off intercepting and drainage ditches, and dry cover application on the remaining regions of the impoundment. For a detailed description, see Lindvall et al. (1999). The intention was to apply 1 m of till as a protective layer in areas with a shallow groundwater table, and in other areas, to apply 1.5 m of unspecified till as a protective layer on top of a 0.3 m thick sealing layer of clayey till. The tailings and the pore water compositions were investigated in 1998 (see Tables 1 and 2), and a detailed description can be found in Holmström et al. (2000). The composition of the unoxidised tailings is dominated by Si, Fe, S and Mg in decreasing order. The most represented minor elements, in decreasing order, are Zn, Cu, Pb and As. The oxidation of the upper part of the tailings resulted in depletion of mainly S, Fe and Mg, for major elements and Zn, Cd, Co, Cu and As for minor elements (in decreasing importance). Based on the mineralogical observations
Table 1. Average major element composition of oxidised and unoxidised tailings at Kristineberg, Impoundment 1 (% weight ±±±± s.d.). Samples affected by secondary enrichment are excluded.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unoxidised tailings (73 samples)</th>
<th>Oxidised tailings (12 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>9.35±1.50</td>
<td>11.40±1.47</td>
</tr>
<tr>
<td>CaO</td>
<td>1.01±0.49</td>
<td>1.24±0.74</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>24.00±5.00</td>
<td>8.45±3.59</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.81±0.40</td>
<td>1.88±0.97</td>
</tr>
<tr>
<td>MgO</td>
<td>7.73±1.46</td>
<td>6.65±3.52</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.12±0.02</td>
<td>0.11±0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.46±0.35</td>
<td>1.46±0.88</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07±0.02</td>
<td>0.08±0.04</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.80±6.70</td>
<td>63.10±7.10</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.30±0.06</td>
<td>0.45±0.07</td>
</tr>
</tbody>
</table>

Table 2. Average minor elements composition of oxidised and unoxidised tailings at Kristineberg, Impoundment 1 (ppm ±±±± s.d.). Analyses for Be, La, Sc, V, Y, and Zr are not reported here.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unoxidised tailings (73 samples)</th>
<th>Oxidised tailings (12 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>183±157</td>
<td>36.2±28.9</td>
</tr>
<tr>
<td>Cd</td>
<td>21.5±12.5</td>
<td>1.47±2.39</td>
</tr>
<tr>
<td>Co</td>
<td>56.4±21.3</td>
<td>7.77±9.18</td>
</tr>
<tr>
<td>Cr</td>
<td>46.2±13.3</td>
<td>60.7±19.9</td>
</tr>
<tr>
<td>Cu</td>
<td>956±316</td>
<td>159±132</td>
</tr>
<tr>
<td>Hg</td>
<td>2.42±1.17</td>
<td>0.94±0.52</td>
</tr>
<tr>
<td>Mo</td>
<td>24.4±5.3</td>
<td>17.7±11.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.95±2.58</td>
<td>4.52±3.35</td>
</tr>
<tr>
<td>Pb</td>
<td>463±283</td>
<td>454±318</td>
</tr>
<tr>
<td>Zn</td>
<td>8861±4744</td>
<td>559±919</td>
</tr>
</tbody>
</table>

and the average composition of the tailings, the amount of sulphides mineral in the unoxidised tailings is estimated to be: 26% pyrite, 1.3% sphalerite, 0.28% chalcopyrite, 0.05% galena, and 0.04% arsenopyrite. In the oxidised tailings, iron oxyhydroxides are common, occurring as grain aggregates or coatings on the silicate minerals. The main gangue minerals for both parts of the tailings are, in decreasing order of abundance: quartz, K-feldspar, Mg-chlorite, talc, plagioclases, muscovite, amphiboles/pyroxenes, and biotite.

2 Methodology

2.1 Sampling

Sampling of the groundwater began in August 1998 and has been performed at 15 different locations across the impoundment (see Figure 1) on more than 25 occasions to date (December 2000). The groundwater sampling has been performed by the use of “Bat®-pipes” which resulted in a minimal sample exposure to atmosphere before analysis (see Torstensson and Petsonk, 1988, for detailed description). Pipe P, installed during August 2000 provides information about the background hydrogeochemistry from the western till slope. Pipes D to I monitor the part with a raised groundwater level, while pipes J to M and O are used for the double-layer dry covered part. In the single-layer part with a raised groundwater level, half of the pipes were installed at a shallow depth of about 3.5 m and the other half deeper at about 8 m at the same locations. Pipes A to C, N and Q are not used in the present study.

The water samples were collected in glass bottles (DURAN®) acid-washed in 5% HNO₃ for three days. The bottles were then emptied and refilled with argon several times, so that the expected amount of oxygen left inside ranged between 0.1 and 0.01%. Before sampling, the groundwater in the Bat-pipes was renewed 3 to 4 times. During the entire sampling, the sampled water was protected from light and heat. The groundwater level has been measured regularly in 29 piezometers across the impoundment, using an electronic probe (location, see Fig. 2).

2.2 In situ analysis

Once sampled, a part of the water was filtered in a small laboratory installed in field (within a delay of 2 to 4 hours) using a vacuum pump with 0.22 µm Millipore® Nitrocellulose membrane filters (φ = 47 mm) washed for three days in 5% acetic acid. The filter holders were acid-washed in 5% HNO₃ prior to use.
Redox and pH were measured with a Metrohm® Pt-electrode and a Metrohm® combined pH-electrode. The pH electrode was calibrated using two Titrisol® pH 4 and 7 buffers. The redox electrode was checked using two Ag/AgCl Reagecon® standards (124 mV and 358 mV). All redox values were adjusted to the standard hydrogen electrode. The conductivity was measured with a Hanna® conductivity meter. Alkalinity was determined by titration with a decimolar Titrisol® HCl solution, using a portable Hach® digital titrator. All measurements were made within a few minutes after the opening of each bottle.

Figure 2. Isopiezometric map of Impoundment 1, 10-10-2000, showing the groundwater table as m above the sea level.

The water left in the bottle was then divided in three subsamples for the analyses performed in laboratories: one for anions analyses (currently chloride, sulphate and nitrate), one for metals and main elements by ICP techniques, and one for dissolved organic content. The water samples for anions analyses were filtered directly into plastic bottles and placed immediately in a refrigerator. The water samples for main elements and metal analyse were also filtered directly in acid washed 60 ml Azlon® HDPE bottles and were acidified with 1% redistilled suprapur HNO₃. The water samples for organic content were filtered using a metal filter-holder and a glass container through Whatman® glass fiber filters (0.7 µm pore size and φ 47mm) burnt before use at 450°C for 24h. The water was then poured into Falcon® plastic tube acidified with 1% two molar hydrochloric acid and put immediately in the refrigerator. Blank analysis using the same methodology with milli-Q water instead of groundwater, verified that the conditions of manipulation and analyses were satisfactory, with less than 2% average relative error on all pipes and elements.

2.3 Analytical methods

The samples, kept cold and in the dark, were brought to a laboratory within 24 hours. Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb and Zn were measured using ICP–SMS (high-resolution ICP-MS), and Ca, K, Mg, Na, S, Si, and Sr were analysed by ICP–AES (Atomic Emission Spectroscopy). The data were reported after three to four runs on each instrument. The quality of the analyses was checked using synthetic standards (Ödman et al., 1999). The precision determined in such conditions as ± one standard deviation was generally better then 5%. The dissolved organic carbon content was determined using high-temperature...
3 Results

Data concerning the general averages across the impoundment, element by element, as well as background values are summarised in Table 3. The concentrations found in the zone with a raised groundwater level are higher than in the zone with the dry cover, except for Ca, Si, Co, Ni and Cl⁻.

Table 3. Average values in year 2000 for the zone with a raised groundwater level, for the entire impoundment, and background values. Levels below the detection limits have been replaced by the detection limits themselves, thus leading to overestimation. Standard deviations are given for the average values recorded per pipe.

<table>
<thead>
<tr>
<th></th>
<th>Average in pipes D to I: zone with a raised groundwater level ± s.d.</th>
<th>Average in pipes J to M and O: zone with a qualified dry cover ± s.d.</th>
<th>Average in the entire impoundment ± s.d. (200 samples)</th>
<th>Background value: pipe P (2 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.3 ± 0.8</td>
<td>5.5 ± 1.2</td>
<td>5.4 ± 1</td>
<td>6.0 ± 0.2</td>
</tr>
<tr>
<td>Redox (mV)</td>
<td>261.7 ± 112.8</td>
<td>205.0 ± 104.8</td>
<td>235.9 ± 107.9</td>
<td>397.5 ± 17.7</td>
</tr>
<tr>
<td>Cond (mS/cm)</td>
<td>6.8 ± 5.7</td>
<td>5.0 ± 3.2</td>
<td>6.0 ± 4.6</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>320.7 ± 169.2</td>
<td>433.2 ± 99.3</td>
<td>372.7 ± 147.8</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>4292 ± 7528</td>
<td>2439.8 ± 2583</td>
<td>3450.1 ± 5472.1</td>
<td>2.4 ± 2.9</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>497 ± 665</td>
<td>266 ± 259</td>
<td>392 ± 512</td>
<td>1.4 ± 0.06</td>
</tr>
<tr>
<td>S (mg/L)</td>
<td>4628 ± 5753</td>
<td>2109 ± 1776</td>
<td>3483 ± 4420</td>
<td>4.9 ± 1.9</td>
</tr>
<tr>
<td>Si (mg/L)</td>
<td>7.0 ± 5.4</td>
<td>10.6 ± 4.7</td>
<td>8.7 ± 5.2</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>Al (µg/L)</td>
<td>67434 ± 101417</td>
<td>14592 ± 29540</td>
<td>43415 ± 79078</td>
<td>11.8 ± 3.3</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>256 ± 602</td>
<td>9.4 ± 14.5</td>
<td>144 ± 445</td>
<td>0.1 ± 0.03</td>
</tr>
<tr>
<td>Cd (µg/L)</td>
<td>0.7 ± 0.68</td>
<td>0.46 ± 0.73</td>
<td>0.59 ± 0.68</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>Co (µg/L)</td>
<td>9.88 ± 23.26</td>
<td>71.38 ± 105.1</td>
<td>37.8 ± 75.6</td>
<td>2.5 ± 0.9</td>
</tr>
<tr>
<td>Cr (µg/L)</td>
<td>243.5 ± 531.4</td>
<td>3.3 ± 3.7</td>
<td>134.3 ± 396.2</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>Cu (µg/L)</td>
<td>26.63 ± 37.15</td>
<td>1.91 ± 0.54</td>
<td>15.4 ± 29.3</td>
<td>0.77 ± 0.12</td>
</tr>
<tr>
<td>Mn (µg/L)</td>
<td>14781 ± 17724</td>
<td>10111 ± 8672</td>
<td>12658 ± 13896</td>
<td>128.9 ± 69.4</td>
</tr>
<tr>
<td>Ni (µg/L)</td>
<td>7.2 ± 7.9</td>
<td>59.7 ± 69.7</td>
<td>31.1 ± 52.2</td>
<td>2.6 ± 0.01</td>
</tr>
<tr>
<td>Pb (µg/L)</td>
<td>4.98 ± 6.57</td>
<td>2.6 ± 2.7</td>
<td>3.7 ± 4.7</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>Zn (µg/L)</td>
<td>508880 ± 934209</td>
<td>3710 ± 5440</td>
<td>279260 ± 711330</td>
<td>15 ± 3</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>13.2 ± 11.4</td>
<td>19.1 ± 23.2</td>
<td>15.9 ± 17</td>
<td>2.4</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>20010 ± 26940</td>
<td>7966 ± 6521</td>
<td>14534 ± 20479</td>
<td>25</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>7.55 ± 7.43</td>
<td>7.4 ± 4.8</td>
<td>7.48 ± 6.08</td>
<td>4.15 ± 0.6</td>
</tr>
</tbody>
</table>

3.1 Hydrology

Ekstav (1989) reported that the vertical permeability is much lower than the horizontal, due to the deposition of the tailings in layers. The field observations provide data for the isopiezometric map of the groundwater shown in Figure 2. In the impoundment, the flow directions of the groundwater remain quite constant all year long. The highest groundwater level is found along the slope in the southwestern part of the impoundment, in pipe V8, and the lowest in the southeastern part. The zone around pipe V8 constitutes a hydrological dome, thus leading the groundwater from this zone to the surrounding areas eastward (see subfigure “flow gradients and directions” in Figure 2).

In some pipes and at some periods the groundwater level rises above ground level (for example in pipe 2H, about one month after the snowmelt). This may be due to the entry of some groundwater from the till slope which is released at a crucial depth in the impoundment at a high pressure, forming artesian water around pipes H and I. This fresh water from the eastern slope, could then rise during mixing with the tailing water, reach the surface in some parts and then follow the surface water paths. This could explain the presence of red iron deposits on top of the till cover around pipes H and I. The drainage areas of the impoundment...
are located around piezometers 1 and 2 for the northern part and around piezometers 3 and 4 for the southeastern part.

The variations in the groundwater level over one year can be illustrated by those observed in pipe V4 (see Figure 3a). The changes in level result in short-term seasonal variations of the geochemistry in the groundwater, as illustrated in Figure 3b.

![Figure 3a. Illustration of the seasonal variations observed in the groundwater level over one year.](image)

![Figure 3b. Illustration of the seasonal variations observed in hydrogeochemistry, of Ba in pipe F. The general trend observed after the beginning of the remediation is expressed by the dashed line. Seasonal variations cause perturbations from the general trend, observed here on the amount of dissolved Ba in pipe F, from May to October. In reference to Fig 3a, the peaks marked “Sm” are likely due to snowmelt and the peaks marked “AR” are likely due to autumn and summer rains.](image)

The two types of cover and the hydrology result in a strong heterogeneity of the hydrogeochemical conditions across the impoundment.

### 3.2 Zone with a raised groundwater level

The average composition of the groundwater in the zone with a raised groundwater level is summarized pipe by pipe in Table 4. Since the hydrogeochemistry of the impoundment still seems to be influenced by the preremediation conditions, averages were reported for year 2000 data. Some pipes show significant and regular decreases of almost all metal concentrations over the past two years. The results are relatively variable with average values ranging from 1.2 to 14.7 mS/cm for conductivity, from 4 to 6.5 for pH, from 81 to 18,800 mg/L Fe, from 331 to 15,040 mg/L S, 0.09 to 1484 µg/L As, 0.04 to 57 µg/L Co, 0.92 to 1,326 µg/L Cr, 2.2 to 87.9 µg/L Cu, 1 to 4,232 µg/L Pb, and 12 to 2,352,000 µg/L Zn.

The deep pipes D and F have quite low concentrations, while the corresponding shallow pipes E and G show much higher values. Dissolved iron, for example, is about 3 times lower in pipe F than in pipe G, and about 50 times lower in pipe D than in pipe E. Pipes H and I display highest concentrations of metal and metalloids recorded across the impoundment, and the deeper pipe shows a higher amount of dissolved metals than the shallower one.

The variations in the concentrations of a few elements over time are shown in Figure 4. To understand the long-term effect of the remediation, seasonal variations illustrated in Figure 3b, and anomalies in the first available data (August 1998, except for pipes M and O) that might be due to the installation of the pipes, should be identified. The concentrations in the samples taken in pipe F clearly show exponentially decreasing trends over time for Fe, Zn, Mn, Mg, bringing for example Fe content from about 4900 mg/L in August 1998 to about 430 mg/L in July 2000. During the same time, pH increased by more than 1.2 units. In pipe F, only Ba shows an increasing trend. It seems that the values taken from pipe G, sampling the groundwater at the same location as F but shallower, follow a similar trend, but with much
lower amplitude. This is particularly clear for Fe, Mn, Co and Zn concentrations. It should be noted, however, that some elements like As, Ca and Sr showed an increasing trend after an initial decrease.

Table 4. Average values in year 2000 for the pipes located in the zone with a raised groundwater level. The missing data correspond to some concentrations found below the detection limits. When an average is reported without s.d., there was only one occurrence above the detection limit. The detection limits change from one sample to the next because of the variable dilution needed to obtain a limited salt content for the ICP techniques analysis.

