MiMi
Mitigation of the environmental
impact from mining waste

MiMi – Performance Assessment Main Report

MiMi 2003:3

Photo: Åsa Sjöblom

Höglund L.O. and Herbert R. (Editors)

Lövgren L., Öhlander B., Neretnieks I.,
Moreno L., Malmström M., Elander P.,
Lindvall M., Lindström B.

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Kristina Skagius, Kemakta Konsult AB
Håkan Svensson, Kemakta Konsult AB
Sara Södergren, Kemakta Konsult AB
Celia Jones, Kemakta Konsult AB

Associated researchers

Steven Banwart, University of Sheffield
Gordon Brown, Stanford University
Embaie Ferrow, Lund University
Johan Ingri, Luleå University of Technology
Barbara Müller, ETH Switzerland
Clara Neuschütz, Stockholm University
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For more information please contact:
Lars Olof Höglund, Programme director
Kemakta Konsult AB
P.O. Box 12655
112 93 Stockholm, SWEDEN
Phone: +46 8 617 67 17
Fax: +46 9 652 16 07
E-mail: loh@kemakta.se

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Preface

This report forms an integrated part of the reporting and communications from the MiMi Programme. The report has benefited by contributions from all participating MiMi researchers and experts through written communications, as well as presentations and discussions during numerous seminars and workshops, which are gratefully acknowledged.

This research was funded by the Swedish Foundation for Strategic Environmental Research (Mistra) through the research programme Mitigation of the Environmental Impact from Mining Waste (MiMi).

Abstract

The MiMi programme has studied the processes in deposits of sulphide containing mine tailings. The aim has been to understand the chemical and transport processes sufficiently well to design methods that will hinder unacceptable releases of acidity, toxic metals and other substances to the environment. The time scales considered have been hundreds to thousands of years. The emphasis has been on methods that will need little or no supervision after closing of the deposit.

Soil cover and water cover designs have been studied. Performance Assessment methodology has been used to assess the long term impact of the tailings deposits on the environment.

The studies have been supported by field observations from a real site as well as numerous laboratory and field experiments.

A methodology has been developed that can be used to assess the performance over time of sulphide containing mine tailings covered by soil or by water.

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Contents

1 Summary

This report is focused on the outcome of the Performance Assessment studies that constitute a central part of MiMi research. The complete reporting from MiMi includes a significant scientific documentation found in supporting documents, in theses presented by the MiMi researchers and in the open scientific literature.

MiMi's vision for mining waste management in the future states that:"….*Methods used for waste disposal and remediation are efficient, robust and reliable so that, when any remediation is completed, a deposit can be left without the need for supervision or maintenance*".

Conclusions

In short, MiMi studies have reached the following conclusions:

- MiMi confirms that the primary objective for remediation of potentially acid generating mine tailings is to restrict the oxygen intrusion.
    - The amount of reacted minerals is determined by the amount of intruded oxygen.
    - For soil covered tailings this requires that the sealing layer can maintain its function over long time.
    - For water covered tailing this requires that the water balance can be maintained over long time, which in turn often requires a functional dam construction.
- For soil covers, there is significant potential for the primary acidity to be neutralised within the tailings.
    - The acid neutralisation by carbonates is most efficient, but aluminium silicates may contribute significantly to the acid neutralisation if the contact time is suitable.
- For soil cover the metals copper, lead and cadmium can often be retained in the tailings whereas iron, zinc and arsenic are not.
    - Secondary sulphides are formed when mobilised copper reacts with the more soluble sulphides pyrrhotite or sphalerite. A similar mechanism is expected also for cadmium and lead.
- The dissolved ferrous iron constitutes a latent acidity which is expressed first when the drainage is further oxidised outside the tailings deposit
    - The latent acidity can only be accommodated by dilution and acid neutralisation upon mixing with the surface runoff.
- The ferrous iron in the effluent from the soil covered deposit will eventually oxidise and form secondary iron precipitates (SIPs) that offer a significant adsorption capacity for trace elements, in particular arsenic
    - If the pH is near neutral the SIPs can adsorb a large part of the released trace elements.
    - Particle formation in recipient waters may be an important capture mechanism for released trace elements.
- For water covers neither the primary acidity nor the released metals are attenuated in the tailings.
    - The primary and the latent acidity can be neutralised in the water volume covering the tailings provided the water flow is sufficiently large.

    - The copper, lead, cadmium and arsenic can be adsorbed in secondary iron precipitates (SIPs) that form in the water due to oxidation of the ferrous iron (Fe^{2+}) and precipitate in the dam.
- The acidity load, the mixing ratio between drainage and surface runoff and the natural alkalinity of the surface runoff are site specific parameters that need consideration.
- The capacity of downstream wetlands as a trap for trace elements has been found to be low in the cold Swedish climate. The main reasons being channelled flow and frozen soils during peak-flow in spring.
- A performance assessment methodology has been adapted and tested for evaluation of the long-term function of tailings deposits. The methodology has been found effective and suitable for assessment of the most important processes governing the complex interactions in disposed sulphidic mine tailings.
- The general methodology and the presented base case evaluations can be used as a guideline, example and reference in future studies of other objects.
- The pros and cons of soil cover and water cover techniques have been studied and compared. The conclusion drawn is that both methods can be applicable and effective. The site specific conditions must be considered when deciding the most appropriate method at a particular site.

Further details and discussions are given in the following sections that elaborate the listed conclusions.

About the programme

MiMi (Mitigation of the environmental impact from mining waste) is a multidisciplinary research programme devoted to development of safe methods for remediation of mining waste and reliable prediction of the long-term function of the disposal sites. The Swedish Foundation for Strategic Environmental Research (Mistra) has funded the MiMi programme for the period 1997-2004. In addition, Swedish mining industry has supported the work with in-kind contributions. The programme is now being finalised (November 2004). The programme has a total budget of about 78 Million SEK, equivalent to about 9 Million EUR. The programme has engaged 35-40 researchers at 7 universities, as well as engineering specialists at consultant companies, the mining companies and the authorities. The participants are listed on the inside cover of this report.

Discussion

The MiMi programme has assessed the performance of soil covers and water covers for the prevention and control of sulphide oxidation in mine tailings. The need for a holistic approach to this assessment has led to a refocus from detailed basic research to the more encompassing and integrated Performance Assessment (PA) methodology. This is a new development in the investigation of mine waste deposits, and requires a detailed analysis of the function of various barriers to oxygen diffusion and water infiltration, and to trace element mobilisation within and discharge from these deposits.

The results of seven years of research within the MiMi programme have provided many opportunities to investigate both well-tested and new approaches to mine drainage mitigation, as well as to study specific processes that affect the environmental impact of mining activities. The research efforts have confirmed our previous understanding of dominating processes in and outside of tailings deposits, but have also led to a re-evaluation and re-interpretation of processes that were not as well understood.

The results from MiMi's performance assessment confirm the necessity that the design criteria for the construction of barriers to oxygen and water intrusion into tailings deposits must be based on local conditions, including the acid neutralisation capacity of recipients. For a given cover construction the produced latent acidity and its impact on the recipient can be predicted. The primary acidity formed due to sulphide weathering may be neutralised by buffering reactions in the tailings, whereas the released latent acidity can only be accommodated by dilution and acid neutralisation due to mixing with the surface runoff. The composition of the mine tailings will obviously affect the effluent quality, and possibilities for minimizing the amount of waste and the sulphide content should be explored in all cases.

The MiMi studies have resulted in improved understanding of the governing processes occurring within the tailings deposits, and have also provided methods to address the long-term function of the deposits.

The chemical processes occurring in sulphidic mine tailings are very complex, but the MiMi research has been able to document and assess the importance of different processes using a holistic approach. By this, it has been possible to distinguish the most important processes for the function of the deposits under different conditions over time.

The processes responsible for acidification and mobilisation of trace elements are well-known. Different processes tend to counteract the acidification, in particular the presence of acid neutralising minerals. The transport and release of trace elements that are mobilised due to weathering are also in many cases influenced by different retention and capture mechanisms. It is interesting to note that even for these fundamental processes and their interactions, new insights regarding their importance in different systems have been gained by the MiMi research.

The MiMi research has confirmed the need to restrict the oxygen intrusion into the disposed mine tailings as the primary objective for any management strategy for potentially acid generating mine waste. A direct correspondence has been found between the amount of oxygen and the amount of sulphides that are oxidised. However, this is true only under conditions where the oxygen access to the tailings is restricted by some barrier so that the oxidation kinetics, i. e. the biogeochemical reaction rate, does not influence the overall oxygen consumption rate. Soil covers as well as water covers can be designed to function as such barriers.

Soil cover

The restricted sulphide oxidation rate has an important effect on the acid neutralisation of the tailings. Besides the fast acid neutralisation offered by carbonates in the tailings, in particular by calcite, different aluminium silicates may significantly contribute to the acid neutralisation. The neutralisation reactions by aluminium silicates are, however, fairly slow. Restricted intrusion rates of oxygen and water, will increase the ability of the slow reacting aluminium silicates to accommodate part of the released acidity. Also a slower transport through the tailings will increase the contact time and improve the local acid neutralisation. At higher sulphide oxidation rates, the acid neutralisation may be less effective. This applies only to the soil cover case.

The oxidation of primarily pyritic sulphur in the tailings to sulphate will produce acidity and since it is formed as a direct result of the primary oxidation in the tailings we will refer to this as the primary acidity. For the soil cover case the MiMi studies have shown that the primary acidity to a large extent will be neutralised by calcite and aluminium silicates within the tailings, before the drainage is expelled from the deposit. Field observations and mass balance estimates at Kristineberg show that 75 – 100 % of the primary acidity may be neutralised within the tailings. Any remaining acidity or alkalinity in the drainage water leaving the tailings deposit is referred to as residual acidity/alkalinity.

For soil covers, the MiMi studies have also confirmed that the primary acidity produced in the tailings near the upstream side and in the central parts of the deposit have a greater likelihood of acid neutralisation during transport through the tailings due to a long travel path to the near recipients (e.g. ditches), as compared with acidity produced near the edges of the deposit. The reason for this is the increased likelihood of contact between acidic drainage waters and acid neutralising mineral surfaces and the longer residence time within the tailings for the longer travel paths. We therefore conclude that these edge effects need to be considered in the remediation plans.

However, when the oxygen intrusion rate is restricted by a barrier the oxygen will be readily consumed when brought in contact with the sulphides present in the tailings. If iron sulphides are exposed to restricted amounts of oxygen in the tailings, it has been found that only the sulphide part is oxidized, not the ferrous iron. Therefore, the amount of ferrous iron that is solubilized in the pore water will increase and eventually be released from the deposit into the near-recipients. Further oxidation of the ferrous iron in the discharge waters will lead to precipitation of ferric iron oxyhydroxides accompanied by the generation of additional acidity. Since the partial oxidation leads to a delayed formation of acidity due to the ferrous iron, we will refer to this as a latent acidity in the drainage water.

The latent acidity is expressed first when the drainage flows out of the tailings deposit. This means that the acid neutralisation can not be offered by the tailings material. Hence, the latent acidity instead needs to be accommodated by mixing with the surface runoff downstream the tailings deposit. This has the important implication that the latent acidity in the drainage from the tailings needs to be neutralised by the surface runoff to protect the downstream recipients from acidification.

It should be noted that the latent acidity is a direct consequence of the primary oxidation of sulphides, in turn directly correlated to the oxygen intrusion in the tailings deposit. Thus, if the predicted oxygen intrusion results in a certain latent acidity, also taking into consideration any residual acidity/alkalinity, the total drainage flow from the tailings deposit gives a total acidity load. This means that, if the acceptable total load of acidity is decided, we may obtain a quantitative measure of the acceptable oxygen intrusion for any given set of local conditions.

To avoid a net acidification of the recipient, the mixing ratio between alkalinity of the surface runoff and the acidity of the drainage water must be large enough to allow the natural alkalinity of the surface runoff to neutralise the drainage acidity. The mixing ratio and the natural alkalinity of the surface runoff are site specific factors. The latent acidity is nearly proportional to the oxygen intrusion rate, whereas the amount of drainage water is given by a water balance over the tailings deposit.

During the primary oxidation of the sulphide minerals in the tailings, ferrous iron and different trace elements bound to the sulphide will be mobilised. The assembly of trace elements found in sulphides may often include zinc, copper, cobalt, cadmium, lead and arsenic. The MiMi studies have shown that different mechanisms are important regulators for the transport and release of the trace elements from the tailings deposits.

The tailings often have a large proportion of iron sulphides among the sulphide minerals. Pyrite is usually the most abundant mineral and can be regarded as a macro component regulating the progress of the sulphide oxidation in the tailings. The pyrite and several of the sulphides formed by trace elements are highly insoluble in water. However, the iron sulphide pyrrhotite is slightly more soluble compared with the other sulphides. Trace elements mobilised by the sulphide oxidation process may then be transported into unoxidised tailings. If pyrrhotite is present in appreciable amount, the dissolved trace elements may out-compete the iron from pyrrhotite and precipitate as less soluble secondary sulphides. The MiMi studies have confirmed such a process for copper, with indications also for lead and cadmium. Field observations and thermodynamic calculations have shown that zinc has a high mobility due to its comparably soluble sulphide. This may explain the high release rates of zinc often observed from tailings deposits. A similar process may be responsible for the low observed release rates of arsenic, although an alternative explanation involving an adsorption process to pyrite is possible.

As a result of the latent acidity, secondary iron precipitates (SIPs) are formed, e.g. in ditches and ponds downstream the tailings deposit. The SIPs are known to be very effective adsorbents for trace elements, in particular arsenic. Hence, despite the negative impact by the SIPs, in terms of acidification and possible aesthetic aspects, a significant capacity to capture trace elements is provided by this process. The MiMi research has provided data that enable quantitative evaluation of such adsorption. Further, estimates have shown that the amount of SIPs formed would have a sufficient capacity to bind a large part of the arsenic and other trace elements released from the tailings. In a similar manner, adsorption to other minerals surfaces in soils and sediments, e.g. silicates, may also offer adsorption sites for trace elements. The adsorption processes are however, dependent on the pH of the drainage. For most metals the adsorption is most efficient at high pH, whereas certain trace elements such as arsenic are best adsorbed at acidic or neutral pH. With a drainage containing a mixture of trace elements it is therefore likely that a near neutral pH is optimum. Consequently, the effectiveness of the adsorption processes, as a means to retain trace elements, therefore couples back to the need for sufficient acid neutralisation by the surface runoff as discussed earlier. The effect on the effluent discharge by adsorption processes is also influenced by the actual flow path for the drainage through the tailings and the natural soil. In general, a long flow path through the tailings and the soil would tend to improve the attenuation of contaminants by adsorption.

Adsorption can also take place on different suspended particles in the recipients. Depending on the chemical conditions in the recipients, the new particles may be formed by precipitation or flocculation and form sediments. Such processes commonly regulate the fluxes of different trace elements in lakes and streams, and are therefore of importance for the fate of trace elements in the recipients downstream the tailings deposits.

The function of wetlands as traps for trace elements has been studied in MiMi. The main conclusion from these studies is, however, that wetlands are not effective traps for trace elements in Swedish climate. Important factors for the studied case were: the wetlands were frozen during the snowmelt when the trace element fluxes were usually high; the wetlands were channelled whereby water residence time became short and the contact surface area between streaming water and the wetland materials was small.

Water cover

There are some important differences between the processes in deposits covered by soil and those covered by water. In the soil covers the pores are partially filled with water and partially by air. The water flows downward through the soil(s) into the underlying tailings. The oxygen diffuses (mostly) downwards in the air filled pores over distances of several tens of centimeters to a metre before it reaches the tailings. There is very little upward diffusion of acidity or dissolved metals into the overlying soil(s). Any upward diffusing species are swept back into the tailings by the downward flowing water.

In the water cover there is no thick layer of soil or sediments (at least in the early stages) that hinder the intrusion of oxygen. The oxygen intrusion is restricted by the low diffusion rate in the water in the tailings. At this early stage, the biogeochemical reaction rates determine the rate of oxygen uptake. This depletes the sulphides in the uppermost layer, which after a short time, on the order of some decades, forms a diffusion barrier of water filled pores in the depleted tailings layer. Already a centimeter layer of depleted tailings makes up a diffusion barrier comparable to that of the soil cover.

Over time, the depleted layer gradually becomes thicker, and therefore the oxygen intrusion rate decreases with time. Any natural sediments formed will further decrease the oxygen intrusion which for a very long time is governed by the diffusion rate. This also points to the possibility to construct of a thin layer of soil or other material as a sediment cover in the impoundment. As mentioned earlier, this could have a large impact on the effluent quality during the early stage.

For a very long time period, the oxygen intrusion with the infiltrating water is small compared to that by diffusion. This has some interesting consequences. Reaction products that are formed, as a consequence of the oxygen intrusion described above, will not be swept downward as readily as in the soil covers. The reaction products will diffuse upward into the water in the water cover. The primary as well as the latent acidity and also the released trace elements will enter the water body above the tailings. If the water is not exchanged, it would with time become acidic with high metal concentrations.

Therefore, in the water cover case, it is essential that the water balance of the impoundment is maintained. This is to ensure that there is always a large water body on top of the tailings, but also that there is sufficient renewal of water to supply the necessary neutralizing alkalinity and dilution to avoid acidification by primary and latent acidity.

The necessary flow rate of water in the water cover case is about twice that needed for the downstream neutralization in the soil cover case for any comparable oxygen intrusion rate. This is because the primary acidity formed in soil covered tailings is neutralized within the tailings. In water covered tailings, the acidity diffuses up into the water column. However, this also has potential advantages over the soil cover case. The latent acidity in the form of ferrous iron when oxidized and neutralized can precipitate on top of the tailings as SIPs. This will add to the diffusion resistance for further oxygen intrusion. The trace elements copper, lead, cadmium and arsenic can be adsorbed on the SIPs that remain in the dam as sediments. With sufficient water flow rate and alkalinity in the water most of the SIPs as well as the mentioned metals could be deposited and remain in the dam and not flow downstream.

It should be noted that it has not been possible to validate the above described processes over long time periods for water covers to the same extent as it was possible for the soil cover case in Kristineberg, where field observations were available of processes and mechanisms acting over several decades.

2 Introduction

This report forms a central part of the reporting from the MiMi programme. The main conclusions of the research investigations are summarised and the general principles and results of performance assessment studies for mine tailings deposits are presented. However, it must be pointed out that a large amount of results are available and can be found in supporting documentation and publications in the open scientific literature. Within the performance assessment work the emphasis has been given to development of a scientifically sound understanding of the governing processes causing the acid mine drainage (AMD) in sulphidic tailings. Two different methods for mine tailings remediation have been studied in particular: Soil cover and Water cover techniques. The conclusions and insights on the function of these methods are reported here.

This Chapter gives a brief introduction to:
– the main concerns related to mining waste, in particular sulphidic tailing,
– the scope of work of the MiMi-programme, and
– some issues of relevance for environmental compliance of a mine waste deposit.

2.1 Background

Swedish mining history

This section on mining history is an excerpt from the PhD thesis presented by Erik Carlsson (Carlsson, 2002). 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 2-1) 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/, 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, Långbans gruvby, Lesjöfors museum, Nordmark gruvby, Hornkullen, and Löa. Old and unremediated mining waste deposits are also reminiscent of this era.

Figure 2-1 Swedish mines 2002. The map also indicates the major ore districts in Sweden. Figure modified from Swedish Geological Survey, SGU.

The Swedish mining industry

Today, Sweden is a major metal producer within the EU[1]. A large share of Europe's iron and metal ore resources and mines is in Scandinavia. Significant mineral exploration is currently taking place in Sweden, opening new possibilities for future mining operation. In a European perspective, the security of metal supplies and the long-term protection of the environment are prioritised areas.

Future exploitation of ore reserves identified during exploration demands knowledge that enables internationally competitive mining operation, with due consideration of increasing environmental demands. Mining operations generally require large areas of land, however, and associated conflicts arise that are primarily related to competing land uses, fugitive dust, vibrations and inevitably, large amounts of mine waste. This waste needs to be managed using principles that control the environmental impact in both short and long term, as well as meet the safety requirements on the deposits over long periods of time. Finding appropriate methods to solve the problems related to mine waste disposal is a prioritised research task, which is addressed by the MiMi programme. While a certain impact on the local environment by disposal of significant amounts of mine wastes within the mine site is inevitable, the impact on the surroundings needs to be negligible. This puts high demands on the management of the mining operation, as well as on the use of appropriate methods for waste disposal and remediation. A factor of particular importance is the need for methods that ensure safe disposal over very long periods of time.

To meet this demand, a research programme was required to establish the necessary scientific and technical basis for mine waste disposal and remediation. The purpose of the MiMi programme has been to provide this basis.

The strategic importance of the mining industry for Swedish society has been recognised in a forward-looking study presented by the Swedish Academy of Engineering Sciences (IVA, 2000). In a report to the Swedish Government, the Swedish Environmental Protection Agency has pointed out the importance of the MiMi programme as a national resource within the area and a need for future support (Swedish Environmental Protection Agency, 2001).

Environmental issues

Significant attention has been given to the effects of mining activities on the environment in the past decades. Large amounts of tailings and waste rock are created as a result of ore extraction. The main concerns of sulphidic tailings impoundments are the potential occurrence of acid mine drainage problems and potential failure of tailings dams that could lead to contamination of downstream areas. In addition, the tailings deposits make use of large areas of land. In Table 2-1, the amount of mine waste produced in Sweden is summarised. The release of metals and acidity from sulphidic mine tailings has been studied extensively throughout the world. The remediation of mine tailings has been recognised as a major cost for the mining companies and the need for environmentally safe and cost effective remediation methods is large. Depending on the local conditions at the site and the characteristics of the particular mine waste, different methods are applied. In Sweden, the most common remediation methods today are to cover the tailings with soil or water.

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[1] (Based on production within the present 25 EU member states in 2002): *Iron 88 %, 1st; Gold 29 %, 1st; Silver 18 %, 2nd; Lead 25 %, 2nd; Copper 11 %, 3rd; Zinc 19 %, 3rd.*

Table 2-1 Mine waste generated in Sweden in 2003.

	Million tonnes	**Percentage**
Sulphidic ore mines total	**45,4**	**77% of all mine waste**
Tailings sand	21,3	86% of all tailings sand
Sulphidic waste rock	10,3	30% of all waste rock
Separately handled sulphide-free waste rock	13,8	41% of all waste rock
Iron ore mines total	**13,5**	**23% of all mine waste**
Tailings sand	3,5	14% of all tailings sand
Waste rock	10	29% of all waste rock
Total all mines	**58,9**	
Tailings sand	24,8	42% of all mine waste
Waste rock	34,1	58% of all mine waste

In a broad perspective, the management of mine tailings should aim at meeting the national environmental goals. In Sweden, the goals of primary relevance are:

- non-toxic environment
- groundwater of high quality
- thriving wetlands
- living lakes and water courses
- sea in balance and living coastal zone
- living forests
- no eutrophication
- only natural acidification

It is realised that the establishment of a mine and deposits of mine tailings will inevitably be connected with a certain environmental load. It is important to consider the actual levels of environmental impact that should be met and are tolerable. The immediate surroundings of the tailings impoundments may be expected to be contaminated by metals and acid released by tailings weathering. However, due to different attenuation processes in the ground and downstream watercourses the environmental loading may decline with increasing distance from the deposit. It may therefore be of interest to assess at which distance the impact from the deposit would attain the same level as the variability of the local natural background.

The Swedish Environmental Protection Agency has compiled reference values to enable assessment of environmental conditions considered to be impacted by human activities. Extensive investigations have also been made to determine the natural background levels in different areas of Sweden. It should be recognised that mining takes place in areas that are commonly heavily mineralised and therefore has a significant background contribution to the observed contaminant levels, often to be classified as polluted even when no anthropogenic exists.

The acceptable contaminant levels can be determined with due consideration to the site-specific conditions, e. g. the anticipated land-use after decommissioned mining operation, proximity to sensitive or protected environments and relevant dispersion pathways for contaminants to critical individuals living nearby the facility.

Past mine waste research in Sweden

The emission of acid mine drainage in Sweden was first reported by Jacks (1976). A research programme carried out in 1983-1988 by the Swedish EPA, increased the understanding of oxygen intrusion as an important factor causing the acid mine drainage (AMD) (Lundgren and Lindahl, 1993). Mathematical models were developed to help design soil covers to reduce oxygen intrusion into the waste deposits (Magnusson and Rasmuson, 1984; Rasmuson and Collin, 1986; 1988). The research results were tested in full scale at the Bersbo deposit (Lundgren, 1997).

Based on this experience the Swedish Waste Research Council (AFR) decided to fund continued research with the following objectives:

- Increase knowledge of the weathering processes of sulphide minerals;
- Improve the prediction tools of transport processes in the waste deposits;
- Study the effects of alternative remedial actions; and
- Develop cost-effective remediation techniques.

About 20 research projects, with a total budget of US$1 million, were carried out during 1994-1997. The Swedish mining industry has also carried out significant research at specific sites. Summaries of Swedish experience is given by Gustafsson (1997) and detailed site-specific studies are reported by e.g. Lindvall et al. (1997a-b); Ljungberg et al. (1997).

2.2 The MiMi Programme

The MiMi initiative

The idea for the MiMi-programme was brought up by AFR jointly with the Swedish mining industry. A steering committee was formed with representatives from the Swedish mining industry, the Swedish EPA, AFR and the Mistra foundation. The steering committee assigned a co-ordinator and an ad-hoc working group, which involved representatives from academia, the mining industry and consultants.

Organisation of the work

The different processes leading to the emission of acid mine drainage (AMD) are complex and span over numerous scientific disciplines. The MiMi-programme is an integrated effort of researchers and engineering specialists from different scientific disciplines; geologists, geochemists, microbiologists, geohydrologists, geotechnical and geophysical expertise, ecologists and botanists.

MiMi has taken on the challenge to provide economically and environmentally efficient and safe waste management solutions that will meet enhanced future demands. Throughout this work, it is important to develop, and communicate, relevant knowledge necessary for finding correct and well-balanced disposal solutions, to the industry and the authorities. In particular, the development of waste disposal technologies that ensure a long-term performance is a true challenge.

Five key areas were pointed out by a steering committee during the planning phase of the MiMi programme, into which the research should be directed:

- Cost-efficient prevention and control methods
- Prediction methods
- Microbial processes and their importance for AMD
- Management of process waters and leachate waters from mines and deposits
- Establishment of vegetation.

Studies of these topics have been the starting point of the MiMi research activities. To assure focussed and co-ordinated efforts by the different research teams, the Kristineberg mine operated by Boliden Mineral AB has been selected as a common study site for the MiMi-programme, and a field-monitoring programme has been established and maintained. Parts of the Kristineberg mine site have been remediated, with plans for remediation of the remaining parts over the next few years. A variety of remediation methods have been applied in the area, which offers excellent opportunities for research studies (Lindvall et al., 1999).

Achievements during MiMi Phase I

The initial phase of the MiMi programme has established a research organisation consisting of several scientific and engineering specialists working together on a common task. A common field site has been selected, the Kristineberg mine, and a field-monitoring programme has been established and maintained.

In essence, the first phase of MiMi was focused on measurements and quantifications of different processes in field and laboratory, as well as on development of predictive models to assist in the interpretation of processes acting over time. During the first phase the programme was organised in projects with the following objectives:

Field studies and characterisation. Studies of mass-balances, improved characterisation methods and process evaluation of dry till covers and water covers, including the effects of vegetation.

Laboratory studies. Resolution of important mechanisms that can be used as chemical, physical or microbial barriers against mobilisation of pollutants and mechanisms leading to retention and containment.

Predictive modelling. Development of models that were based on and increased the understanding of processes acting on the system over time. The increased model precision was used to quantify the performance of different remediation methods in the short and long term.

Prevention and control. Finding improved, efficient and economic methods for remediation. Studies included different management strategies for waste, active and passive barrier systems, vegetation of deposits and natural attenuation processes.

Coordination, integration and communication. Special efforts were set aside to coordinate and integrate the work and collaboration between research groups. A steering committee was appointed, responsible for analysis and synthesis guiding the ongoing work. Contacts and collaboration with different Swedish and international parties ensures the exchange of information and ideas. An important task has been the communication of the results to identified end-users to ascertain that findings will result in practical and correct implementation.

The field and laboratory observations have been continuously interpreted on a conceptual basis and have also been compared with quantitative model evaluations. Identified deviations between observations and predictions have been used for refining and improving the understanding and to initiate further research and model development.

State-of-the-art reports have been produced on a number of important areas. In addition, scientific results have been published in peer-reviewed international scientific journals, as well as at international conferences. A summary report of the results from the first phase of the programme, to some extent updated during phase II, is found in the report *MiMi - Results and Synthesis Report for Phase 1, 1998-2001* (MiMi Report 2002:3).

The network of researchers, engineering specialists and industry representatives established during Phase I, provided a platform necessary for the work in Phase II. In many respects this has offered unique possibilities for collaborative research, including both in-depth basic research and more applied aspects of mine waste management. The process to establish this collaboration is further detailed in Höglund et al. (2001a) and in a MiMi report compiled by the MiMi board and steering committee (MiMi, 2004).

Soil Covered Tailings

Detailed studies on Impoundment 1 in Kristineberg show that the soil cover is efficient with respect to limiting the oxygen intrusion. Any remaining oxidation is now occurring under dysoxic conditions, possibly with contribution from Fe^{3+} as an oxidant in acidified parts. A diverse microbial community that may play a role in this context has been observed. An extensive study of the groundwater geochemistry indicates that the rate of sulphide oxidation has decreased, but that it will take another 5-10 years until the overall groundwater quality has been improved. A raised groundwater table results in wash out of weathering products retained in the tailings. Hydraulic conductivity tests on compacted low permeable till barriers indicate that their efficiency is very sensitive to compaction during construction. Repeated freezing and thawing also indicate that such barriers may be affected by frost action, if not protected by a sufficient cover. Furthermore, modelling results show that deterioration or quality variations in a low permeable barrier may have a significant effect on the overall intrusion of oxygen.