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<td>6.5 ± 0.18</td>
<td>6.0 ± 0.19</td>
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<td>Redox (mV)</td>
<td>112.4 ± 20.06</td>
<td>135.4 ± 16.62</td>
<td>293.6 ± 28.32</td>
<td>392.4 ± 33.5</td>
<td>339.8 ± 10.6</td>
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<tr>
<td>Cond (mS/cm)</td>
<td>1.6 ± 1.07</td>
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<td>14.7 ± 10</td>
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<tr>
<td>Ca (mg/L)</td>
<td>529.6 ± 16.21</td>
<td>363.6 ± 11.33</td>
<td>31 ± 0.76</td>
<td>239.8 ± 85.76</td>
<td>387.6 ± 22.7</td>
<td>372.6 ± 19.8</td>
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<tr>
<td>Fe (mg/L)</td>
<td>81.6 ± 4.27</td>
<td>4206 ± 252.4</td>
<td>449 ± 26.5</td>
<td>1396.6 ± 483.8</td>
<td>18800 ± 2003</td>
<td>848.4 ± 639.3</td>
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<td>Mg (mg/L)</td>
<td>50 ± 3.46</td>
<td>251.2 ± 3.63</td>
<td>29.9 ± 0.8</td>
<td>99.6 ± 39.6</td>
<td>1702 ± 103</td>
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<td>S (mg/L)</td>
<td>541.2 ± 31.11</td>
<td>3006 ± 89.6</td>
<td>331.6 ± 21.7</td>
<td>1326.6 ± 476.9</td>
<td>15040 ± 829</td>
<td>7520 ± 343</td>
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<td>Si (mg/L)</td>
<td>2.1 ± 0.19</td>
<td>15.1 ± 0.34</td>
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<td>5.2 ± 0.72</td>
<td>8.2 ± 0.2</td>
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<td>Al (µg/L)</td>
<td>21.9 ± 34.40</td>
<td>62.8 ± 17.5</td>
<td>1196 ± 209</td>
<td>91100 ± 33009</td>
<td>262000 ± 14446</td>
<td>52000 ± 3779</td>
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<tr>
<td>As (µg/L)</td>
<td>0.3 ± 0.10</td>
<td>5.1 ± 0.8</td>
<td>&lt;0.20</td>
<td>1484 ± 73.69</td>
<td>41.6 ± 2.8</td>
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<tr>
<td>Cd (µg/L)</td>
<td>0.07 ± 0.04</td>
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<td>1.77 ± 1.37</td>
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<tr>
<td>Co (µg/L)</td>
<td>0.04 ± 0.01</td>
<td>0.17 ± 0.05</td>
<td>0.11</td>
<td>-</td>
<td>57.36 ± 25.06</td>
<td>1.01 ± -</td>
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<tr>
<td>Cr (µg/L)</td>
<td>0.97 ± 0.70</td>
<td>0.92 ± 0.19</td>
<td>4.37 ± 0.4</td>
<td>40.56 ± 15.27</td>
<td>1326 ± 158.7</td>
<td>88.16 ± 11.4</td>
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<tr>
<td>Cu (µg/L)</td>
<td>2.38 ± 1.5</td>
<td>4.22 ± 2.20</td>
<td>-</td>
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<td>87.90 ± -</td>
<td>58.10 ± 11</td>
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<td>Mn (µg/L)</td>
<td>987.2 ± 57.5</td>
<td>11960 ± 371</td>
<td>1590 ± 163.6</td>
<td>3210 ± 877</td>
<td>45680 ± 1689</td>
<td>25280 ± 1076</td>
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<tr>
<td>Ni (µg/L)</td>
<td>1.6 ± 1.2</td>
<td>2.7 ± 1.6</td>
<td>1.1 ± 0.2</td>
<td>21.9 ± 9.69</td>
<td>&lt;10.00 ± -</td>
<td>6.1 ± 0.2</td>
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<tr>
<td>Pb (µg/L)</td>
<td>0.99 ± 1.14</td>
<td>0.96 ± 0.18</td>
<td>0.76</td>
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<td>5.06 ± 1.15</td>
<td>16.14 ± 35.9</td>
<td>4.32 ± 1.1</td>
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<tr>
<td>Zn (µg/L)</td>
<td>12 ± 3</td>
<td>578 ± 76</td>
<td>6652 ± 1176</td>
<td>78040 ± 22803</td>
<td>2352000 ± 358287</td>
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<tr>
<td>Cl (mg/L)</td>
<td>7.7 ± 9.8</td>
<td>29.3 ± 48.3</td>
<td>2.6 ± 1.9</td>
<td>3.6 ± 0.1</td>
<td>25.57 ± 35.6</td>
<td>10.48 ± 14.5</td>
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<tr>
<td>SO4²⁻ (mg/L)</td>
<td>1695 ± 236</td>
<td>11675 ± 2454</td>
<td>1540 ± 627</td>
<td>5280 ± 2715</td>
<td>70850 ± 21931.5</td>
<td>290000 ± 8569.7</td>
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<tr>
<td>DOC (mg/L)</td>
<td>3.8 ± 1.4</td>
<td>4.5 ± 1.9</td>
<td>3.5 ± 0.7</td>
<td>3.6 ± 1.9</td>
<td>22.4 ± 5.7</td>
<td>7.5 ± 2.6</td>
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For pipe D, only a few clear trends could be observed: increased concentrations of Fe, S, SO4²⁻, Ca, Mg, and Sr, and decrease of redox and Ba. Once again, the coupled pipe E shows similar trends with lower amplitude, except for Ca, Ba, and Cl, which do not seem to follow any specific tendency, and Si, which increases. Few trends could be defined in pipe F, which maintains high levels of concentrations for almost all metal and shows strong seasonal variations. Fe and Zn show a regular increase after a short period of decrease, while Si has a clearly decreasing trend. The measured pH seems to increase and redox seems to decrease, but to a very slight extent over the past two years. The values obtained from pipe I also show few obvious trends. Since the first sampling was performed, pH increased slightly, about 0.5, while redox decreased about 50 mV. During the same time, Fe increased slightly and Pb decreased strongly with the same pattern as the one observed for the metals in pipe F. No such clear decrease could be observed for other metals, such as Zn.
3.3 Zone with the dry cover

The average composition of the groundwater in the zone with the dry cover is summarized pipe-by-pipe in Table 5. The concentrations vary largely across the area, but less than for the zone with a raised groundwater level. The average values taken in year 2000 range from 1.85 to 8.5 mS/cm for conductivity, from 3.8 to 7 for pH, from 41 to 6,096 mg/L Fe, from 440 to 4,550 mg/L S, 0.2 to 244 µg/L Co, 0.3 to 8.6 µg/L Cr, 1.3 to 2.5 µg/L Cu, less than 0.3 to 7 µg/L Pb, and 21 to 12,700 µg/L Zn.

From a general point of view, pipes M and O present quite low amounts of metals and metalloids, while pipes J, K and L present rather high values. Pipes J and K are somehow coupled, as they are both installed very close together, but pipe K samples the groundwater deeper down, in the till below the tailings. The observed trend with depth is the same as the one observed in the couples D-E or F-G, higher concentrations at a shallower depth, closer to the former oxidation front. Taking Zn as an example for the year 2000, the water sampled in pipe J has an average concentration of zinc of 12734 µg/L, while pipe K has only 386 µg/L, pipe L 4,962 µg/L, pipe O 429 µg/L and pipe M has a quite low amount with 21 µg/L.

The variations in the concentrations of different elements over time are presented in Figure 5. Pipe J shows clearly increasing trends for Fe and Zn, while Co, and Ni are decreasing. Zn shows an unusual trend with rather constant autumn and winter values and increasing spring and summer values. The trends observed for Mg or Mn are not very clear, and more data over a longer period are required. However, the Mg concentrations seem relatively constant, and the Mn concentrations seem to decrease. The pH is the lowest observed on the entire impoundment, but seems to be increasing slightly from 3.4 in 1998 to 3.8 during autumn 2000. During the same period, pipe K, sampling water from 4 meters below J in the underlying till, showed quite different results, with a rather high and stable pH of around 5.3, and increasing amounts of Ni, Co and As. Relatively close to J and K, pipe M, sampling water from a shallow point below the oxidation front shows stable and low concentrations of Fe (around 40 mg/L) and Zn, and increasing Ca, Mo, Sr and pH. The pH is very high for natural conditions, recently reaching 7.2 (background value for pH is 6.2). Installation of pipes O and L are quite similar to pipes K and J. O is sampling relatively deep in the tailings and L is sampling below in the underlying till. However, neither the average values nor the trends are comparable. Pipe L displays a regular and rather linear increase over the past two years for Fe, S, Mg, and Mn. Co increases as well, and Pb decreases. The pH increases regularly, recently reaching a value around 5. Pipe O has a higher pH, slightly increasing from 5.8 in 1998 to 6.2 during autumn 2000. Fe, S, Mn and Mg contents rose recently after an initial slight decrease during 1998-99.
Table 5. Average values for year 2000 for the pipes located in the zone with the dry cover. The missing data correspond to some concentrations measured below the detection limits. When an average is reported without s.d., there was only one occurrence above the detection limit. The detection limits change from one sample to the next because of the variable dilution needed to obtain a limited salt content for the ICP techniques analysis.

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<td>Redox (mV)</td>
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<td>Cond (mS/cm)</td>
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<td>Ca (mg/L)</td>
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<td>Fe (mg/L)</td>
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<td>Mg (mg/L)</td>
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<td>S (mg/L)</td>
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<td>Al (µg/L)</td>
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<td>34.96</td>
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<td>Cd (µg/L)</td>
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<td>Mn (µg/L)</td>
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<td>Ni (µg/L)</td>
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<td>Pb (µg/L)</td>
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<td>Zn (µg/L)</td>
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<td>Cl− (mg/L)</td>
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<td>DOC (mg/L)</td>
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<td>0.83</td>
<td>4.2</td>
<td>1.34</td>
<td>3.6</td>
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The pH and redox measurements show similar trends over the impoundment. In all studied pipes, the pH is increasing and the redox is decreasing. However, these trends are not so pronounced for some pipes. The DOC showed in general an initial period of decrease followed in 2000 by an increase, except for pipe H in which it continued to decrease.
4 Discussion

There is a good correlation between Fe, S, and Mg for all values over the entire impoundment ($R^2$ about 0.99). Dissolved Fe and S are linked because they both originate from dissolution of the pyrite. Dissolved Mg comes from the dissolution of the chlorite, present in large amounts in the tailings, and also from carbonates. These reactions are closely linked to the dissolution of the pyrite due to their buffering capacity. A good correlation was also found between Fe and Mn ($R^2$ about 0.92), both likely to form complex precipitates by oxidation. The amounts of dissolved metals are clearly linked to pH (an illustration is given with Zn in Figure 6). Large amounts of Zn occur in a dissolved form at a pH below 5.5, while higher pH results in adsorption and immobilisation of Zn (Krauskopf, 1956; Kooner, 1993). The hydrogeochemistry varies strongly over the impoundment, except for DOC, which seems to be more influenced by seasonal variations than by the prevailing conditions in the impoundment. However, some characteristics can be explained for the different areas.
4.1 Characterisation by zone

The zone in which H and I are installed does not give clear signs of remediation, with concentrations of most elements remaining high. This zone has a very complex hydrology, with some evidence of up-welling water from the southwestern slope. The high metal and metalloid concentrations could be linked to the high DOC in this water. Some underlying peat was found during drilling in the area, and some complexation with soluble organic matter could then occur (Ranville, 1997; Yanful et al., 2000). Further, when sampling in pipes H or I, some odourless gas is released from the groundwater, which remains green whereas some red iron precipitations occur after some time in the samples coming from the other pipes. Another explanation could be that the remediation was not fully effective upward, periodically leaving some tailings in the unsaturated zone. Drillings performed during February 2000 brought dry tailings to the surface. Nevertheless, the true explanation for the high concentrations is probably more complex in relation to the hydrology, since the deeper pipe H has higher dissolved amounts than the shallow pipe I, the latter sampling closer to the probable local source of pollutants, the former oxidation front. However, the decreasing trend for redox and the slightly increasing one for pH indicate an improvement in local general conditions. The decreasing trend found for Si is supporting the pH decrease, suggesting the precipitation of amorphous Si around pipe H. Silica gels form rapidly at a moderately low pH, (Siever, 1962). Saturation indices, calculated using the geochemical equilibrium model PHREEQC (Parkurst, 1995) with the MINTEQ database (Allison et al., 1991), were found to be 0.45 for quartz (SiO₂) and 3.75 for kaolinite (Al₂Si₂O₅(OH)₄) in October 2000. However, Fe and Zn are still increasing, probably due to transport over quite large distances.

The zone in which pipes F and G are installed, shows encouraging trends, with clear decreases in almost all dissolved elements, although the levels reached remain high in comparison to the background values (see Tables 3 and 4). Pipe G, closer to the surface, shows slower decreases, as some vertical transports probably still take place from the former oxidation front. Holmström et al (2000) reported that a washout of oxidation products secondarily retained below the oxidation front was occurring as a result of the raised groundwater level.

The zone in which pipes D and E are installed has rather low average concentrations of almost all dissolved elements, but the observed trends show an increase. The pH observed in pipe D and the amount of Ca are quite high compared to the rest of the available values. This could indicate that the liming performed before the covering is still affecting the chemistry in the deep part of this area. Pipe E shows a comparable behaviour to pipe G, suggesting that some vertical transports of metals and metalloids are still taking place. This could thus mean that the lime was consumed by buffering reactions and that dissolutions, probably essentially of secondary minerals, continued to occur afterwards. The low concentrations recorded may be due to the position of pipes D and E, which are installed downstream from a large
horizontal pipe transporting freshwater to the mine, and retaining surface water in a small lake (see Figure 1). Infiltration of the lake water possibly locally dilutes the groundwater. Pre-remediation concentrations in this area are also lower than in the rest of the impoundment (Ekstav, 1989).

The zone in which pipe M is installed shows a high pH which leads to very low concentrations of almost all measured elements due to adsorption and precipitation. However, the high pH recorded (up to 7.2) indicates that the effect of the liming is still present, rendering the remediation effective. Nevertheless, if the hypotheses made for pipes D and E are correct under a different type of remediation, we could, in the long run, expect the lime to be consumed and some increases in metal concentration to appear. The increase observed for Ca could be due to vertical transport of dissolved lime.

The zone in which pipes K and J are installed is comparable to the zone in which M is installed. As these pipes are much deeper, they are probably not strongly affected by the local oxidation front, and the values registered probably depend more on horizontal flows from the west, which are much faster than the vertical one (Axelsson et al., 1986).

For the same reasons, pipes O and L are probably principally affected by the moderately deep horizontal flows coming from the southern part of the impoundment.

4.2 General chemistry of the impoundment

By comparing the elemental concentrations in the tailings (see Tables 1 and 2) with the results obtained for the closest groundwater pipes (P3 with H and I, P5 with F and G, P6 with D and E, and P7 with O, see Figure 1), it appears that the amount of metals in the groundwater is not correlated to the local concentration in the tailings, and thus that the dissolved amounts do not come uniquely from local sources. The geochemistry of the groundwater in the Impoundment 1 is very likely influenced by metal transport. Based on a comparison between oxidised and unoxidised tailings, Holmström et al. (2000) reported the following order of mobility: Zn > Cd > S > Co > Cu > As > Fe > Ni > Pb. This illustrates the different behaviour of Zn and Pb, for example. Zn is present in large amounts at almost every location, whereas Pb occurs in low concentrations or was among the few elements showing a rapid and significant decrease, as in pipe I.

The pore water characteristics in profiles P4 and P6, reported by Holmström et al. (2000) close to pipes F-G and D-E respectively (see Fig. 1), may help us to achieve a better understanding of the vertical fluxes and differences. It was concluded that in the pore water, which was sampled during 1998, there was in general a kind of segregation between heavy metals such as Cd, Co, Cu, Ni, Pb and Zn having higher concentrations in a shallow zone below the oxidation front, while Ca, Fe, Mn, Mg and S showed higher concentrations at deeper levels (below about 5m). This was also reported for pre-remediation groundwater by Ekstav (1989). The average pre-remediation groundwater composition (Ekstav, 1989) is reported in Table 6. Although important decreases appear in some zones, and pH and redox values indicate an improvement of the situation all over the impoundment (cf. Figs. 4 and 5), the average concentrations of groundwater today are comparable with the pre-remediation averages, suggesting that the dissolved elements have not left the impoundment yet, however Cu, Pb and Cd have decreased drastically, probably due to a slowing down of the source reactions in the tailings (see Holmström et al., 2000), and also because of co-precipitation with Fe-oxyhydroxides or adsorption on mineral surfaces (Kooner, 1993; Coston et al., 1995; Herbert, 1996). All these observations suggest that Ca, Fe, Mn, Mg, S could be easily transported from one place to another in the impoundment and heavy metals depend more on local conditions. A relatively high mobility of these elements fits well with the observed variations in the impoundment, but Zn should also be added to the list, and Mn depends probably more than others on local conditions, as shown by pipe M and the lower degree of correlation existing between S and Mn. Sequential extractions performed and reported by Carlsson (2000) showed that Zn, S, Fe and Mg just below the oxidation front occur to a large
extent in the adsorbed fraction, indicating that these elements were probably primarily transported, and could be easily remobilised and transported again if changes of pH occur.

Table 6. Average composition of the groundwater during the period 1983 to 1988 reported by Ekstav (1989).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average ± s.d. pipes “3 and 4”, area of pipe F</th>
<th>pipe “5”, area of pipe D</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.88 ± 0.37</td>
<td>4.98</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>297 ± 124</td>
<td>250</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>3906 ± 1270</td>
<td>4727</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>277 ± 119</td>
<td>343</td>
</tr>
<tr>
<td>Cd (µg/L)</td>
<td>80 ± 30</td>
<td>93</td>
</tr>
<tr>
<td>Cr (µg/L)</td>
<td>50 ± 30</td>
<td>57</td>
</tr>
<tr>
<td>Cu (µg/L)</td>
<td>2500 ± 1670</td>
<td>3230</td>
</tr>
<tr>
<td>Pb (µg/L)</td>
<td>1390 ± 570</td>
<td>1690</td>
</tr>
<tr>
<td>Zn (µg/L)</td>
<td>333000 ± 197000</td>
<td>463000</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>8620 ± 3174</td>
<td>10514</td>
</tr>
</tbody>
</table>

If migration of elements could take place on a much larger scale, the zone where the groundwater was allowed to remobilise and dissolve secondarily retained oxidation products below the former oxidation front, in the south western area remediated by raising the groundwater level above the tailings, could then be considered as the main source of metals and metalloids (cf. Öhlander et al., 2000). This is referred to as the first washout in Figure 7a. Considering that the flow of main pollutants, such as Fe and SO₄ follows the groundwater displacements (Johnson et al., 2000), clean groundwater coming from the western till slope would then wash away the dissolved elements from the zone remediated by a raised groundwater level. This is referred to as the second washout in Figure 7a. If we consider that the groundwater level was raised almost instantaneously in comparison to the groundwater flow, a squared concentration peak should be observed in the pipes around the piezometric dome located around V8. However, the mobilization of the pollutants was probably progressive, leading to the formation of a peak due to the first washout with a delay, also for the pipes located in distant parts of the area with a raised groundwater level, such as pipe D (see Figure 4, increases observed for pipe D). Considering the late decreasing trend of this peak (second washout, marked 3 on Figure 7a) and seen from the surrounding pipes, we can assume that the flow of dissolved elements is equivalent to the flow that would result if a certain amount of dissolved elements were originating from a unique point located around the summit of the hydraulic dome. This model would result in a narrower peak than what should be observed, but this should not influence transfer time calculations much.

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Figure 7a. Illustration of the “washout peak” for a mobile element under the prevailing conditions. At 1, the groundwater has pre-remediation concentration of dissolved elements. At 2, the elements secondarily retained below the oxidation front are remobilised and an increase is observed in the groundwater. At 3, clean groundwater coming from the western till slope (with the same properties as the background water) washes away the mobile elements. At 4, a stable and low level of concentration is reached.

Figure 7b. Hypothetical variations in the dissolved iron content in pipes J and F for the period 1996-2002.
We can then try to calculate the time needed for this washout peak to reach each pipe by estimating the speed of the groundwater flow, which is given by the following formula, derived from the Darcy equation:

\[ V = \frac{Kh}{\alpha l} \]

where \( V \) is the speed of the water, \( K \) is the hydraulic conductivity, \( h/l \) is the hydraulic gradient, and \( \alpha \) is the effective porosity.

The previous hydrological study performed in the field and reported by Axelsson (1986), gave a hydraulic conductivity ranging from \( 2 \times 10^{-5} \) to \( 5 \times 10^{-5} \) m/s. Carlsson (2000) reported a porosity ranging from about 35% to 45% on several solid samples taken from drillings. Depending on the exact location of the piezometric dome, and on the values taken for \( \alpha \) and \( K \) (considering that \( K \) and \( \alpha \) are related), the transfer times vary of about one to two years for each pipe position. The tailing sands were discharged in the impoundment by a water flow originating from a spigotting point located about 100 metres southwest of F and G. The sedimentary processes that occurred resulted in the deposition of more coarse grains in this area, and more fines farther away. The permeability data reported by Axelsson (1986) is an average for the entire impoundment, and the porosity reported by Carlsson (2000) was measured on material located in the centre of the impoundment (P4, see Figure 1). If we take into account these sedimentary processes, we should obtain a smaller porosity and a larger hydraulic conductivity for pipes F and G, and higher porosity and smaller hydraulic conductivity farther away. By taking average values of \( K \) and \( \alpha \), we are then overestimating the transfer time for the pipes located in the south-western part of the impoundment and underestimating the other ones.

Assuming a \( K \) value of \( 3.5 \times 10^{-5} \) m/s, and a \( \alpha \) value of 40%, the maximum of the washout peak should reach pipes D and E about four years after remediation (after raising the groundwater level), one and a half years after remediation for pipes F and G, four years for pipes H and I, three years for pipe J, about six years for pipe O, and four and a half years for pipe M. Calculations for pipes K and L are not given, since the hydraulic conductivity and the porosity of the layers from which groundwater is sampled are not known. These transfer times may explain the observed variation of dissolved metal and metalloids, especially of Fe, S and Mg. These calculations suggest that the washout peak in the area of pipes F and G occurred shortly before the first sampling, and the concentrations have been decreasing since that time, to reach a rather stable level in 1999, three years after remediation (see Figure 7b). This same peak should reach pipes D and E during 2000, explaining the observed regular increases for Fe, Mg, and S, for example. We can thus expect a general decrease for the year 2001 or 2002 in those pipes. In a porous media, the peak shape widens and flattens with increasing distance. For pipe J, the observed increase was quite slow, and the decrease should not be as radical as the one observed in pipe F, as illustrated in Figure 7b. The regular increases found in pipes H and I can be explained by this washout effect as well, and we should observe a decrease for year 2001. Based on the calculations made, the increase observed in pipe J should have stopped in 2000. The observed delay is probably due to the reduced hydraulic conductivity and the increased porosity in distant locations compared to pipes F-G and D-E. However, some decreases were observed for Mn, Ni or Co, which can be either due to local conditions or to a macroscopic separation of different elements of the peak with distance due to adsorption, complexation, and precipitation. The decrease in Co and Ni in pipe J is probably linked to their increase in the underlying till sampled by pipe K, since the pH values and variations measured in both pipes are comparable. This indicates that some vertical transport probably occurs for these elements in this area or at this depth sampled by pipes J and K. Pipe J probably intercepts much of the water coming from the northern part of the impoundment. The unusual behaviour of Zn, showing a stable winter level and increasing summer levels, can then be explained by the washout effect as well. During the seasonal
events an increase in the available dissolved Zn in the surroundings occurs, indicating that even if a Zn peak should reach pipe J, its mobility is limited in time to the high flow periods, probably in relation to a lower pH. Carlsson (2000) reported that a significant part of the Zn in solid tailings is adsorbed onto mineral surfaces, and may be easily remobilised during such events. Based on the assumptions mentioned above, pipes M and O should show washout peaks in 2000 and in 2002, respectively. However, the effect of liming probably masks any increases in pipe M, and O, as a distant pipe should receive a rather flattened peak (probably poorly detectable among the seasonal variations) with some delay.

Conclusions
The measurements of pH and redox show encouraging trends, after remediation. The pH is generally increasing and the redox is generally decreasing across Impoundment 1, where some areas show quicker changes than others. The reactions producing the acid waters and the dissolution of metals and metalloids seem to have slowed down, and a general decrease in the dissolved amounts should be observed on the impoundment within 3 to 4 years, due to the second washout effect caused by clean water from the southwestern slope. The surface water infiltrating through the dry cover does not lead to an important release of pollutants to the groundwater.

Some hypothesis can be suggested about the behaviour of different elements. It seems that Cu, Cd and Pb concentrations in the groundwater decreased drastically with the remediation. They might have adsorbed or co-precipitated due to the imposed change of conditions. The oxidation of sulphides, which was the source of metals, thus seems to have slowed down or stopped. Since the conditions are relatively variable across the impoundment, some elements could be trapped locally because of liming. These traps may constitute secondary sources in the long run. Some elements, like Fe, Mg, and S continue to migrate downward in the tailings from the oxidised zone, as shown by the higher levels registered in shallow pipes. Deeper down, some vertical transport could also affect Ni and Co concentrations, as shown in pipes J and K. It seems, however, that horizontal transport of Fe, S, Mg and to a less extend of Mn, Sr and Ca, are much more important. Zn showed a particular behaviour in some areas, with a high mobility and high capacities of adsorption during winter and desorption during summer. All these elements are released by the washout effect generated by the raising of the groundwater level in the northwestern part, and follow more or less the displacement of the groundwater.

Pipes H and I show a rather different behaviour with high concentrations in metals and metalloids, though they seem affected by the washout effect as well. This is probably caused by an imperfect cover in combination with a complex hydrology with artesian phenomena. The possible role of the organic complexations has to be further investigated. Some improvements in the remediation of the impoundment in this area, such as the addition of a dry cover, could be performed.

In the future, more data are required in order to achieve a better understanding of the importance of the seasonal variations and to identify the long-term trends for various elements.

Acknowledgements
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Investigation of repeated cycles of freezing and thawing effects on a clayey till used as sealing layer over sulphide-rich tailings at the Kristineberg mine, northern Sweden.


Carlsson E., and Elander P.
Investigation of repeated cycles of freezing and thawing effects on a clayey till used as sealing layer over sulphide-rich tailings at the Kristineberg mine, Northern Sweden.

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Abstract:
To minimise oxidation of a sulphide-rich tailings deposit by reducing the flow of oxygen and water into the tailings, remediation actions based on a compacted clayey till as a sealing layer have been implemented at Impoundment 1, Kristineberg mine, Northern Sweden. On top of a 0.30 m compacted clayey till, 1.5 m of unspecified till is used as a protective cover. Possible long-term effects such as cyclic freezing and thawing, are presumed to affect the remediation efficiency by increasing water and oxygen transport into the tailings with time. The objective of this work is to study whether a change in the hydraulic conductivity due to repeated freezing and thawing is significant for the function of the sealing layer. The material used in the investigation was collected during field investigations in 1998 at the impoundment two years following reclamation. In the laboratory, eight repeated cycles of freezing and thawing were performed on four samples of the clayey till, compacted at the same water ratio and to the same compaction degree as during the construction of the sealing layer. After freeze/thaw cycle 1, 2, 4, 6, and 8 the hydraulic conductivity was measured. The results indicated that sealing layers of compacted clayey till can be sensitive to frost penetration. However, three out of four samples showed minor increases in hydraulic conductivity, between 1.2-3.5 times compared to the initial hydraulic conductivity measurement. To control whether the low increase depended on the rather high initial hydraulic conductivity a second series of two permeameters compacted to a maximum degree according to modified Proctor standard was set-up. These two permeameters had very low initial hydraulic conductivity, 3.5-7*10⁻¹⁰ m/s, but after four cycles of freeze/thaw it increased to 8*10⁻⁹ - 1.8*10⁻⁸ m/s. This result indicate that the hydraulic conductivity for a compacted clayey till can vary within a wide range depending on e.g. compaction rate. The sensitivity to freeze/thaw actions also depends on the initial hydraulic conductivity according to this investigation. The obtained difference in this study between samples with limited compaction (95% of modified Proctor maximum) and fully compacted samples using the modified Proctor compaction was 2-3 orders of magnitude in hydraulic conductivity. After being subject to freeze/thaw actions this difference decreased.

Introduction
For remediation of sulphide-rich mine tailings two main methods are used in Sweden, soil cover and wet cover. The objective of both types is to prevent oxygen diffusion into the waste. For dry cover a number of different designs has been tried out with various results during the past decades (Aubertin et al., 1997; Bell et al., 1994; Lundgren, 1995; Lundgren, 1997; MEND, 1994; Tremblay, 1994).
For the construction of low permeability barriers on mine waste, clayey till is the commonly used soil material in Sweden. To clarify how the hydraulic conductivity (permeability) of such a material responds to repeated cycles of freezing and thawing, and to which depth frost may penetrate, studies are performed within the Swedish research programme MiMi (Mitigation of the Environmental Impact from Mining Waste) (MiMi 2000). It is assumed that an increase in hydraulic conductivity also will lead to an increased diffusion of oxygen.

Studies of the effects of cyclic freezing and thawing on fine-grained soils often show an increase in hydraulic conductivity caused by altered geotechnical properties and soil structure. Such alterations may include changes in volume, strength, compressibility, mechanical properties, and formation of cracks and particle movements (Chamberlain et al., 1990; Benson and Othman, 1993; Benson et al., 1995).

In Viklander and Knutsson (1997) and Viklander (1998) laboratory studies of the effects of frost penetration on a fine-grained (silty) till with low clay content was performed. The results showed changed hydraulic conductivity but no significant particle movements for till exposed to 10-18 cycles of freezing and thawing. For samples having initial large void ratio (a loose structure) the hydraulic conductivity decreased 1.4 to 50 times while samples with smaller void ratios (a dense structure) gave hydraulic conductivity increase in the range of 1-11 times.

The present investigation was initiated to verify whether the observations made by Viklander and Knutsson (1997) and Viklander (1998) on fine-grained till is due also for clayey till that is suitable for sealing layers.

**Area description**

The Kristineberg mining area is located in the western part of the Skellefteå ore district, approximately 120 km west of Skellefteå in Northern Sweden (Figure 1). The largest orebody in the area is the Kristineberg Zn-Cu deposit, which was discovered in 1918. It was not until 1940 that Boliden Mineral AB started mining activities, and mining is still in progress. The annual precipitation in the area varies between 400 and 800 mm/y (Axelsson et al., 1991) and the annual mean temperature is 0.7°C (Axelsson et al., 1986). The vegetation consists mainly of coniferous forest, but some deciduous forest is also present in the area. Boglands are common. The major soil type in the area is podzol weathered till (Granlund and Wennerholm, 1935; Granlund, 1943).

Five tailings impoundments are located within the Kristineberg mining area. As many as 10 different ores from the western part of the Skellefte mining district were processed in the processing plant, and thus the impoundments contain a mix of several different kinds of tailings. Impoundment 1 was investigated in this study (Figure 1). It is the oldest within the mining area. It has a surface area of about 0.10 km² and was used for disposal of tailings until the early-1950s (Boliden Mineral AB, 1995). The impoundment is located in a valley and underlain by peat and till. The thickness of the tailings ranges from a few metres to approximately 11 m. The average thickness is between 6 and 8 m. The unoxidised tailings contain high concentrations of metals and metalloids with average values of 183 ppm As, 21.5 ppm Cd, 56.4 ppm Co, 956 ppm Cu, 463 ppm Pb, 14.4 wt% S, and 8861 ppm Zn.
In 1996 the impoundment was remediated by application of till coverage, the groundwater table was raised, and the site was finally seeded with grass (Lindvall et al., 1999). In water saturated areas of the impoundment 1 m of unspecified till is used as a protective cover. In areas with unsaturated tailings a 0.3 m sealing layer of compacted clayey till was constructed as an oxygen barrier. The barrier was covered by 1.5 m of till as protection against superficial processes, e.g. erosion, frost, and root penetration, that may affect it’s efficiency. During the construction of the compacted clayey till, cobbles and gravel larger than 100 mm in diameter were excluded. The compacted clayey till layer was compacted in two 0.15 m lifts. The quality demand for the compaction was 93% of modified Proctor maximum ($R_D$), Eq. 1.

$$R_D = \frac{\rho_D^{\text{in-situ}}}{\rho_D^{\text{max}}}$$

$\rho_D^{\text{in-situ}}$ is dry density measured after compaction in the field and $\rho_D^{\text{max}}$ the corresponding maximum dry density obtained in laboratory compaction according to the Modified Proctor procedure (ASTM D-1557).

The quality control during construction of the sealing layer consisted of Troxler measurements (measurements of density based on absorption of gamma radiation) to verify compaction results and test pits to verify layer thickness for every 2000 m² of sealing layer constructed.