Water Covered Tailings

One method to limit the supply of oxygen to mine waste is to cover the waste with water. Flooding by raising tailings impoundment dams is an important remediation method. Detailed geochemical studies of the flooded, sulphide-rich tailings at Kristineberg and Stekenjokk show that flooding is an efficient method from a geochemical point of view, and that there is little leakage of metals from the tailings to the pond water. Washout of old weathering products may, however, be a problem for water covering old waste. At Kristineberg, the flooded pond is limed and functions as an efficient trap for metals released from upstream impoundments. If flooding should be a real walk-away solution, long-term dam stability is critical. The high pH in the limed pond has a strong inhibitory effect on bacteria, whereas nutrients are not lacking. If plants are established in a pond, the water depth may be shallower than otherwise. Introductory studies show that it may be possible to establish vegetation in flooded impoundments. Studies of metal uptake show that different species have very different metal accumulation capacities.

Biogeochemical Barriers

A pilot-scale barrier system has been installed for the treatment of groundwater discharging from Impoundment 1, and has been monitored at regular intervals. Analyses of treated water indicate that acid neutralisation is proceeding as expected. However, the maintenance of a viable population of sulphate-reducing bacteria has proved to be difficult, probably because of the relatively low water residence time in the system. Laboratory experiments, nevertheless, have yielded encouraging results and demonstrate that by reducing water flow in the field system and by inoculating with bacteria, it should be possible to maintain a population of sulphate-reducing bacteria for an extended period of time.

Co-disposal Technique

Full-scale pumping tests (in the order of 100 000 tonnes) with a slurry of tailings and crushed waste rock have shown that drained deposits with inherent stability and natural landscape forms can be achieved. However, in these tests co-disposal including pumping of waste rock was not found to be economically competitive to traditional disposal techniques. Pilot-scale tests with co-disposal utilising traditional transport methods have shown favourable results with regard to stability. However, the retention of tailings sand in coarse waste rock structures needs to be improved.

Wetlands as Metal Traps

A field-monitoring programme was established to study metal removal in the wetland system down-gradient from Impoundment 4. Results from this study demonstrated that water flow in the wetland system is highly channellised, with a major fraction of the metal flux concentrated during snowmelt when the wetland is still frozen. Little metal precipitation occurs in the wetland sediments. Metal attenuation in the wetland is due primarily to dilution, while increases in metal concentration can be attributed to metal sources in mineralised regions of the catchment area. A conclusion of this study is that the studied wetland system is inefficient for capturing metals, but that a constructed wetland may be properly designed for sufficient water treatment. A method was developed for the determination of aqueous metal complexes with organic matter, and indicated that copper, for example, occurs primarily in complexes with natural organic matter.

Surface Water Systems

Particles play a significant role in the distribution of metals in surface waters within the mining area and in the recipient (R. Vormbäcken). The particulate phase consists of organic and inorganic matter, such as secondary iron precipitates formed by oxidation of ferrous iron, with particle sizes ranging from colloids (<0.22 µm) to suspended solids. The uptake of contaminants to particles is determined by the chemical conditions. Association of contaminants with particles forms a potential basis for utilisation of natural attenuation processes in active as well as passive treatment systems. It was estimated that, under optimal conditions, the adsorption capacity of the secondary iron precipitates is sufficient to immobilise a significant fraction of the heavy metals released by sulphide weathering.

Phase 2

When starting the second phase of MiMi, significant amounts of data were available and also continuously collected. Therefore, during the second phase effort has been put on the interpretation and integration of the different research results in the context of the function of mine tailings deposits over time. Conceptual and mathematical models have been developed and used in the systematization and synthesis of knowledge.

The **overall goal** for the second phase of the MiMi programme was formulated:

> ***To devise methods for the safe disposal of mining waste and for the reliable prediction of their function over very long periods of time.***

In order to achieve this goal, the research activities during the second phase have been focused on the following main tasks:

I. *Developing scientifically sound conceptual models as a means to understand the importance of different processes in disposed mine tailings and in the far field.*

II. *Devising methods for characterisation* of the disposed mine tailings in *order to define basic measurable input data* necessary for *the performance assessment* of the function of different disposal methods *over long periods of time*.

III. *Using studies of natural analogues to evaluate the importance of processes acting over long time-scales*, inaccessible by experiments and other means of observations, with the purpose to apply the findings to mine waste disposal.

IV. *Applying a performance assessment methodology for reliable long-term prediction based on a synthesis of conceptual models, data acquired by characterisation of the disposed tailings, and studies of natural analogues*.

V. *Training of PhD students* and involving *senior researchers and engineering specialists, that may* act as *carriers of competence*, as well *as to establish technical and scientific networks*. The purpose has been to *contribute to the future competence needs* of industry and society, and *to assure appropriate implementation of results*.

Reporting from the MiMi programme

This report forms a central part of the reporting from the MiMi programme. The main conclusions of the research investigations are summarised and the general principles and results of performance assessment studies for mine waste deposits are presented. Additional details can be found in complementary reporting in the programme.

Within MiMi, a number of scientific and technical reports have been published, where detailed results are provided. In addition to this, a significant publication of scientific material has resulted from the MiMi programme; to date six PhD-theses, ten licentiate theses, and numerous scientific contributions to journals and conferences. A report has been compiled that lists the different MiMi reports and publications, in many cases with short abstracts describing the scope, *Reports and Publications from MiMi (2004)*. The MiMi publications and references to all scientific contributions are available on a searchable CD-rom, as well as through the MiMi web site *www.mimi.kiruna.se* or *www.mistra.org/mimi* where a web application is also available for guidance. An e-learning kit for self-studies, based on material from the MiMi end-user workshops, is also available on CD and on the web. An overview of available information from the MiMi programme is given in Figure 2-1.

The reporting from the MiMi programme is extensive and significant efforts have been set aside to present the research results in a comprehensible form. To achieve this, a book has been written in a popular scientific style directed to a Swedish audience of non-specialists. The ambitions with the book has however been that the information should be relevant, up to date and provide interesting insights also for the specialists in the field (in Swedish only).

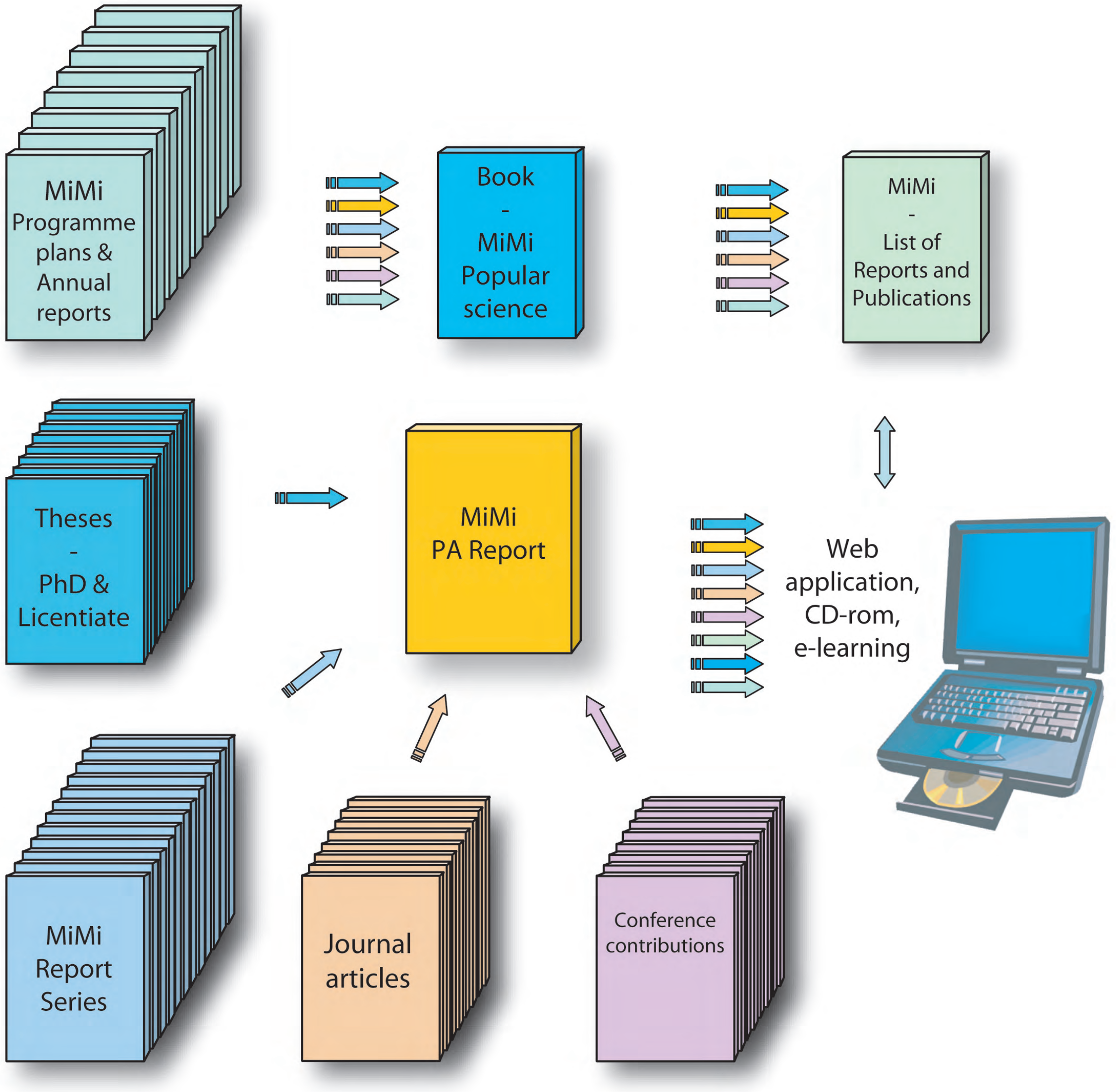


Figure 2-1 Information available from MiMi.

2.3 Scope of work

The MiMi-programme has sulphidic tailings impoundments as its main focus. This report is entirely concerned with tailings impoundments, the function of different remediation methods and different down-stream measures and effects. In many respects, the results may also be of relevance for waste rock deposits, but this has not been studied specifically within MiMi. The crucial question for the disposal of mining waste is to demonstrate in a solid scientific - technical way the effects of the selected prevention and control actions over very long time periods. To address this question, an approach based on performance assessment has been adopted. Performance assessment is a methodology developed by researchers in the area of radioactive waste management.

In the present study, it is presumed that the tailings are contained in impoundments and when necessary for the functionality equipped with long-term stable dam constructions. Therefore, issues related to dam stability are not a primary focus in this report.

2.4 Structure of the report

The report has different parts. The first part comprises chapters 2-3. The second part comprises chapters 4-9. The third part comprises chapters 10-14. This is followed by conclusions and recommendations presented in Chapter 15.

The first part gives the background with a generic problem description and presents the aim of the MiMi programme (Chapter 2). The performance assessment methodology is introduced to the reader in Chapter 3.

In the second part, we describe the site and the waste, emphasising those properties that we at present deem to be of importance for assessing the rate of release of contaminants. An overview of the methods that are used to prevent and control the release and the main mechanical, physical, chemical, biochemical and transport processes that need to be considered are described.

Different processes dominate in different regions. The waste itself is the source of the contaminants and is thought of as a source term. There is a considerable resistance to release due to solubility limitations, provided the chemical environment is not disturbed. The waste is described in Chapter 5.

The waste itself and the material immediately under and over the waste is called the near field. The near field offers a resistance to intruding water and air and may attenuate leaking contaminants by different processes. The near field can be influenced by design and especially the cover is of central importance. Different prevention and control methods are described in Chapter 6. In Chapter 7, processes of importance for the function of near field are described in some detail.

The region outside the waste and the engineered barriers is called the far field where additional attenuation mechanisms are active. The far field is commonly not changed by engineering measures. A description of the far field conditions at the MiMi field site at Kristineberg is presented in Chapter 8. In Chapter 9, processes of importance for natural attenuation in the far field are described.

The third part sets out to quantify the various processes in order to assess the rate of release from the source to the near field, from the near field to the far field and from the far field to the surface waters and thus the biosphere.

The quantification is made using models. The models are mathematical formulations of the various processes and mechanisms that were described in the second section of the report. They make it possible to account for the many complex interaction processes e.g. chemical changes in the near field as influenced by exposure to air and water.

The models need data that are of general nature such as e.g. basic chemical data as well as specific for the site such as e.g. site geometry and physical properties of different materials.

There are a large number of uncertainties both in basic data and in such information as e.g. future rainfall. It must thus be expected that there will be different answers for different choices of input data. In order to accommodate the uncertainties and the natural variability of the system two somewhat different techniques are used. Firstly, a sensitivity analysis is used to assess how a choice of a different value of a parameter will influence the results. Secondly, a scenario analysis is used to illustrate the results of “What-If” questions. That could be e.g. what if there is a longer period of dry weather or rise in temperature etc.

Both approaches start with defining a base case. In the base case the input data are chosen so that they are realistic based on what is known at present. For example the chemical composition of the waste is fairly well known but can vary. Then one could choose a mean value. Rainfall can be based on historic records and a value near the mean would be typically chosen. Based on the base case data the models are used to calculate the reactions and other processes that lead to mobilisation of the contaminants and their subsequent fate through the different regions.

Not to lose transparency of the modelling and to gain insight into which processes dominate and which processes are of secondary importance, the different processes are quantitatively described in the different regions. The resulting rate of release of the contaminants is the final result.

In the sensitivity analysis those processes are sought out that were found to have a large impact on the results. Systematically the parameters of those processes are varied within reasonable ranges and their influence on the release is determined.

In the scenario analysis, reasonably possible scenarios are defined and their impact on the release calculated, when possible, or is assessed by other means. A systematic methodology for scenario analysis and documentation is described and exemplified.

Finally, in Chapter 15, a synthesis is made of the research results, the field observations, the performance assessment studies and research results available in the international scientific literature. The conclusions drawn are presented and discussed. Important issues that require further research studies are suggested.

3 Performance assessment methodology

The MiMi vision states that *"…The MiMi programme has made it possible to predict the extent of environmental impact and has provided tools and methods to control and design processes and waste treatment systems already from investigation of the mineralogical and chemical composition of the ore and the wall rocks, and the local hydrology and topography…"*

A systematic approach is required to address the function of mine tailings deposits over long time. Performance assessment studies for the final storage of radioactive and other toxic wastes have addressed similar questions for decades. The application of a simple, but robust methodology, based on fundamental and well-established scientific principles such as thermodynamic and mass-balance approaches, has been very successful. Thus, the same basic concept has been found appropriate for long-term performance assessments of governing processes in mine waste deposits.

It is essential to be able to describe the function and in quantitative terms assess the long-term properties of different remediation alternatives. Preferably, this should be conducted already during the planning phase for a new mine, so that the results of the evaluations can be used as a basis for improving and optimising the design. This is the objective of the performance assessment studies.

3.1 Problem description

While sulphidic mine waste-related environmental problems and required remediation techniques may be complex, the fundamental source of these problems is simple. The key issues that are the root of these environmental problems are:

- Mine waste often contains metal sulphides
- Sulphides oxidise when exposed to oxygen and water
- Sulphide oxidation creates an acidic metal-laden leachate water
- Large amounts of waste have the potential to result in leachate generation over long periods of time.

The primary consequence of these key issues is that the applied prevention and control methods must have a very long functional lifetime. Therefore, the methods used for the construction of waste deposits with covers and dams need to result in stable structures. The crucial question for the disposal of mining waste is to demonstrate, in a solid scientific - technical way, the effects of the selected prevention and control actions over very long time. In this context, the relevant time scales are on the order of hundreds or even thousands of years.

Even for mine wastes that do not contain sulphides, like tailings from iron oxide mining, the long-term stability of waste containment, is a critical factor.

In order to demonstrate that the effects of selected remediation methods are viable over very long time, different prediction tools are required. Two types of tools are necessary for this: – experimental methods to characterise the waste material, – and quantitative models for predictions of metal release and transport over long time.

Figure 3-1 gives a schematic illustration of the origin of acid mine drainage and various treatment options at a mine site. When integrated system solutions are used for reclamation of complex mine sites the performance assessments must take a holistic perspective.

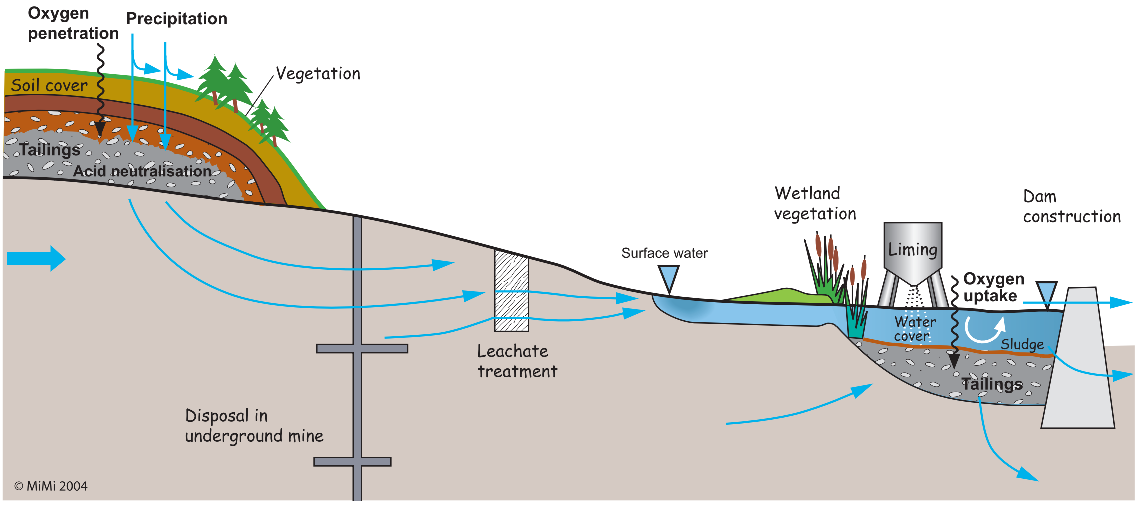


Figure 3-1 A schematic illustration to causes and remedies for generation of acid mine drainage.

3.2 Problem Structuring

The basic features of mine waste deposits can be structured in three parts, *i) the Source term*, *ii) the Near field*, and *iii) the Far field*, as illustrated in Figure 3-2.

The *Source term* concerns different aspects of the waste that is produced, such as the amounts and characteristics of the waste, the possibilities to alter its chemical and mineralogical composition, and different aspects of the reactivity of the waste.

The *Near field* covers all aspects of the waste deposits and the engineered barriers. The fundamental remediation approach for the near field can be denoted *passive prevention*, i.e. methods applied to preclude oxidation of the waste and thereby avoiding subsequent problems. Critical questions include the mobilisation of metals from the waste, the longevity and sustained function of the cover layers and of dam constructions built to confine the waste and to prevent oxygen from reaching the waste.

The *Far field* comprises the area outside the constructed deposits that receives drainage water from the deposits. It is important to understand and be able to quantify different natural attenuation processes in the far field for the assessment of the environmental impact of a constructed deposit. Studies of the far field also include different *passive treatment* methods for mine drainage water that can be efficient in combination with the containment methods applied in the near field.

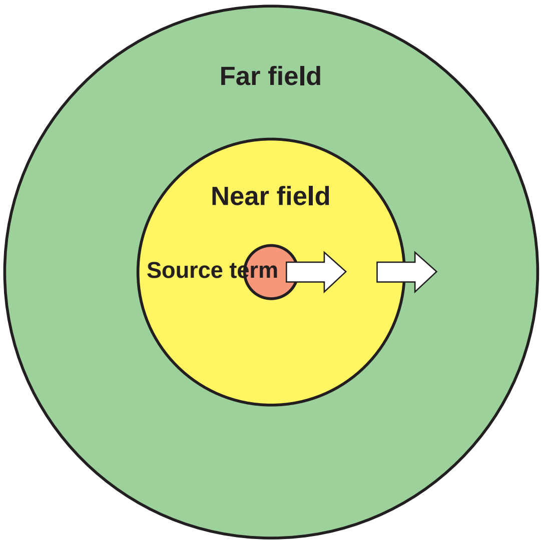


Figure 3-2 Illustration of the propagation of trace elements and acidity mobilised from the source term, transport through the near field and the release into the far field.

This approach follows the propagation of trace elements and acidity mobilised from the source term, transport through the near field and the release into the far field. The investigated problem can then be conceptually simplified to:” *by reducing the amount of leachable metals in the source term, and by reducing the inflow of oxidants in the near field, we can thereby decrease the trace element release rate. In addition, trace elements and acidity that do escape from the near field are retained in the far field by accounting for the capacity of natural attenuation processes.”*

Studies have been undertaken within the MiMi programme on the feasibility of different methods:

- to reduce the source term strength,
- to mitigate the release of contaminants from the source term and the transport in the near-field, and
- to explore the possibilities to increase the natural attenuation in the far field.

3.3 Methodology

In order to demonstrate that the effects of selected remediation methods are viable over very long periods of time, different prediction tools are required. Two types of tools are necessary for this:

- experimental methods to characterise the waste material,
- and quantitative models for predictions of metal release and transport over long time periods.

The prediction of the environmental impact from mining waste over long periods of time is complex and requires an integrated approach, with due consideration to multiple and interacting processes, e.g. chemical, microbial, physical and mechanical processes. The performance assessment methodology has been developed to handle such complex systems and has been shown to be reliable.

Performance assessment is a methodology developed by researchers in the area of radioactive waste management. The primary question addressed here is: *How can we assess the performance of a proposed disposal design over a period of time that by far exceeds the period for which experimental evidence can be provided?*

The approach relies on basic and well-established scientific knowledge, such as found for thermodynamic processes in combination with mass-balances, to scrutinise the function of a proposed design from any possible angle, successively increasing the complexity of the addressed issues when found necessary. In essence, the performance assessment uses an assembly of conceptual and mathematical models. The models are used to describe and quantify the main processes that govern the release, transport, as well as the chemical and biochemical reactions of the contaminants in the whole chain from the source term to a final recipient. This methodology can be used to study e.g. how changes in the design of the near field influence the final release. It also allows the identification of crucial mechanisms and design issues.

To support the evaluation of the long-term effects of different processes, studies of natural analogues can give valuable additional information. In Sweden, many quaternary geological formations such as dense till formations and sulphidic clays, as well as weathering of massive sulphide rocks, are available that can give valuable information on processes acting over periods of 5 000-10 000 years.

It is important to describe the studied systems in a clear and transparent way to make it possible to distinguish between significant and negligible processes. Such evaluations also need to be made at different times. For a mine waste deposit three different stages are of interest:

- The operational stage (e.g. during the first decades)
- The short-term – mid-term stage (e.g. within the first hundred years after closure)
- The long-term stage (i.e. hundreds to thousands of years after closure)

In this report, the main focus is on the long-term stage, although the short- and mid-term stage will also be addressed. A systematic approach to address the complex interaction of different processes can greatly facilitate the performance assessment work. One method developed for performance assessment is the so-called interaction matrices used to assist in structuring and documenting the work needed for establishing conceptual models of complex systems. The method is also suitable for keeping record of priorities given to different processes, as well as documentation of the underlying scientific basis. The interaction matrix method can also be used as a platform for studies of the impact on the function of studied remediation technologies by changes in the design or the external conditions, e.g. changes of climate. Systematic studies of such changes are commonly denoted scenario analysis, which is an integrated part of the performance assessment. The use of e.g. interaction matrices provides a structure to formulate and document reasonable scenarios.

By the performance assessment approach, a successive development of the conceptual understanding and quantification of a complex system is enabled. A simple illustration of a mine site where a system of remediation methods has been applied is presented in Figure 3-1. The experience from radioactive waste management in using the performance assessment methodology has shown that it is an effective pivot for synthesis of research results and for identification of critical tasks, which need further scientific research. This can create a dynamic research process, as illustrated in Figure 3-3, where the performance assessment is used to set priorities for the research activities.

The performance assessment framework is used for the following purposes:

- to identify and document the processes judged important for the different technologies and methods studied,
- to establish conceptual models based on the scientific comprehension of the interacting processes,
- to set up simple mathematical tools to evaluate the importance of different processes, and
- to successively include additional processes in more elaborate prediction models.

Whenever applicable, available models and modelling tools are used for exploratory calculations. For specific needs, further developments and adaptation of the existing models are made when necessary. At all levels of the performance assessment the models are used to study the sensitivity to the fundamental assumptions, systematically testing alternative model concepts, as well as the sensitivity to uncertainties in the basic input data.

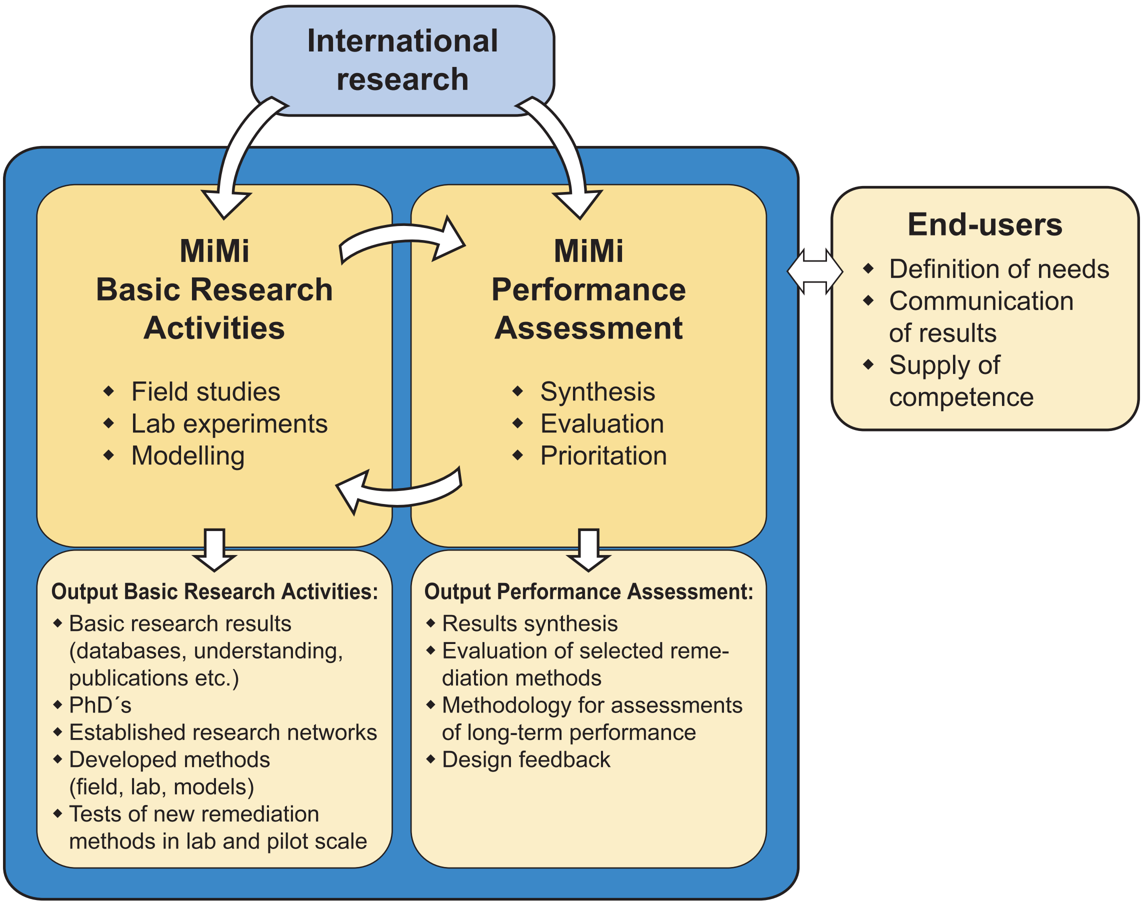


Figure 3-3 A systematic performance assessment methodology in the MiMi synthesis work provides a toolbox for evaluation and guidance for on-going research work.

With its main focus on sulphidic tailings and long-term performance, a methodology for the performance assessment work has been developed within MiMi which is briefly described below. For each of the studied remediation methods the continuous and recurrent methodology includes:

- A thorough and detailed definition of the environmental situation at the site is given and the anticipated function of the proposed/studied remediation method is described.

- A Base case definition is set up for the studied remediation method. Only very basic features and processes are included in the Base case definition. This ensures simplicity and transparency.

- Simple models, both conceptual and mathematical, are applied to study and to quantify the effectiveness of the method. Initial evaluations, process by process, are made for idealised conditions.

- Throughout the evaluations, processes of quantitative importance are pinpointed and the conditions under which they are of importance are documented.

- The complexity is gradually increased by considering additional processes, as well as by accounting for process interactions. Scientifically stringent process descriptions are set up and interactions between processes are identified and documented in a structured way. A structured methodology is applied, e.g. development of so called interaction matrices, to define scenarios, caused e.g. by changing environmental conditions. It is essential to document assumptions and judgements made throughout this work.

- Predictions are made for the defined scenarios and the results are used to assess whether the performance of the remediation technique is adequate.

- Sensitivity calculations are performed for different processes to study the impact on the overall performance. Alternative conceptual and mathematical models are applied and compared, and when applicable, alternative data sets are tested for consistency.

- The models upon which the performance assessment simulations are based are continuously compared with field and laboratory observations, making use of identified deviations for refining and improving the understanding, for improving the system definitions and to initiate further research and model development. In addition, observations of natural analogues are used to validate the models.