In the protective cover boulders larger than 50 cm were removed. A few years after remediation the impoundment is now almost completely covered by grass.
Materials and methods

Material collection and characterization
During field installations in October 1998 disturbed samples of the compacted clayey till layer were collected in situ from Impoundment 1. The collected compacted clayey till was characterized with regard to grain density, modified Proctor tests and particle size distribution. These results were compared to available pre-remediation data for the clayey till material (Mattson 1992) to verify sample representativity. The clay content in the pre-remediation investigations showed an average of 7.7 wt%. For the material collected in situ at Impoundment 1 and used in the four permeameters the clay content as well as most of the other soil fractions, according to Figure 3, is within the shaded area representing the spread of the samples analysed in the pre-remediation study by Mattson (1992). The compacted clayey till was dried and re-wetted to the desired water content prior to compaction into the permeameters.

Table 1 Characteristics for the clayey till

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Clayey till</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρs</td>
<td>2.71 ton/m³ (metric)</td>
</tr>
<tr>
<td>ρD max (modified Proctor)</td>
<td>2.19 ton/m³ (metric)</td>
</tr>
<tr>
<td>wopt (at ρD max)</td>
<td>6.3 wt%</td>
</tr>
<tr>
<td>RD in-situ (Troxler control)</td>
<td>96.5%</td>
</tr>
<tr>
<td>win-situ</td>
<td>7.3 wt%</td>
</tr>
</tbody>
</table>

Figure 2 modified Proctor compaction curve

Figure 3 Particle size distribution for collected sealing layer material used in the freeze/thaw set-up. Shaded area indicates sample spread in pre-remediation investigation by Mattson (1992). Dotted lines indicate particle size distributions for clayey till from Impoundment 1.
Laboratory set-up and methodology

After verification of the representativity of the sampled material a first series of four rigid wall permeameters were prepared for freezing/thawing experiments by two different set-ups. The compactions of the samples were performed in five layers and aimed at reaching the average compaction level obtained in field. A weight was dropped on a rod from a given distance with the same level of energy as for a modified Proctor compaction. After compaction of each layer the density was calculated, to verify that the desired compaction rate was achieved for the sample. When all layers were compacted the overall compaction level could be estimated for the samples (Table 2). Spare soil from the compaction was used to determine the water content in the soil. Since three different batches of soil were used, the water content deviated slightly between the four permeameters. Three of the permeameters were compacted slightly on the wet side and one close to the optimum water content. According to modified Proctor compaction tests optimum water content is about 6.3 wt%, giving a maximum dry density of 2.19 metric ton/m$^3$.

Table 2 Compaction rate and water content during the initial sample set-up. R_D defined according to equation 1.

<table>
<thead>
<tr>
<th>Permeameter</th>
<th>Type</th>
<th>Compaction rate (R_D):</th>
<th>Water content (w):</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Small, non-transparent</td>
<td>95.9 %</td>
<td>7.38 wt%</td>
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<tr>
<td>4</td>
<td>Small, non-transparent</td>
<td>97.2 %</td>
<td>7.38 wt%</td>
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<tr>
<td>C</td>
<td>Large, transparent</td>
<td>95.3 %</td>
<td>6.47 wt%</td>
</tr>
<tr>
<td>U</td>
<td>Large, transparent</td>
<td>96.2 %</td>
<td>6.88 wt%</td>
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</tbody>
</table>

The second series consisted of two samples compacted to a maximum degree at a water content of 7.92 wt% according to the modified Proctor standard. These permeameters were similar to permeameter 3 and 4 in the first series. One of these two samples (MF) consisted of clayey till collected from the till pit and was also used to refill the field installation area. The other sample (MP2) was from the batch used in the first series and thus collected from the sealing layer at Impoundment 1.

Two different methods were used for freezing and thawing the samples. Both methods presumed one-dimensional (1-D) freezing from the top of the permeameter. At the sides, the permeameters were insulated, and the base was at level with the water table, enabling pore water suction into the soil sample through the bottom valve during freezing, a so-called open system. This set-up was presumed to mimic freezing and thawing in the field reasonably well. The first method was based on the use of ambient air as a freezing medium using the large (110 mm inner diameter) transparent permeameters C and U (Figure 4). For this method an ambient air temperature of −5°C was applied during freezing and a temperature of +5°C during thaw. The second method used an alcohol/water mixture, circulating inside specially-designed caps, as the freezing/thawing medium (Figure 4). For this method the smaller (50 mm inner diameter) non-transparent permeameters 3 and 4 were used. Ambient air temperature in this case during both the freezing and thawing was +2°C and the freeze/thaw temperature was −5°C and +5°C respectively.

To prevent unwanted effects during compaction due to large grains in the selected soil, compared to the diameter of the permeameters, it was decided that the samples should consist of soil particles ≤20 mm. After sieving it was evident that, in the selected soil, only a small amount of soil particles were larger than 20 mm. The chosen degree of compaction for the first series (R_D=96%, water content 7 wt%) was based on average Troxler measurements in field during the full-scale remediation in 1996. Using the modified Proctor compaction curve a density corresponding to the Troxler readings was calculated and the permeameters were
compacted as near the desired level of compaction as possible and at the desired water content, as described above. Prior to the compaction the inner walls of the permeameter were greased to prevent seepage during the hydraulic conductivity measurements. The larger transparent permeameters C and U could be controlled visually for cracks and leakage during the water saturation as well as during the measurements. For the smaller non-transparent permeameters no such visual control could be made but intermediate changes in hydraulic conductivity during measurement could be used to indicate seepage around the walls of the container and/or sample contraction during measurement.

![Permeameter Diagram](image)

**Figure 4** Freeze/thaw set-up. The ambient air froze the left permeameter and the alcohol/water mixture froze the permeameter to the right.

During the freezing/thawing experiment the permeameter samples carried an overburden pressure corresponding approximately to the load of 1.5 m of till (33 kPa). The load was applied by inserting a pipe with a slightly smaller diameter than the inner diameter of the permeameter onto the top cap (for the larger permeameter) or atop of the freezing puck (for the smaller permeameter). The load was then applied to the pipe.

After the initial hydraulic conductivity measurement eight freeze/thaw cycles were performed for the first series and four for the second. The freeze/thaw cycles were performed as follows: 1) Freezing of the samples during at least one week. When inserting the samples in the water bath, air trapped in the valve below the water table was evacuated by flooding it with a syringe filled with water attached to a fine tubing. 2) After freezing, the permeameters frozen by the ambient temperature were moved to a refrigerator with a temperature of +5°C. The permeameters frozen by the cooled liquid were thawed by increasing the temperature of the liquid to +5°C. The thawing continued for at least one week. 3) Before the next hydraulic conductivity measurement the permeameter was adjusted to 20°C about one day prior to the start of the measurement to adjust to measurement temperature. At this stage the top caps were
installed, fixated and the load was removed. The fixation of the sample was done to prevent alteration prior to and during the hydraulic conductivity measurement.

The vertical saturated hydraulic conductivity was measured using a back-pressure technique in a triaxial apparatus. Prior to every measurement the sample was saturated with water through the bottom valve at a low pressure (6-8 kPa) to get rid of possible air trapped in the sample. During the actual measurement intermediate volume and time readings were performed to ascertain whether the hydraulic conductivity changed during the measurement. Normally the hydraulic conductivity varied less than 10 % as an average for all intermediate measurements and no obvious trend was visible. Pressure levels used depended on the sample length. This is due to the constant pressure gradient used for all samples. The total pressure applied in the first series of freeze/thaw (54-60 kPa) was the applied back-pressure (33 kPa) plus the required pressure to obtain the chosen pressure gradient, \( i = 15 \) where \( \Delta h \) represents the pressure difference and \( l \) the sample length, Eq. 2.

\[
i = \frac{\Delta h}{l}
\]

were \( \Delta h \) and \( l \) are in the unit m

For the second series a higher saturation pressure was applied (80 kPa) and during the measurement a gradient of 57 was used resulting in a total pressure of 83 (MF) and 97 (MP2) at the same back-pressure as for the first series. At present four cycles of freeze/thaw has been made. The increased gradient was used due to the lower hydraulic conductivity in these samples.

Hydraulic conductivity measurements for the first series were conducted for the cycles 0, 1, 2, 4, 6, and 8. When the eight cycles were completed, the four permeameters were saturated once again from bottom up at low pressure. Then the samples were sliced from bottom to the top in about two-cm thick slices. The slices were dried and the water content calculated. For two of the permeameters (3 and 4), the density of the clayey till was determined.

Results

As can be seen from Figure 5, the overall changes in hydraulic conductivity during the eight cycles for three out of four permeameters in the first series may be considered as minor. If the hydraulic conductivity values are normalised towards the initial measurement for the permeameter, the ratios presented in Figure 5 are obtained. The non-dimensional parameter \( HC_{\text{Norm}} \) is defined as the ratio between the hydraulic conductivity obtained in the thawed soil after \( N \) cycles of freeze/thaw (\( k_N \)) and the hydraulic conductivity measured in unfrozen soil (\( k_0 \)), Eq. 3.

\[
HC_{\text{Norm}} = \frac{k_N}{k_0}
\]

were \( k_N \) and \( k_0 \) are both in m/s

From Figure 5 it can be concluded that the kind of permeameter used does not seem to affect the initial or the final results. The three permeameters 3, U, and C converge towards the same level of hydraulic conductivity after cycle 2. In cycle 4 and 6 these samples continue to stay within the same range until cycle 8, when they converge towards a hydraulic conductivity slightly higher than the level after 2 cycles. After the final cycle all exhibit a hydraulic conductivity of about \( 1.2*10^{-7} \) m/s. Permeameter 4 hardly seem to be affected at all. It is more or less stable at around \( 2.0*10^{-8} \) m/s during the eight cycles. From the \( HC_{\text{Norm}} \)-ratio it is evident that permeameter C exhibits the largest change with a hydraulic conductivity increase of around 3 times after eight cycles. The permeameters 4 and U also increase, but less than 1.5 times while permeameter 3 is the most stable throughout the freeze/thaw cycles according to the \( HC_{\text{Norm}} \)-ratio.
The water content (w) of the sliced samples and the calculated porosity (n) after eight freeze/thaw cycles are presented in Figures 6 and 7, respectively. Note that the data are presented as a function of slice number, not length. Slice 1 represents the bottom slice and the highest number the top slice of the sample. Both the water content and thus also the porosity possibly exhibit a minor increase, in general, with increasing slice number but the increase is not statistically significant due to the large variations within each permeameter.

\[
n = 1 - \frac{\rho}{\rho_s (w + 1)} \tag{4}\n\]

If \( \rho \) (bulk density) is presumed equal with \( \rho_{\text{sat}} \) (saturated density) after the saturation of the sample, then \( \rho \) can be derived by the use of Eq. 5.

\[
w = \frac{1 - \rho_{\text{sat}}/\rho_s}{\rho_{\text{sat}}/\rho_w - 1} \tag{5}\n\]

Calculated porosity is in the range of 0.200-0.245.
Between the freeze/thaw cycles the changes in sample length was monitored. The change in sample length was used to calculate porosity and void ratio.

Table 3 Sample length after freeze/thaw cycle

<table>
<thead>
<tr>
<th>Permeameter</th>
<th>0 (Initial length)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
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<tbody>
<tr>
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<tr>
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</tr>
<tr>
<td>U</td>
<td>142</td>
<td>144</td>
<td>144</td>
<td>145</td>
<td>145</td>
<td>142</td>
</tr>
</tbody>
</table>

The two samples, MF and MP2, compacted to a maximum $R_D$ exhibit a quite different behaviour compared to the four samples compacted to a lower degree. Prior to the first freeze/thaw cycle it is evident that these samples obtained a much lower initial hydraulic conductivity. The permeameter MF had $3.54 \times 10^{-10}$ m/s and MP2 $6.97 \times 10^{-10}$ m/s. At present, four cycles of freeze/thaw has been made and an increase in hydraulic conductivity of 23 times for MF to $8.49 \times 10^{-9}$ and almost 25 times for MP2 to $1.73 \times 10^{-8}$ is detectable. Freezing and thawing will continue until eight cycles has been performed or more.
Discussion

The initial hydraulic conductivity in the first series of freeze/thaw experiments is higher, about $10^{-7}$-$10^{-8}$ m/s, as compared to an average of $1.1\times10^{-9}$ m/s in the investigation prior to the remediation, by Mattson (1992). Most likely this difference depends on different compaction of the samples and also possibly by using different measuring techniques and pressure gradients. The compaction level, as well as the hydraulic gradient used in measurements of the hydraulic conductivity in the pre-remediation investigation, is not presented by Mattson (1992). For the fully compacted samples MF and MP2 a significantly lower initial or pre-freeze/thaw hydraulic conductivity was found. The difference in compaction level might be the reason for the initially lower hydraulic conductivity. However, measurements after the following freeze/thaw cycles show that, when compacted to a high degree of compaction, the (low) hydraulic conductivity of a clayey till most probably is affected by freeze/thaw actions. The fact that no significant or only minor changes occurred for the samples 3, 4, C, and U in the first test series, possibly show that the initial hydraulic conductivity coincided with a possible “residual” hydraulic conductivity level that the clayey till achieve after freeze/thaw actions. This explanation is supported by the results presented by Viklander and Knutsson (1997) and Viklander 1998.

According to Benson and Othman (1993) an over-burden pressure could prevent a change in the hydraulic conductivity by limiting the growth of ice lenses, since the negative pore pressure in the frozen fringe is reduced. The hydraulic conductivity of the frozen fringe is also reduced, and after thawing the voids are compressed and the hydraulic conductivity is thereby reduced. The change in hydraulic conductivity due to freeze and thaw actions is less as a higher overburden pressure is applied. However, the overburden pressure of 33 kPa used in this study is low compared to the overburden pressure applied by Benson and Othman (1993). In that investigation, an overburden pressure of 70 kPa was applied during freezing and thawing and no change in hydraulic conductivity was observed. On the other hand, Ravaska and Kujala (1997) found that an overburden pressure of 15 kPa, was too low to re-compact soil-bentonite mixtures affected by freeze/thaw cycles, and the hydraulic conductivity thereby exhibited a considerable increase. The increase for the second series in the present investigation indicate that a load approximately corresponding to 1.5 m of till is not sufficient to prevent freeze/thaw effects in the clayey till, resulting in an increased hydraulic conductivity.

As can be seen from Figure 5, the largest change in hydraulic conductivity for the first series occurred in sample C, which also had the lowest degree of compaction. According to the modified Proctor compaction curve, this sample was compacted close to optimum water content. Generally, when a soil is compacted in the field it is considered common practice to do this slightly on the wet side since clayey sealing layers generally exhibit a lower hydraulic conductivity when compacted slightly on the wet side (Mitchell et al., 1965). This is common practice although the same dry density might be obtained at both the dry side and the wet side. In a dry soil the grain skeleton is easier to disturb since there are no capillary forces increasing the strength in the soil. Thus larger settlements might develop in a dry soil compared to a wet one (Viklander 1997).

The height changes for the samples during the freeze/thaw cycles make it possible to calculate the void ratio using Eq. 6, since the amount of dry till used in the permeameter and the level of compaction are known. It is assumed that the volume of soil is constant ($V_s$) and that the variable parameter is the pore volume ($V_p$).

$$ e = \frac{V_p}{V_s} $$

(6)
From Figure 9 it is possible to conclude that, for most of the permeameters, the largest increase in the void ratio occurred in freeze/thaw cycles 2 to 4. Towards the end of the freeze/thaw period a decrease in the void ratio is visible. Only test C exhibits a considerably higher void ratio after eight completed cycles of freeze/thaw.

![Figure 9 Void ratio versus freeze/thaw cycle](image)

The fact that permeameters 3, 4, and U converge towards the same void ratio, around 0.265-0.275, might indicate that these samples follow the relationship derived by Viklander (1998), where a fine-grained till with initial void ratios between 0.25 and 0.42 tended to move towards a “residual” void ratio after repeated freezing and thawing independent of the initial one. The till in the investigation by Viklander was quite similar to the till used in the sealing layer at Impoundment 1 in Kristineberg, although the clay content is lower. The obtained residual void ratio in the investigation by Viklander (1998) was 0.31. Permeameter C obtained a final void ratio close to this value, this might depend on the similarities in particle size distribution between the two soils although the clay content in general was lower in the till used by Viklander. Changes in hydraulic conductivity for dense soils (low initial void ratios) in the investigation by Viklander (1998) exhibited an increase in the range of 1-10 times. The soil used in this investigation had increased hydraulic conductivity in the range of 1-3.5 times, which is within the same range. A difference between these two investigations was the overburden applied (33 kPa) in this investigation, which will to some extent decrease the impact of freeze/thaw. Another difference is that, in this investigation, the permeameters were frozen in an open system, whereas Viklander used a closed system.

No measurement of soil temperature inside the permeameter was made during the freezing, but, based on previous experience from freeze/thaw tests, it is presumed unlikely that both freezing methods have failed to freeze the samples. The lower porosity in the bottom slices of the permeameters are most likely caused by the compaction in successive layers, that may lead to a higher compaction degree in the lower layers. Water ratios in the sliced samples are quite homogenous through the length of the samples, but a possible increase in the upper part is visible. This is probably also an effect of the compaction procedure, which affected the porosity. A higher porosity enables higher water content within the soil.

**Conclusions**

Based on the hydraulic conductivity measurements it can be concluded that clayey till can be susceptible to freeze/thaw effects affecting the hydraulic conductivity. In all four samples a change in void ratio and porosity can be traced under the eight cycles of freeze/thaw. Although
these changes are visible, the change in hydraulic conductivity for the samples, except for C, may be considered negligible. For most of the samples, the void ratio and porosity decreases during the final cycles. This could indicate that a normalisation/stabilisation within the samples occurs with regard to freeze/thaw effects. It is thus possible that the same soil, compacted to a higher degree of compaction and a lower hydraulic conductivity, will show a much higher sensibility to freezing and thawing. The result from the second test series makes this assumption probable since the increase for both samples after four cycles of freeze/thaw is about 25 times.

It is also evident from the results that the hydraulic conductivity for a clayey till can vary within a wide range depending on relatively small differences in compaction results. This further underlines the (well-known) importance of appropriate investigations of the sealing layer material prior to remediation, and appropriate construction requirements and control.

Future work
Presently, effects of freezing and thawing on water infiltration and oxygen transport through a barrier of compacted clayey till are being studied in field (Werner et al., 2001). For these studies, three different test areas with different thickness of the protection cover have been constructed. Besides observation with time of water and oxygen flow through the different barriers, soil temperature profiles and frost depth variations are measured. To be able to evaluate the behaviour also climate conditions (precipitation, snow accumulation, air temperature and humidity and solar radiation) are observed with time. Field data will be evaluated using the laboratory results on the effects of freeze/thaw for the clayey till.

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References


Oxygen- and water fluxes into a soil-cover remediated mill tailings deposit: Evaluation of field data from the Kristineberg mine site, Northern Sweden.


Werner K., Carlsson E., and Berglund S
Oxygen and water fluxes into a soil-cover remediated mill tailings deposit: Evaluation of field data from the Kristineberg mine site, Northern Sweden

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Abstract: Oxygen and water fluxes into a soil-cover remediated mill tailings deposit at the Kristineberg mine site in Northern Sweden are estimated by evaluating field data from oxygen and water lysimeters and oxygen probes. The results of the evaluation are used in combination with data on groundwater levels and local precipitation to identify critical processes controlling the fluxes of oxygen and water, and hence the generation and transport of contaminants within the tailings. The results of the study show that in the investigated part of the deposit the diffusion coefficient in the soil cover (and the associated oxygen flux) is small and that it exhibits seasonal variability. The measured water infiltration, and thereby the groundwater recharge, is also small within the studied area. Hence, the results indicate that the composite soil cover provides an efficient oxygen and water barrier. The field data also suggest that oxygen fluxes are strongly influenced by periodic accumulation of water in the protective (upper) cover layer. In the case of the soil cover being an efficient water barrier, temporal fluctuations of the groundwater level in the tailings may be a dominant factor for contaminant recharge into the groundwater. Hence, observation of groundwater levels in the soil cover and in the tailings may provide key components in monitoring of soil cover remediation performance.

Background and Site Description

In recent years, there has been a growing interest in the efficiency of different methods to reduce the leaching of acidity, heavy metals and other potentially hazardous substances from sulphide-bearing mill tailings. The primary factor controlling contaminant generation within sulphidic tailings is commonly considered to be oxygen diffusion in air-filled pores within the water-unsaturated zone of the tailings. Further, contaminant recharge into the groundwater takes place by means of unsaturated water flow and/or groundwater level fluctuations in the tailings.

Soil-cover remediation means that the tailings deposit is remediated by application of an oxygen and water barrier, which aims to reduce the fluxes of oxygen and water into the tailings and thereby decrease the discharge of contaminants to the surrounding...
environment. Hence, the estimation of field-scale oxygen and water fluxes is a necessary component of performance assessment of soil-cover remediation. Previous studies of soil-cover effects for mill tailings have mainly focused on the estimation of oxygen (e.g. Nicholson et al., 1989) or water fluxes (e.g. Herbert, 1992) into the tailings. However, relatively few studies have been reported on site specific and coupled soil-cover effects on oxygen and water fluxes.

The aim of the Swedish research programme MiMi (Mitigation of the Environmental Impact from Mining Waste) is to develop new and improved methods for remediation of mining waste (MiMi, 2000). Mill tailings impoundment 1 (Fig. 1a) at the Kristineberg mine site, situated approximately 120 km west of Skellefteå in Northern Sweden, was the main study object within the first phase (1998-2000) of the MiMi programme. Sulphide-bearing tailings were deposited into the impoundment during the 1940s. In 1995-96, the impoundment was remediated by application of till cover layers as an oxygen and water barrier, and part of an upstream cut-off ditch was sealed in order to reduce the depth of the water-unsaturated zone within the tailings (Lindvall et al., 1999).

![Figure 1a. Mill tailings impoundment 1 at the Kristineberg mine site.](image)

![b. Overview of the installation area on impoundment 1.](image)

Laboratory investigations of the clayey till used in the lower layer of the composite cover showed an average clay content of about 8 % and an average hydraulic conductivity after compaction of approximately $10^{-9}$ m s$^{-1}$ (Lindvall et al., 1999). The effects of remediation on the geochemical conditions within the impoundment were investigated by Carlsson (2000), who concluded that contaminants are retained above the mean groundwater level in the tailings, and are remobilized due to fluctuations of the groundwater level. Werner
found that the actual, overall remediation effects on the impoundment are likely to be influenced by the degree of heterogeneity in the hydraulic properties of the soil cover, as well as by spatio-temporal variations of the groundwater level. Both these factors affect the conditions for transport of oxygen and contaminants within the tailings.

The purpose of this study is to evaluate some of the post-remediation field data collected during the period 1998-2000 in order to assess the effects of the remediation on oxygen and water fluxes into the tailings. Moreover, the evaluation also aims to identify critical factors controlling these fluxes, and hence some key issues for relevant monitoring of soil-cover remediation performance.

Field Installations and Data Collection

In order to quantify the fluxes of oxygen and water through the composite cover into the tailings, field installations were made in the composite soil-covered part of the impoundment (see Figs. 1a-b and 2). For quantification of the diffusion coefficient in the composite cover, three oxygen lysimeters (named OL1-OL3) were installed below the low-permeable till layer, with a protective till layer depth varying between 1.5 m at OL1 and 0.3 m at OL3 (see Fig. 2). About 0.5 m below the low-permeable till layer, three water lysimeters (WL1-WL3) were installed to quantify the infiltration of water through the cover. Further, two oxygen probes (OP3 and OP10) were installed and used for measurement of gas-phase oxygen concentrations in the tailings immediately below the low-permeable till layer.

In order to investigate whether water accumulates within the cover, nine groundwater observation wells (Mv1-Mv9) were installed in the protective till layer, each with a water intake screen immediately above the low-permeable till layer. A weather station, including a rain gauge (RG1; Environmental Measurements Ltd. ARG100), was set up at the installation area, and a similar rain gauge (RG2) was also set up approximately 2 km from impoundment 1. The previously installed groundwater observation well V7 (see Fig. 1b) is located in the installation area and was used to measure the groundwater level in the tailings.

Figure 2. Schematic cross-section of the installations on impoundment 1.
The lysimeters (OL1-OL3 and WL1-WL3) are open upwards, and each lysimeter has a total volume of 1.6×1.6×0.2 m$^3$. The oxygen lysimeters (OL1-OL3) are sealed against the low-permeable till layer and against the tailings with concrete and bentonite powder, filled with cleaned quartzite, and covered with a geotextile layer. Two pipes are connected to two opposing sides to allow circulation of gas through each lysimeter and measurement of the gas composition, and a water drainage pipe is connected to the bottom of the lysimeter to prevent flooding. The bottom of the water lysimeters (WL1-WL3) consists of a drainage layer of quartzite between two geotextile layers, and the lysimeters are filled with tailings to prevent capillary barrier effects. A single pipe is connected to one of the corners, and each water lysimeter is slightly angled towards the pipe to facilitate pumping of water.

After the oxygen lysimeter installation, about 4 m$^3$ of N$_2$ gas was circulated through the two connected pipes to ensure a close-to-zero initial oxygen concentration within the lysimeters. The outgoing N$_2$-O$_2$ gas mixture was evacuated into an open water vessel to create an atmospheric total gas pressure within the lysimeters before the gas circulation system was closed. During the period until the next oxygen concentration measurement, diffusion of oxygen through the composite soil cover partly replaces the nitrogen gas within the lysimeters.

The oxygen probes (OP3 and OP10) consist of a quartzite-filled geotextile bag, and the oxygen concentration is measured at the ground surface in a pipe connected to each bag (Fig. 2). A thermistor (not shown in Fig. 2) was also installed at the same depth as OP3 and OP10 to measure the temperature within the tailings. An ANSTO Portable Automatic Oxygen Analyser and a fuel cell (Teledyne Class B-1) were used to measure the oxygen concentration in the oxygen lysimeters and in the oxygen probes. Before each measurement, the instrument was zero-calibrated in N$_2$ gas and thereafter allowed to stabilize in the open air. In order to obtain a stable concentration value, the gas mixture to be measured was pumped through the instrument in three separate series, each with three concentration readings.

Evaluation of Field Data

Oxygen fluxes

The diffusive oxygen flux $F_c$ [ML$^{-2}$T$^{-1}$] through the composite soil cover can be calculated according to

$$F_c(t) = D \frac{C_0 - C_{lm}}{\Delta z_c}$$  \hspace{1cm} (1)

where $D$ is the effective diffusion coefficient [L$^2$T$^{-1}$] in the cover, $C_{lm}$ is the oxygen concentration [ML$^{-3}$] in the oxygen lysimeter at time $t$, and $\Delta z_c$ is the depth of the cover. In the present study, a simple analytical model is adopted to estimate $D$ in the cover, using the oxygen concentration measured in each oxygen lysimeter as input. Assuming
that the gas flux takes place under quasi steady-state conditions, Cussler (1984) showed that an approximate expression for $D$ in a porous layer can be obtained by combining equation (1) with mass balances for two well-stirred volumes separated by the layer. The oxygen flux into the oxygen lysimeter (with void volume $V_v$ and cross-sectional area $A$) is

$$F_c(t) = \left( \frac{V_v}{A} \right) \frac{dC_{lm}}{dt}$$

(2)

For the initial condition $C_{lm}(0) = 0$, i.e. zero oxygen concentration within the lysimeter immediately subsequent to circulation with N$_2$ gas at $t = 0$, combination of (1) and (2) yields (cf. Cussler, 1984)

$$C_{lm}(t) = C_0 \left[ 1 - \exp(-\beta t) \right]$$

(3)

where the atmospheric oxygen concentration $C_0 = 20.95$ vol-% and $\beta \equiv AD/V_v \Delta z_c$.

Rearranging (3), the expression for $D$ is

$$D = \ln \left( \frac{C_0}{C_0 - C_{lm}(t)} \right) \frac{V_v \Delta z_c}{At}$$

(4)

Table 2 below shows values of $D$ calculated by (4) with $t = t_p$, where $t_p$ is the period between N$_2$ gas circulation (at $t = 0$) and measurement of $C_{lm}$, for different measurement periods in the three oxygen lysimeters OL1-OL3. It should be noted that even though $D$ can be expected to vary with time (attributed to a time-dependent water content within the cover), (4) assumes temporally constant parameters. Hence, the values of $D$ in Table 2 should be interpreted as “effective” values for the specified periods. In (4), the cross-sectional area of each lysimeter is $A = 2.56$ m$^2$, and the void volume (total volume times the porosity) $V_v \approx 0.237$ m$^3$ (E. Carlsson, unpublished data). Since only small volumes of water infiltrated into the lysimeters during the investigated periods (see the next section), the reduction of $V_v$ with time is neglected in the analysis.

<table>
<thead>
<tr>
<th>Period</th>
<th>$t_p$ (days)</th>
<th>$C_{lm}$ (vol-%)</th>
<th>$D$ ($\times 10^{-5}$ m$^2$ d$^{-1}$)</th>
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<td>99/08/24-00/03/29</td>
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</tr>
<tr>
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<td>39</td>
<td>0.22</td>
<td>4.58</td>
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</table>

Table 2. Values of $D$ in the composite cover calculated by equation (4).

OL1 ($\Delta z_c = 1.8$ m)
Table 2. Continued.

OL2 (Δz_c = 1.3 m)

<table>
<thead>
<tr>
<th>Period</th>
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<th>C_{lm} (vol-%)</th>
<th>D (×10^{-5} m^2 d^{-1})</th>
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<tbody>
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OL3 (Δz_c = 0.6 m)

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<th>Period</th>
<th>t_p (days)</th>
<th>C_{lm} (vol-%)</th>
<th>D (×10^{-5} m^2 d^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>00/05/29-00/06/05</td>
<td>7</td>
<td>0.62</td>
<td>23.91</td>
</tr>
<tr>
<td>00/06/05-00/08/18</td>
<td>74</td>
<td>0.63</td>
<td>2.28</td>
</tr>
<tr>
<td>00/08/18-00/09/26</td>
<td>39</td>
<td>0.86</td>
<td>5.97</td>
</tr>
</tbody>
</table>

^1yr/mth/day. ^2Measurements could not be taken during the cold winter period.

The results in Table 2 show that the estimated values of D are low, on the order of 10^{-4} m^2 d^{-1}. As expected, D varies with time, being approximately one order of magnitude lower (10^{-5} m^2 d^{-1}) during some periods. Accounting for diffusion in both air- and water-filled pores at high water content, Collin and Rasmuson (1988) used a constitutive relationship to calculate D as function of the water saturation S = water content/porosity. For instance, for a porosity of 0.5 they showed that D decreases from about 5×10^{-4} to 5×10^{-6} m^2 d^{-1} when S increases from 0.9 to 1. Hence, Table 2 suggests that the soil cover remained at high or complete water saturation during the investigated periods.

The gas-phase oxygen concentration, C_{interface}, was measured in two oxygen probes (OP3 and OP10; see Figs. 1b and 2), located at the cover/tailings interface. By use of (1), the values of C_{interface}, combined with the values of D in Table 2 allow estimation of the oxygen flux through the cover, F_c. Table 3 below shows F_c calculated by (1), with C_{lm} replaced by C_{interface} and with Δz_c = 1.8 m (cf. Fig. 2). The equation of state for an ideal gas (C_M = p/RT), assuming that the total gas pressures are atmospheric, was used to convert the gas-phase oxygen concentrations into units of M = mol m^{-3}. Temperature data from the thermistor and the local weather stations (see the previous section) were used to obtain T.

Table 3. Estimated values of F_c using (1) with D at OL1 from Table 2.

<table>
<thead>
<tr>
<th>OP3</th>
<th>C_0 (mol m^{-3})</th>
<th>C_{interface} (mol m^{-3})</th>
<th>F_c (×10^{-4} mol m^{-2} d^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>00/03/29</td>
<td>9.19</td>
<td>0.084</td>
<td>0.25</td>
</tr>
<tr>
<td>00/05/18</td>
<td>8.92</td>
<td>0.065</td>
<td>2.2</td>
</tr>
<tr>
<td>00/06/05</td>
<td>9.08</td>
<td>0.031</td>
<td>1.7</td>
</tr>
<tr>
<td>00/09/26</td>
<td>9.23</td>
<td>0.24</td>
<td>0.23</td>
</tr>
</tbody>
</table>
The calculated values of $F_c$ are on the order of $10^{-3}$ mol m$^{-2}$ d$^{-1}$ or less, exhibiting temporal variations of the same magnitude as those for $D$ (Table 2). The values of $F_c$ in Table 3 are about 2-3 orders of magnitude lower than those reported by Elberling and Nicholson (1996) for uncovered oxidized tailings at a mine site in Canada with a groundwater table depth of 0.65 m. Further, they reported that a 0.2 m thick cover, consisting of fine sand, reduced the oxygen flux by 2 orders of magnitude compared to uncovered conditions.