- The results of the performance assessment provide important feedback in the design process to encourage new and improved remediation techniques.

4 Site description

The Kristineberg mine in northern Sweden was chosen as the main field site for the MiMi research programme since it has a number of tailings deposits subject to remediation using a variety of methods. Further, an extensive pre-reclamation database related to the site was available. The reclamation programme started 1996, and one of the tailings impoundments still remains to be completely decommissioned. Field studies, sampling and analysis under the auspices of the MiMi programme started 1998.

4.1 Mining history and geology

The Kristineberg has been operated by Boliden since the commissioning of the operations 1940. The mining area is located in the western part of the Skellefte ore district, approximately 175 km south-west of Luleå (Figure 4-1). The bedrock consists of ca. 1.9 Ga metamorphosed ore-bearing volcanic rocks overlain by metasedimentary rocks. The metasupracrustals display a marked foliation and extensive sericitization (Vivallo and Willdén, 1988). Pyrite-rich massive sulphide ores are intercalated within a stratigraphic unit consisting of mainly basic volcanics and redeposited volcano-clastic rocks (Willdén, 1986). Common ore minerals are pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and magnetite (Fe_3O_4). Common gangue minerals include quartz (SiO_2), sericite ($KAl_2(AlSi_3)O_{10}(OH)_2$), chlorite ($(Fe,Mg,Al)_{4-6}(Si,Al)_4O_{10}(OH)_8$, talc ($Mg_3Si_4O_{10}(OH)_2$), biotite ($K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$), and calcite ($CaCO_3$) (Holmström et al., 2001).

The largest ore in the area is the Kristineberg Zn-Cu deposit. This deposit was discovered as early as 1918. In 1940, the mine was brought into production to support Sweden’s supply of alloy metals during the war. A mill and a 96 km long tramway were constructed to convey the products to the Boliden mine for further transport to the smelter. In the past, ten different mines within 50 km distance from Kristineberg have provided ore to the Kristineberg mill, but today the Kristineberg mine is the only remaining active mine in the area. The mine produces ca. 490 000 tonnes of ore per year. The tramway was replaced by highway trucks in 1988, and the Kristineberg mill was closed in 1991. Today, processing of the ore takes place in the Boliden mill.

Sulphide-rich tailings have been deposited in the five impoundments 1, 1B, 2, 3 and 4, all located along a small valley (Figure 4-1). Impoundments 1 and 2 are the oldest, used until the early 1950s when impoundment 3 was constructed. Later, impoundment 4 was constructed further downstream. Low-grade pyrite and pyrrhotite concentrates, intended to be used as a sulphur source for production of sulphuric acid, were deposited in impoundment 1B. However, the market for these concentrates never developed, and the impoundment was incorporated in the reclamation programme.

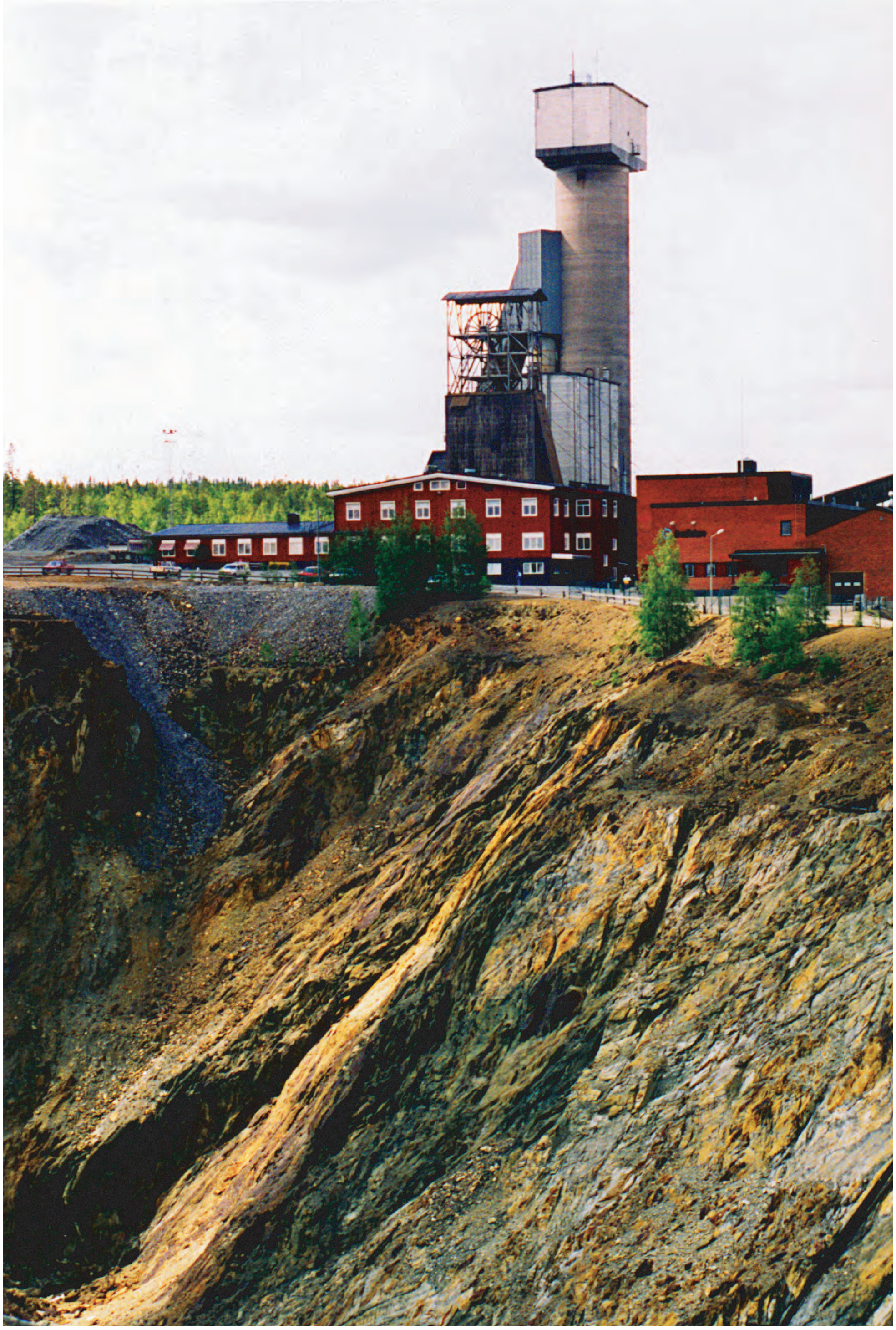


Illustration: The Kristineberg mine with the old open pit in the foreground.

Figure 4-1 Map of the mine area with the impoundments 1, 1B, 2, 3 and 4 with the surrounding catchment area, and location of Kristineberg in Sweden.

4.2 Remediation activities

The tailings impoundments are in the final stage of remediation (Lindvall et al., 1999). Both dry covers with till as cover material and flooding have been applied. A brief description of the current remediation activities at Kristineberg is presented below; additional details are discussed in Chapter 6.4.

Impoundments 1 and 1B were covered with till in 1996. A layer of crushed limestone was distributed on the surface of the tailings before the cover was applied. On impoundment 1B, a composite cover was applied as a sealing layer, where 0.3 m compacted till with a maximum hydraulic conductivity of $5 \cdot 10^{-9}$ m/s was applied. On top of that layer, a protective layer of 1.2 - 1.5 m unspecified till was applied. This system was also used on the north-eastern part of impoundment 1, covering approximately half the impoundment area. On the remaining part of the impoundment, 1 m of unspecified till was applied on the tailings and the new concept of groundwater saturation was applied. Groundwater saturation was maintained by water management, whereby existing drainage ditches were backfilled to allow groundwater and surface water to enter the area from up-gradient areas. By covering the area with 1 m of unspecified till, this allowed a further raising of the phreatic level. In this area, the groundwater table now is shallow, completely covering the tailings and occasionally reaching the ground surface. The till surface was hydroseeded with grass, and today grass covers the surface and higher vegetation has started to establish itself.

On the major part of impoundment 2, the same method for groundwater saturation was applied. The easternmost part of impoundment 2 consisted of an impoundment, which was left flooded. To allow access to the area for the contractor equipment without costly access roads construction, the cover was applied during winter when the ground was frozen.

Until recently, impoundment 3 has been used as a component in the mine water treatment process. This impoundment constituted a sedimentation impoundment for the sludge generated by the straight liming process being used both during mill operations and also after the mill was closed. As a result of this, the tailings in the lower part of impoundment 3 are covered by hydroxide sludge. The western part of impoundment 3 has been covered with 1 m unspecified till according to the groundwater saturation method described above, and in the eastern part the groundwater almost reaches the covered surface. The entire impoundment 3 will eventually be covered with till.

Impoundment 4 covers an area of 0.74 km^2, and was flooded by raising the existing dykes by 1.5 m. The water depth varies from approximately 1.5 to 2.5 m, and the impoundment is ice-covered from late October to early June. Erosion-protection material will be applied in shallow areas. The water flowing from impoundment 3 is treated with lime before it reaches impoundment 4. Treated water is finally discharged to Vormbäcken.

The remediation plan for Kristineberg, described above, is a system approach used to manage drainage water from the impoundments during the transition phase following remediation. A washout of weathering products from the various impoundments has been predicted to occur for several years after covering and raising the groundwater level. By controlling the pH with the addition of lime, thereby reducing metal mobility, the water-covered downstream impoundment (i.e. impoundment 4) acts as a trap for metals released from the areas upstream. When remediation is completed after mine closure, the long-term water balance will be ensured by re-directing the river Vormbäcken, presently channelled to bypass the tailings impoundments, back into the water-covered impoundment 4. Liming will be discontinued when the water quality is satisfactory, and natural sedimentation is foreseen to contribute to the containment of metals by the sediments in the impoundment.

Illustration: The Kristineberg mine area – view from across the valley.

5 Source term - Deposited waste

5.1 Introduction

The long-term chemical and physical stability of mine tailings is intimately related to both the quantity and composition of the tailings. It is therefore important that, whenever possible, the composition of the tailings should be controlled in order to provide a material that ensures this long-term stability. This chapter begins by discussing the necessity for source term limitation, and then presents available data on the amount and composition of tailings that have been deposited as a result of mining activities in Kristineberg. Furthermore, the physical properties of the tailings are discussed, such as grain-size, porosity, and water retention properties, which are important parameters influencing the flow of gases (e.g. oxygen) and water in the deposit.

In order to compare results from this mine tailings study and performance assessment, it is important to indicate if the properties of the Kristineberg tailings are representative of values for other Swedish and non-Swedish mine tailings. Therefore, this chapter is concluded with such a comparison of the various properties of the tailings from impoundment 1 and values from other deposits cited in literature.

5.2 Source term limitation

Environmental problems related to mining waste often originate from historic industrial activities. It is not until the 1970s that the selective management of waste products based on their potential environmental impact found a wider spread. Numerous examples exist, in roads, dams and other geotechnical installations in which sulphidic material was used, sometimes causing severe environmental problems with acid rock drainage.

The relevant management of waste products based on their inherent geochemical properties provides opportunities for source term limitation. Source term, as defined by MiMi, equals the material’s pollutant generation potential as a function of each mineral constituent’s properties. In this context, every stage of the production process needs to be considered and each of the intermediate and final products evaluated. Different intermediate products in a milling process, by definition, have individual properties and may therefore possess drastically different geochemical properties. A fundamental example of this is the pyrite and calcite content in sub-products in milling processes for base metals.

The term *source term limitation* includes an evaluation of opportunities for pre-treatment. Obvious examples are pyrite recovery and separate management/deposition, with the design of the deposit based on the need to prevent pyrite oxidation. On the other hand, the residual product, normally silicate dominated, requires only basic measures and may, in the most favourable alternative, be sold as a product e.g. for construction purposes. Alternatives for the management of the pyrite product may be deposition under water or use as backfill material in the mines. Another alternative, studied by MiMi, is the biooxidation of the pyrite in the waste, so as to deplete the source term in a controlled fashion.

A general requirement is cost-efficiency – as the materials in question are waste products without commercial value, additional costs for management must be covered by reduced costs for waste management or, should sales of the products be possible, by the income from that business.

5.3 *Waste amounts and pre-remediation conditions*

The Kristineberg mill was commissioned in 1940. Originally, only ore from the Kristineberg mine was treated, but after discoveries of other ore deposits nearby, the mill was expanded to treat a number of ores, all complex sulphides. As many as ten different mines up to 50 km away have been active in this area, all providing ore to the mill. Today, the only mine still in operation is the original Kristineberg mine. The mill was closed in 1991 due to decreasing tonnage to the mill and increasing milling costs as a consequence of the closure of a number of small mines. The Kristineberg area was then incorporated into the nearby Boliden area, where the concentrator recently had been expanded.

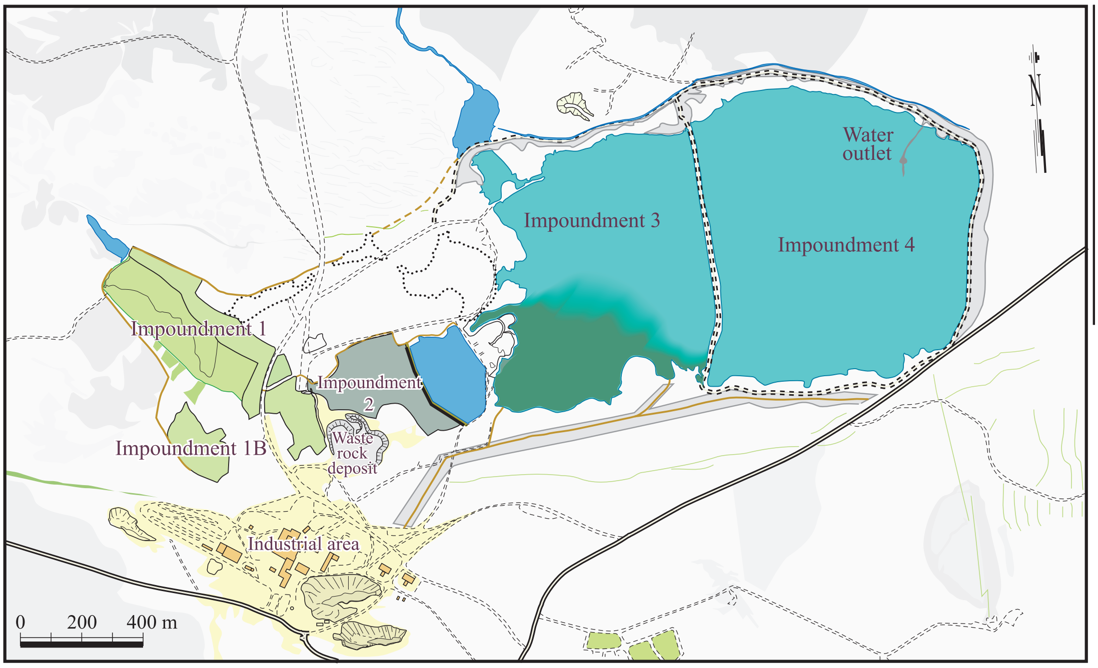


Figure 5-1 Map of the mine area at Kristineberg and the location of the tailings impoundments 1, 1B, 2, 3 and 4.

During its operation, the mill capacity was gradually expanded from the original level of 300 000 tonnes per year, up to 1 million tonnes per year, a level that prevailed during the 1970´s and the 1980´s. The main products recovered from the ore were zinc, copper and lead concentrates. However, in the early days, pyrite for sulphuric acid production was also an important product. In the mill, flotation was used as the concentration process. The flotation process required that the ore was ground to a particle size normally below 0.1 mm.

The tailings impoundments are located in a valley between two mountain ridges (see Figures 4-1 and 5-1). Initially, the tailings were deposited in two impoundments, no. 1 and 2, along the Rävlidmyrbäcken creek, which was diverted to bypass the deposits. Around 1950, these impoundments filled up, and a new impoundment, no. 3, was constructed south of the confluence between Rävlidmyrbäcken and Vormbäcken. Later, a fourth impoundment was constructed downstream. The impoundments 3 and 4 contain most of the tonnage. A fifth impoundment, 1B, was constructed to be used as intermediate storage for low grade pyrite and pyrrhotite, which was intended to be sold for sulphuric acid production. As the market for such products never developed, the material was left in the impoundment.

During operations, the tailings were deposited hydraulically, using a discharge ditch to the impoundment. The discharge point to impoundment 1 was moved along the SW upstream limit, to distribute the tailings evenly. In impoundment 2, the tailings were deposited using a fixed discharge point, onto a flat cone with its highest level at the SE corner of the impoundment. Discharge into impoundments no 3 and 4 was arranged by extending the ditch to the SE corner of impoundment 3. By this practice, the tailings were spread out in the impoundments in an irregular pattern of thin layers with horizontal stratification. In general, coarse and heavy particles sediment in the area close to the discharge point, while fines migrate further to the distal regions of the impoundments.

At closure, the tailings area consisted of five individual impoundments (Figure 5-1), containing pyrite-rich tailings. The area includes three old drained impoundments containing weathered tailings (impoundments 1, 1B and 2); one recently operated impoundment containing unweathered material (impoundment 4); and one deposit also containing substantial quantities of precipitates from the treatment of acidic mine water (impoundment 3). The total tonnage and size of each impoundment is reported in Table 5-1, along with the average composition of tailings. It should be noted that tailings composition is quite variable because of the stratification, so these values are only a rough indication of the material quality.

Table 5-1 General composition and quantities of tailings

Impoundment	1[†]	2	1b[‡]	3	4
Area, ha	12	12	2	42	74
Tonnage, Mt	1.2	1.2	0.1	9.5	8
% S	14.4 ± 4.7	3.5	9.80 ± 5.49	14.5	14.5
% Zn	0.89 ± 0.47	0.22	0.012 ± 0.004	0.95	0.95
% Cu	0.10 ± 0.03	0.06	0.066 ± 0.023	0.15	0.15
% Pb	0.05 ±0.03	0.02	0.044 ± 0.029	0.35	0.35

† Unoxidized tailings, Holmström et al. (2001)
‡ Unoxidized tailings, Öhlander et al. (2001)

The upper impoundments, with an unsaturated surface layer, have undergone weathering with depletion of the metals and sulphur content. This zonation is described in several MiMi-publications (e.g. Holmström et al., 2001; Holmström, 2000), but in general, the oxidised zone varies from 0.1 m up to 1 m. In this zone, a substantial fraction of the metals and pyrite are gone.

5.4 Site characterisation of Kristineberg

Over the years, and prior to the start of the MiMi programme, several studies have been conducted in the Kristineberg tailings area. Early in the 1970´s, impoundments 1 and 2 were sites for Boliden´s first field tests on remediation. During the 1980´s, they were used in a governmental research programme investigating several cover techniques. Although these early remediation activities were unsuccessful, they produced valuable documents on geochemistry and hydrogeology, which could be used in the final design of the decommissioning plan for the mine site. A review of the available data on the hydrogeology and geochemistry of impoundment 1 is provided in Malmström et al. (2001). In general, much of the pre-remediation information is from investigations by Qvarfort (1983, 1989), Axelsson and Karlqvist (1986) and Axelsson et al. (1984, 1986, 1991a, 1991b). Starting 1990, Boliden undertook a series of investigations (Boliden Mineral, 1994, 1995) aiming at a comprehensive decommissioning plan. The plan was submitted to the authorities during 1994 and 1995.

The tailings impoundments in Kristineberg have been studied in a number of relatively large field investigations during the period 1998 – 2003. In addition, groundwater and surface water has been sampled at regular intervals since the start of the MiMi programme. A list of the major field campaigns and their purpose are summarized in Table 5-2. This table only indicates field investigations that are related to the characterization of source term and near field components in impoundment 1, as this is the main focus of this report. A map of the field site with groundwater sampling points and boring locations is shown in Figure 5-2.

Table 5-2 Investigations of impoundment 1 as part of the MiMi programme.

Date	Purpose of field investigation	Reference
Jul 1998	Installation of BAT-tubes for groundwater sampling. Steel pipes installed for measuring groundwater level. HDPE wells were installed for groundwater sampling without the BAT technique.	MiMi Årsrapport 1998
Jul 1998	Groundwater samples analyzed for organic material and total bacterial content.	MiMi Årsrapport 1998
Oct 1998	Groundwater wells installed, as above. Seven borings were performed through the soil cover and into the tailings. Pore water was removed from the samples in 4 of these bore profiles. Solid phase samples collected and analyzed for chemical and mineralogical composition. Suction lysimeters installed for sampling water from the unsaturated soil cover and underlying tailings.	MiMi Årsrapport 1998 Holmström et al. (2001) Carlsson et al. (2003)
Dec 1998	Climate station in operation on impoundment 1.	
1999, 2000	Surface water sampling around impoundment 1.	MiMi Årsrapport 1999 MiMi Årsrapport 2000
2001	Gas composition determined in groundwater samples. Groundwater analyzed for organic acids.	MiMi Årsrapport 2001
Oct 2001	Sampling of saturated tailings for detailed studies of pore water chemistry, microbiology, and physical properties.	Herbert (2003a,b)
Sep 2003	Sampling of saturated and unsaturated tailings for studies of pore water chemistry, solid phase composition, microbiology, and physical properties. Groundwater sampled regularly during 1998 – 2003. Suction lysimeters sampled 1999 – 2000.	Corregé (2001)
2003-2004	Monitoring of surface water flow and chemistry in drainage ditches around impoundment 1.	Svensson and Höglund (2004)

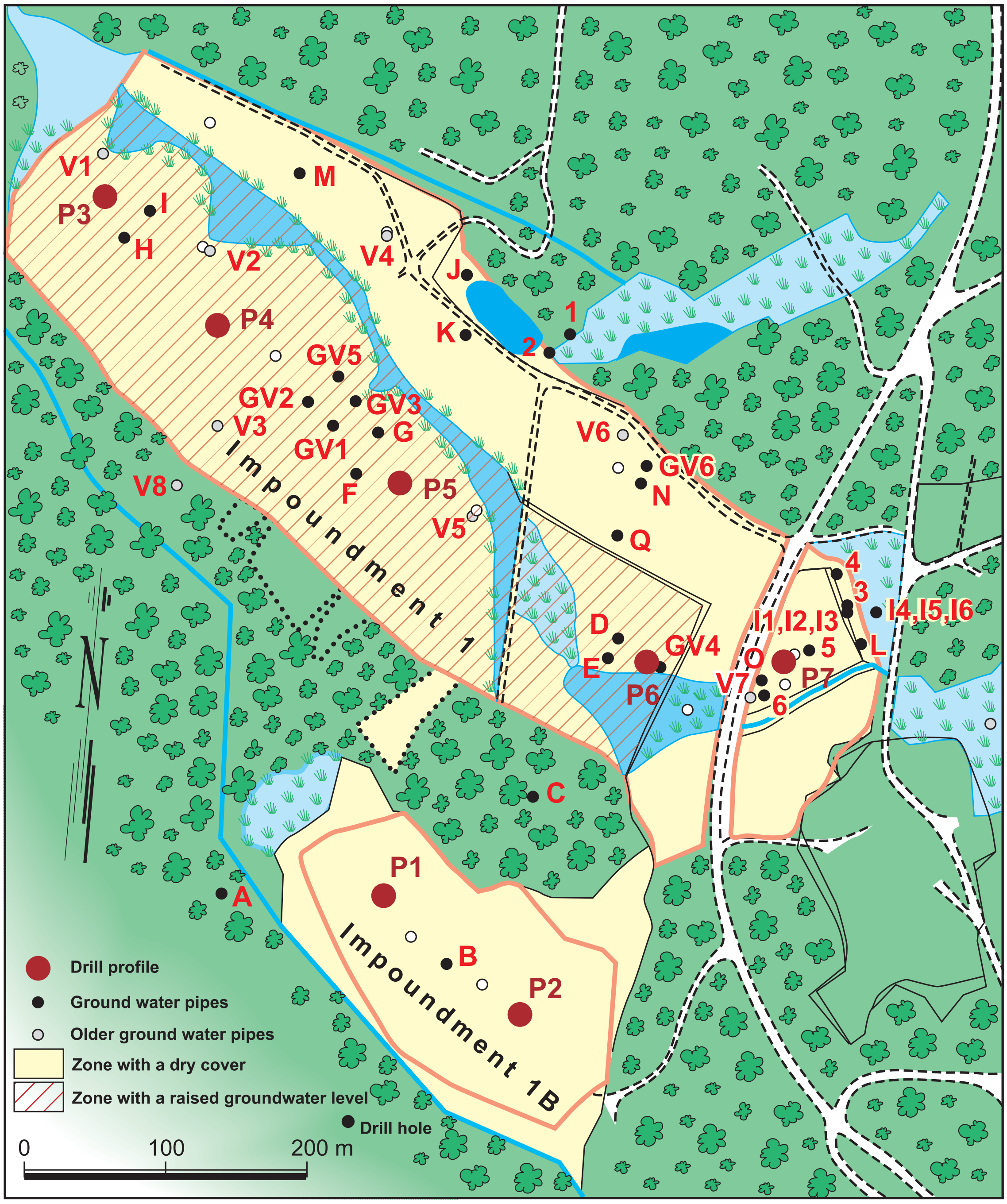


Figure 5-2 Map showing impoundments 1 and 1B at Kristineberg. P1-P7 = drill profiles, A-O and I1-I6 = groundwater pipes (BAT system), 1-6 and Mv1-Mv9 = HDPE-pipes, GV1-GV6 = steel pipes, V1-V8 = older pipes for monitoring of groundwater levels.

5.5 Waste characterisation

MiMi vision states "…*The MiMi programme has made it possible to predict the extent of environmental impact and has provided tools and methods to control and design processes and waste treatment systems already from investigation of the mineralogical and chemical composition of the ore and the wall rocks, and the local hydrology and topography*. ..." Following this vision it is clear that exploration data need to provide such data that are necessary for development of correct waste management strategies already at the early planning stages of a mine. This approach has the obvious advantage that strategies for material handling and waste disposal do not need to be changed during the operational phase, which will probably save costs over the entire life-cycle of the mine. Further, a reasonable knowledge of the correct costs in each stage of the life-cycle will give an adequate basis for decision on investments. Hence, this approach points out an economic incentive to carry out adequate waste characterisation.

Different characterisation methods have been tested and compared within MiMi (Öhlander et al, 2004). The tests include different standard methods, such as ABA-tests (Acid Base Accounting), Humidity Cell-tests, paste-pH, etc. However, in addition to this, complementary characterisation methods, as described in following sections, have been applied to improve the understanding of governing processes and mechanisms and to provide the necessary data for quantitative assessments of the long-term function of the waste during the disposal phase. Quantitative evaluations, including the use of modelling tools for interpretation, have been made within the performance assessment framework (PA).

In sections below, a number of tailings properties are presented, which are considered important for the performance assessment and the long-term evaluation of reclamation measures.

Tailings Mineralogy

The mineralogy of tailings from impoundments 1 and 1B has been investigated by Holmström et al. (2001), Öhlander et al. (2004), and Gleisner et al. (2003). Some information about the tailings in impoundment 4 was given by Widerlund et al. (2001). In general, the primary tailings mineralogy in impoundment 1 is determined by the composition of ores processed by the Kristineberg ore concentrator from 1940 to the early 1950s. Although ore from several mines were processed at Kristineberg, the tailings in impoundment 1 originate from the Kristineberg mine. The tailings from other ores processed in the Kristineberg concentrator were deposited in the younger impoundments.

Tailings were discharged as a slurry into impoundment 1 over a period of more than ten years, and the discharge point was moved on numerous occasions. Variations in ore quality and discharge point have resulted in vertical and horizontal variability in tailings composition. Thus, a single tailings profile cannot be expected to represent a compositional profile of the entire impoundment, but rather of the local environment in the vicinity of the profile. Therefore, average values are presented of tailings composition, but the variability in this data must be considered as well (cf. Holmstöm et al., 2001; Öhlander et al., 2004).

Sample mineralogy has been determined from the examination of polished thin sections by optical microscopy, and by using powder x-ray diffractometry. On a few occasions, other methods such as energy dispersive X-ray spectroscopy have been used as a complement to the traditional techniques.

There is a distinct zonation in the tailings in impoundment 1, with an oxidized zone above the unoxidized tailings. As estimated from the drill cores examined in Holmström et al. (2001), and tailings cores collected in 2001 and 2003, the thickness of the oxidized zone formed prior to remediation is between 0.1 and 1.15 m thick, with thickness increasing towards the southeast where the depth to the water table was greater. The sulphide mineral content ranges from 10 to more than 30 wt. % in the unoxidized tailings. Pyrite is by far the most common sulphide mineral, followed by pyrrhotite, sphalerite, chalcopyrite, galena, covellite and arsenopyrite (Table 5-3).

Table 5-3 Sulphide mineralogy of tailings from impoundment 1.

Sulphide mineral	Formula	Holmström et al., 2001* wt. %	Gleisner et al., 2003[†] vol. %	Gleisner et al., 2003[‡] vol. %	Herbert et al., 2003[#] wt. %
Pyrite	FeS_2	26	16.7	22.1	25.0
Pyrrhotite**	Fe_7S_8**	--	3.25	0.30	--
Sphalerite	ZnS	1.3	1.4	0.05	1.19
Chalcopyrite	$CuFeS_2$	0.28	0.70	0.53	0.2
Galena	PbS	0.05	0.10	n.d.	0.07
Arsenopyrite	AsFeS	0.04	0.10	n.d.	--

* Unoxidised tailings. Estimated from average chemical composition. Results in wt.%.

** Herbert (2002) showed that S:Fe ratio in pyrrhotite grains is close to 8:7. Trace levels of Zn present.

[†] Coarse-grained tailings, determined by point counting. Results in volume %.