**Water fluxes**

The water infiltration $I$ [L] into the tailings during different periods was calculated as the volume of water accumulated in each of the water lysimeters WL1-WL3 during these periods divided by their respective cross-sectional areas. The results showed that $I$ was between 0 and 5% of the precipitation measured in the rain gauges RG1 and RG2. These results indicate that most of the precipitation is accumulated within the soil cover, from which it discharges to the surroundings and/or is removed by evapotranspiration. Similar results, from a study performed at a tailings impoundment in Canada, were presented by Yanful (1993), who reported that during a two-year period no water accumulated in water lysimeters installed under a three-layer cover.

The efficiency of the composite cover as a water barrier is further illustrated in Table 4. This table shows the water level (m) in the protective till layer of the cover, measured in groundwater observation wells Mv1-Mv9 (Figs. 1b and 2), expressed as level above the upper surface of the low-permeable till layer. For comparison, the table also shows the depth (m) to the groundwater level, expressed as depth below the cover/tailings interface, measured in groundwater observation well V7. It should be noted that the depth of the water-unsaturated zone within the tailings at well V7 may be much smaller than that showed in Table 4, due to the presence of a capillary-saturated zone. However, the height of this zone has not been evaluated.

**Table 3.** Continued.

<table>
<thead>
<tr>
<th>OP10</th>
<th>$C_0$ (mol m$^{-3}$)</th>
<th>$C_{\text{interface}}$ (mol m$^{-3}$)</th>
<th>$F_c$ ($\times 10^{-3}$ mol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00/06/05</td>
<td>9.08</td>
<td>0.043</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 4.** Water levels in Mv1-Mv9 and depth to the groundwater level in V7 (m)$^3$.

<table>
<thead>
<tr>
<th>Date</th>
<th>Mv1</th>
<th>Mv2</th>
<th>Mv3</th>
<th>Mv4</th>
<th>Mv5</th>
<th>Mv6</th>
<th>Mv7</th>
<th>Mv8</th>
<th>Mv9</th>
<th>V7</th>
</tr>
</thead>
<tbody>
<tr>
<td>98/10/22</td>
<td>0</td>
<td>0.01</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>0.12</td>
<td>0.12</td>
<td>0.15</td>
<td>0</td>
<td>1.91</td>
</tr>
<tr>
<td>98/11/09</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0</td>
<td>0.025</td>
<td>0.03</td>
<td>0.02</td>
<td>0.015</td>
<td>0</td>
<td>2.23</td>
</tr>
<tr>
<td>98/11/25</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>2.57</td>
</tr>
<tr>
<td>99/05/11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>0.005</td>
<td>0</td>
<td>0.03</td>
<td>0.034</td>
<td>2.57</td>
</tr>
<tr>
<td>99/05/28</td>
<td>0.13</td>
<td>0.30</td>
<td>0.06</td>
<td>0.20</td>
<td>0.04</td>
<td>0.28</td>
<td>0.29</td>
<td>0.41</td>
<td>0.18</td>
<td>2.03</td>
</tr>
<tr>
<td>99/06/11</td>
<td>0.13</td>
<td>0.30</td>
<td>0.06</td>
<td>0.20</td>
<td>0.04</td>
<td>0.28</td>
<td>0.29</td>
<td>0.41</td>
<td>0.18</td>
<td>2.03</td>
</tr>
</tbody>
</table>
The water-level data for wells Mv1-Mv9 show that on many occasions, water remained accumulated in the protective till layer; the water level there was up to 1.3 m (Aug. 17, 2000). This periodic accumulation of water within the soil cover, resulting in high or complete water saturation, is in qualitative accordance with the small values for $D$ in the cover (Table 2). Hence, the overall results indicate that the low-permeable till layer acts as an efficient water barrier, resulting in small groundwater recharge within the deposit. Thereby, the regional groundwater flow may have a relatively large influence on the groundwater level fluctuations, and hence on contaminant transport within the deposit.

The above conclusion is at least qualitatively supported by a comparison between the water levels measured in the soil cover (wells Mv-Mv9) and the groundwater levels measured in the tailings (well V7). The groundwater level in well V7 fluctuated about 2.2 m during the measurement period, but does not show any obvious co-variation in time with the water levels measured in the soil cover, further indicating that groundwater recharge within the deposit is small.

### Discussion and Conclusions

The evaluation of oxygen lysimeter data for 1999-2000 from impoundment 1 at the Kristineberg mine site in Northern Sweden indicates that the diffusion coefficient $D$ in the composite cover is low. The model-fitted values of $D$, and the associated diffusive oxygen flux, varied approximately one order of magnitude between different periods. For instance, at oxygen lysimeter OL1 with a total cover depth of 1.8 m, $D$ was about $3 \times 10^{-4}$ m$^2$ d$^{-1}$ during the early summer 2000 and about $5 \times 10^{-5}$ m$^2$ d$^{-1}$ during the early autumn the same year. However, the data did not provide sufficient support for any general conclusions on typical seasonal variations of $D$. Further, the results did not show any consistent connection between the thickness of the composite cover and its performance.
as an oxygen barrier. Either the methodology used for data collection (i.e., instrumentation and sampling frequency) is no more accurate than the variations we tried to identify, or diffusion is dominated by other, unstudied parameters.

Data from groundwater wells installed within the protective (upper) till layer in the soil cover suggest that there is periodic accumulation of water within the soil cover, resulting in small oxygen fluxes and hence reduced contaminant generation within the tailings. On the other hand, during extended periods of little or no precipitation, the water retention properties of the low-permeable till layer and the depth to the groundwater level may be critical for the efficiency of the cover as an oxygen barrier.

The evaluation of water lysimeter data indicates that only a small fraction of the precipitation infiltrates into the part of the deposit remediated by the composite soil cover, resulting in small groundwater recharge within that part of the deposit. In the case of water fluxes being small for the whole deposit, groundwater level fluctuations may be a dominant factor for contaminant recharge into the groundwater. Hence, observation of groundwater levels in the soil cover and in the tailings may provide key components in monitoring of soil-cover remediation performance.

The results of this study show that soil-cover remediation of mill tailings deposits can lead to very small oxygen and water fluxes, and hence large reduction in contaminant discharge to the surroundings, provided that part of the cover is well compacted and low permeable. It should be noted that at the installation area, the average Proctor maximum was 96% for compaction of the low-permeable till layer, compared to a required 93% compaction during remediation (Hedman, 1996). Hence, it is likely that the cover at the installation area is more compacted than practically feasible in large-scale remediation programmes. Moreover, as the total precipitation during the investigation period was 25% greater than normal (SMHI, 1998-2000), further studies are required in order to investigate the sensitivity of the actual soil-cover effects to the hydrological conditions.

Long-term monitoring of groundwater levels and oxygen concentrations, not only in the part of the impoundment investigated in this study, but also in other parts, is required to improve our understanding of the overall remediation effects on the generation and transport of contaminants within the deposit.

Acknowledgements

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Abstract
Oxygen and water fluxes through the sealing layer at the soil cover remediated tailings Impoundment 1, at the Kristineberg mine in northern Sweden have been monitored between August 1999 and September 2002. Oxygen diffusion rates were compared for three different protective cover thicknesses; 1.5, 1.0, and 0.3 m, respectively. The installation area with 1.0 m of protective cover exhibited approximately 10 times higher oxygen diffusion rate at most measurements. However, during the dry summer 2002 with only 240 mm of precipitation between May 1st and September 12th, but also during late autumn 2001 the area with 0.3 of protective cover dried and the oxygen diffusion rate increased to the level of the 1.0 m area. The area with 1.5 m of cover remained unaffected at the same level as earlier. Oxygen concentrations in the protective cover are at times very low. This results in diffusion of oxygen from the lysimeters to the protective cover. The major oxygen diffusion period seems to be from May to September, with small fluxes occurring from late autumn until spring. This implies that the oxygen diffusion is very low during the winter. Periodically a perched water table is present in the protective cover, mainly during snowmelt and late autumn during the intense rains. This perched water table is an effective hinder for oxygen diffusion although it never lasts long. Compared with the pre-remediation conditions the oxidation rate can be estimated to have decreased about 2-3 orders of magnitude depending on which test area to compare with. Since the climate probably will be warmer in the future with shorter and milder winters, the design demands for the protective cover might have to be changed from preventing frost penetration into the sealing layer to instead be designed to provide enough retained water available for evapotranspiration, to prevent desiccation of the sealing layer. A dry sealing layer is much less efficient (as was shown by the 0.3 m area), and it still remains to see whether the damage formed during the dry summer 2002 was irreparable. Frost penetration of the sealing layer has not yet occurred, and the effects in field scale of frost actions on cover efficiency are still uncertain. Since the 1.5 m cover area was unaffected by the dry conditions, it seems as if this cover was thick enough to sustain the dry conditions. It is likely that this thickness of the protective cover is the most appropriate of the three.

Introduction
Wastes from sulphide ore mining are nowadays considered as a possible threat to the surrounding environment due to the environmental impact of metal release which can be connected to the oxidation of sulphides. Such sulphide-rich tailings and waste rock dumps thus require actions to be taken to minimize the availability of oxygen. To monitor the efficiency of the remediation actions performed at the Kristineberg mine, field installations were constructed during the autumn 1999 as a part of the Swedish MiMi-program. The sulphide-rich tailings at Impoundment 1 at the Kristineberg mine were left unremediated for almost 50 years until remediation actions were finished in 1996. The tailings at Impoundment 1 were remediated by the application of unspecified till and a raised groundwater table in the areas of impoundment 1 where the groundwater table prior to the remediation were situated close to the tailings surface. In other areas with a deeper groundwater table, a more advanced till cover consisting of a 0.3 m compacted clayey till underly
constructed (Figure 1). Previous studies at the site regarding the effectiveness of the chosen remediation methodology are among others Holmström et al. (2001) who studied the mineralogy and chemistry of the solid fraction as well as the pore water, and Corregé et al. (2001) in which a prediction of the future behaviour of the groundwater composition was presented. Carlsson et al. (2002a) studied, by using sequential extractions, the speciation of the elements at different depths in the tailings. Studies of the sealing layer and its sensitivity to frost with regard to the hydraulic conductivity was presented in Carlsson et al. (2001) and the efficiency of the sealing layer regarding oxygen diffusion and water infiltration for the first one and a half year after installation was evaluated in Werner et al. (2001). In the present paper the efficiency of the soil cover remediation for the area incorporating the sealing layer methodology, is further evaluated and compared to past oxidation rates at the impoundment as well as making predictions for the future efficiency of the soil cover. The seasonal variation of the oxygen diffusion through the sealing layer is also presented.

Figure 1. Impoundment 1, Kristineberg mine.

Measurements of oxygen and water fluxes in tailings, waste rock piles, and field scale investigations have been performed since the 1980s (e.g. Harries and Ritchie, 1985). The mechanisms dictating the transport of oxygen during different conditions have been relatively
well known since the late 1980s. At that time also modelling efforts to predict the behaviour and efficiency of different remediation strategies was initiated (e.g. Magnuson and Rasmuson, 1983) simulated the function of different soil cover designs.

**Area description**

The Kristineberg mining area is located in the western part of the Skellefte ore district, approximately 175 km south-west of Luleå (Figure 1). The approximately 1.9 G a old ore-bearing volcanic rocks are overlain by sedimentary rocks. The metamorphosed volcanic and sedimentary rocks display a marked foliation and extensive sericitization (Vivallo and Willdén, 1988). Pyrite-rich sulphide ores are intercalated within a stratigraphic unit mainly consisting of basic volcanics and redeposited volcano-elastic rocks (Willdén, 1986). For further description of the area and its geology and ores, see Du Rietz (1951), Gavelin (1943), Gavelin and Kulling (1955) and Grip (1973).

The largest orebody in the area is the Kristineberg Zn-Cu deposit, which was discovered in 1918. It was not until 1940 that Boliden Mineral AB started mining activities and mining is still in progress. Other mines close to the Kristineberg mine are the Kimheden, Hornträsk, Rävliden and Rävlidmyr mines, all of which are closed and remediated. The annual precipitation in the area varies between 400-800 mm/y (Axelsson et al., 1991) and the annual mean temperature is 0.7°C (Axelsson et al., 1986). In general, the impoundment is snow-covered between late October/early November and late April/early May (Axelsson et al., 1986). The vegetation consists mainly of coniferous forest, but some deciduous forest is also present in the area. Boglands are common. The major soil type in the area is podzol weathered till (Granlund and Wennerholm, 1935; Granlund, 1943). Five tailings impoundments are located within the Kristineberg mining area. As many as 10 different ores from the western part of the Skellefte field mining district were processed in the processing plant, and thus the impoundments contain a mix of several different kind of tailings. In this study Impoundment 1 was investigated (Figure 1). It is the oldest within the mining area. It has a surface area of about 0.10 km² and until the early 1950s it was used for tailings disposal (Boliden Mineral AB, 1995). The tailings discharge was located along the southern hill slope. In the years 1976 and 1978 attempts were made to sow grass seed. In 1996 the impoundment was remediated by till covering, raising the groundwater table and seeding with grass (Lindvall et al., 1999).

After the remediation, the groundwater table is shallow. At some parts of the impoundment, it reaches the surface. The intention was to use 1 m of unspecified till as a protective layer in areas with a shallow groundwater table. In other areas 1.5 m of till was applied above a 0.3 m sealing layer. The sealing layer consists of a compacted clayey till. Prior to the application of the till cover 10 kg/m² of lime was added to the top of the tailings. The impoundment is located in a valley and underlain by peat and till. The thickness of the tailings ranges from a few metres up to approximately 11 m. The average thickness is between 6 and 8 m. The oxidation zone reaches about 50 cm depth in the tailings at the sampled location studied here. After the application of till cover the upper part of the oxidised zone is approximately 150 cm below the surface.

**Description of the tailings and the installation area**

In the area of the installation, the oxidation depth was based on visual inspection during several drilling occasions and excavations, but also from solid tailings analyses. Generally the colour in the oxidised zone is red-yellow and at some levels a slightly greenish tone is discernible. Reddish coloured tailings were also interlayered in what seemed to be unoxidised tailings in the lower part of the oxidised zone. During tailings disposal the spigotting location for the tailings was positioned in the opposite (northwestern) end of the impoundment. It is
probable that the installation area was at times dry during the tailings discharge, which could have resulted in oxidation of the tailings during the use of the impoundment. The oxidised tailings were from time to time covered with fresh tailings resulting in the layered structure. The area of the installation has been remediated with a qualified 0.3 m thick sealing layer of compacted clayey till. Above this layer a 1.5 m thick protective layer of unspecified till has been applied.

Mineralogy
In the unoxidised tailings, the sulphide mineral content ranges from 10 to more than 30%. The average sulphide mineral concentration is approximately 27.5%. The most common sulphide minerals are, in decreasing order, pyrite, pyrrhotite, sphalerite, chalcopyrite, galena, and covellite. Pyrite is by far the most common sulphide mineral. Some of the Fe-hydroxides identified in the tailings were formed by evaporation of pore water after sampling, so-called tertiary minerals (Jambor, 1994). Gypsum occurs as massive euhedral grains, some of which also appear to be of tertiary origin.

In the oxidised tailings, the sulphide content is generally around 1 to 2%. The most common sulphide minerals are, in decreasing order, pyrite, chalcopyrite, pyrrhotite, sphalerite, and galena.

The most common gangue minerals in both types of tailings are quartz, K-feldspar, Mg-chlorite, talc, plagioclase, muscovite, amphiboles/pyroxenes and biotite. Ilmenite, magnetite, hematite, titanite, epidote, sericite, zirkon, apatite, and calcite also occur, but in minor amounts.

Materials and methods
Oxygen diffusion and water infiltration measurements
Oxygen diffusion was measured in three separate oxygen diffusion lysimeters with the cross-section area 1.6*1.6 m² and a height of 0.2 m. They are manufactured in stainless steel (Figure 2). These lysimeters were installed in the tailings horizontally. High-quality concrete was used to make certain that, after the application of the compacted clayey till and the protective soil cover, the lysimeters would stay in the correct position. Around the oxygen lysimeters bentonite was added to the upper part of the concrete at least to a distance of 0.5 m out from the side of the lysimeter. This together with the uppermost part of the sides of the lysimeters raised about one centimetre atop of the concrete was supposed to work as a seal towards the oxygen consuming surroundings. Rather coarse crushed quartzite was used to fill the oxygen diffusion lysimeters (average size-range 30-50 mm), and calculated porosity for the filling material was 0.47. This gives a resulting pore volume inside the lysimeter of 0.24 m³. The water infiltration lysimeters have the same area and height as the oxygen diffusion lysimeters, but are slightly tilted towards the end of the lysimeter containing the water outlet. The water infiltration lysimeters are installed at a depth of about 0.5 m in the tailings (Figure 3) and filled with tailings. Oxygen diffusion lysimeters have three pipes attached to the bottom (water outlet), front and back walls (oxygen sampling and oxygen evacuation pipes). All pipe connections have been sealed to prevent oxygen leakage. One oxygen diffusion lysimeter and one water infiltration lysimeter is installed in each of the three test areas (Figure 3). The test areas have a sealing layer of 0.3 m compacted clayey till except for the area with 0.3 m of protective cover, which has 0.5 m. For the other two test areas the protective cover is 1.5 and 1.0 m, respectively. A tentative outline of the installation is presented in Figure 3.
Oxygen diffusion lysimeter

Oxygen measurement pipe

Water evacuation pipe

Figure 2. Oxygen diffusion and water infiltration lysimeters.

Water infiltration lysimeter

Water evacuation pipe

Figure 3. Oxygen diffusion and water infiltration lysimeter installation.

Oxygen probes
Oxygen probes were installed on top of and underneath the sealing layer. The probes consist of a geotextile bag filled with quartzite into which a tube has been inserted. The tube is extending to the ground surface. Sealing is installed to prevent oxygen transport along the tubing.

Oxygen measurement
Oxygen analyses were performed using an ANSTO Portable Automatic Oxygen Analyzer equipped with a micro fuel cell, Teledyne Class B-1. The range for measurement is 0-20.95 volume-% with a resolution of 0.03 volume-%, and an accuracy of ±0.10 volume-%. Prior to measurements, the oxygen analyser was calibrated using nitrogen gas. During the measurement the oxygen analyser was controlled against the atmosphere concentration.

Results
Measurements of oxygen diffusion and water infiltration rates were initiated after the installation was finished 24th of August 1999. Models for diffusion are based on Fick’s first law:

$$F = -D \frac{dc}{dz}$$  \hspace{1cm} (1)
which are transformed into

\[ F = -D_{\text{eff}} \left( \frac{\Delta c}{\Delta z} \right) \]  

(2)

where \( D_{\text{eff}} \) is an experimentally determined effective value of \( D \).

The \( \Delta c \) corresponds to the difference in concentration of, in this case, oxygen and the \( \Delta z \) is the distance between the two points of oxygen measurements. Although the diffusive transport over the sealing layer is random, the net flow is from the higher concentration to the lower until they are equilibrated at which time the net flow is zero. However, in a sulphide-rich tailings or organic rich environment oxygen is consumed and the net flow therefore rarely reaches equilibrium. Using Fick’s first law to calculate the flux through a porous layer (such as a soil) requires the user to presume approximate steady-state diffusion for the period. It has also to be combined with mass-balances for two well-stirred volumes, separated by the porous soil layer. Such an approximative expression for \( D \) was presented by Cussler (1984). If the lysimeter volume is \( V \) and has a cross-section area \( A \), this is illustrated by:

\[ F_{\text{lm}} = \left( \frac{V}{A} \right) \frac{dC_{\text{lm}}}{dt} \]  

(3)

Here \( F_{\text{lm}} \) mean “Flow in lysimeter” and \( C_{\text{lm}} \) correspondingly means “Concentration in lysimeter”. For approximate steady-state conditions, the flux through the soil layer (Eq. 2) equals the flux indicated by the change in concentration in the lysimeter (Eq. 3). Hence,

\[ -D_{\text{eff}} \left( \frac{\Delta c}{\Delta z} \right) = \left( \frac{V}{A} \right) \frac{dC_{\text{lm}}}{dt} \]  

(4)

where \( \Delta c = C_{\text{lm}} - C_0 \)  

(5)

Rearranging Eq. 4 using Eq. 5

\[ - \frac{D_{\text{eff}} A}{\Delta z V} (C_{\text{lm}} - C_0) = \frac{dC_{\text{lm}}}{dt} \]  

(6)

and introducing \( \beta = \frac{D_{\text{eff}} A}{\Delta z V} \)

(7)

gives the expression in Eq. 8.

\[ - \beta (C_{\text{lm}} - C_0) = \frac{dC_{\text{lm}}}{dt} \]  

(8)

This (Eq. 8) is a separable differential equation and can be integrated, using the initial condition with zero oxygen concentration in the lysimeter immediately after flushing the system with N\(_2\) gas at \( t=0 \) when \( C_{\text{lm}}(0)= 0 \), i.e.
\[
\int_0^t -\beta dt = \int_0^t \frac{dC_{im}}{C_{im} - C_0}
\]

Then it is possible to obtain
\[
C_{im}(t) = C_0 \left[1 - \exp(-\beta t)\right]
\]

where \(C_0\) is the atmospheric oxygen, if rearranging to obtain \(D_{eff}\) it is written as in Eq. 11.

\[
D_{eff} = \ln\left(\frac{C_0}{C_0 - C_{im}(t)}\right) \frac{V_V \Delta z_c}{A t}
\]

Once \(D_{eff}\) is determined \(F\) can be calculated using Eq. 2.

The derived equations can also be adjusted with regard to infiltrating water. However, the volume of the infiltrating water is small compared to the pore volume of the lysimeter and is in this case neglected.

To check the validity of the assumed steady-state diffusive flux through the soil layer, the time to reach steady-state, \(t_{ss}\) (Eq. 12) can be estimated (Crank, 1979),

\[
t_{ss} = \frac{0.45 (\Delta z)^2}{D_{air}}
\]

where \(D_{air}\) is the oxygen diffusion coefficient in the soil gas and \(\Delta z\) is the soil cover thickness.

Using an estimated value of \(1.8 \times 10^{-5}\) m²/s = 1.6 m²/d (CRC Handbook of Chemistry and Physics, 1981) and a soil cover thickness (\(\Delta z\)) of 1.5 m, a time to reach steady-state conditions of about 0.7 day is calculated. Hence, the approximation seems to be appropriate.

The results from oxygen diffusion lysimeters are evaluated by the use of Eq. 11, where \(C_0\) denotes the oxygen concentration in the air, \(V_V\) is the pore volume and \(A\) is the bottom area while \(C_{im}(t)\) is the oxygen concentration in the lysimeter for measurement \(t\) subtracted with measurement \(t-1\). The depth from the surface down to the till-tailings boundary is \(\Delta z_c\) and \(t\) is time in days. Calculated D coefficients for the oxygen diffusion lysimeters is presented in Table 1. The \(D_{eff}\) coefficient should be interpreted as an effective value of \(D\). The \(D_{eff}\) value is then used in the calculation of flux of oxygen per square meter and time, Eq. 2. Here \(\Delta C\) is the difference between \(C_0\) (atmospheric oxygen concentration) and \(C_{interface}\) which is the oxygen concentration in the uppermost part of the tailings underneath the sealing layer. \(\Delta z_c\) is the same as in the calculations of \(D_{eff}\). To have the transport in mol m⁻² d⁻¹ the concentration has to be converged from volume-%. If applying the ideal gas law at atmospheric pressure it can be converted to moles of oxygen. Then the diffusive flux of oxygen over the sealing layer is possible to calculate and the results are converted from days to year prior to incorporating them into Table 1. Calculations of the flux are performed with the measurements from the oxygen probe underlying the sealing layer at each location except for the area with 0.3 m of protective cover for which the oxygen concentration underneath the area with 1.0 of cover was used due to installed in the old impoundment dam wall. Thus, the total flux (mole O₂/m²) for the period is to be calculated according to equation 13.
In Table 1, flux for periods with a negative diffusion coefficient has not been calculated. A negative flux is not occurring in the field; however it is possible to presume a low flux into the tailings for the negative periods.

Table 1 The * denotes zeroing the lysimeter by nitrogen gas. D_{Average} is calculated for the positive values. D_{Average} for the two periods are calculated separately. F_c for 0.3 m of protective cover are calculated using oxygen probe concentrations from the 1.0 m area due to installed in the former impoundment dam.

<table>
<thead>
<tr>
<th>Period: Days:</th>
<th>Cover:</th>
<th>D_{Average}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000-06-05* to 2000-08-18</td>
<td>74</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2000-08-18 to 2000-09-26</td>
<td>39</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2000-09-26 to 2001-04-05</td>
<td>191</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2001-04-05 to 2001-05-30</td>
<td>55</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2001-05-30 to 2001-07-05</td>
<td>36</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2001-07-05 to 2001-09-21</td>
<td>78</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2001-09-21 to 2001-11-22</td>
<td>62</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2001-11-22 to 2002-05-03</td>
<td>161</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2002-05-03* to 2002-07-23</td>
<td>81</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2002-07-23 to 2002-09-12</td>
<td>51</td>
<td>1.5 m</td>
</tr>
<tr>
<td>2000-06-05* to 2000-08-18</td>
<td>74</td>
<td>1.0 m</td>
</tr>
<tr>
<td>2000-08-18 to 2000-09-26</td>
<td>39</td>
<td>1.0 m</td>
</tr>
<tr>
<td>2000-09-26 to 2001-07-05</td>
<td>282</td>
<td>1.0 m</td>
</tr>
<tr>
<td>2001-07-05 to 2001-11-22</td>
<td>140</td>
<td>1.0 m</td>
</tr>
<tr>
<td>2001-11-22 to 2002-05-03</td>
<td>161</td>
<td>1.0 m</td>
</tr>
<tr>
<td>2002-05-03* to 2002-07-23</td>
<td>81</td>
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<td>2002-07-23 to 2002-09-12</td>
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<td>74</td>
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</tr>
<tr>
<td>2000-08-18 to 2000-09-26</td>
<td>39</td>
<td>0.3 m</td>
</tr>
<tr>
<td>2000-09-26 to 2000-11-14</td>
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</tr>
<tr>
<td>2000-11-14 to 2001-05-30</td>
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</tr>
<tr>
<td>2001-05-30 to 2001-07-05</td>
<td>36</td>
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</tr>
<tr>
<td>2001-07-05 to 2001-09-21</td>
<td>78</td>
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<td>81</td>
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</tr>
<tr>
<td>2002-07-23 to 2002-09-12</td>
<td>51</td>
<td>0.3 m</td>
</tr>
</tbody>
</table>

The amount of oxygen entering the tailings dissolved in water can be calculated using the water infiltration rates, and choose an oxygen concentration of 10 mg/l (which approximately represents saturated conditions). These values are presented in Table 2.
Table 2

<table>
<thead>
<tr>
<th></th>
<th>Cover:</th>
<th>Water infiltration [l/m², year]:</th>
<th>Oxygen transport [mole O₂/m², year]:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water infiltration lysimeter</td>
<td>1.5</td>
<td>1.47</td>
<td>4.61*10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>3.57</td>
<td>1.12*10⁻³</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen diffusion lysimeter</td>
<td>1.5</td>
<td>1.25</td>
<td>3.92*10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>9.06</td>
<td>2.83*10⁻³</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>3.57</td>
<td>1.12*10⁻³</td>
</tr>
</tbody>
</table>

Oxygen probe measurements on top of the sealing layer have been possible to perform occasionally due to the perched groundwater table forming on top of the sealing layer from time to time and saturating the oxygen probes. In the area with 1.0 m of protective cover two oxygen probes were installed in the protective cover on top of the sealing layer. On the other two areas only one oxygen probe per area were installed.

Discussion

Diffusion coefficient and oxygen flux

It is in general assumed that effective oxygen transport through the sealing layer only occurs during the snow-free period of the year since water in the form of snow is accumulating on the ground surface during the winter. During the snow-covered period the snow as well as the frozen soil is effective in hindering the diffusion of oxygen (Werner, 2000). As could be seen from Table 1, negative diffusion coefficient values (D) seem to occur for certain periods. In Figure 4 measurements of depleted oxygen concentrations in the protective cover are also visible. The calculated negative D values (and correspondingly negative fluxes of oxygen) presented in Table 1 could appear due to several different reasons:
• leakage to the oxygen consuming tailings;
• a reversed diffusion due to a higher oxygen concentration within the lysimeter compared to the protective cover during certain time periods;
• by the inflow of unsaturated water into the lysimeter, reducing the oxygen rate or by diffusion into the hanging water in the sealing layer;
• oxygen consumption within the oxygen diffusion lysimeter by organic matter.

The last of the above stated possible explanations are also probably the least probable since the lysimeter was filled with quartzite. Prior to the installation the quarzite was washed using a high-pressure hose. At the same time it was also verified that the material used actually also were quartzite. Secondly, a consumption of oxygen within the lysimeters seems unlikely since the absolute values of the diffusion coefficient varies one order of magnitude as can be seen from Figure 5 and Table 1.

![Deff](image)

**Figure 5.** Calculated diffusion coefficients for the three oxygen diffusion lysimeters

The same reason can explain why oxygen leakage to the surrounding tailings, the first explanation, probably is not valid. It also seems that the upward diffusion mainly takes place when measurements have been performed in late autumn or early spring (March, April). Early spring values can be explained by a low diffusion of oxygen into the protective cover. As can be seen in Figure 4, the oxygen level in the protective cover is for the measurement in March 2000 less than 2 volume-%. This is about the level of, or lower than, the concentrations in the lysimeters and correspondingly, the net diffusion for the lysimeters upwards. This results in a very low transport of oxygen into the tailings through the sealing layer.
For the third explanation it is possible to test whether the decreasing oxygen levels could be due to dissolution of gaseous oxygen in unsaturated infiltrating water. As could be seen from Table 2, the average annual infiltration measured in the oxygen diffusion lysimeters are less than 5 l/m²·y. This low infiltration rate can be explained by a low hydraulic conductivity through the sealing layer (Carlsson and Elander, 2001), but a major effect is likely surface run-off and lateral run-off on top of the sealing layer since the installation area is sloping. Transformed water paths leading to a transport of infiltrating water around the lysimeter is not detectable since the water infiltration lysimeters (Table 2) show the same level of infiltration although these were filled with tailings. Setting the inflow to 5 l/m²·y gives a total volume of 12.8 l per year and lysimeter, and a gas volume of 227.2 l remain in the lysimeter, since the total volume is 512 l and the quartzite have a porosity of 0.47. As can be seen from Table 4, ΔO₂-% between measurements can be up to 2 volume-% (negative values). Thus, the removed fraction of oxygen is 4.54 l. If atmospheric pressure is presumed, this corresponds to 0.203 moles of O₂. Using the ideal gas law (Eq. 13) then 6.3 g of oxygen is removed presuming a temperature at the sealing layer of 4 ºC.

\[
P V = n R T
\]

where

- \( P \) = Atmospheric pressure (1 atm = 101.3 kPa)
- \( V \) = Volume (m³)
- \( n \) = mole
- \( R \) = 8.314 J/(mole K)
- \( T \) = Temperature (in K)

Considering the solubility of oxygen in water (~10 mg/l), this would require the infiltration of ~630 l of water depleted in dissolved oxygen. This is several orders of magnitude higher than the measured infiltration and can not be presumed to be a likely explanation. However, it can also be presumed that oxygen is to be dissolved in the water present in the sealing layer. This can be tested, assuming that oxygen is diffusing into the water withheld in the sealing layer. Presuming that this retained water is entirely oxygen free, the volume of soil available for diffusion (considering 1-dimensional diffusion) are the lysimeters cross-section area (2.56 m²) multiplied by the thickness of the sealing layer (0.3 m) multiplied by the porosity of the sealing layer (0.2). This volume of water is 0.154 m³. Consider that the previously calculated 6.3 g of oxygen are to be dissolved in this amount of water. The result is that 41 mg/l have to be dissolved to explain the decrease. However, still unsatisfactory, it might be a part of the explanation although there ought to be a reason for why the water withheld in the sealing layer is depleted in oxygen. One such reason could be soil respiration.