[‡] Fine-grained tailings, determined by point counting. Results in volume %.

[#] Average composition of 9 samples examined in sterilisation experiments. Mineralogy estimated from chemical composition. Results in wt.%.

The most common silicate minerals in the unoxidised tailings are quartz, chlorite, and talc, followed by numerous other, less common gangue minerals. Calcite occurs but in small amounts. The composition of common and trace gangue minerals identified in impoundment 1 is presented in Table 5-4. In terms of total mineral content, the relative abundance has been determined to the following sequence: quartz ≥ chlorite ≥ pyrite > talc > muscovite > feldspar > calcite (Holmström et al., 2001).

Table 5-4 Composition of gangue minerals in tailings from impoundment 1 (Holmström et al., 2001).

Common minerals	Formula	Trace minerals	Formula
Quartz	SiO2	Ilmenite	$FeTiO_3$
K-feldspar	$KAlSi_3O_8$	Magnetite	Fe_3O_4
Chlorite	$(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$ ***	Hematite	$\alpha\text{-}Fe_2O_3$
Talc	$Mg_3Si_4O_{10}(OH)_2$	Titanite	$CaTiSiO_5$
Plagioclase	$NaAlSi_3O_8$ - $CaAl_2Si_2O_8$	Epidote	$Ca_2(Al,Fe)_3(SiO_4)_3(OH)$
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$	Sericite	$KAl_2(AlSi_3)O_{10}(OH)_2$
Amphiboles	$(X,Y,Z)_{7\text{-}8}(Al,Si)_2Si_6O_{22}(OH)_2$*	Zircon	$ZrSiO_4$
Pyroxenes	$XY(Al,Si)_2O_6$**	Apatite	$Ca_5(PO4)_3(OH,F,Cl)$
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	Calcite	$CaCO_3$

* X,Y,Z = Fe(III), Cr(III), Al, Ti

** X = Ca, Na, Zn, Li Y=Cr, Al, Fe(III), Ti, V

*** variable composition with Fe- and Mg-rich end-members. Herbert (2002) measured compositions that ranged from $(Fe^{II}_{2.46}Mg_{1.96}Al_{1.52}[\ ]_{0.06})(Si_{2.54}Al_{1.46})O_{10}(OH)_8$ to $(Fe^{II}_{1.15}Mg_{3.63}Al_{1.15}[\ ]_{0.07})(Si_{2.95}Al_{1.05})O_{10}(OH)_8$ where [ ] corresponds to impurities such as Mn.

In the oxidized tailings the sulphide mineral content is generally around 1 to 2%. The most common sulphide minerals are, in decreasing order, pyrite, chalcopyrite, pyrrhotite, sphalerite and galena. Fe-oxyhydroxides are common. They occur as individual grains or aggregates, as well as coatings on the silicate minerals, which are more abundant than in the unoxidized tailings.

In impoundment 1B the sulphide mineral content is generally < 20%. Pyrite-rich parts or layers alternate with pyrrhotite-rich layers. Other sulphides are less abundant than in impoundment 1, but sphalerite and chalcopyrite occur. Galena is rare and a few grains of native silver have been observed. The most common silicates are quartz, plagioclase, K-feldspar, chlorite, amphiboles, biotite and muscovite. Magnetite, hematite, zircon and apatite occur in trace amounts.

In impoundment 4, tailings mineralogy was investigated by Widerlund et al. (2001). The following ore minerals have been identified: pyrite, pyrrhotite, sphalerite, galena, arsenopyrite, ilmenite and chalcopyrite. The occurrence of gangue minerals is similar to impoundment 1.

Chemical composition

The chemical composition of tailings from impoundments 1 and 1B has been investigated by Holmström et al. (2001), Gleisner et al. (2003), Öhlander et al. (2004), and Herbert et al. (2003). Analytical techniques for the determination of total elemental concentrations are presented in Holmström et al. (2001). Some information about the tailings in impoundment 4 is given by Widerlund et al. (2001). As noted above in the discussion of mineralogical composition (section 5.4), the tailings composition in impoundment 1 is determined by the composition of ores processed by the Kristineberg ore concentrator. For impoundment 1, the tailings originate from the Kristineberg mine. The tailings from other ores (e.g. Petiknäs, Renström) processed in the Kristineberg concentrator were deposited in the younger impoundments.

The average composition of tailings collected in impoundments 1, 1B, and 4 is shown in Table 5-5. The unoxidized tailings in impoundment 1 contain high concentrations of sulphur, metals and metalloids with average values of 14.4% S, 183 mg/kg As, 21.5 mg/kg Cd, 56.4 mg/kg Co, 956 mg/kg Cu, 463 mg/kg Pb and 8 861 mg/kg Zn. The sulphide-bound metals and S have, to a large extent, been depleted in the oxidized zone, with the exception of Pb, and the content of the silicate-bound elements Si, Al, Ca, K, Mg, Na, Ti, Ba, Cr, Sr and Ti has increased. There is, however, considerable variability both horizontally across the impoundment and vertically within a profile. This is illustrated in Figure 5-3 by the Zn concentration (proxy for sphalerite content) for one drill profiles through the tailings. As shown in Figure 5-3, the vertical variability of Zn concentration is higher than 50% of the average, and the average values for the two profiles differ significantly. The low Zn concentrations in the till cover and the oxidised tailings are clearly shown in the figure.

Despite fluctuations between individual points, the concentration profiles of different elements versus depth in the tailings material generally show relatively constant trends with depth in unoxidized tailings in all profiles (an exception to this is the enrichment of Cu under the oxidized zone; this process is described in more detail in Chapter 7). This is also illustrated in the standard deviation values in Table 5-5, which are often in the same order of magnitude as the mean values. The variations in metal concentration with depth are primarily a function of ore quality during processing and distance to tailings discharge, resulting in graded bedding due to grain size and weight differences of different minerals during deposition. These factors result in substantial changes in sediment structure and composition with depth; magnetic susceptibility measurements performed on tailings cores indicate that significant changes in sediment structure and composition are common in tailings profiles and occur rapidly over short depth intervals (< 10 cm) (Herbert, 2003a).

Impoundment 1B has lower content of S and several metals than impoundment 1, but slightly higher content of Cu. The differences between the oxidized and unoxidized tailings in impoundment 1B are similar to those in impoundment 1. The chemical composition of unoxidised tailings in impoundment 4, based on one profile from Widerlund et al. (2001), is given in Table 5-5. These tailings have higher concentrations of S, Cu and Pb than those in impoundment 1, but slightly lower concentrations of Zn.

Table 5-5 Average composition of tailings samples collected in impoundments 1, 1B, and 4 in Kristineberg. All major elements except S are expressed as the corresponding oxides (Holmström et al., 2001; Öhlander et al., 2004; Widerlund et al., 2001).

Element	Unoxidised tailings impoundment 1 (73 samples)	Oxidised tailings impoundment 1 (12 samples)	Unoxidised tailings impoundment 1B (22 samples)	Oxidised tailings impoundment 1B (7 samples)	Tailings impoundment 4 (mean 1 profile)
	[weight%±s.d]	[weight%±s.d]	[weight%±s.d]	[weight%±s.d]	[weight%±s.d]
SiO_2	42.8±6.7	63.1±7.1	37.0±10.8	67.9±2.6	30.6 ± 1.2
Al_2O_3	9.35±1.50	11.4±1.5	7.51±3.16	10.9±0.7	7.47 ± 0.34
CaO	1.01±0.49	1.24±0.74	0.99±0.55	0.78±0.33	4.23 ± 0.40
Fe_2O_3	24.0±5.0	8.45±3.59	33.8±14.1	7.70±1.75	19.1 ± 3.8
K_2O	0.81±0.40	1.88±0.97	1.07±0.35	2.08±0.50	0.637 ± 0.067
MgO	7.73±1.46	6.65±3.52	4.69±4.18	4.10±1.31	8.14 ± 0.59
MnO_2	0.12±0.02	0.11±0.02	0.09±0.03	0.06±0.03	0.199 ± 0.008
Na_2O	0.46±0.35	1.46±0.88	0.83±0.39	1.52±0.60	0.325 ± 0.052
P_2O_5	0.07±0.02	0.08±0.04	0.06±0.02	0.05±0.02	0.040 ± 0.002
TiO_2	0.30±0.06	0.45±0.07	0.24±0.09	0.36±0.06	0.164 ± 0.007
S	14.4±4.7	1.81±2.79	9.80±5.49	3.01±2.41	16.8 ± 0.9
LOI	12.4±2.6	5.03±3.00	12.4±3.2	4.72±1.43	15.2 ± 0.8
	[mg/kg±s.d]	[mg/kg±s.d]	[mg/kg±s.d]	[mg/kg±s.d]	[mg/kg±s.d]
As	183±157	36.2±28.9	186±460	22.5±11.7	8263 ± 1434
Ba	281±79	481±193	379±100	561±94	176 ± 10
Cd	21.5±12.5	1.47±2.39	6.38±5.42	2.52±3.36	24 ± 4
Co	56.4±21.3	7.77±9.18	22.9±24.8	20.3±19.9	62 ± 3
Cr	46.2±13.3	60.7±19.9	64.0±27.0	119.4±173	67 ± 14
Cu	956±316	159±132	663±225	408±413	1203 ± 208
Hg	2.42±1.17	0.94±0.52	1.95±1.01	0.54±0.28	6.03 ± 1.05
La	22.4±5.3	25.7±5.5	13.7±9.0	16.5±6.1	15 ± 3
Mo	24.0±6.7	17.7±11.3	12.1±7.4	11.3±6.0	7.3 ± 2.4
Ni	5.95±2.58	4.52±3.35	19.5±9.0	5.42±2.59	21 ± 5
Pb	463±283	454±318	442±292	130±53	1550 ± 200
Sc	5.90±1.38	7.46±1.10	5.78±2.67	7.41±1.50	6.4 ± 0.9
Sr	40.1±21.0	90.5±51.8	58.3±22.5	85.6±32.6	34 ± 3
V	26.9±8.1	34.3±8.9	24.4±13.3	20.8±9.2	46 ± 9
Y	17.6±3.1	21.2±3.3	15.2±5.2	18.5±2.6	
Zn	8861±4744	559±919	2674±2400	805±1039	8197 ± 1191
Zr	117±41	205±78	121±44	185±33	86 ± 7

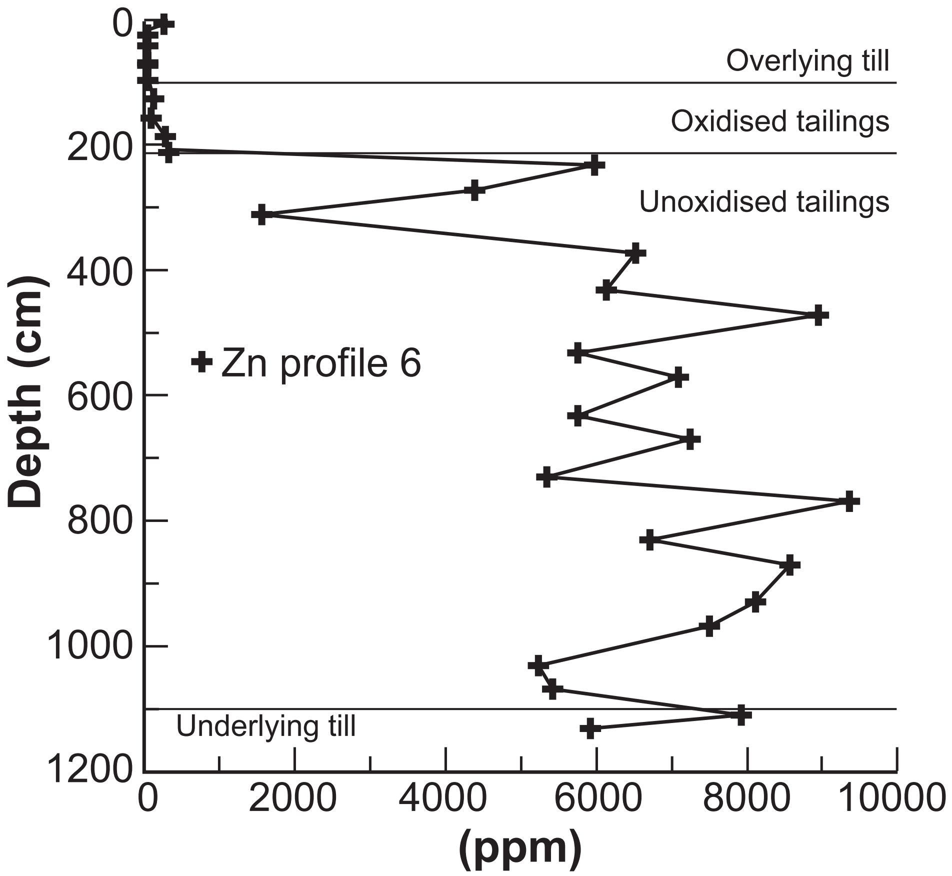


Figure 5-3 Concentration of Zn (mg/kg) versus depth in drill profile 6 (see Figure 5-2) in impoundment 1.

Physical properties of tailings

The deposition of tailings in a pond involves sedimentation of the particles under water and a successive consolidation of the grain skeleton with time. If the impoundment is allowed to drain after the deposition is completed, further consolidation takes place due to the increased effective stress as the pore water pressure decreases. The consolidation generally leads to an increasing density and a decreasing porosity with depth. However, variations in the production process implies heterogeneity in grain density and grain size distribution and varying location of the discharge leads to variations in the distribution of tailings with different properties over the impoundment.

According to the baseline investigations, the water content (m_w/m_s) for the unoxidised tailings in impoundment 1 varies between 18 and 25 %, the dry bulk density varies between 1 760 and 2 100 kg/m^3 and the grain density varies between 3 020 and 3 760 kg/m^3. With respect to the grain size distribution the tailings can be characterised as sandy silt (Figure 5-4) with porosity varying within the interval 35-46 % as calculated from measurements of grain density, bulk density and water content at saturation (Öhlander et al., 2004).

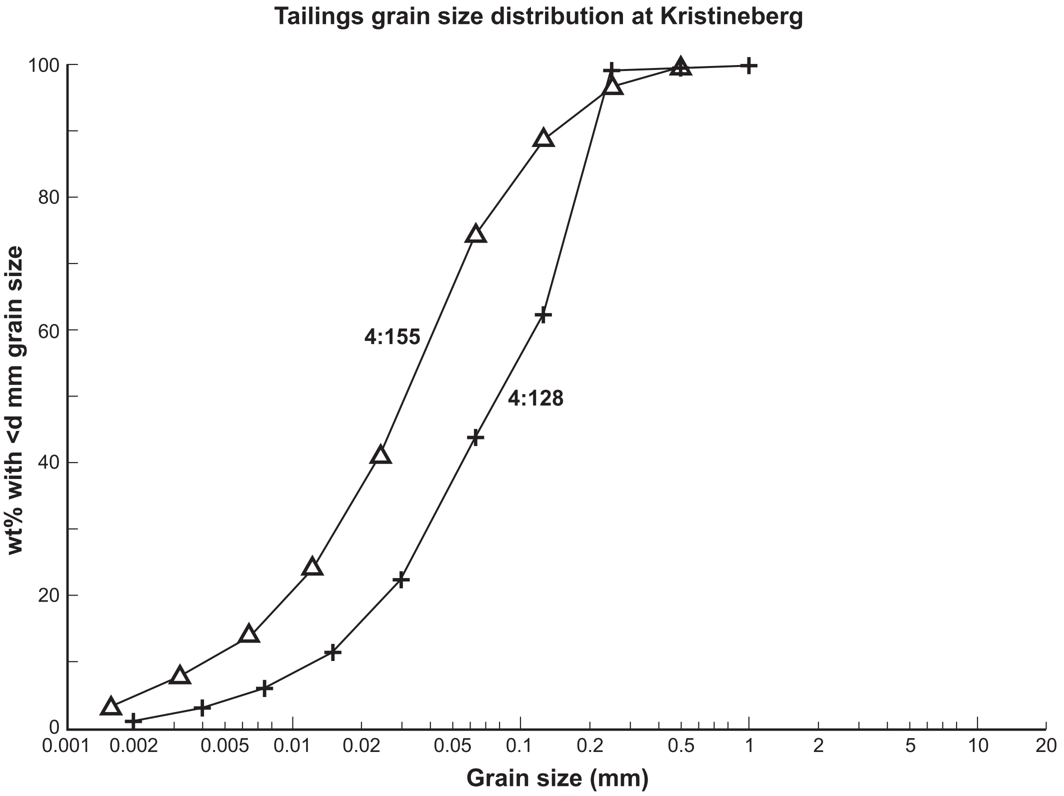


Figure 5-4 Grain size distribution for two samples (Profile 4) from the tailings (Öhlander et. al., 2004).

The deformation characteristics of a soil depend on factors such as the pre-consolidation stress, grain size distribution and porosity. Generally, fine grained soils with high porosity consolidated at low pre-consolidation stresses show low deformation modulus. Provided the tailings are consolidated for the actual stress conditions including pore pressure (governed by the groundwater level) before a load is applied, the resulting deformation for a given load normally are estimated from a deformation modulus and increased vertical effective stress. The changed stress condition depends on the level and the distribution of the external load that is applied, but also on possible changes in the pore pressure (groundwater level) that may arise.

In the case of an evenly distributed surface load, e.g. a soil cover, horizontal deformations can be neglected and the deformation is calculated as a one-dimensional vertical compression. The compression modulus M for an increasing load in soil can in general be expressed by (e.g. Larsson 1995):

$$M=m\sigma_j'(\sigma'/\sigma_j')^{1-\beta} \qquad (5\text{-}1)$$

where
M = compression modulus, kPa
m = modulus number
β = stress exponent
σ' = effective vertical pressure, kPa
σ_j' = comparison pressure, kPa (normally 100 kPa)

Typical values for m and β for different soils have been compiled by Janbu (1970). According to his compilation the compression modulus index can vary between 10 and 1000 depending on grain size with the lowest value for fine silt. The stress exponent for silt was reported to vary between 0 and 0.5.

Variations in the distribution of tailings over an impoundment implies both horizontal and vertical variations of deformation characteristics. According to empirical observations of relations between the saturated water content and the modulus number, m, for the tailings in Kristineberg can be expected to vary between 20 and 100 (Janbu, 1970).

For stability analyses of silty soils like tailings, effective stress analysis using the drained shear strength according to the Mohr-Coulomb soil model normally is relevant. The drained shear strength is expressed by a cohesion intercept (c’) and a friction angle (ϕ') and varies with the effective stress according to equation 5-2:

$$c'=\sigma'\tan\phi' \qquad (5\text{-}2)$$

where
c'= undrained shear strength, kPa
σ' = effective vertical pressure normal to the shear plane, kPa
ϕ' = internal friction angle

The friction angle for natural silt soils with grain size distribution similar to tailings is reported to vary between 24° and 39° (Larsson, 1995). Factors that affect the friction angle are mineralogy, grain shape, grain size distribution, stress level and the degree of consolidation. (Larsson, 1989). The most important factor that causes the wide variation in reported friction angles probably is the degree of consolidation. Similar values are reported from triaxial tests and shear tests on iron ore tailings, with values between 19° and 41° (Ygland, 2000; Eurenius, 1989). From these tests it can be concluded that low friction angles are more common in tailings that have settled below the water table near the dam. These tailings also are more fine-grained and less consolidated than tailings on the beach. However, also tailings underlying the beach at a certain depth have settled under water and are correspondingly fine-grained. These tailings normally show higher values on the friction angle than tailings close to the dam as they are consolidated for a higher stress level.

The hydraulic conductivity of a soil normally varies with porosity and pore size distribution and thus indirectly with grain size distribution and degree of consolidation. The saturated hydraulic conductivity measured in laboratory on two samples of unweathered and two samples of weathered sand from impoundment 1 in Kristineberg varies between $8\cdot10^{-8}$ and $8\cdot10^{-7}$ m/s, as shown in Table 5-6.

Table 5-6 Results from laboratory measurements of hydraulic conductivity on samples of tailings from impoundment 1 in Kristineberg.

Sample	Porosity %	Hydraulic conductivity m/s
Unweathered tailings	46.8	$1.1\cdot10^{-7}$
Unweathered tailings	48.4	$7.8\cdot10^{-7}$
Weathered tailings	48.7	$1.3\cdot10^{-7}$
Weathered tailings	48.3	$0.8\cdot10^{-7}$

Water retention characteristics can, like the hydraulic conductivity, be expected to vary with pore size distribution and thus indirectly with grain size distribution and degree of consolidation. For the tailings in Kristineberg impoundment 1, water retention characteristics have been investigated on one general sample of unoxidised and one general sample of oxidised tailings. The results are shown in Figure 5-5.

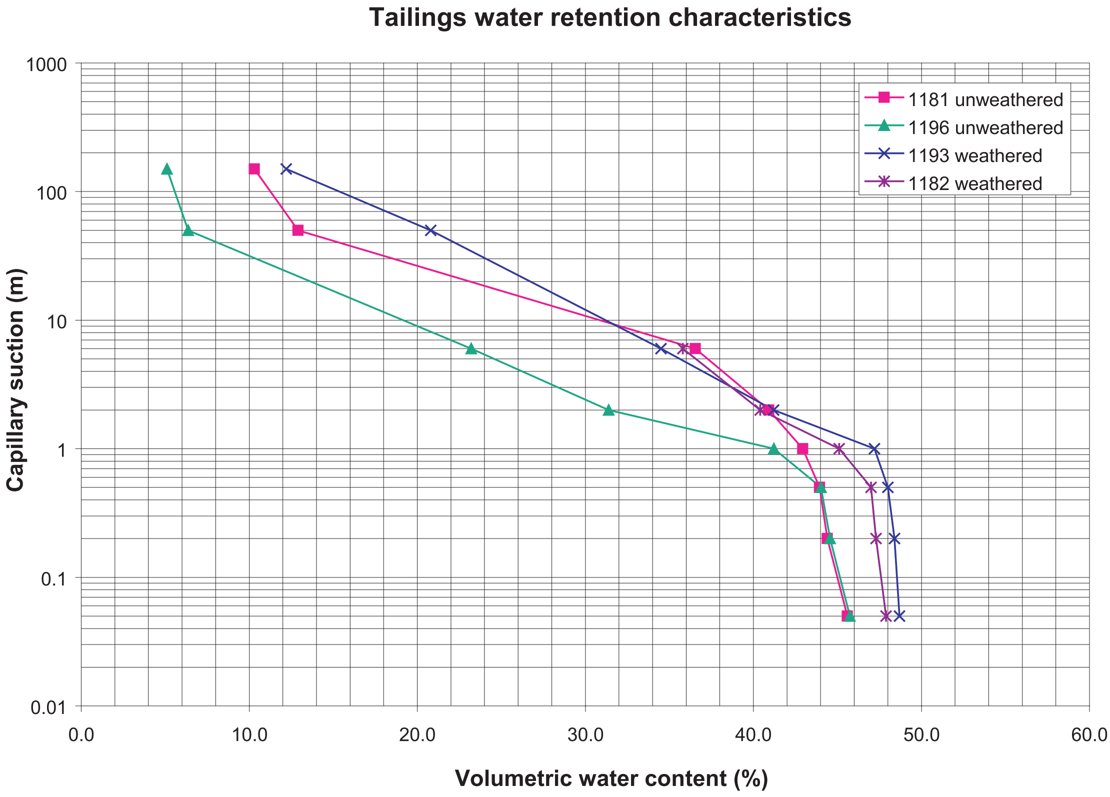


Figure 5-5 Water retention characteristics of tailings in Kristineberg impoundment 1.

Surface area – measured values for sulphides

Tailings consist of a number of minerals distributed over a wide range of particle sizes. Thus, the assessment of individual specific mineral surface areas is difficult to accomplish. In the following, a number of BET-measurements on pure sulphides (pyrite, sphalerite, bornite, chalcopyrite, and arsenopyrite) and two sulphide concentrates from tailings from impoundment 1 in Kristineberg have been used instead of full tailings samples. The BET-measurements were performed as one-point nitrogen gas adsorption/desorption determinations. The areas, as obtained from adsorption and desorption, always agreed within a factor of two in a single determination. The samples had been size fractionated using sieves, and ultrafine particles had been removed by repetitive ultrasonication in ethanol prior to drying at 60 ^{o}C before BET-determinations. The BET-areas are averages of 2-5 repetitive measurements on each sample. It should be noted that BET-areas of tailings samples have shown a dependence on degassing temperature (Salmon (2003), personal communication). In this analysis, particle radius (*r*) is estimated as half the value of cut-off sizes for the used sieves. The sulphide concentrates had been obtained by size, density, and magnetic fractionation. (Unpublished results).

Figure 5-6 shows an overview of the obtained BET surface areas (A_{BET}). The figure shows that most of the obtained values corresponds to a surface area of 0.05 – 0.2 m^2/g, and an internal surface area of $10^5 < A_{spec, int} < 10^6$ m^{-1}. See Chapter 7 for further discussion of surface area.

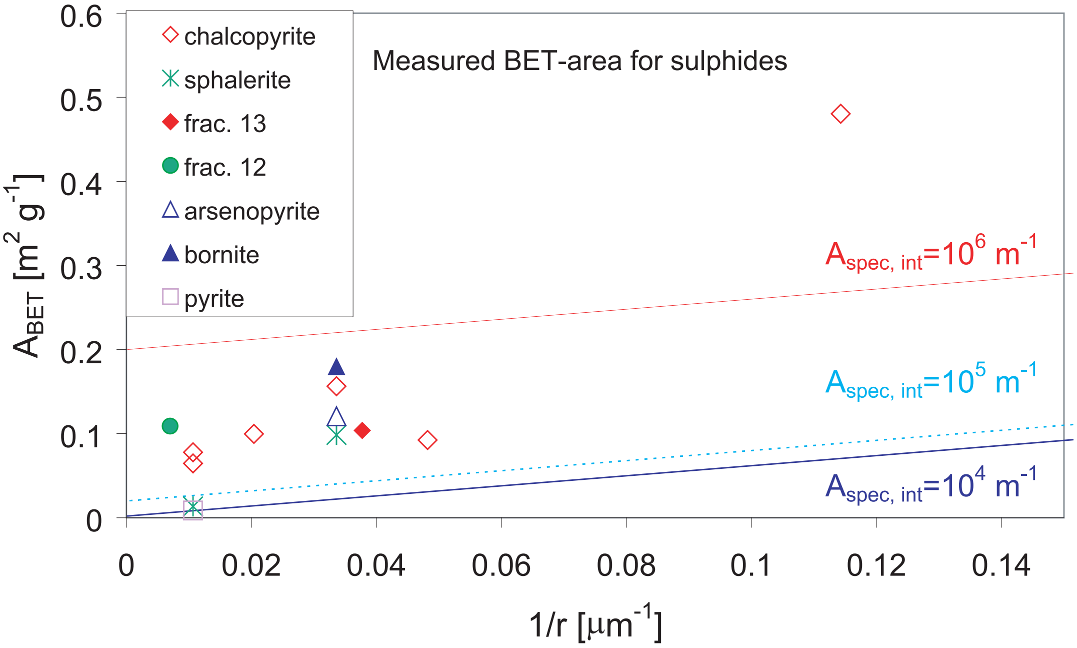


Figure 5-6 Measured BET-areas for size fractions of chalcopyrite, bornite, sphalerite, arsenopyrite, pyrite, and sulphide concentrates from tailings from impoundment 1 in Kristineberg as function of 1/r. Lines show the theoretical A_{BET} as estimated from $A_{tot,spec}$ for spherical or cubic particles for different assumed specific internal areas $A_{spec,int}$.

5.6 Comparison of Kristineberg with other mine sites

The potential environmental impact of a mine waste deposit is intricately related to the source term (i.e. the composition of the waste and its various properties). Ideally, there should be some method by which the source term from a particular mine tailings impoundment could be compared with another source term from, for example, another mine site. However, there are a great number of different properties and parameters that can be compared in the source term, such as ore type, tailings composition, pore water composition, and hydraulic properties. The identification of only few relevant, common parameters is difficult.

In terms of environmental impact, an important property of a waste material is the material's capacity for acid generation or, conversely, the material's capacity for neutralizing acidity. One method for assessing the acidification potential (AP) and the neutralisation potential (NP) of a waste material is Acid-Base Accounting (ABA). This is a common static test method to estimate the balance between the acid – producing and buffering capacity of a material (British Columbia Acid Mine Drainage Task Force, 1989). In ABA, both AP and NP are expressed in units of kg $CaCO_3$ per ton material, where the AP is equivalent to the amount of $CaCO_3$ required to neutralize the acidity generated by pyrite oxidation, according to the following reaction:

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2 \qquad (5\text{-}3)$$

This reaction indicates that the four protons produced as a result of pyrite oxidation, iron oxidation and ferric iron precipitation are consumed by calcite dissolution. In addition, this reaction is assumed to proceed under acidic conditions, since CO_2 is the reaction product and not bicarbonate (HCO_3^-). The reader is referred to Chapter 7 for further details on pyrite oxidation and carbonate buffering.

There are a number of experimental methods for determining the AP and NP of a material, such as humidity cell tests (Öhlander et al., 2004), but AP and NP can also be estimated directly from chemical analyses of the material. The AP is estimated from the total sulphur concentration or pyrite concentration (equation 5-4). When determined experimentally (e.g. in humidity cell tests), NP is determined from the net neutralization produced by both carbonate and silicate buffering. However, without this data, the NP can be assumed to be equal to the calcium carbonate content (equation 5-5).

$$\text{AP (kg } CaCO_3 \text{ / ton material) = sulphur content (wt\%)} \times 31.25 \qquad (5\text{-}4)$$

$$\text{NP (kg } CaCO_3 \text{ / ton material) = } CaCO_3 \text{ content (wt\%)} \times 10 \qquad (5\text{-}5)$$

For equation 5-4, the multiplication factor accounts for the difference in formula weight between sulphur in pyrite and $CaCO_3$, and the fact that two moles $CaCO_3$ are consumed for every mole FeS_2 that is oxidized. For equation 5-5, the multiplication factor is needed for the conversion in units from wt% to kg/ton.

According to the ABA method, the net neutralization potential (NNP) of a material is determined as the difference NP-AP. For a material where NNP>0, acid generation in the tailings should always be compensated by acid neutralization (e.g. calcite dissolution). For NNP<0, acid generation may eventually exceed acid neutralization when calcite is completely consumed, and acidic conditions will prevail in impoundment pore water unless additional measures are considered (e.g. liming)

In Figure 5-7, the AP and NP of various mine tailings from Sweden and Canada are presented for comparison. As shown in this figure, many of the materials are net acid – producing (NNP<0). It should be noted, however, that acidification will not occur until the neutralisation potential of a material is consumed. This is exemplified with the Stekenjokk impoundment, where NNP<0 but pore water pH is greater than 7 because of a low rate of pyrite oxidation under the water cover (cf. Chapter 6) and a high carbonate content. Thus, the NNP does not necessarily indicate the present status of the environmental impact of a deposit (e.g. acidification), but gives rather an indication of the *potential impact* of a deposit if no remedial activities (e.g. soil cover, water cover) were employed.

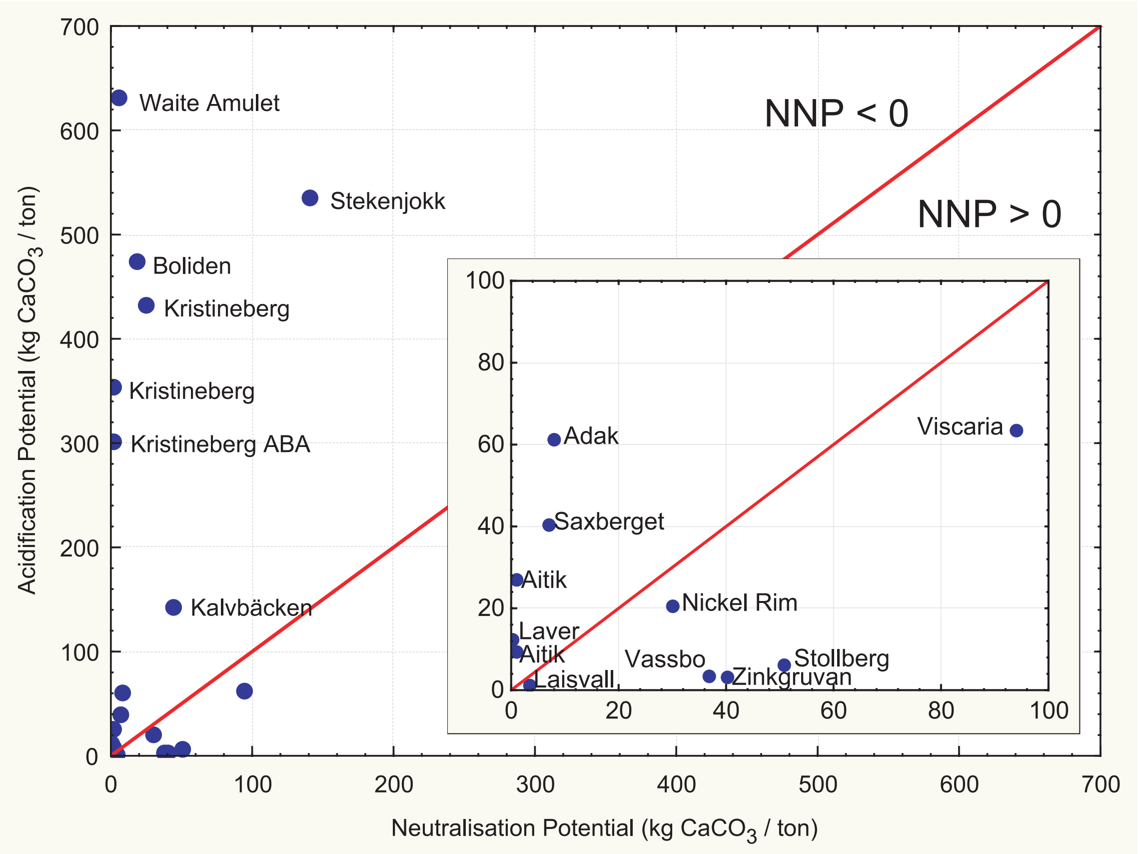


Figure 5-7. Comparison of net neutralisation potential of various mine tailings in Sweden and in Canada. Data has been selected that represents the composition of unoxidised tailings below the water table. Compilation of data from Coggans et al. (1999), Johnson (1993), Qvarfort (1989). “Kristineberg ABA” refers to results from ABA tests performed on Kristineberg tailings (Öhlander et al., 2004).

Illustration: Site characterisation – where theory meets practice.

6 Near field - Prevention and control methods

The *near field* covers all aspects of the waste deposits and the engineered barriers. Critical questions include the mobilisation of metals from the waste, the longevity and sustained function of the cover layers and of dam constructions built to confine the waste and to prevent oxygen from reaching the waste.

The fundamental remediation approach for the near field can be denoted *passive prevention*, i.e. methods applied to preclude oxidation of the waste and thereby avoiding subsequent problems. Some fundamental demands on feasible closure options have been formulated:

- Very long functional life-time is required
- Passive methods must be applied
- All constructions must be robust and stable
- The longevity needs to be demonstrated beforehand in a robust scientific way
- The relevant time-scales are hundreds to thousands of years
- Ecological integration is necessary - we must learn from nature

6.1 Overview of different cover techniques

Covering of sulphidic mine waste mainly aims at reducing the transport of oxygen into the waste dump, thereby preventing the oxidation of sulphides and the generation of acidic drainage and the release of metals. By covering of mine waste dumps, the rate of oxygen diffusion into the dump normally becomes the determining factor for the weathering of pyrite (Magnusson and Rasmuson 1983, MEND 1994). Another goal, that sometimes is considered equally important to limit the oxygen transport, is limiting the infiltration of precipitation into the waste dump. Such a reduction also leads to a reduction of the formation of leachate, and thereby limits the quantity of contaminated effluent from the dump.

In the next two sections, various types of covers are discussed that function as barriers to oxygen and water intrusion. These barriers are designed as covers composed of soil, either as single layer or multiple layer covers of varying material.

Some basic principles for remediation of tailings deposits are depicted in Figure 6-1, and a general classification of covers according to their function is shown in Table 6-1.

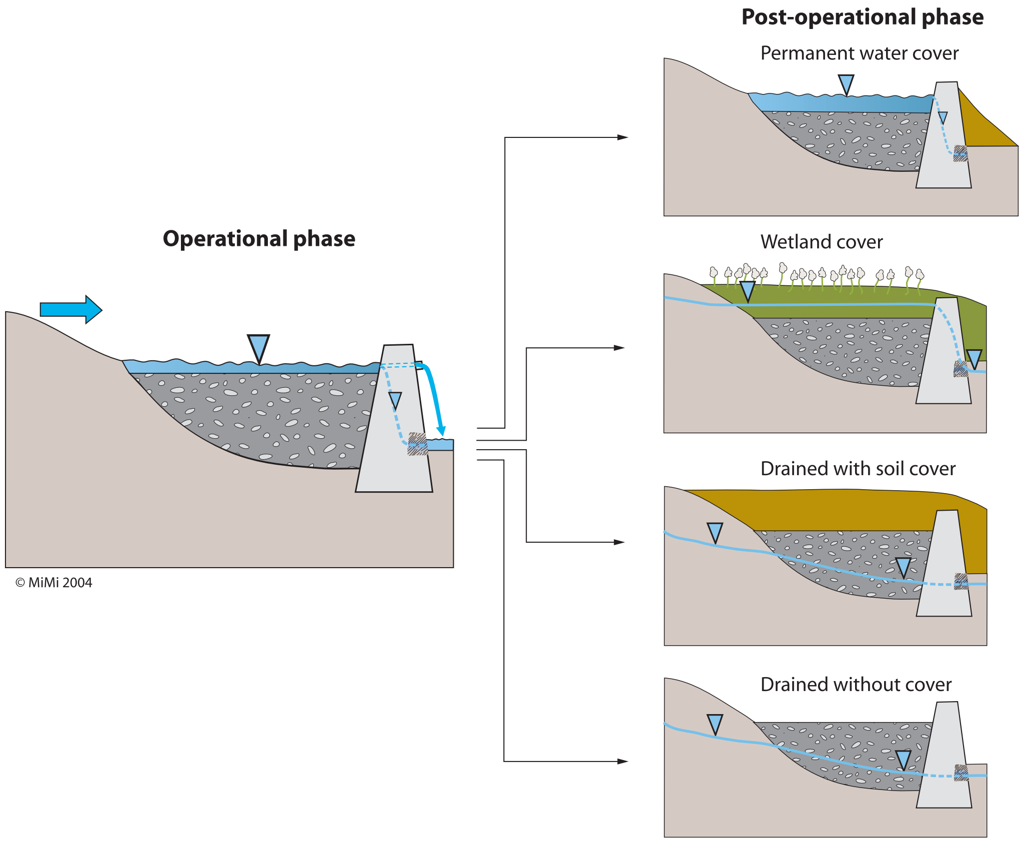


Figure 6-1 Illustration of some basic alternatives for tailings remediation. The last alternative is not considered feasible for tailings.

Table 6-1 Cover types and their primary function.

Cover type	**Example of cover material**	**Primary function**
1. Oxygen diffusion barriers (soil covers)	Soil, till	To limit the transport of oxygen by acting as a barrier against the diffusion of oxygen to the waste.
2. Capillary barriers	Gravel	To prevent the transport of water into a deposit.
3. Oxygen consuming barriers	Sludge, peat	To limit the transport of oxygen by consumption of oxygen which penetrates into the cover.
4. Low permeability barriers	Clay	To limit the transport of oxygen and the formation of leachate by acting as a barrier against the diffusion of oxygen, as well as against the infiltration of precipitation.
5. Reaction inhibiting barriers	Phosphate, bactericides	To provide a favourable environment to limit reaction rates and metal release
6. Water covers	Water	To limit the transport of oxygen by acting as a barrier against the diffusion of oxygen to the waste. Oxygen concentration in waste is limited by its solubility in water.

6.2 Soil Covers

Oxygen diffusion barriers – Primary function

Since the purpose of most covers is to ultimately minimize oxygen diffusion into a deposit, these covers could be classified as ‘oxygen diffusion barriers’. However, in order to facilitate the division of the various cover techniques into identifiable categories, only traditional soil covers are discussed as “oxygen diffusion barriers”. It should be understood that oxygen-consuming barriers composed of peat, and low permeability barriers composed of clay, are also oxygen diffusion barriers but are discussed separately.

If a cover should perform as a barrier against oxygen transport from the atmosphere into a deposit, a layer with a low effective diffusivity for oxygen must be included in the cover. The effective diffusivity in a porous media is strongly dependent on the degree of water saturation (Millington and Shearer, 1971; Collin and Rasmuson, 1988). In water-saturated soils, the diffusivity generally is low, and any saturated soil theoretically should be an excellent barrier against oxygen transport. However, the effective diffusivity increases very rapidly as the soil dries and the water content decreases which, depending on the climatic conditions, periodically happens in most superficial soil layers. Consequently, to act as an effective barrier against oxygen transport, the barrier material must be able to withstand drying and to retain water in the cover structure.

In brief, the water retention capacity of a material is a function of the pore size and is generally enhanced by fine pore size (see Figure 5-5; Collin and Rasmuson, 1987; Nicholson et al., 1991; Tremblay, 1995). The degree of saturation is affected by capillary suction, which is a function of the elevation above the groundwater table. With increasing distance between the soil cover and the underlying groundwater surface, an increasingly higher capillary suction acts to withdraw water from the cover. Moreover, evaporation at the ground surface leads to a capillary transport of water upwards and can affect the water content to a considerable depth during dry periods. Regarding this, materials used in oxygen transport barriers must be able to maintain a high degree of saturation at high capillary suction (e.g. clayey till, cf. Figure 5-5). Furthermore, the best efficiency of an oxygen transport barrier can be expected at sites where the capillary suction that acts on the barrier is limited, naturally or by artificial means.

To meet the requirements on an oxygen diffusion barrier, a single layer cover should be constructed of a material with mainly fine pores, which is generally true for fine grained materials (clays, clayey silts) and well–graded materials with a high content of fines (clayey and silty glacial tills). A single layer cover can be an efficient oxygen transport barrier particularly at sites where the ground water table is close to the ground surface, where the conditions are favourable to maintain a high degree of water saturation in the cover. Depending on the hydrogeology, such conditions can be found in certain tailings deposits.

Single layer soil covers

In order to obtain the greatest possible water saturation in a soil cover, without actually flooding the impoundment with water, a potential solution involves raising the water table so that it lies within the cover material. This is accomplished by filling pre-existing ditches, so that runoff from the deposits is limited and there is an increase in water storage in the deposit. As the material is entirely water saturated, further oxidation is inhibited. The basis for such a measure is careful groundwater modelling, taking into account the influence from surface water management and groundwater-raising dykes. This technique has been applied in Kristineberg, Sweden, where two tailings impoundments have been reclaimed with single layer covers of till ensuring a high degree of water saturation (Lindvall et al., 1995).

Illustration: Single-layer soil cover at impoundment 1 in Kristineberg.

At locations with greater depth to ground water, there is an obvious risk that the cover will be drained and the transport of oxygen will increase during dry periods. However, depending on the character of the waste, the requirements on the cover efficiency can vary and single layer covers can still be applied under certain conditions.

Within the research program ”Deposits of waste from mining industry” financed by the Swedish Environmental Protection Agency, it was estimated that a single layer cover constructed with 1.0 m till should result in a reduction of the pyrite weathering rate (and metal release) by about 80% in an ordinary tailings deposit (SEPA, 1993). For a cover constructed with 1.5 m till, the corresponding reduction was calculated at about 90 %. For advanced multiple layer covers including an effective low permeability barrier, the calculated reduction was estimated at about 99 %. After the research program was completed, decommissioning plans including single layer covers have been established for some Swedish deposits. Numerical simulations of the effects for some deposits show better results than previously calculated. For the tailings impoundment at Aitik, the reduction is calculated at 99 % using a 1.0 m single till layer (Lindvall et al., 1997). Sulphide oxidation rates under field conditions have been estimated by Elberling et al. (1993).

Illustration: Construction of soil cover at the Aitik mine.

Experience of single layer soil covers

Single layer dry covers are generally not used in Sweden, since the water table must extend above the tailings, into the cover itself, and this hydrological condition would be very difficult to maintain at many mine sites. An exception to this is the use of a single layer cover on two impoundments in Kristineberg (impoundments 1 and 2), which both contain strongly weathered material. Since the Kristineberg deposits lie in a valley, it is possible to maintain water saturation in these impoundments by limiting discharge from the saturated zone; this was accomplished by filling drainage ditches surrounding the impoundments.

In Canada and USA, single layer covers not aiming primarily at the reduction of oxygen supply, but to facilitate re-vegetation, are often applied. Instead, other methods such as leachate treatment are used to prevent the effects of AMD. In arid climatic zones, the high rate of evaporation is exploited in a technique called “charge and regain”. Rainfall that infiltrates into a soil cover quickly evaporates from the upper soil horizons. Thus, significant volumes of water rarely percolate to the underlying tailings.

Capillary barriers

Theoretically, the so-called capillary barrier effect can be used in order to maintain a water saturated layer in the cover protected from losses due to evaporation or drainage. A capillary barrier can be generated when a fine-graded material with a high capacity to bind water by capillary forces is placed between two coarse-grained materials with no ability to transfer capillary suction (Rasmuson and Eriksson, 1987).

Modelling of covers including a capillary barrier suggests that it seems quite feasible to keep the fine grained layer at high water content and thereby significantly reduce the diffusion transport of oxygen (Collin and Rasmuson, 1986). It has also been suggested that a capillary barrier can act as an infiltration barrier by the lateral transport of water under unsaturated conditions, thereby avoiding positive pore water pressures on the barrier, which is theoretically needed to achieve vertical flow through the barrier. However, for normal Swedish conditions, this seems possible to achieve only occasionally. To act as an effective infiltration barrier, the capillary layer instead must have a sufficiently low permeability (Rasmuson and Eriksson, 1987).

The possibilities to utilise a capillary barrier have been investigated in laboratory columns by Aachib et al. (1994). The barrier consisted of (from top to bottom) 0.2 m sand, 0.5 m non-reactive tailings and 0.3 m of sand placed on top of tailings sand. The capillary layer (non-reactive tailings) could be characterised as silt with a high air entry value indicating that suction pressures up to about 25 kPa could be applied before the material should start to drain. The column was instrumented with tensiometers for measurement of suction pressure and TDR (Time Domain Reflectometry) probes for measurement of volumetric water content. The results indicated that the water content in the capillary layer should be maintained at a high degree of saturation and consequently that tailings can be of interest to use as a water retention layer in capillary barriers.

Experience of capillary barriers

At the field scale, the capillary barrier concept has been investigated by e.g. Bell et al (1994). The tests were carried out as a reclamation of a waste rock pile with an area of 2 500 m^2 at Heath Steele Mine, New Brunswick, Canada. A compacted fine-grained till was used as the 0.6 m thick capillary layer and was placed in-between two layers of 0.3 m sand. The barrier was covered with a 0.1 m superficial layer as protection against erosion. The cover was established in September 1991. Field hydraulic conductivity tests by single-ring infiltrometers indicated a hydraulic conductivity in the capillary layer of $1 \cdot 10^{-8}$ m/s. An assessment of the cover performance showed no significant change in the water content of the till during the reported period (until May 1993), i.e. during the first 1.5 years after placement. The oxygen concentration in the pile decreased successively from 18-21 % in May 1991 to 0.8-1.1 % in May 1992 to 0.1-0.2 % in May 1993. The temperature decreased in a similar way and the pH in the leachate increased.

A similar construction was investigated at Waite Amulet, Quebec, Canada (Yanful et al., 1994). Test plots were constructed with a capillary layer of 0.6 m compacted clay placed between two layers of 0.3 m sand and protected against erosion by a gravel crust. The water content in the clay remained close to the construction content at a degree of saturation ≥93 % during the assessment period (1990-1993). Modelling of oxygen transport based on field measurements indicated a barrier effect of >99.9 % regarding oxygen transport. Furthermore, the compacted clay had a significant effect as a barrier against infiltration due to its fairly low permeability (estimated at about $1 \cdot 10^{-9}$ m/s).

One problem involved in the establishment of capillary barriers is the supply of appropriately fine-grained cover materials. Bussiére et al. (1997) have investigated the possibilities to use desulphurized tailings as the capillary layer in a capillary barrier. Column experiments, including reference columns as well as columns with capillary barriers constructed of tailings with different (but low) sulphur contents, were carried out. Results were measured as oxygen-consumption values (Elberling et al., 1994). The column, with a capillary barrier constructed of desulphurized tailings with the lowest concentration of sulphur (0.14 %), showed a reduction of the oxidation rate by a factor 20 (95 %) compared to the reference column.

A similar capillary barrier, with non-acid generating tailings in the barrier, has been constructed in full scale at Les Terrains Auriferes in Quebec, Canada (Ricard et al., 1997). AMD modelling showed that a multi-layered cover with an effective oxygen diffusivity of $1 \cdot 10^{-8}$ m^2/s with a thickness of 0.8 m would be adequate to inhibit acid production from the underlying tailings. To achieve this, the tailings in the barrier must be saturated at 85 % or more according to the characterisation of the material. For design of the construction, the HELP and SEEP/W models were used for two-dimensional evaluation of the water budget. The cover was constructed during the winter of 1995/96, which called for a strict QA/QC program to ensure that minimum standards were met. Winter construction was chosen to avoid trafficability problems since the performance of the cover would have been more jeopardised by these problems than by those encountered during winter construction. The first six months of monitoring of the cover's performance showed an average saturation of 86.0 % on top of the dump and 84.4 % in the slopes. Implementation of oxygen consumption measurements indicates a reduction of the rate of oxygen flux to the underlying tailings by a factor of 75.

Showed to be an economic feasible alternative, covers with a capillary barrier have been the subject of several studies and have also been established in full scale. However, the importance of adequate characterisation of the construction materials and modelling of the actual site and water budget prior to design and construction of a multi-layer barrier should be stressed (Aubertin et al., 1997; Ricard et al., 1997). For example, 2D numerical finite element investigations of a large scale deposit show that the capillary barrier effect is dependent not only on the properties of the used capillary materials but also on the geometry of the deposit, and illustrate the risk of desaturation of a portion of the cover if the slope is too steep or too long.

Oxygen consuming barriers

Oxygen transport to the waste can also be reduced by covering the deposit with an oxygen consuming material. Examples of such material include paper and pulp wastes, wood wastes, sewage sludge, and peat.

Experience of oxygen consuming barriers

Tremblay (1994) reports from the reclamation of the East Sullivan Mine in Quebec, where dumping of wood wastes on tailings began in 1984. In 1990, reclamation activities focused on covering the tailings deposit with wood wastes. The cover consists of 2 m of organic waste (85 % bark, 10 % pulpwood and 5 % sawdust). An evaluation of the cover during 1991 showed that the oxygen decreased with depth in the cover. At a depth of 0.7 m the oxygen content was 1.5 %. Monitoring also showed increasing pH and decreasing metal release in leachate from the covered areas. Some organic contamination by small concentrations of phenol and tannin occurred. Further monitoring and tests are planned with different cover designs and will study the effect of the covers on oxidised and fresh tailings.

Three different organic materials (peat, lime stabilised sewage sludge, and municipal solid waste compost) were investigated in a combination of bench and pilot scale laboratory test in order to evaluate their effectiveness as oxygen consuming covers (Elliot et al., 1997). To provide comparative data, a cover with desulphurized tailings was also tested. From these studies it was concluded that lime stabilised sewage sludge appeared to offer the greatest potential for reducing metal loading to the environment. This is achieved by changing the underlying tailings environment by reversing the AMD processes with an increase in pH, decreased metal concentrations and formation of a reducing environment at the tailings - cover interface. For the compost cover a significant decrease in oxygen concentration with depth was observed. The oxygen content at the tailings interface at 0.9 m depth was close to zero, indicating that the material worked as an oxygen barrier. However, the effect on metal release from the underlying tailings was moderate, probably because these were already partly oxidised and no change in pH was achieved. The peat layer showed a minor decrease in oxygen concentration with depth indicating that the oxygen consumption in the material was too low to function as an oxygen transport barrier. This was probably due to the character of the peat as an older, highly decomposed material.

At the Galgberget impoundment in Falun, Sweden, a cover with a high content of organic material was constructed from fly ash, paper mill sludge, and wood waste; the latter two materials will consume oxygen during their decomposition. On the top of the tailings impoundment, a 1 m thick layer of fly ash mixed with paper mill sludge was laid out and compacted in two layers and thereafter covered with a 0.5 m layer of wood waste and coarse till. This cover is believed to form an effective barrier against oxygen transport partly due to consumption of oxygen in the cover and partly due to a physical barrier effect in the compacted low permeable mixture of fly ash and paper mill sludge (i.e. a ‘low permeability barrier’; see below). The hydraulic conductivity of the mixture was measured in the laboratory at $\leq 5 \cdot 10^{-9}$ m/s and the water retention capacity was measured and considered satisfactory to maintain a high degree of saturation in the barrier, similar to natural clay (Mattson, 1987). A similar cover design was used at the Ingarv impoundment in Falun. En evaluation of the physical barrier effect of alternative designs was done using a transient two-dimensional finite element model. The results indicated a small risk for dry-out of the cover during dry periods in the upper parts of the slopes near the edges of the deposit (Höglund et al, 1995).

Illustration: Cover construction of fly ash and paper mill sludge at Ingarv impoundment, Falun.

Other possible positive effects are the inhibition of acidophilic iron- and sulphide-oxidising bacteria due to the high pH of the percolating water, derived from the interaction of water with the calcium hydroxide–rich fly ash. In addition, it is possible that an anaerobic environment could be created under the cover which would be favourable for the growth of sulphate-reducing bacteria. These bacteria would produce hydrogen sulphide that precipitates metals. However, there is also a risk that the combination of organic compounds and iron hydroxides in the upper (oxidised) part of the deposit could result in bacterial iron reduction that would release co-precipitated heavy metals. The evaluation and monitoring indicated that the oxidation of sulphides had decreased and that the pH at the site was higher than at the reference site. No evidence of any significant bacterial sulphate reduction was noticed (Granhagen et al., 1996).

Low permeability barriers

Low permeability barriers are commonly used to limit the infiltration of precipitation into landfills. In addition, low permeability soil generally shows favourable water retention properties and maintains a high degree of saturation in the barrier. The limited percolation of water through the barrier also leads to water saturation in a second cover placed above the low permeability layer for long periods, unless this layer is drained. Consequently, low permeability barriers also act as water saturated layers preventing oxygen transport, provided they are covered by a protective layer (cf. multi-layer covers, below).

Being a barrier against both the diffusion of oxygen and percolating water, covers including low permeability barriers often show high potentials for limiting AMD and metal release from mine waste dumps. Estimates based on modelling within the former Swedish research program ”Deposits of waste from mining industry” indicate a possible reduction of the oxidation rate from 95 % up to more than 99 % and a probable reduction of the percolation rate from 80 % up to more than 95 % depending on the barrier soil (SEPA, 1993). Hence, pollutant transport is reduced in proportion to the reduced infiltration.

Low permeability barriers can be constructed of fine-grained soils, mainly clay and clayey till, geosynthetic clay liners (geotextile/bentonite liners), geomembranes (plastic liners), cement-stabilised products and some fine-grained residues from industrial processes (mainly sludge) (MEND, 1994; Lundgren, 1995).

Experience of low permeability barriers

When used as covers on mine waste deposits, low permeability barriers are commonly covered with more permeable protective covers. Because of the low infiltration capacity of such materials, surface runoff from such barriers would be significant. Therefore, a protective cover is needed to prevent the erosion of the low permeability barrier. In the section below, low permeability barriers are discussed as a component in multi-layer barriers, in association with protective covers.

Adak. At the reclaimed tailings deposit in Adak, Sweden, the cover is constructed with 0.5 m compacted till overlain with 1.5 m uncompacted till. The permeability of the barrier layer is relatively low, about $5 \cdot 10^{-8}$ m/s, but not sufficient to act as a barrier against infiltration of precipitation. The groundwater table is about 5 m below the interface between tailings and barrier layer. The oxygen flux for this construction is estimated to be ca. 0.2 mol/m^2/year (Höglund et al., 1993; Brandberg et al., 1993).

Illustration: Soil covered tailings deposit at the Adak mine.

Bersbo. During 1987-1989, the deposits of mining waste and metal contaminated ground areas in Bersbo were remediated (Lundgren, 1997). The waste (ca. 750 000 m^3) was produced during a long period of mining activities reaching back to the 13th century. The mine was closed in 1901. The remediation activities became a pilot project for the decommissioning of the waste deposits from mining of sulphidic ores, which followed and still are under way in Sweden. Since 1989, a series of investigations has been conducted in Bersbo with the objective to show the results of the remediation measures. The post-remediation studies can be divided in four main programs, which study the following:

- The efficiency of the dry covers on the two waste rock deposits
- The efficiency of other counter measures in the mining area
- The quality of the surface waters affected by AMD from the mining area
- The effect of the measures on the ecology of the area that was (and still is) affected by AMD.

The post-remediation studies of cover efficiency show that the cover on the Steffenburg deposit works very well and the water quality monitoring verifies that the transport of metals from this deposit has been reduced to low levels. The cover on the Storgruve deposit has not functioned equally satisfactory, because of air leakage from the old galleries in the mine. Supplementary sealing operations have been carried out and the results have been studied for 1.5 years. The supplementary sealing measures have had some effects which are too early to specify.

Illustration: The Bersbo deposit about ten years after finalised remediation.

The drainage from the Storgruve deposit is also charged with an acid drainage from the mine. This AMD is generated by a quite large mass of waste rock (250 000 m^3) that was dumped under the groundwater level in the mine shafts in order to limit contact with oxygen. It has been shown that the drainage from the mine increased significantly due to secondary oxidation and leaching of this mass of waste rock and that the drainage from the waste rock deposit was significantly reduced. Even if there are indications of improvements, the resulting transport of AMD in the common outlet from the mine and the deposit to Lake Gruvsjön is still about the same as before remediation.

On the Storgruve deposit, the cover consists of a 0.25 m thick sealing layer of cement - stabilised coal fly ash (”Cefyll”) which was grouted as a slurry in a crushed rock aggregate. This layer was covered by a protective layer of 2.0 m of glacial clay. On the Steffenburg deposit, the sealing layer consists of glacial clay, which was compacted in three lifts and protected by 2.0 m of glacial till. The saturated, hydraulic conductivity of the Cefyll-layer was measured on small samples to around $1 \cdot 10^{-9}$ m/s which was the specification set up for the sealing layers. The corresponding conductivity of the compacted clay was measured as $1 \cdot 10^{-10}$ m/s, i.e. 10 times lower than the specifications. The vertical, full scale percolation of water through the sealing layers registered as the leachate production rate corresponds to 3-5 times the saturated conductivity of the clay liner but only 0.5 times the saturated conductivity of the Cefyll liner. The latter result suggests that the sealing layer is not fully water saturated, which is caused by the capillary conditions in the Cefyll liner on the long slope of this deposit.