The last possibility is that soil respiration in the protective cover is responsible for a negative flux over the sealing layer of oxygen from the oxygen diffusion lysimeter, mainly during late autumns. In September 2001 a maximum CO₂ concentration of 14 volume-% was measured in the protective cover at the test site with 1.0 m of till. In the other oxygen probes high CO₂ concentrations were also measured, although lower than 14 volume-%. Those oxygen probes had a concentration between 3.9 and 10.2 volume-%. Total pore volume in the area with 1.0m of protective cover is 0.3 m³ since the porosity can be approximated to 0.3. The CO₂ thus occupies the volume of 42 l, corresponding to ~1.875 moles. This corresponds to ~22.5 g of organic C/m³ of till. If the approximate bulk density of the till is ~2000 kg/m³, then this corresponds to a decomposition of 11.25 mg Org C/m³ of till. According to Flanagan and Van Cleve (1977), 200 g of Org C/m³ down to a depth of 18 cm can decompose annually in a
forest soil in Alaska. This corresponds to an Org C content of 555 mg/kg till decomposed annually (corresponding to an org C concentration of ~0.06%). From solid till analyses of the protective cover the average loss on ignition (LOI) for 39 samples are 0.82%. Although the LOI incorporates losses from minerals such as CaCO₃, which will be oxidised to CO₂, as well as chemically bound water and physically harder bound water in excess to the organic content (Gembert 1991), it is common practice to consider that approximately half of the LOI is corresponding to organic C in a till. According to Rowell (1994) a useful value is 58%. In the till used for the protective cover at Kristineberg the amount of CaCO₃ can be considered as negligible (Holmström et al., 2001). Thus the amount of Org C decomposition required to produce 14 volume-% of CO₂ seems reasonable. Soil respiration could be a possible explanation for the decreased oxygen concentrations in the protective cover, creating the forces required for a negative flux. It has also been shown that soil respiration are dependant on the temperature of the soil, showing an Arrhenius relationship with an approximately rate increase of 2 when the temperature increase 10 °C (Russel 1973). When correlating the soil temperature and the change in oxygen concentration for the oxygen diffusion lysimeters it is somewhat evident that for measurements occurring after the soil temperature peak, oxygen concentrations in general have decreased compared to the previous measurement, shown as negative ∆O₂ values in Figure 6.

Figure 6. Soil temperature and change in oxygen concentration between measurements. A positive ∆O₂ indicate an increase compared to previous measurement and a negative a decreased oxygen concentration. Between mid-April 2001 and August 2001 soil temperatures have been interpolated.

Several times it was not possible to sample the oxygen probes on top of the sealing layer, in the protective cover, due to the presence of water. At most occasions during 2000 and 2001 when sampling was possible (Figure 4) the oxygen concentration was rather low (<4 volume-%, except for the oxygen probe underneath 0.3 m of cover which could be up to ~12 volume-%). In the year 2002, with much drier conditions than the two previous years, the oxygen
content in the protective till cover was much higher, especially for the September measurement where the level was between 17 and 20.7 volume-%. The oxygen concentration in the protective cover seems to be dependent on the current water content of the soil. The intense rains during autumn (with ongoing soil respiration) create an environment in the protective cover depleted in oxygen. This could mean that the diffusion of oxygen in the lysimeters during some periods is reversed; both because of soil respiration which during early autumn create a low-oxygen pore gas when the soil temperature is high but also due to the fact that a perched water tables from time to time is formed on top of the sealing layer and thus, when it is removed by evapotranspiration or lateral run-off, oxygen might be transported both from the atmosphere as well as from the oxygen diffusion lysimeter.

In the protective cover around the installation area a number of open groundwater pipes have been installed (Figure 1) to monitor the characteristics of the perched water table (Mv1-Mv9). The depth of the protective cover varies between 150 and 170 cm (the shaded area in Figure 7). During shorter periods of time, a perched water table has been detected on top of the sealing layer, mainly during snowmelt but also during the intense rains occurring in late autumn. A perched water table decreases the oxygen transport through the sealing layer. It is generally considered that for typical hydrological conditions in northern Sweden, water is accumulating in the form of snow on the ground surface or in the form of ice in the upper part of the soil. During the field work, a layer of ice was found on top of the ground under the snow cover. This is usually depending on melt-refreeze cycles before the beginning of the main period of snow-melt (Engelmark 1988). During the freezing of the upper part of the soil, water suction is induced on water in the pores at greater depth. Such suction can form cracks in soils like clay if it is situated too close to the surface freezing fringe. However, during the winter, infiltration of water and diffusion of oxygen are practically zero into the soil due to the formation of the ice layer in and on top of the surface soil. During a relatively short period of time, late April and early May, the accumulated snow pack melts and a peak in the groundwater occurs. This is evident in the measurements of the perched groundwater table which shows maximum levels during and just after snowmelt has occurred. The soil is rapidly saturated and water is transported from the soil mainly by run-off, or as a lateral flow of water, perched on the sealing layer. During the summer evapotranspiration is rather high, and normally rain intensity is rather low compared to the late summer and early parts of the autumn. At this time groundwater formation is low underneath the sealing layer since evapotranspiration is occurring in the protective cover and no perched water table has been monitored. Water is to a larger degree remaining within the sealing layer, enabling it to continue to function as an oxygen barrier until the water available for evapotranspiration in the protective cover is very low. At this point, water is withdrawn also from the sealing layer, and its efficiency as a diffusive barrier against oxygen transport to the tailings is decreased. It is thus important to design the protective cover thick enough to protect the sealing layer against desiccation. Summer infiltration is mainly accumulated within the protective cover and stored there upon evapotranspiration. During autumn, however, evapotranspiration is low and the rain intensity rather high. Perched groundwater tables on top of the sealing layer have been monitored at this time. Realizing this, it is evident that totally flat sealing layers impose that lateral run-off is hindered and the perched water table is leading to an increased water infiltration through the sealing layer due to the hydraulic gradient. However, the perched groundwater table (Figure 7) is nevertheless effective in hindering the diffusion of oxygen. The behaviour of the perched table groundwater, as experienced from field measurements, has been successfully simulated by using the HELP3 model ((Schroeder et al., 1994a and 1994b) and climatic data from the site, also the low infiltration level from the field measurements 1999-2002 was verified by the simulation.
As could be seen from the measurements of the effective diffusion coefficients over the years 2000, 2001, and 2002, a 0.3 m of protective cover was thick enough to provide a protection against drought during rather wet summers with a precipitation of 576 mm for 2000 and a slightly lower figure for 2001 during the period between 1\textsuperscript{st} of May and 12\textsuperscript{th} of September. Autumn 2001 was nevertheless rather dry and an increased diffusion coefficient resulting for the area with 0.3 m of protective cover. However, corresponding period during 2002, precipitation was lower with a precipitation of only 244 mm, and the 0.3 protective cover dried. This lead to a decreased efficiency of the sealing layer situated underneath since the drought enabled it to desiccate. Although the sealing layer is 0.5 m thick and underlying 0.3 m of protective cover, the effective diffusion coefficient for the sealing layer increased from an average of 5.2x10^{-5} m\textsuperscript{2}/d to 1.1x10^{-4} m\textsuperscript{2}/d for the summer 2002. As could be expected the other two areas with a thicker protective cover coped better with the dry conditions. For the 1.5 m protective cover area the increase was almost not detectable, from an average of 3.8x10^{-5} m\textsuperscript{2}/d (average for positive values summer 2000 and 2001) to 5.1x10^{-5} m\textsuperscript{2}/d. For the area with 1.0 m of protective cover there was no increase at all. Here it instead decreased from 1.4x10^{-4} to 1.3x10^{-4} m\textsuperscript{2}/s. The reason for not detecting any change in the area with 1.0 m of protective cover most likely depends on the level to which the desiccation extended in the soil profile. The tension lysimeter, measuring pore water pressure, installed at 50 cm depth indicated during the second half of the summer extremely dry conditions, the tension lysimeter at 100 cm depth indicated a more normal behaviour (Figure 8). The figure can roughly be interpreted as the higher the value (in kPa) the lower is the soils water content.
Figure 8. Tensimeter readings in the protective cover. Values between mid-April 2001 and July 2001 is missing.

The reason for the higher coefficient in this area although, compacted in the same way as well as with the same material, is yet not known. It is possible that upon closing measurements and re-investigating the installations a probable explanation can be detected. During the summers 2000-2001 the oxygen concentration within the protective cover were rather low. During the sampling occasions when the oxygen probes on top of the sealing layer in the protective cover were possible to sample, the concentration was between 0.5 and 10 volume-%. During the summer 2002, the concentrations in July were between 7.5 (for 1.0 m of protective cover) and 17.3 (for 0.3 m of protective cover) volume-%. In September measurements between 7.5 and 17.8 volume-% was recorded for the 1.0 m protective cover, and for the area with 0.3 m protective cover the measured oxygen concentration was 20.1 volume-%. The importance of water content in the soil can not be stressed enough.

Penetration of frost has not been monitored over these three seasons into the sealing layer. Recorded frost penetrations varied between 30 and about 50 cm, where the deepest is from the year prior to the installation. The major explanation for this is rather wet autumns with a high precipitation enabling the formation of a protective cover with rather high water content. Then in late October or early November, snow has arrived, and only after the snow cover has been established temperatures started to decrease strongly. At this point the protective cover have had two protections against frost penetration. Snow acting as insulation against freezing temperatures and the large amounts of water in the protective cover prevents the soil from freezing since the system of soil and a lot of water requires a higher amount of energy to be frozen compared to the soil with lower water content.
Oxidation depth models

A simple comparison of the oxidation rates for the three different test areas versus an estimation of the pre-remediation oxidation based on available parameters, and the possible evolution of the oxidation rate with time is presented in Figure 9. A simplistic shrinking-core model (Levenspiel, 1972; Höglund L. O., pers. comm.) was used to illustrate the difference between pre-remediation and the present possible oxidation rates. To illustrate the pre-remediation case, without any cover, equation 14 was used.

\[
t = \frac{Q_C x^2}{2 D_1^i C_S}
\]  

(14)

Here \(Q_C\) is the concentration of pyrite (4563.8 mol/m\(^3\)) in the tailings (all sulphides is approximated as pyrite), \(x\) is the depth into the tailings (m), \(D_1^i\) is the effective diffusion coefficient for the tailings, approximately 2.4-3.8x10\(^{-7}\) m\(^2\)/s as estimated by Banwart and Malmström (2001). In the following calculations the average value of 3.1x10\(^{-7}\) m\(^2\)/s was used. \(C_S\) is the oxygen concentration in the atmosphere-tailings boundary (mole/m\(^3\)). To illustrate the case with a cover applied Eq. 14 was extended into Eq. 15.

\[
t = \frac{Q_C \left( x + \frac{D_1^i}{D_c^2} x \right)^2 - Q_C \left( \frac{D_1^i}{D_c^2} x \right)^2}{2 D_1^i C_S}
\]

(15)

The parameter introduced, \(D_c^2\), is the effective diffusion coefficient of the cover. Used values for the different cover thicknesses were \(D_{\text{Average}}\) for the two periods as presented in Table 1.

It is evident from Figure 9 that the oxidation seems to have been reduced by an order of 2 to 3 magnitudes due to the application of the cover. However, during the summer 2002 an increased transport rate resulting in a decreased efficiency for the area with 0.3 m of protective cover occurred. This is due to an increase in the effective diffusion coefficient. Nevertheless, the cover system is still efficient in decreasing the oxidation compared to the pre-remediation condition, but the results show that to protect the sealing layer component in a composite soil cover from the forces acting upon it and decreasing its efficiency, like freezing (which has not happened yet) an drying (which occurred during 2002) is important.
Figure 9. Movement of the oxidation front according to the shrinking core model. Note the log$_{10}$ scale for the x axis. Tailings indicate that no cover at all is protecting the tailings from oxidation.

When comparing the diffusive fluxes in (Table 1) with the oxygen transported dissolved in water (Table 2) it is possible to conclude that during one year, the net flow of oxygen dissolved in water is approximately 1 to 2 orders of magnitude lower. This result was derived by using Eq. 13. A typical example is the period 2000-06-05 to 2000-08-18 for the area with 1.5 m of protective cover. The diffusive flow is estimated to be $3.1 \times 10^{-2}$ mole/m$^2$, whereas the total dissolved transport for oxygen in water during the entire year was about $3.9-4.6 \times 10^{-4}$ mole depending on whether the oxygen diffusion lysimeter or water infiltration lysimeter rate is used (Table 2).

Predictions for the future

Climatic models or scenarios for the future can and should be incorporated when predicting the efficiency of the cover system in the years to come. According to the Swedish Regional Climate Modelling Programme (Sweclim), funded by the Swedish Foundation for Strategic Research (MISTRA), the following scenario is likely within 100 years from now. The precipitation in the Kristineberg area will increase with approximately 15 to 20 % compared with the current situation (Figure 10), and the average winter temperature increase by 4 to 5 degrees (Figure 11) (Sweclim, 2000). Thus a reduction in the freezing index (Figure 12) will occur which, in combination with the increased precipitation as rain, likely reduces the frost penetration depth. Based on estimations by Sweclim (2001) on measured frost penetration in central and northern Finland, the estimated frost penetration on snow-free soil is to be reduced from 100-150 cm to 50-100 cm in central Finland, and for northern Finland from 200-300 cm
to 100-200 cm. When applying a snow cover, these depths are further reduced. A protective cover, if accepting these predictions, of 150 cm should thus be thick enough to prevent freezing of the sealing layer at most instances in the future. Then remains the possibility of desiccation of the sealing layer during extended periods of drought. This can be prevented if the protective cover contains enough water for evapotranspiration. The climate models, as previously described, predict an increase in average yearly precipitation. In combination with the increased temperature during the winter (decreased freezing index) the prediction is that the snowmelt is to be less important for the groundwater formation and that there is a more general increase over the entire year. Also considering the prolonged growth season, predicted to be is approximately 1-2 months longer around 2100 due to the increased average temperature (Sweclim, 2000), the possibility of an increased evaporation as well as an increased water demand from plants due to the prolonged growth season are thus important parameters to take into account. It might be necessary to increase the thickness of the protective cover for preventing desiccation of the sealing layer rather than from frost penetration in the future. However, this have to be investigated carefully in the future designs of soil cover remediation systems. As was observed during the summer 2002 at the test area in Kristineberg, the 1.5 m protective cover was thick enough to protect the sealing layer from desiccation whereas the total soil thickness of 0.8 m in the area with a protective cover of 0.3 m (thus having a sealing layer of 0.5 m) showed one order of magnitude in increase of the effective diffusion coefficient. If this increase in the effective diffusion coefficient was temporary or not for the 0.3 m area remain to be seen. A protective cover thickness of 1.5 m should also be thick enough to protect the waste from frost during most winters that might occur.

**Figure 10.** Precipitation modified from Sweclim (2000). Observed values 1961-1990 (in mm) to the left, then the predicted change (in %) and to the right the predicted precipitation (in mm) (modified from Sweclim, 2000).
**Figure 11.** Observed and predicted average winter temperatures. To the left observed average winter temperatures 1961-1990 (°C), in the middle predicted change (°C) and to the right the predicted average winter temperatures (°C) (modified from Sweclim, 2000).

**Figure 12.** Freezing index for the winter period (sum of the daily negative averages during a winter) present and around the year 2100 (modified from Sweclim, 2000).
**Conclusions**

Currently the sealing layer established at the test area at Impoundment 1 Kristineberg indicate reduced oxygen diffusion in the order of 2-3 magnitudes, and a water infiltration rate which have been reduced by approximately 98% compared to pre-remediation data. The reason for the one order of magnitude higher oxygen diffusion in the test area with 1.0 m of protective cover for the years 1999/2000 and 2000/2001 has not been solved. However, dry conditions prevailed during the summer 2002, and an increased diffusion rate of one magnitude was detected for the test area protected by 0.3 m of protective cover and 0.5 m of sealing layer. It was now in level with the diffusion rate for the area with 1.0 m of protective cover. Thus, to establish an increase of this magnitude it is probable that the desiccation extended to about 0.8 m depth. Measured precipitation between May 1 and mid-September 2002 as about half that of the previous years. This effect from drought extending almost 1 m down into the cover was preliminary verified by the behaviour of the tension lysimeters installed at 50 and 100 cm depth, respectively. Thus, to establish a protective cover thick enough to prevent desiccation of the sealing layer is probably as important as to protect it from freezing. Freezing conditions in the sealing layer have not been detected during the three winter seasons since installation. For future predictions of the behaviour it is important to investigate the probable relation between precipitation and evapotranspiration. If presuming that the future climate is to be similar with the summer 2002 it seem as if 1.5 m of protective cover was enough to prevent desiccation of the sealing layer whereas a total cover thickness of 0.8 was not. It still remains to see whether the diffusion effect is reversible or if the damage is irreparable. It is thus suggested that measurements on the test site should continue, and that upon closure, the sealing layers are thoroughly investigated to possible find the reason for the higher diffusion into the lysimeters installed below 1.0 m of protective cover.

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