The transport of oxygen through the clay liner is very slow and the oxygen concentration is normally below 0.5 % with a seasonal fluctuation between less than 0.1 % and 1 %. The transport of oxygen through the Cefyll liner is higher, normally between 1 % and 3 % but with seasonal fluctuations between 0.1 % and 5 %. The peaks in oxygen concentration are caused by the seasonal low groundwater levels in the cover, which take place in August-September each year. Due to the low oxygen diffusivity of the sealing layers, the peaks are not registered until 6 months later when the groundwater levels are normally the highest during the years.

In conclusion, the clay liner acts as a good water and oxygen barrier, while the Cefyll liner acts as a comparatively good water barrier but a less good oxygen barrier. As previously mentioned the Storgruve deposit has also suffered from leakage of air with advective transport of oxygen to the waste. Chemical analysis shows that the higher oxygen transport rates in the Storgruve deposit have a smaller effect on the metal concentrations in the discharges from the deposits than the very low oxygen transport to the waste in the Steffenburg deposit.

Beside the wet and dry cover on mining wastes, the countermeasures in Bersbo included rinsing of wastes and concentrating the waste to the two main deposits. This led to a 50 % reduction of the size of the ground area that was exposed to AMD. The post-reclamation studies show that both the surface water and the ground water quality rather quickly and significantly improved in certain subareas while high concentrations of sulphate and metals still can be found after more than 8 years in other subareas.

Saxberget. The Saxberg mine was in operation from 1892 to 1988. Waste products from the mining activities were deposited in the Saxdalen Village, where the first beneficiation plant was situated, at the Boliden Mineral AB mine site (from 1957), and in two large impoundments containing mill tailings. The decommissioning, which was a joint project between the Swedish Environmental Protection Agency and Boliden Mineral AB, started in 1991 with the remediation of the old plant site in the village and disposing of some 100 000 m^3 of mining wastes and contaminated soils in one of the tailings impoundments.

The most costly and time-consuming part of the project was the coverage of the two large tailings impoundments which was carried out between 1993 and 1995. The cover consists of a sealing layer and a protective layer. The sealing layer, 0.3 m thick, consists of a clayey glacial till that was compacted in 2-3 lifts. The protective layer consists of a 1.5 m thick layer of sandy, glacial till. Both till types were found close to the impoundments and were used without treatment other than the removal of stones bigger than 150 mm.

The original specification of the sealing layer material was that it should be compacted to 95 % modified Proctor and give a hydraulic conductivity that is less than $5{\cdot}10^{-9}$ m/s. This turned out to be difficult to achieve with the selected materials at site which resulted in that a minor part of the sealing layer may have a slightly higher conductivity. The specified conductivity of the sealing layer is too high to result in efficient water barrier properties. However, according to numerical modelling it should be low enough to create saturated conditions in the bottom part of the cover during a large period during the year. Oxygen transport should only be possible during one or two months in the dry season. Numerical modelling performed for hydraulic conductivities of the sealing layer between $5{\cdot}10^{-9}$ and $1{\cdot}10^{-8}$ m/s showed oxygen intrusion rates of about 0.1–0.2 mol/m^2/year (Höglund et al, 1994).

Post-reclamation studies of the Saxberget impoundment have shown that the oxygen concentration under the cover is very low, only occasionally above 0.5 %. Hence, the cover must act as a good oxygen barrier. However, the monitoring also shows that the air transport processes are very sensitive to leakage through discontinuities in the cover. The reason for this is probably, like in Bersbo, that gas pressure changes take place in the covered deposit, over both short and long time intervals. Short-term (diurnal) changes are due to tidal effects (gravitational) and possibly atmospheric air pressure variations. The long-term effects are due to variations in groundwater levels.

Post-reclamation monitoring of water levels in the cover indicates that not only seasonal but also spatial variations in the water balance of the cover are significant. So far, it is too early to specify what effect the cover has on the transport of metals from the tailings impoundments to surface and ground waters.

Ranstad. At Ranstad, uranium mill tailings have been reclaimed using a cover including a low permeability till layer, similar to the construction in Saxberget.

Examples from Canada. At a waste rock dump in British Colombia, Canada, a cover including a low permeability barrier was constructed with a fine-grained till classified as SC-CL using the Unified Soils Classification System (clayey – silty to silty – clayey till according to the Swedish classification system; Wilson et al., 1995). On the top of the deposit, a barrier of 0.5 m compacted till with a saturated hydraulic conductivity estimated at $2 \cdot 10^{-9}$ m/s was established and covered with 0.3 m loose till as a protective layer. Modelling based on short term monitoring indicated that the water flux into the dump was reduced by approximately 99 % and that the oxygen flux was reduced up to 99.7 % compared to the uncovered waste rock.

The capillary barrier construction established at the Waite Amulet site in Quebec (see above) is also shown to act as a low permeability barrier (Yanful et al., 1994). The barrier consists of 0.6 m compacted clay between two 0.3 m sand layers. The hydraulic conductivity of the clay barrier was measured in field at about $1 \cdot 10^{-9}$ m/s. Monitoring of the infiltration through the cover by means of a lysimeter below the barrier yielded 37 mm of leachate during a year. Simulation of 20 years varying climate data and calculations of the resulting infiltration through the barrier with the quasi-two-dimensional deterministic HELP (Hydrologic Evaluation of Leachate Performance) model indicated an average infiltration rate of 39 mm/year. Finite element modelling simplified to steady state conditions supports the results indicating an infiltration rate of 34 mm/year. As previously noticed, the reduction of oxygen transport was estimated at >99.9 %.

In the case of a shortage of low permeability soil at the mine site, low permeability barriers often involve high costs for transportation or processing of materials. In certain cases it is possible to reduce the cost by the use of alternative materials supplied by nearby industries. The earlier described rehabilitation of the tailings impoundment at Galgberget in Falun is such an example (see above). At the Eustis mine site in Quebec, a similar low permeability barrier was constructed with de-inking sludge from the recycling of paper (Cabral et al., 1997). An experimental cell was built with partly oxidised tailings covered with a barrier of 1.2 m of compacted de-inking sludge and a vegetated cover of 0.3 m compost mixed with de-inking sludge. Prior to the covering, the upper 0.3 m of oxidised tailings was mixed with alkaline sludge in order to increase the pH.

The de-inking sludge had very high water content, equal to a water quotient of 160-185 %. The sludge consisted of 38-50 % kaolin clay and organics. The permeability according to laboratory measurements of compacted samples varied between $5 \cdot 10^{-10}$ - $2 \cdot 10^{-9}$ m/s. The sludge also showed favourable water retention characteristics with an air entry value of 35-45 kPa.

Experiences showed that the sludge, unlike fine-grained soils, could be compacted in a wide range of water contents and still show low permeability, which was calculated from lysimeter readings (comparable to the values measured in laboratory). Monitoring also showed that the oxygen content in the cover generally was below detection limits at a depth of 0.5 m, indicating an excellent barrier against oxygen transport. The temperature profile in the cover showed heat generation, which could be associated with degradation of the organics. It is likely that the oxygen diffusion barrier effect was strengthened by oxygen consumption in the barrier.

Tests on a barrier consisting of residues from pulp and paper has been reported by Cabral et al. (2000).

Reaction inhibiting barriers

While the use of soil (above) or water covers (see below) are the most common methods of limiting oxygen diffusion to mine wastes, other barrier techniques that inhibit the sulphide oxidation process have been tested.

The application of bactericides to wastes (e.g. Parisi et al., 1994; Schippers et al., 1998) is effective in suppressing the activity of iron- and sulphur-oxidizing bacteria, but these methods require the essentially continual application of bactericides for effective treatment (Evangelou and Zhang, 1995). Schippers et al. (1996) showed that that there was a rapid decrease in the activity of *Thiobacillus ferrooxidans* after the addition of sodium dodecyl sulphate (SDS), a sulphonated surfactant. However, this compound is quickly degraded by microorganisms or adsorbed to clay minerals, so that additional doses are needed to maintain a low activity of *T. ferrooxidans*. The addition of alkaline compounds such as calcium carbonate and concrete to mine wastes also has an inhibitory effect on the activity of iron-oxidizing bacteria (Schippers et al., 1996, 1998), but this inhibition is the result of the high pH environment, which greatly depresses the activity of the acidophilic bacteria.

Novel prevention technologies, such as the passivation of pyrite surfaces with ferric phosphate (Evangelou, 1994; Evangelou and Zhang, 1995; Kalin et al., 1997) or silica (Evangelou et al., 1998) surface precipitates, have been tested in bench-scale experiments. In the former case, pyrite – rich mine wastes are treated with hydrogen peroxide (H_2O_2), KH_2PO_4, and a pH buffer. Hydrogen peroxide oxidizes the pyrite and produces Fe^{3+}, which subsequently precipitates on the pyrite surfaces as a ferric phosphate surface coating. According to Evangelou and Zhang (1995), the successful application of a surface coating methodology in the field could mean a long-term solution to certain types of AMD problems. Investigations by Elsetinow et al. (2001) have confirmed that pyrite oxidation is indeed inhibited by phosphate additions at $pH > 4$. However, at low pH ($pH < 3$), oxidation inhibition by ferric phosphate was not observed.

6.3 Water Cover

Since the solubility (8.6 g/m^3 at 25 ^{o}C) and diffusivity (2·10^{-9} m^2/s) of oxygen in water are low compared with their corresponding values in air (285 g/m^3 and 1.78·10^{-5} m^2/s, respectively), the covering of mining waste with water has become an established remediation method. In the absence of convection, oxygen transport through water is considered to be slow, so that the oxidation rate of sulphidic mine waste decreases to a level that is acceptable. Water coverage may be obtained by underwater disposal of tailings during production, either in natural lakes or in tailings ponds that are deep enough. Conventionally operated impoundments, with discharge along a beach, may also be permanently protected by a water cover after mine closure by raising the dam walls along existing tailings impoundments. Another possibility in complex mining areas is to deposit tailings in pit lakes, which may have anoxic bottom waters.

Water covers are generally regarded as one of the most cost effective methods for the mitigation of potentially acid-generating mine tailings. Among the benefits of using water covers are the reasonably low maintenance required and beneficial side effects such as the prevention of dust formation. A major drawback of the method involves the construction of dams and dikes that often need maintenance and monitoring for long periods of time. It remains to be proven that dams built to reasonable costs are effective for time scales of hundreds to thousands of years. This effectiveness includes both the geotechnical stability of the dam structures, and the long-term water balance for the water cover. A schematic illustration of dam constructions for tailings dams is shown in Figure 6-2.

Illustration: Water covered tailings at impoundment 2 in Kristineberg.

To secure the deposit, some design parameters need to be established. The most important one is the design water depth, ruled by the water balance and the wind conditions. Depending on the exchange rate of the water, the design must accommodate for the losses due to evaporation and dyke leakage during dry periods. The minimum water depth is ruled by the wave action combined with the particle size, which yields a shear force or an erosion velocity at the sediment surface, which must not be exceeded.

A potential problem when using shallow water covers is that wind driven turbulence may increase the supply of oxygen in the water body, such that the resuspension of sulphides in water covered tailings ponds may lead to increased sulphide oxidation.

If plants are established in water covered impoundments, the water depth in the impoundment may be reduced since the risk for tailings resuspension decreases. This reduces the costs. Establishment of vegetation in shallow ponds may also result in formation of a sediment layer rich in organic material on top of the tailings. It is possible that the decay of this organic matter further reduces the oxygen flux, and that the changes of the physiochemical environment caused by the organic matter are positive for metal immobilisation. However, some plants have the ability to actively transport oxygen to the roots and release oxygen in the root zone, thereby potentially increasing the oxygen supply in the tailings. This needs consideration in the remediation design.

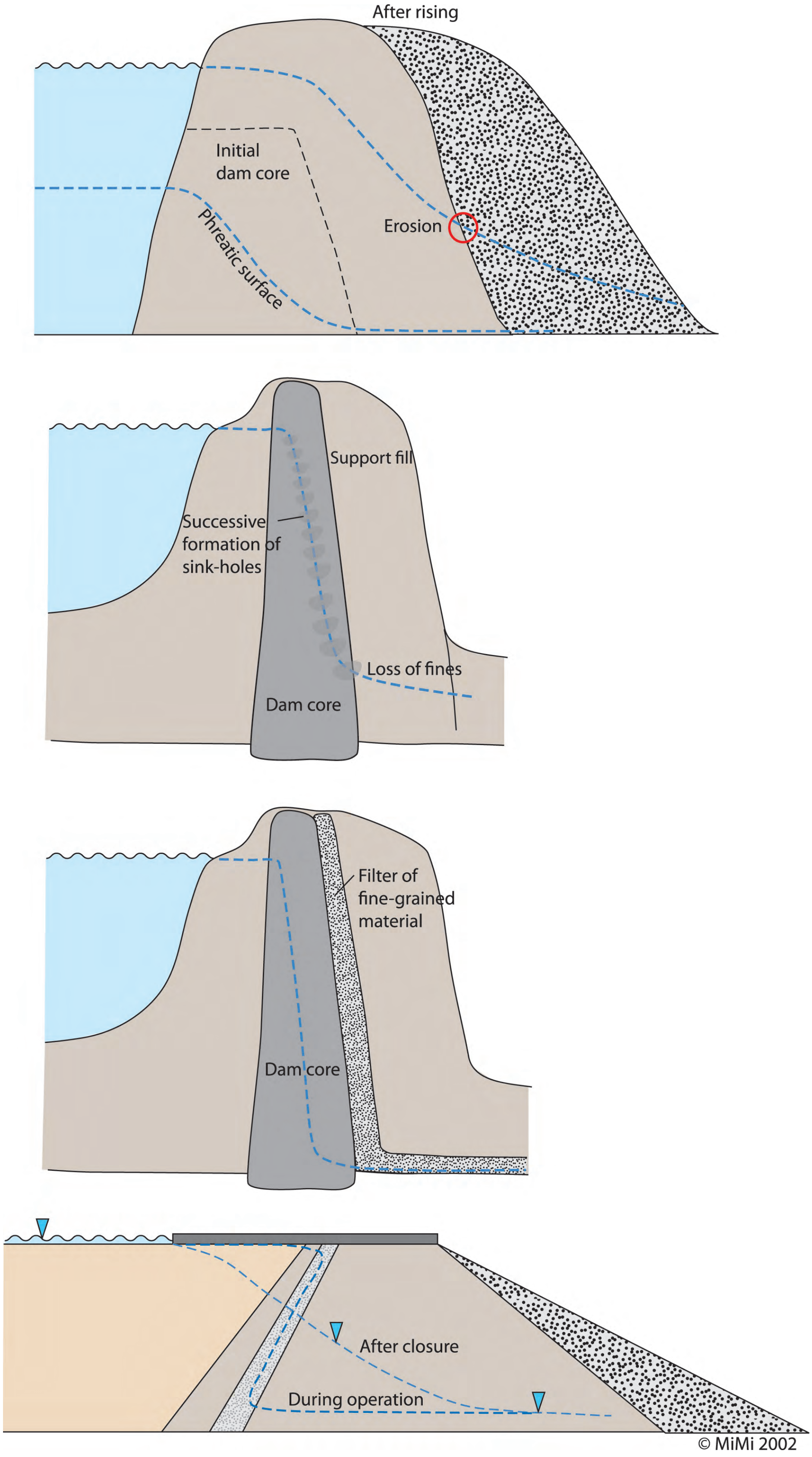


Figure 6-2 Schematic illustration of dam constructions for tailings dams.

Flooding of tailings impoundments

Conventionally operated impoundments, with discharge along a beach, may be permanently protected by a water cover after mine closure. To accomplish this, the water level needs to be raised. In conjunction with an increase in water level, it is usually necessary to raise the height of the surrounding dam walls. In some cases, surface of the material can be flattened out to reduce the need for dyke height.

A problem that needs to be addressed is the content of weathering products in the material, originating from oxidation during dry periods prior to flooding. When the water level is raised, often following major excavation work in the impoundment, substantial amounts of metals and salts are mobilised, complicating the evaluation of the oxidation rate of the bottom sediments.

Apart from the high decommissioning costs, the post closure flooding option is associated with a few drawbacks during operation. One is the behaviour of the beach, which during unfavourable weather conditions may result in the dispersal of fugitive dust. Additionally, the exposed tailings may weather, yielding an increased metal and sulphate content in the impoundment water. This is common for all mines operating conventionally managed tailings impoundments.

Experiences from the flooding of tailings impoundments

In Sweden, the Stekenjokk mine was closed 1988, and the operator Boliden worked out a decommissioning plan for the area focusing on the tailings impoundment. At that time, the use of soil covers for the prevention of sulphide oxidation was the method that was predominantly discussed, but this was currently only used on small deposits and the effectiveness of the method had not been satisfactorily proven. Due to the circumstances (i.e. a lack of soil cover material), Boliden chose the post-closure flooding method with elevation of the dykes and the redistribution of some material to reduce required dam height. The results are very satisfactory, and Stekenjokk has since become the reference object for flooded tailings impoundments.

In order to avoid the resuspension of sulphides in water covered tailings ponds, Boliden uses breakwaters and waste rock to reduce the wave forces and stabilise the bottom in the shallow parts of the flooded tailings impoundments.

Important references on post-closure flooding are located in Canada. In the uranium mining district Elliot Lake, a number of pyrite containing tailings impoundments have been subject to flooding, which now constitute a system of artificial lakes. The project has been carefully evaluated, and a research centre administrated by CANMET has been founded in Elliot Lake.

Impoundment 4 in Kristineberg covers an area of 0.74 km^2, and was flooded by raising the existing dykes by 1.5 m. The water depth varies from approximately 1.5 to 2.5 m, and the impoundment is ice-covered from late October to early June. Erosion protection material will be applied in shallow areas. The water flowing from impoundment 3 is treated with lime before it reaches impoundment 4. This impoundment is at present an efficient trap for metals transported by drainage from the upstream areas (Widerlund et al., 2001). Liming will continue until the transport of acidity and metals has decreased to acceptable levels. Further details on impoundment 4 are given later in this chapter.

Illustration: Water covered tailings at Stekenjokk mine.

Continuous underwater deposition

In its most fundamental form, underwater deposition means the discharge of tailings at or below the water surface. No beach is allowed to develop. Fluctuations of the water level must not take place to such an extent that the tailings surface is exposed. As the angle of distribution is steeper below surface than above, the depth of the lake or impoundment is important.

The management of the deposit involves strict planning. The tailings are discharged using a floating pipeline, and to minimise the need for changing the set-up, bathymetric measurements need to be carried out. Based on these measurements, the pipeline is directed along an intended line, anchored and in sequences shortened to create an underwater ridge of tailings. Depending on the fineness of the tailings and the depth of the impoundment, more or less frequent relocation of the discharge point is required. In the best case, the method does not call for more frequent changes than conventional discharge onto a beach.

Important scientific work was undertaken by among others NIVA (Norsk Institutt for Vannforskning), who developed methods for the quantification and prediction of the metal release from sediments. Based on this work, the underwater deposition method was developed for application also on previously drained and oxidised material.

Disadvantages with this method are the relatively high initial costs due to preparatory dyke construction to the final height and expensive pipeline arrangement. Apart from the benefits of a water cover that inhibit oxidation, the costs for decommissioning an underwater deposit are low. Under the most favourable conditions, only the removal of the pipeline and the final cleanup of the area are required. This is under the circumstances that the dyke stability is sufficient and that the dykes are built using appropriate material or already covered when the dyke material is sulphidic.

Experience from continuous underwater deposition

Pioneering work on underwater deposition methods for tailings was carried out in Norway during the 1980s. At the mines Løkken and Hjerkinn, sulphide rich tailings were distributed in impoundments using floating pipelines, never allowing access of air to the tailings. The record proved that the pyrite oxidation rate under water was extremely low, and that metal release was orders of magnitude lower than in the drained deposit case.

An early example in Sweden was the Grängesberg mine, which practised underwater deposition mainly aiming at the reduction of fugitive dust until closing in 1986.

In some cases ocean deposits have been operated. Two such examples are Titania in Norway and Greenex in Greenland. Titania, producing inert titanium ore tailings, was forced by the regulators to move the deposit from a fjord to an area on land. Greenex, which closed operations in 1990, utilised the fjord with only limited recorded impact on the aquatic life. After closure, the metal content in the species is declining towards the background value.

Within the research programme MEND/NEDEM in Canada, important investigations of underwater deposition practises have been undertaken. A number of lakes in Canada being used for continuous underwater deposition of sulphidic tailings were studied. The signs of disturbances due to slimes etc. were limited, except within close proximity of the discharge points. The positive experience regarding the chemical stability of the material together with the favourable visual impression of the deposit, even when it is in operation, has caused Canadian mining companies to strongly consider the method for future projects. One of the most recent projects, the Louvicourt mine in Quebec, is operating a continuous underwater deposition impoundment.

Pit lakes

Pit lakes are artificial water bodies formed in open pits when production and dewatering cease. There is a potential to deposit sulphide-bearing mine waste in pit lakes. To improve the understanding of the geochemistry of pit lakes, the Rävlidmyran and Udden pit lakes situated in the Skellefte Ore District in Northern Sweden were studied within the MiMi programme (Lu, 2002; Ramstedt et al., 2002; Lu et al., 2002a,b; Lu et al., 2004). Both lakes have low pH and high content of sulphate and metals, but show distinctly different limnological and geochemical characteristics.

Rävlidmyran pit lake is oligotrophic and meromictic. The lake is permanently stratified with three layers: the mixolimnion at the top, the chemocline below and the monimolimnion further below. Groundwater discharge and water stratification control the elemental distribution in the lake. The oxygen concentration in the monimolimnion is very low, but redox is still too high for sulphate to be reduced. Elements such as Ca, Mg, Na, K, S (as sulphate), Mn, Fe and Zn have lowest and almost constant concentration in the mixolimnion. The concentrations of these elements increase in the chemocline and keep rising in the monimolimnion. Fe is removed from the mixolimnion due to oxidation and precipitation, but is redissolved in the monimolimnion.

Illustration: Pit lake at the Rävlidmyran mine.

Udden is a dimictic lake. Distinct overturn of the lake occurs both in spring and autumn during which the whole lake, except a few metres of bottom water, is completely mixed and most elements homogeneously distributed. With the exception of the bottom water, the whole water column is oxygenated. During summer and winter, the lake is thermally stratified. Three layers, the epilimnion at the top, the metalimnion below and the hypolimnion at depth could be identified. However, the thermal stratification does not control the elemental distribution. During stratification, the concentration of dissolved elements appears to be constant at most depths. Variations mainly occur in the top and bottom waters. Elements such as Ca, Mg, Na, K, S (as sulphate), Mn, Cu, Al and Zn have lowest concentration in the epilimnion. Concentrations increase in the metalimnion, and keep constant in the hypolimnion. The distribution of Fe-concentration reflects the changes of redox potential. High amounts of Fe(II) reaching the surface waters by drainage from closely situated waste rock dumps cause higher dissolved Fe concentration and lower redox potential in the uppermost 10 m of the water column. Precipitation of dissolved Fe occurs in deeper water where the redox potential is higher (Ramstedt et al., 2002).

In both lakes, a strong relationship between Cu and Al was found. An Al-rich phase, possibly gibbsite, is important since it controls the dissolved concentrations of both Al and Cu by precipitation and adsorption. Otherwise, scavenging processes by particles are not important for controlling the concentration of most elements due to the low concentration of suspended particles in both lakes.

In permanently stratified lakes such as Rävlidmyran, it may be favourable to deposit waste rich in iron sulphides due to the low oxygen concentration in most of the water column.

Interaction of surrounding watercourses with flooded deposits

A mechanism recently focused on in e.g. Kristineberg is the influence of natural sediments at the top of the sand. Simulations carried out by NIVA suggested that even a shallow inert sediment layer would reduce the transport of oxygen and metals to fractions of the base case. Hitherto realised decommissioning projects have been aiming at isolating the deposits from the surrounding environment, without taking into account any benefit from natural sediments. In Kristineberg, the regional watercourse is planned to be directed through the tailings impoundment, aiming at a rapid restoration of the impoundment to a lake with normal aquatic life.

Today's knowledge of the rehabilitation process is limited. As one example, the establishment of fish in the impoundments is investigated only to a limited extent. There is a need to follow the immigration of various species into the restored environment.

Combined flooding and wetlands

One modification to the flooding of tailings impoundments is to allow water-growing plants to grow in the water cover. These plants may either establish themselves naturally in the water cover, or may be introduced as part of the remediation plan. With time, a layer of organic material will develop on the bottom, acting as an oxygen-consuming barrier. Eventually, the system will evolve into a wetland.

One advantage of allowing plants to grow in the water cover is the possibility of reducing the water depth in the cover, since an active wetland provides protection from wave forces and hence resuspension. In addition, the decay of organic matter in the sediment will consume oxygen and reduce the diffusion of oxygen into the tailings. It should be emphasized that the main objective with such a solution is not the biological treatment of water, but rather the establishment of a living barrier for the consumption of oxygen and the reduction of wave action.

Although the degradation of organic matter at the sediment surface will consume oxygen, various studies have shown that water-growing plants actually transport oxygen to their roots. This is potentially a disadvantage to promoting wetland growth in a water cover. Estimates indicate that a water-growing plant can transport from 0.9 to 11 mg O_2/hour to its roots. If approximately 12 plants grow per m^2, and the efficiency of oxygen exchange is limited to 77%, then the oxygen transport to the roots (and sediment) is a minimum of 200 mg O_2/m^2/day or 6.24 mmol O_2/m^2/day. The growing season in northern Sweden is approximately 100 days, so the annual transport rate is in the range of 0.6 – 7.7 mol O_2/m^2/year. This range of transport rates is generally greater than the rate of oxygen diffusion through a partially saturated soil cover (see Chapters 10 and 11), as defined in the MiMi Base Case, and can thus be considered relatively large. However, oxygen transport to the roots may be offset by the consumption of oxygen during the decay of organic material. If the rate of decay exceeds the rate of transport to the roots, and depending on the depth of the root zone compared to the depth of the organic material, then the establishment of a wetland in a water cover might be beneficial to the performance of the flooding method.

6.4 Tailings disposal with the use of seepage dams

For the deposition of tailings with low sulphide content, for which weathering processes are considered not be a main concern for the environment, disposal of tailings using seepage dams may be possible. This technique, which has been investigated within the MiMi programme for disposal of iron ore tailings, uses permeable dam walls (seepage dams) in order to allow the tailings to drain successively with the disposal. The idea is to avoid high pore pressures within the dam wall and the disposed tailings, thereby increasing the stability for the dam. Using seepage dams, successively built up in several levels with decreasing area, it will also be possible to create hill-like formations.

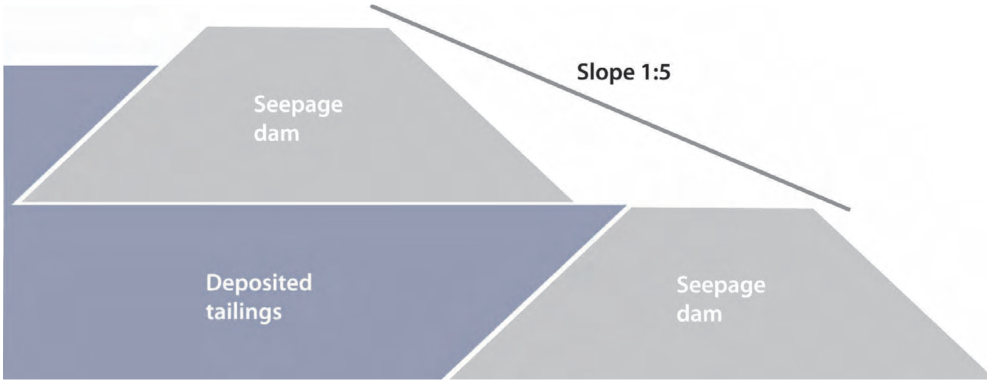


Illustration: Schematic cross-section of tailings disposed in seepage dams.

A possibility investigated is to use waste rock for the construction of seepage dams. The use of waste rock as the main component in dam constructions would also imply a very cost effective method for disposal. However, as the difference in grain size between waste rock and tailings normally is very large, the construction of filters in order to maintain the tailings within the dam as the water drains through the dam becomes crucial. In the performed investigations, different fractions of crushed, well graded, waste rock that emanates from the mill have been tested as filter materials as well as two different geotextiles.

Dimensioning for the filter is the active disposal phase during which significant amounts of water will pass through the seepage dam in order to drain the excess water from the tailings slurry. Laboratory investigations and pilot scale field tests with crushed waste rock as filter materials have shown that generally accepted filter criteria for construction of filters in dam construction, as expected, are valid also for dimensioning of filters of crushed rocks in seepage dams. However, the filtration efficiency was shown to be good also when the filter criteria only was partially fulfilled (Åkerlund, 2004).

Almost 100 % filtration efficiency was achieved using well graded crushed rock as filter as well as with the geotextiles. No substantial difference was noticed between the two geotextiles (non-woven mechanically bonded continous filament), a one-layer and a two-layer geotextile manufactured especially to serve as a filter.

Measurements of pore pressures in the pilot scale field test during disposal and a following period of consolidation showed drainage effects immediately as disposal were started, with a pore pressure profile generally lower than hydrostatic pressure. When filling ceased, the pore pressures decreased with time independent of rain events, indicationg a free drainage. In spite of this, a free water surface was noticed above the tailings in the downstream parts of the test cells during the entire period, indicating a higher horizontal than vertical permeability. The free water surface was achieved as differential settlements following consolidation created a depression upstream the seepage dam (on the dam slope smaller settlements develop than inside the cell due to decreasing depths of tailings).

The largest differences compared to hydrostatic pore pressures were measured at the bottom, although the test cells were lined with an impermeable membrane in order not to allow vertical drainage downwards, indicating a faster drainage in the lower parts of the cells. This is most likely an effect of segregation of particles during settlement, as coarser particles in general settles more rapidly than finer particles according to Stoke's law.

Large scale field tests have in general confirmed the conclusions from the laboratory investigations and pilot scale field tests, even if there seem to have been a larger loss of particles in the large scale tests. In the large scale tests, also the effects of continued disposal in partly filled cells which have been allowed to freeze during a winter break. Upon the continued disposal it was showed that the ice lens that had formed during the break did not thaw, thereby creating higher pore pressures above the lens and drained conditions below the lens (Bohlin och Jonasson 2002). This is an implication with the technique which has to be taken into consideration during operation and need further attention.

Another factor that needs attention is the risk for erosion of disposed tailings under a dam wall when this is constructed on earlier disposed tailings. The seepage create substantial flow through the dam wall and thereby high water velocities at the interface between the highly permeable dam walls and the underlying moderately to low permeable tailings. This create a risk for erosion of the underlying tailings which may have implications for the stability and has not yet been considered, though tendencies to erosion have been noticed in the large scale tests where concentrated flow has developed.

Laboratory investigations of the shear strength of disposed tailings in the large scale seepage dams by triaxial tests and direct shear tests showed large variations. Determined internal friction angles varied from 23° to 45°. Similar variations have earlier been noticed for tailings disposed in traditional dams (Ygland, 2000; Eurenius, 1989). The governing mechanisms resulting in these large differences need further attention to be clarified and, if possible, used to create tailings impoundment with high strength in order to improve the long term stability, in seepage dams as well as in traditional dams.

Illustration: Seepage dams during testing at Malmberget mine.

6.5 Pre-decommissioning planning of the Kristineberg impoundments

Prior to the decommissioning of the Kristineberg impoundments, the investigation plan included a broad range of activities (Lindvall et al., 1999, and references therein). The initial phase was the documentation of the topography with a 3-dimensional terrain model, which was an important tool for the construction work. A comprehensive hydrogeological investigation was carried out. The investigation included the calculation of the water balance for various remedial alternatives to be applied to different sections of the area. Detailed groundwater modelling was carried out to determine the effects of the various decommissioning alternatives. Field studies were performed to estimate the depth of the weathered zone in the various deposits.

The various impoundments were sampled and laboratory tests were carried out to define the acid production rate and potential as well as neutralising characteristics of the deposited material. Leaching tests determined both the chemical stability of the tailings and the amount of weathering products mobilised if dry areas were to be covered by water. An important factor to take into account was the wave dynamics in a flooded impoundment. Calculations using maximum wind strengths and fetch lengths were performed in order to determine the water depth required to avoid wave-induced resuspension of tailings and sludge. Some areas located at high elevations in the catchment area were obvious candidates for dry covering. Special attention was paid to the cover design, taking into account the site-specific conditions. In relation to this work the glacial till deposits in the area were investigated.

The long-term stability of the dykes is of key importance for the success of the project. Specialists in dam construction were hired to produce the final design of the dams. All results were used, together with relevant existing data, to compile a comprehensive decommissioning plan for the area.

Flooding of impoundments 3 and 4

An efficient way of limiting the oxidation rate of sulphide minerals is to flood the material with water and thereby limit the rate by which oxygen can be supplied by diffusion. In many cases, the supply of oxygen is the limiting factor controlling the oxidation rate of sulphide minerals. One important factor to consider in designing a water cover is the influence of wave induced stress on the deposited material which can cause resuspension and increased circulation of oxygenated water through the top layer of the deposited material. Resuspended material may also be transported out of the impoundment with the effluent, and thereby increase the load of metals to the environment.

Until recently, impoundment 3 has been used as a sedimentation impoundment for the sludge from the mine water treatment using a straight liming process. Since the use of impoundment 3 as a sedimentation impoundment has continued even after the mill was closed, the tailings are partly covered by hydroxide sludge. The final stage in the water treatment process was to adjust the pH of the water when entering impoundment 4, resulting in part of the tailings being covered by a calcite-gypsum sludge. This sludge is more prone to resuspension by wave action than the tailings. The investigations conducted showed that for the given sludge properties, hydrological and meteorological conditions, a water cover of 1.5 m would prevent resuspension of the sludge. Various alternatives were investigated on how to control or avoid the potential resuspension of sludge and tailings, including construction of wave breakers or raising the dams. As a result of these studies, the conclusion was that the dykes around impoundment 4 should be raised by 1.5 m. This increase in the height of the dam would allow for a water cover with a minimum depth of 1.4 m. In the shoreline areas, which are shallow, a till layer will be applied to the surface to prevent erosion and resuspension. Later, the final height of the dam has been reconsidered, and the areas with bottom stabilisation will be increased.

The chemical stability of the deposited sludge differs from tailings material. However, the chemical investigations undertaken on the sludge indicate that it is chemically stable, and that the dissolved metal concentrations will be low at the predicted conditions in the water cover. In this context, the inflow of surface water from the river Vormbäcken will play a central role. The river water transports suspended solid material, both organic material and mineral particles. When this material settles in the impoundment, an oxygen consuming diffusion layer is developed, which will potentially further enhance the performance of the water cover (cf. Holmström and Öhlander, 2001).

The Downstream Dam

For many years, drainage through the downstream dam has been a matter of concern. Several investigations have addressed the problem but the cause is both simple and obvious – the dam material contains pyrite which is generating acid rock drainage. To remediate the problem, the drainage water has been collected for a long time, and returned to the tailings impoundments using a collection ditch and a pumping station. Since the decommissioning plan includes reducing the angle of the slope of the dam, the ditch at the toe of the dam will be affected. There will be a need to collect and return the water for proper treatment until the cover on the dam, designed as a composite cover, has reached full performance and the acid rock drainage has been washed out.

Groundwater Saturation of a Single Layer Cover

The tailings area provided a complete range of hydrogeological conditions, from completely drained deposits to permanent underwater deposits. Between these extremes, there were extensive areas with a shallow groundwater table, only a fraction of a meter under the surface. The material below the depth of the groundwater table is permanently protected from oxidation, which was confirmed by field sampling results. Considering this, it appeared unreasonable to apply a cover several times more extensive than the material it was intended to protect.

A viable treatment alternative in areas with a high water table is to further raise the water table so that the tailings are completely water saturated. However, one risk with this method is that soluble oxidation products (e.g. iron sulphates, gypsum), present in the oxidised zone, would be flushed from this area when the water table was raised. The results from the leaching tests indicated that the content of soluble, secondarily retained weathering products in areas with a shallow groundwater table was limited, corresponding to a load of less than one year of weathering. Correlation with the measured load of metals at various checkpoints in the area confirmed the conclusion that the metals were leached out more or less in the same rate as they were supplied by the weathering process. No obvious accumulation of weathering products was detected. The interpretation was that the annual fluctuations in groundwater level and the intense snowmelt and autumn rains had flushed out most of the weathering products, leaving a layer of weathered tailings depleted of weathering products. A limited flushing of old weathering product was predicted, which could be trapped in the limed downstream impoundment 4 until the flushing ceased.

Boliden therefore developed a new approach: the groundwater saturation of tailings. The level of the groundwater table is controlled by the interaction between the supply of water from precipitation and lateral ground and surface water flow, the loss of water due to drainage and evapotranspiration, and the hydraulic properties of the soil and tailings. In ground with relatively homogeneous hydraulic properties, with modest variations in surface gradients and elevation, the groundwater table follows the surface at a more or less constant depth. If a till cover is applied on a tailings deposit, with similar hydraulic properties for the two material types, the groundwater table will rise due to capillary forces. By designing a cover which raises the groundwater level above the unsaturated zone, the tailings will be permanently water saturated.

The benefit of the method is, apart from the reduced thickness of the cover, the lack of need for compaction of the cover and the drastically reduced quality requirements on the cover material.

Illustration: Single-layer soil cover with high phreatic surface at impoundment 2, Kristineberg.

Low Permeability Cover

The hydrogeological investigation showed that neither flooding nor groundwater saturation could be accomplished on impoundment 1B and on approximately half the area of impoundment 1. This implied that a more complex and expensive solution had to be used. Hydrogeological modelling of various composite covers indicated that permanent water saturation could be reached in the cover using a 0.3 m thick sealing layer with a maximum hydraulic conductivity of $5 \cdot 10^{-9}$m/s and a protective layer of 1 m unspecified till. By applying such a cover, an artificial groundwater surface would be created in the sealing layer above the tailings, thereby minimising the oxygen diffusion to the tailings.

The purpose of the protective layer is not only to act as a water storage layer and protect the sealing layer from drying out, but also to protect the sealing layer from erosion, frost and root penetration. Finally the protective layer also provides a substrate for the establishment of vegetation.

Mapping showed that there was a deposit of well graded till with high clay content (8%) 4 km from the tailings area. Laboratory investigations of the till concluded that it could be used in the sealing layer of the proposed composite cover. The average measured hydraulic conductivity after compaction was $1 \cdot 10^{-9}$ m/s. A deposit of unspecified till, suitable for the protective layer, was found close to the tailings area. This finding contributed to reducing the costs. In earlier applications, e.g. the Saxberget tailings impoundments in south central Sweden, this kind of composite covers had cost approximately 80 SEK/m^2. At Kristineberg the cost was only about 55 SEK/m^2.

After applying a thin layer of crushed limestone on the surface of the tailings, the sealing layer was emplaced and compacted in two 0.15 m thick layers directly on top of the tailings. Particle sizes greater than 100 mm were excluded. In some areas of impoundment 1, with low mechanical stability, it was necessary to apply a 0.5 m thick layer of waste rock before placing the sealing layer in order stabilise the surface to meet the requirements of compaction.

The composite cover was finalised in 1996 and its performance as an oxygen diffusion barrier is now thoroughly monitored.

6.6 Final Reclamation Design

Impoundment 1 – Soil cover

The design of the soil cover at impoundment 1 was based on different criteria. In one part of impoundment 1, the groundwater table was raised and a protective cover of ordinary till was applied. The water balance was studied by geohydrological modelling (Axelsson et al, 1992) and the implementation included filling in ditches near the impoundment. In another part of the impoundment, were the groundwater table is deeper, at composite till cover consisting of a 0.3 m sealing layer of compacted till and a 1.5 m protective layer of ordinary till was constructed. The dimension of the sealing layer and the protective cover were based on the water retention capacity and the expected frost penetration.

Physical properties of the till

The till used as a sealing material can be characterized as a fine-grained and well-graded, clayey till. The clay content varies between 5 and 12 % (see Figure 6-3) and the grain density was determined as 2710 kg/m^3.

Two modified Proctor compaction tests show a maximum dry density of 2190 kg/m^3 and 2220 kg/m^3 obtained at water contents of 6.3 % and 6.0 % respectively. The hydraulic conductivity obtained for samples compacted to maximum density according to modified Proctor tests varied between 4×10^{-10} m/s and 8×10^{-10} m/s while the hydraulic conductivity for samples compacted to 95% - 97 % of the maximum Proctor density varied between 2×10^{-8} m/s and 1×10^{-7} m/s. As the design criteria for the sealing layer was chosen to 5×10^{-9} m/s expressed in terms of hydraulic conductivity, it is obvious that the compaction result was essential to obtain a low enough hydraulic conductivity during construction.

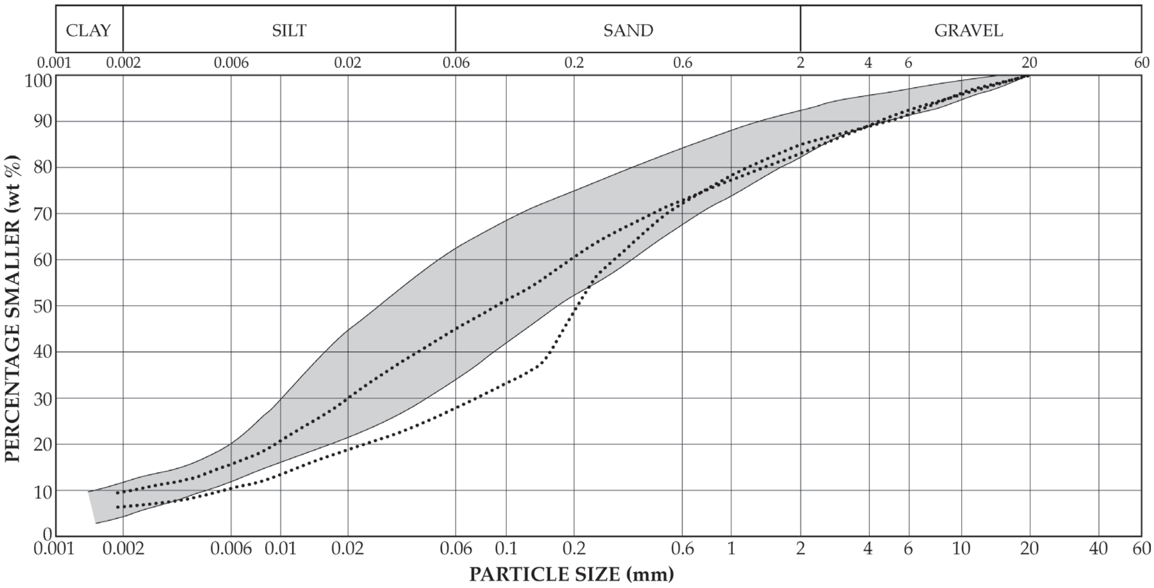


Figure 6-3. Grain size distribution of the clayey till used as sealing layer. The shaded area represents grain size intervals for earlier investigations (Mattson, 1992) while the dotted lines represent samples collected from the constructed layer during MiMi field investigations.

Dimensioning of cover – water retention in sealing layer

Based on hydraulic conductivity data for the sealing layer, water retention characteristics estimated from grain size distribution data, and local climatic data, model calculations were performed to study the variation in water saturation in the sealing layer over time. From the water saturation estimates the oxygen intrusion through the sealing layer was calculated using the TRUST code package (Collin et al., 1990; Collin and Rasmuson, 1990). The results showed that for a hydraulic conductivity of $1 \cdot 10^{-9}$ m/s in a 0.3 m sealing layer, the oxygen intrusion would be about 0.06 mol/m^2/year (Lindgren and Pers, 1995). Water retention characteristics measured within the MiMi programme are shown in Figure 6-4.

Illustration: A sample of compacted till from the sealing layer at impoundment 1, Kristineberg.

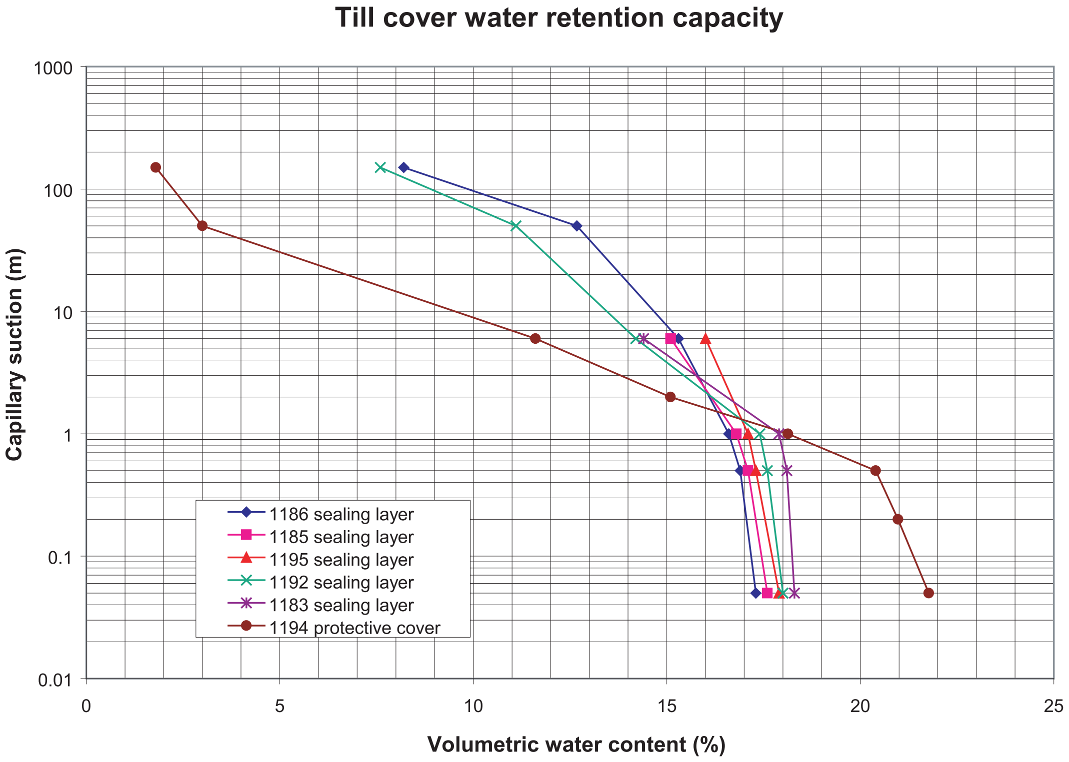


Figure 6-4 Water retention characteristics of the till cover on impoundment 1 in Kristineberg.

Dimensioning of cover – protection of sealing layer

With respect to the efficiency in the long time perspective, it is important that the properties of the sealing layer do not change with time. The short-term efficiency of a dry cover can decrease in the long term as a consequence of different destructive processes that may cause cracks or other discontinuities in barrier layers. Such processes are erosion, frost action, drying, differential settlements, root penetration, digging animals and manmade intrusion.

Investigations show that the sealing layer should be protected primarily against drying and frost action, while the compaction that is applied during construction should be appropriate to protect from root intrusion in the sealing layer as long as no other processes (like e.g. frost action) act to decrease the rate of compaction.

The maximum frost depth was investigated as a part of the remediation plan for the Kristineberg mine by Boliden (1995a). The results were accounted for when designing the protective cover.

Various aspects of processes such as freeze and thaw, root penetration and long-term stability are further elaborated, including calculated examples, in section 7.8.

Illustration: Digging exercise in the protective till cover at impoundment 1, Kristineberg.

Mineralogy of the till

Rock fragments dominate the till. Major minerals are quartz, plagioclase and microcline-perthite. Biotite and hornblende are rather common. The biotite is often altered to chlorite, and the feldspars are often sericitized. Other clay minerals as alteration products of feldspars have been observed, but not identified. Primary chlorite also occurs. Trace amounts of pyroxenes, tremolite-actinolite, olivine, serpentine, epidote, zircon, apatite, calcite, titanite, garnet, iddingsite and tourmaline occur. The content of opaque minerals is generally 1-2%, dominated by magnetite and ilmenite. Small amounts of sulphides, dominated by pyrite and pyrrhotite occur, mainly as inclusions in silicates. Free grains are strongly altered to Fe-oxyhydroxides. Hematite, rutile and a few grains of chalcopyrite have been observed.

Chemical composition of the till

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, Si, Na, K, Ca, Sr, Ba, Zr and Ti, and has a lower content of heavy metals than the underlying tailings. As would be expected from the mineralogical composition with a very low content of sulphide minerals, the heavy metal content is low.

Since quartz and feldspars are the most common minerals in the till, the content of Si, Al, Na and K is rather high, whereas the content of elements such as Fe, Mg, Mn and Ti, mainly occurring in minerals such as amphiboles, pyroxenes, biotite and chlorite, is rather low. This is a common composition of till in Sweden, although the Kristineberg till may have a somewhat higher content of quartz (and thus of Si) than average till in northern Sweden (e.g. Land *et al.*, 1999).

Impoundment 4 – Water cover

Water balance and dimensioning of water depth

A study of the conditions at Kristineberg performed prior to the decommissioning of the site suggested that the hydro meteorological conditions were suitable for flooding of impoundment 4 (Axelsson et al., 1991). The water balance was modelled for normal conditions (precipitation: 669 mm/yr) and dry conditions defined as a reduced annual precipitation with a probability of 0.1%, i.e., an annual precipitation likely to occur once every 1000 years (precipitation: 364 mm/yr).

To maintain the water balance in impoundment 4 during normal conditions requires that runoff from the catchment of the impoundment contributes to the water supply. Under these conditions, an annual water surplus of 242 mm would be achieved (Axelsson et al., 1991). In contrast, during one year with dry conditions, modelling indicated a water deficit of 259 mm/yr.

The tailings impoundments at Kristineberg are located in a valley, with water from impoundments 1–3 draining into impoundment 4. Therefore, modelling of the water balance of impoundment 4 was also performed taking into account the inflow of the surplus water from impoundments 1–3. To prevent drying out of the impoundment during a period of 3 consecutive years representing a sequence of normal – dry – normal conditions, a water level of 441 mm would be required. Modelling showed that this water level can be maintained with the surplus water from impoundments 1–3 (Axelsson et al., 1991). The present-day water balance of impoundment 4 is presented in Table 6-2.

Table 6-2 Water balance for impoundment 4, for the period 1 June 1999 – 31 May 2000.

Parameter	Water flow (10^3 m^3/year)
Inputs	
Surface water inflow (Q_{in})	1400 ± 370
Groundwater inflow (Q_{gw})	3400 ± 1000[a]
Precipitation (Q_p)	520 ± 52
Total inputs	5300 ± 1500
Outputs	
Surface water outflow (Q_{out})	4900 ± 520
Leakage through dyke (Q_d)	160
Evaporation (Q_e)	300 ± 74
Total outputs	5300 ± 590

[a] Groundwater inflow is estimated as Sum(Q_{out}+Q_d+Q_e) - Sum(Q_{in}+Q_p)

The surface water outflow from impoundment 4 is continuously monitored at a constructed pipe outflow. The mean annual surface water outflow (4.9 Mm^3/year, Table 6-2) shows a fairly strong seasonal variation, with discharges varying from 90 l/s (February – March 2000) to 490 l/s (spring flood in late April 2000).

The water depth in impoundment 4 is also dimensioned to minimize the risk for resuspension of the mining waste deposited in the impoundment. For a dimensioning wind speed of 17 m/s it was calculated that a water depth of 1.5 m would be sufficient to prevent resuspension of the fine-grained calcite – gypsum sludge that covers the tailings in impoundment 4 (Bjørdal, 1994).

Illustration: Water covered tailings and spillway at impoundment 4, Kristineberg.

Liming and surface water management

The water-covered impoundment 4 is an integrated part of the system approach applied at the Kristineberg site (Öhlander et al., 2003), and surface drainage water from impoundments 1, 1B, 2 and 3 with high dissolved metal concentrations (Table 6-3) are diverted into this impoundment. Liming is performed continuously at the inlet of impoundment 4, with an average addition of 610 tonnes of CaO per year resulting in an average pH of 10.18±1.71 for the period 990507–000614 (Table 6-3). This liming will continue until acidity and metal concentrations in the leachate from impoundments 1–3 have decreased to acceptable levels. Due to the liming, precipitation, coprecipitation and adsorption reactions are initiated in impoundment 4, which strongly reduces the dissolved metal concentrations at the outlet from the impoundment (Table 6-3). In addition, liming has also resulted in the formation of a 5–45 cm thick layer of calcite–gypsum–iron oxyhydroxide sludge that covers the tailings in impoundment 4 (Widerlund et al., 2001). It is estimated that approximately 12 000 tonnes of this sludge had precipitated in the impoundment in 1999, with the following inventories of metals: Cd = 710 kg; Cu = 34 000 kg and Zn = 293 000 kg. Sludges of this type may subsequently be resolubilised if pH is reduced, and the geochemical behaviour and stability of this sludge may have important implications for the effluent metal levels from the impoundment. Sequential extraction of the Kristineberg sludge shows that more than 97% of the total content of Cd, Cu and Zn in the sludge is bound in operationally defined carbonate and oxide fractions (Widerlund et al., 2004). Thus, in a long-term perspective, metals bound in these fractions may potentially be remobilised by dissolution of calcite and reductive dissolution of iron oxyhydroxides if the sludge is subject to a soil environment with reduced dissolved Ca concentrations, pH and redox.

Table 6-3. Average pH, redox potential (E_h), conductivity and concentrations in the inlet and outlet of impoundment 2, and in the outlet of impoundment 4. All available data are used (990507–000614). The number of measurements is given in parentheses.

Parameter	Impoundment 2 inlet Average±std.dev.	Impoundment 2 outlet Average±std.dev.	Impoundment 4 outlet Average±std.dev.
pH	4.56±1.26 (20)	3.25±0.35 (21)	10.18±1.71 (28)
E_h (mV)	273±127 (20)	417±51 (21)	46.5±40.0 (28)
Cond. (mS/cm)	3.10±0.91 (20)	3.27±0.33 (21)	1.88±0.37 (28)
[mg/l]			
Ca	680±315 (17)	547±94 (21)	400±79 (26)
Fe	63.0±87.6 (17)	80.1±20.4 (21)	1.48±5.95 (24)
K	22.9±13.4 (17)	18.4±6.5 (21)	10.4±3.3 (26)
Mg	65.5±43.4 (17)	89.4±23.6 (21)	5.60±9.02 (26)
Na	24.7±13.0 (17)	20.7±5.4 (21)	15.6±13.6 (26)
S	686±235 (17)	703±83 (21)	332±88 (26)
Si	3.65±4.03 (17)	7.63±1.61 (21)	0.786±0.413 (26)
Cl^-	29.9±57.0 (17)	28.3±50.9 (21)	18.3±49.4 (26)
$NH4^+$	3.71±2.02 (17)	3.25±2.04 (21)	0.604±0.645 (24)
$NO3^-$	3.86±2.09 (16)	4.18±3.65 (21)	1.38±1.11 (26)
SO_4^{2-}	1850±680 (17)	2310±1180 (21)	937±331 (26)
TOC	7.13±7.45 (16)	4.04±1.00 (15)	3.25±1.25 (20)
[μg/l]			
Al	5430±6390 (17)	24 800±7600 (21)	132±200 (26)
As	4.51±5.90 (16)	2.22±2.64 (18)	0.235±0.071 (22)
Ba	20.1±6.2 (17)	19.5±5.3 (21)	11.6±2.1 (26)
Cd	9.58±12.1 (17)	64.3±25.5 (21)	0.55±1.33 (25)
Co	31.2±33.1 (17)	115±24 (21)	1.50±4.69 (26)
Cr	1.70±2.55 (15)	6.78±2.87 (21)	0.383±0.229 (25)
Cu	422±860 (17)	2950±890 (21)	8.1±23.0 (26)
Hg	0.00711±0.00694 (16)	0.00366±0.00077 (16)	0.0027 (1)
Mn	1160±980 (17)	2520±520 (21)	68±205 (25)
Mo	0.376±0.633 (9)	1.45±3.58 (15)	5.31±2.15 (26)
Ni	14.6±15.0 (17)	51.5±13.6 (21)	1.14±2.61
Pb	7.3±10.5 (15)	42.8±20.2 (21)	0.0999±0.0748 (7)
Sr	713±350 (17)	606±126 (21)	410±101 (26)
Zn	3210±3680 (17)	31 200±6700 (21)	220±662 (26)

Dam wall reinforcement

The main component in the flooding system for impoundment 4 is obviously the downstream dam. The dam at closure consisted of several individual lifts using various techniques. The redesign of the dam was done using recommended standards for long-term stable dams. According to available guidelines, the outer slope should be 1:3, which called for additional fill material.

The support fill was identified as a problem of its own, as the material contained pyrite which caused oxidation and acid drainage. For many years, this drainage from the downstream dyke had been a matter of concern. Several investigations had addressed the problem but the cause was finally determined to be both simple and obvious – the dyke's content of pyrite, generating acid rock drainage (ARD).

In reality, the dam wall constituted an ARD-generating waste rock dump, and the reclamation principle was covering the dam with a composite cover, at the same time reducing the slope to the required angle. Also, flooding of the pond called for a specific water depth, provided that no particular erosion protection bottom layers were placed in shallow areas. Significant areas had water depth less than 1 m, which meant either the dam wall needed to be raised or the shallow areas needed to be stabilised using e.g. coarse material.

To prepare for both alternatives, the dam crest was widened inwards and an erosion protection layer was placed along the inner slope. The outer slope was flattened out and covered with till. In the upper section, a composite cover consisting of a 0.3 m low permeable material + 1.5 m protective cover. In the lower sections, the cover thickness was extensive enough to enable the use of a single layer cover. The surface of the cover was sown with grass seeds.

Illustration: Construction work – reinforcement of the dam at impoundment 4 in Kristineberg.

To address the ARD-problem, the water had been collected for several years, and returned to the tailings ponds using a collection ditch and a pumping station. Since the decommissioning plan included reduction of the angle of the outer slope of the dyke, the ditch at the toe of the dyke was affected. To enable collection and returning the water to the treatment system until the cover on the dyke had reached full performance and the acid rock drainage has been washed out, a covered drainage ditch was constructed.

The ditch was filled with coarse waste rock in order to create a hydraulic conductor underneath the expanded toe of the dyke. The drainage is collected using a concrete well through the cover and submersible, acid-proof pumps. When the drainage-water quality is considered acceptable, the pumps will be removed and the well filled with till. Since the dam wall was covered, a significant improvement of the water quality has been recorded.

Quality assurance during construction

For the supervision of the different decommissioning activities, an external controller was designated by the County Council. The controller supervised the daily activities including level measurements before and after decommissioning, investigation and approval of cover material quality, cover material thickness measurements including test excavation, Proctor laboratory tests and field compaction tests with Troxler equipment.

Area Recovery

After covering impoundments 1 and 1B with till, the surface was hydroseeded with grass. In earlier projects within Boliden, various methods for re-vegetation have been tested. At an early stage it was noticed that in many areas where pine has been planted directly onto the till surface, the plants have shown poor development. The conclusion was that the natural succession needs to be followed, i.e. with grass or other pioneering species, followed by herbs, bushes and trees. It was not possible to establish and support tree growth without having the undergrowth in place. The ecosystem needed all components to become permanent. This is in line with experience from revegetation of other Swedish mine sites reported by Ledin (1999).

On impoundments 1B and 1, there is a grass cover, and trees are starting to grow. Protected by the grass, they will have a good opportunity to develop during the coming years.

The redirection of the river Vormbäcken is envisaged to speed up the biological recovery of the area and also to provide additional safety margins as sediments will build up, and form an organic diffusion barrier on top of the tailings and the sludge in impoundment 4.

Post-reclamation MiMi analysis of the system approach used at Kristineberg

The efficiency of the system approach used at Kristineberg was evaluated by Öhlander et al. (2003). Progressive changes of water quality from groundwater in the upstream till-covered impoundments via surface streams within the impoundment system to the water in the flooded downstream impoundment and its outlet were described. The results show that the system approach used in the design of the remediation programme works as planned. The results show that the groundwater characteristics vary considerably in impoundment 1, even under the same type of cover, but pH is generally increasing and redox is generally decreasing with time.This indicates that the sulphide oxidation rate has decreased in the till-covered impoundments. As predicted, there is a flushing of old weathering products which will continue for at least five years before equilibrium is reached. The groundwater in the till-covered impoundments has high concentrations of Fe, S, Mg and Zn, but the concentrations of metals such as Cu, Cd and Pb are much lower than before the till cover was applied. The limed impoundment 4 is an efficient metal trap, with concentrations as high as 2.76% Zn and 0.28% Cu in the calcite-gypsum sludge developed on the tailings. The outlet from the flooded impoundment, and thus from the whole mining area, releases small amounts of metals to the recipient in comparison to the amounts that are in movement within the mining area. The results from Kristineberg show that in planning remediation of complex mining areas, a system approach is preferred in which different methods are used on different parts of the area along the flow path of the drainage water, whereas flooding of the downstream impoundment is the key to the performance of the entire system. Liming the water flowing into impoundment 4 must continue until the water entering the impoundment (i.e. drainage water from impoundments 1, 1B, 2 and 3) has a high enough pH and low enough metal concentrations so as to obtain an acceptable water quality in the flooded impoundment.

6.7 Summary of remediation activities at specific mine sites

Soil and water covers are generally used in Sweden for the reclamation of mine tailings impoundments. A summary of some of the remediation activities at Swedish mine sites is presented in Table 6-4.

Table 6-4 Selected mine sites in Sweden along with cover type. Data from the Swedish Environmental Protection Agency (1998, 2002) and Qvarfort (1989).

Mine	Area deposit (ha)	Tailings cover
Kristineberg impoundment 1	12	Low permeability soil cover / water saturated single layer soil cover
Kristineberg impoundment 2	18	Water saturated single layer soil cover
Kristineberg impoundment 3	56	Water cover
Kristineberg impoundment 4	74	Water cover
Adak	47	Sealing layer 0.5 m packed till, protective cover 1.5 m till
Aitik	1000 +2.6 (tailings + rock dump)	Tailings: vegetated Rock dump: Sealing layer 2 x 0.5 m till, protective cover 0.3 m till
Bersbo	19	Rock dump: Sealing layer 0.3 m clay, protective cover 2 m till Sealing layer: 0.3 m Cefyll, protective cover 2 m till
Enåsen	31	Sealing layer 0.8 m packed till, protective cover 0.3 m till
Galgberget	18.8	Sealing layer 0.5 m fly ash and sludge, protective cover 0.5 m bark or till
Ranstad	25	Sealing layer 0.2 m, drainage layer (limestone) 0.2 m, protective cover 1.2 m, soil for vegetation
Saxberget	54	Sealing layer 0.3 m clayey till, protective cover 1.5m till
Stekenjokk	10	Water cover, >2.2 m deep
Stollberg	20	Soil cover, 0.3 m till

7 Near field processes

In this Chapter, different processes of concern for understanding the function of the near-field are presented. However, several of the processes are of general character and are, therefore, applicable also to the Far-field descriptions.

7.1 Process overview

General

The different processes leading to the emission of acidic leachates are complex and span over numerous scientific disciplines. The initial oxidation of sulphide minerals requires oxygen and water. Remediation of mining waste is, therefore, usually directed towards limiting oxygen transport to the waste. Important remediation methods are to cover the waste with water, and to cover the waste with material with low hydraulic conductivity (Feasby et al., 1997). In both cases, the supply of oxygen to the waste is limited, and in the case of soil covers with low hydraulic conductivity, the supply of water may also decrease.

The most important processes in the near-nield of a mine waste deposit are the intrusion of water and oxygen and the chemical reactions occurring within it. A schematic picture for a typical waste deposit with soil cover is shown in Figure 7-1.

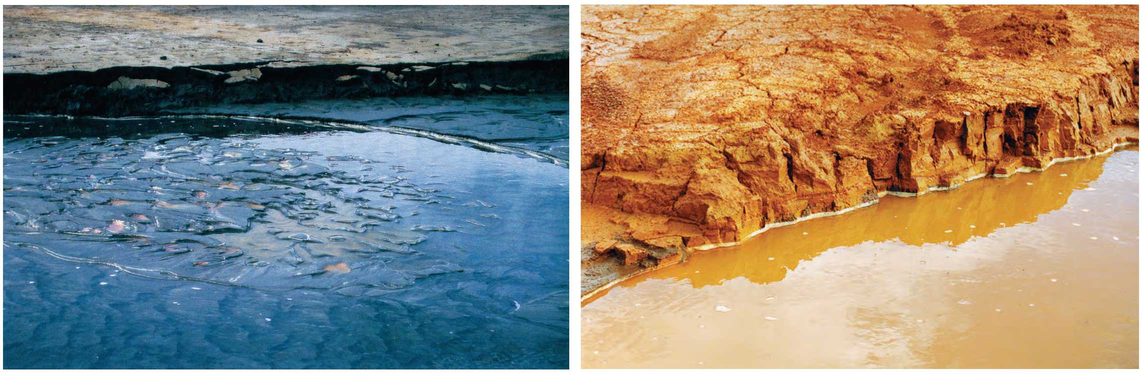


Illustration: Unoxidised tailings to the left and oxidised tailings to the right.

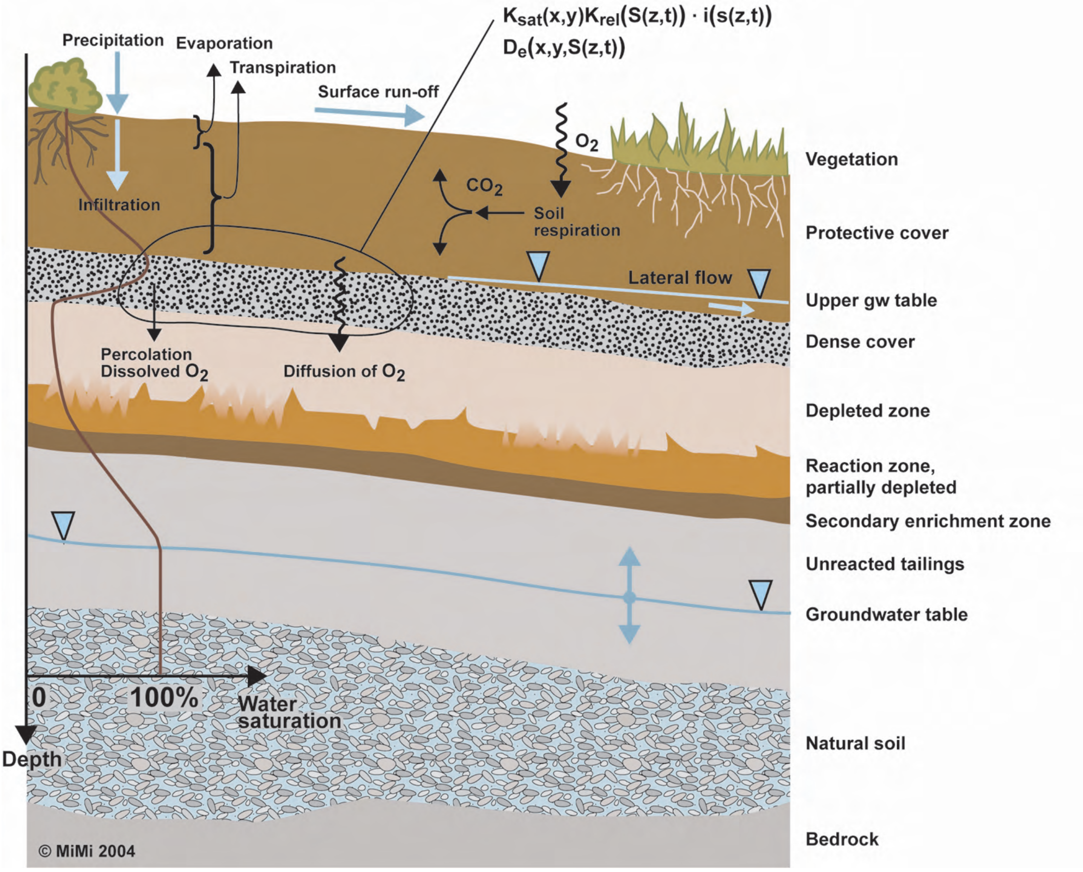


Figure 7-1 Schematic picture of a waste deposit where a soil cover has been applied on previously weathered tailings. Underneath the tailings, a natural soil layer covers the bedrock.

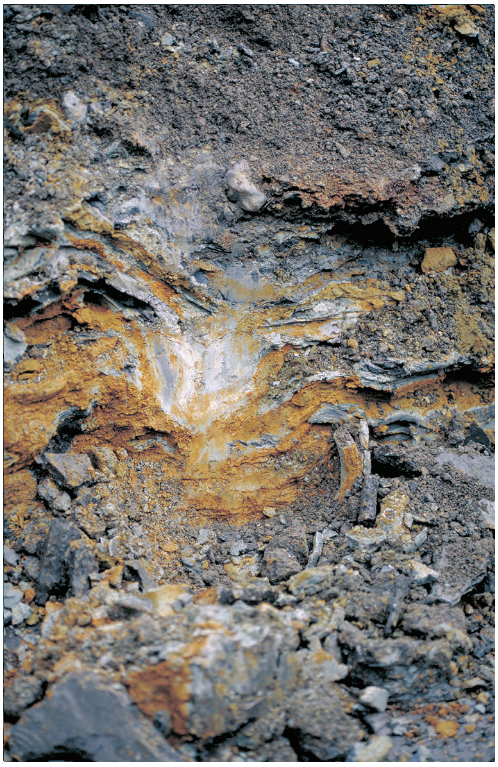


Illustration:
Zonations revealed during excavation.

7.2 Oxygen and water transport

Basic principles

The intrusion of water into a waste deposit is due mainly to precipitation. However, only a fraction of the precipitation finally reaches the tailings in the waste deposit. A part of the precipitation is evaporated directly from the protective cover and another part can flow along the top the protective cover (surface run-off). The remaining precipitation after evaporation and run-off constitutes the infiltration as shown in Figure 7-1. Moreover, a part of this water may be lost by transpiration or may flow on the sealing layer, if a perched groundwater table exists. Finally, the rest corresponds to the water that will percolate through the sealing layer into the tailings. In general is expected that the permeability of the protective cover will be large and not will limit water flow through it. Since the hydraulic conductivity of the sealing layer is small, it will take long time for the water to flow through this barrier. As a result, water may be accumulated inside the protective cover, on top of the sealing layer, and a lateral flow can take place.

The water flow in a water-saturated soil is given by the hydraulic conductivity times the hydraulic gradient. The hydraulic conductivity is a material parameter that can be measured for a specific material. The hydraulic gradient is determined by the overall hydraulic situation and is usually determined by direct measurements of groundwater levels or by calculations.

Since the hydraulic conductivity of the bedrock is expected to be lower than in the overlying natural soil and the tailings, it is anticipated that a predominantly horizontal water flow takes place through the natural soil and the tailings. The water flow is determined by the hydraulic conductivity of these materials and the hydraulic gradient.

In partially water-saturated soils, the water flow may be significantly reduced since the largest pores are occupied by gas. As a result, the hydraulic conductivity needs to be adjusted to accommodate for this phenomenon. Different methods for corrections have been developed to obtain an effective hydraulic conductivity, see e.g. van Genuchten (1980), commonly based on data for particle size distributions for the soil material. In a similar manner, the diffusion rate of oxygen through a partially water-saturated soil needs to be adjusted for the presence of both water and gas in the pores.

The transport rate of oxygen is fast in air in comparison with the transport through water. In flowing water the predominant transport process is oxygen dissolved in the water. Oxygen transport in air can be very fast if the air is flowing, but even for stagnant air the molecular diffusion rate of oxygen is fast. In stagnant water, oxygen may also diffuse, but owing to the low oxygen solubility in the water and the slow diffusion rate of oxygen dissolved in water, the overall transport rate of oxygen is very low. The transport rate in stagnant water is on the order of 1/10 000 of the rate in stagnant air.

Oxygen may be transport into the waste deposit through either or a combination of these processes: through advective or conductive flow of air, dissolved in the percolating water and by diffusion through the pores of the covers. The advective or conductive flow of air must be avoided; this may be a problem in coarse materials such as waste rock, but is less common for fine grained tailings and will not be addressed here. For the second case, the amount of oxygen transported is simply given by the water flow rate times the dissolved oxygen concentration. Since the solubility of the oxygen in water is small, only about 10 mg/l at the temperatures found in the deposit, the maximum amount of oxygen possible to be transported by the percolating water is quite small. Thus, diffusion is usually the dominating mechanism for the transport of oxygen into tailings.

However, to restrict the intrusion of atmospheric oxygen into deposited mining waste, different types of covers are commonly applied, such as soil covers or water covers (see Chapter 6). Both soil and water covers are passive cover techniques, which restrict the oxygen intrusion by decreasing the diffusion rates.

Oxygen and water transport in soil covers

For the multilayer soil cover, two sub-layers with different properties and functions may be distinguished: the protective cover and the sealing layer (Chapter 6). The protective cover is constituted mainly by unclassified till with a relatively coarse particle size and small fraction of fines. Therefore, it is expected that the hydraulic conductivity of the protective cover is high and its water retention low. The most important function of this cover is to prevent damage to the sealing layer.

The sealing layer has as function to reduce the intrusion of oxygen into the waste deposit. Since the diffusion of oxygen is strongly reduced if the transport occurs through a porous barrier that is totally (or almost) water-saturated, water retention of the sealing layer would preferably be high. This is achieved by using a well graded material with a certain content of fines; e.g., clayey till material. The water saturation is low in the protective cover and high at the sealing layer. Another function of the sealing layer is to reduce the infiltration of water to the tailings. Therefore, the hydraulic conductivity of the sealing layer would be low (very low). The expected water saturation profile through the protective cover and sealing layer is shown schematically in Figure 7-1.

Regarding the oxygen transport, the protective cover is not considered as an oxygen barrier. However, some oxygen may be consumed there by reaction with organic material. The main function of the sealing layer is to be a barrier to the oxygen transport. If the water saturation is very high, the transport by diffusion will be very small. In summary, the most important properties of the sealing layer are a low hydraulic conductivity and large water retention.

In a soil cover, the oxygen diffusion takes place in the pores of the soil material. If the soil has significant water content the oxygen must diffuse through water filled pores, a process that is very slow. If the soil is dry, the pores are filled with air and the diffusion rate of oxygen is high, restricted only by the pore structure of the soil. Hence, by maintaining a high degree of water saturation in parts of a soil cover the oxygen transport rate can be controlled.

In the other situation, diffusion takes place in a partially water saturated medium. In general, the oxygen transport occurs mainly through the gas phase. However, if the water saturation of the soil is high, the effective diffusion through it will be strongly diminished. This is due to that the small pores and a part of the large pores are partially filled with water and the gas-filled spaces are reduced. For example, a porous barrier with a saturation of 90 % has an effective diffusion coefficient that is about 3 orders of magnitude less than the diffusion of oxygen in air. Different investigations have demonstrated that the relationship between the diffusion rate and the degree of water-saturation is strong and highly non-linear. Figure 7-2 shows the ratio between the effective diffusion coefficient for porous material with a given water saturation and the diffusion in air as proposed by Collin (1987).

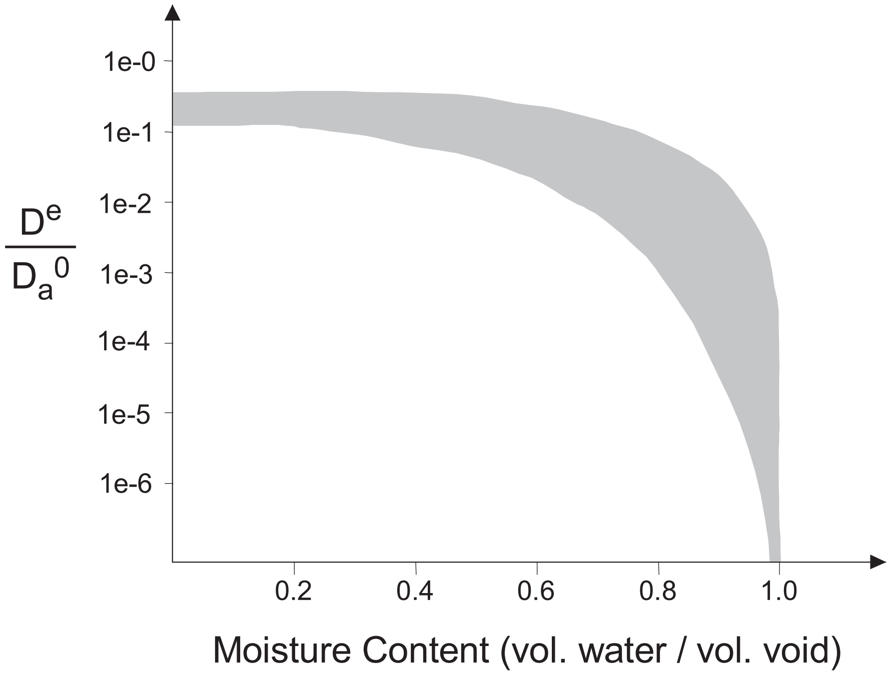


Figure 7-2 Ratio between the effective diffusion coefficient in a porous material partially water-saturated and the diffusion in air.

The capacity of the barrier to retain water can be described by the water retention characteristics of the barrier soil and is related to the grain size distribution and saturated hydraulic conductivity. In general, fine-grained soils with low hydraulic conductivity show favourable water retention capacities. The grain size distribution for the till used as sealing layer in Kristineberg is shown in Figure 7-3.

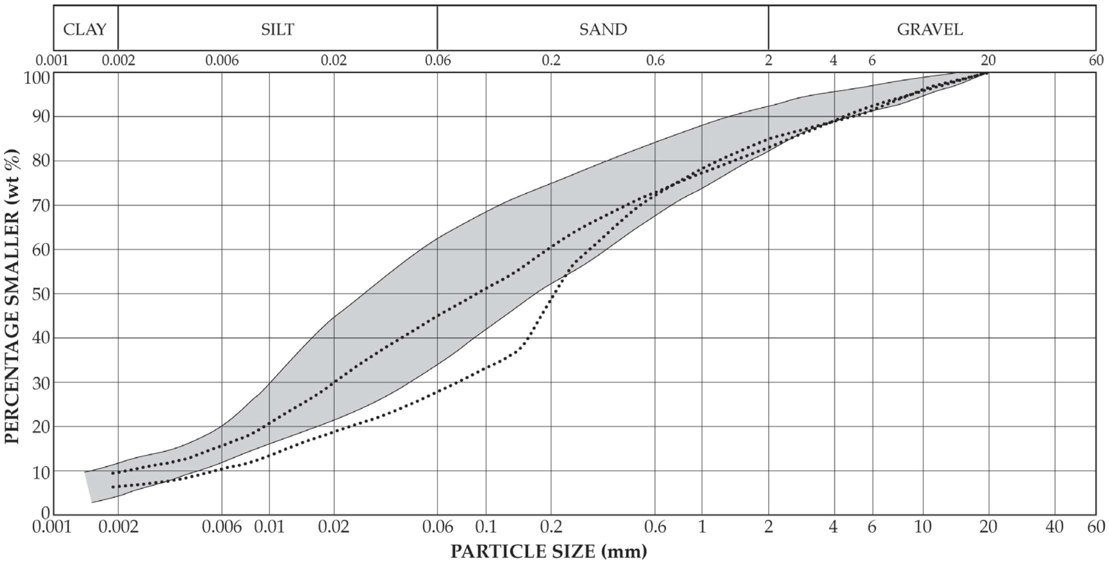


Figure 7-3 Grain size distributions for the sealing layer used at impoundment 1 in Kristineberg. The shaded interval represents determinations prior to reclamation (Mattson, 1992), and the broken lines show results obtained with samples taken from the constructed barrier (Öhlander et al, 2004).

Oxygen and water transport in water covers

The transport of oxygen from a water cover into water-covered tailings is controlled by the rate of the diffusional supply of oxygen, and the rate of net oxygen consumption per unit volume of tailings. In the water column, various mixing processes, which can be referred to as turbulent diffusion, are important transport process for oxygen, while adjacent to the tailings – water interface, viscous forces cause a thin (≤ 1mm thick) film of water (diffusive boundary layer, DBL) to develop close to the tailings surface (cf. Gundersen and Jørgensen, 1990). Within the DBL, the transport of oxygen occurs by molecular diffusion, whereas turbulent diffusion is insignificant. The DBL thus constitutes a diffusional barrier, which limits the oxygen supply to the tailings. Oxygen microelectrodes permitting a vertical measuring resolution of 25–50 µm are an ideal tool for detailed studies of the oxygen supply across the tailings – water interface (e.g., Revsbech and Jørgensen, 1986; Holmström and Öhlander, 1999; Elberling and Damgaard, 2001; Vigneault et al., 2001).

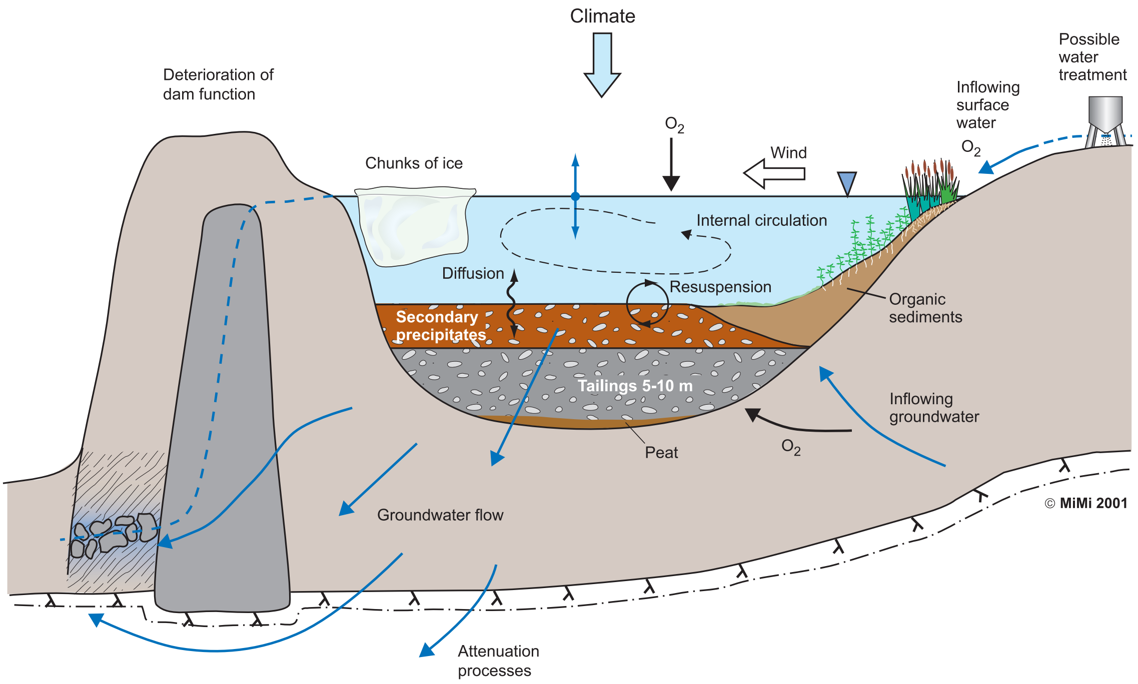


Figure 7-4 Schematic illustration of the function of water covered tailings impoundments.

Internal circulation of the water column (Figure 7-4) caused by wind mixing and/or thermal convection will result in oxygen transport to the tailings – water interface, maintaining the diffusive oxygen transport across the DBL. A thermal or chemical stratification of the water column of a flooded impoundment would tend to reduce the supply of atmospheric oxygen to the tailings surface. The type of stratification and its stability will depend on interactions between climate, water depth and water chemistry, and would be similar to the types of stratifications encountered in natural lakes (Wetzel, 2001). Typical temperate ponds and lakes undergo two periods of mixing, one in the spring and one in the autumn, with stable normal and inverse thermal stratifications prevailing during summer and winter, respectively. However, the water depth in most flooded impoundments is fairly shallow, and a more or less continous wind mixing of the entire water column can probably be expected as long as an impoundment is ice-free. In cold-climate regions, low temperatures will increase the solubility of oxygen in water. However, if an ice cover preventing gas exchange between the atmosphere and the water column is present in an impoundment, this effect may reduce the oxygen exposure during certain periods of the year.

The water in flooded impoundments can be expected to interact with the ground water. Similar to natural lakes, flooded impoundments can be classified as discharge lakes, recharge lakes or flow-through lakes depending on their mode of interaction with the ground water (Figure 7-4). A discharge lake receives ground-water discharge throughout its entire bed, while a recharge lake loses water as seepage to the ground water. Most lakes are flow-through types, receiving inflow over part of their bed, and losing water elsewhere. In natural lakes, most of the ground-water inflow typically occurs near the shore, and a similar flow pattern can probably be expected in flooded tailings impoundments. Inflow of ground-water with significant concentrations of dissolved oxygen would result in an advective transport of oxygen into the tailings, with a potential risk of sulphide oxidation and generation of acid mine drainage. In flooded impoundments containing saline leachate, seepage of this saline water into underlying ground water may be enhanced by the density difference between leachate and ground water (Narayan and Simmons, 1998).

Although most dam constructions surrounding flooded impoundments contain a dam core with low hydraulic conductivity, percolation of water through dams is a common phenomenon (Figure 7-4). In cases where sulphidic mining waste is used as construction material in dams, there is thus a potential risk for sulphide oxidation if advective transport of oxygen into this material should occur.

7.3 Main biogeochemical processes in the deposit

The quality of soil water and groundwater in tailings is largely determined by water-rock-atmosphere interactions. The chemical composition of the aqueous phase is governed not only by the mineral composition of the tailings but also of the presence of dissolved gases which may interfere with the mineral surfaces, mainly dissolved oxygen and carbon dioxide. Also many microorganisms are capable of affecting geochemical processes. Below, an overview is given of biogeochemical processes significant primarily for the source term and near field. Several of these processes are equally relevant for the far field perspective.

After a short discussion of the parent mineralogical composition of tailings the oxidation of sulphide minerals will be treated. The effect of microbial activities on the sulphide oxidation reactions is considered. As for other living organisms, the evolution of bacterial populations is dependent on the conditions provided by the environment in which the organisms dwell. Therefore, this chapter includes a section on microbial ecology.

Besides loss of the parent solid matter, the major effects of sulphide oxidation are generation of acidity and release of heavy metal ions and sulphate. The acidity will be partly, in some cases even completely, neutralised by weathering of non-sulphidic minerals. pH-buffering reactions are overviewed with focus on silicate and carbonate weathering.

Metals released may escape the tailings via groundwater discharge, but may also be attenuated by various processes in which the metal ions are re-associated with the solid matter. This includes precipitation of secondary solid minerals under both anaerobic and aerobic conditions and also adsorption of metals to mineral surfaces.

The chapter is concluded with a discussion of aspects that are specific for soil covered tailings and flooded tailings.

Source term – mineral composition of the tailings

The mineralogical composition of the tailings has a direct impact on the quality of water discharging from tailings impoundments. Tailings from sulphide ores will always contain a certain concentration of sulphide minerals, along with gangue minerals including silicates, oxides, and carbonates. The chemical and/or microbial reactions between these minerals and water percolating into the tailings will leave an imprint on the water composition. These various reactions depend on the tailings composition and the chemical properties of the water (e.g. oxygen content, pH, dissolved solutes), and will be discussed in subsequent sections. It should be noted that the solid matrix of mine tailings is almost completely composed of mineral matter. The organic content of tailings is generally very low (< 0.1 wt%; Herbert, unpublished data), and can probably be attributed to bacterial biomass that is always present in the environment (see below).

The main sulphide mineral in most sulphidic tailings is pyrite (FeS_2), but also pyrrhotite ($Fe_{1-x}S$), covellite (CuS), arsenopyrite (AsFeS), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and many other sulphur containing mineral phases are present in varying amounts (Plumlee, 1999). Besides the sulphides, unweathered tailings consists of gangue minerals, consisting mainly of a variety of aluminosilicate and oxide minerals with a substantial variation in reactivity with respect to chemical weathering and more easily weathered carbonates.

Silicates formed by crystallisation from magmas at high temperature (e.g. olivine, pyroxene and calcic plagioclase), are found to be more reactive than minerals crystallised at lower temperatures (e.g. quartz (SiO_2), feldspars, such as K-feldspar ($KAlSi_3O_8$) and plagioclase ($NaAlSi_3O_8$ - $CaAl_2Si_2O_8$), chlorite ($(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$), micas, mainly muscovite ($KAl_2AlSi_3O_{10}(OH)_2$), biotite $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$) and sericite ($KAl_2(AlSi_3)O_{10}(OH)_2$), amphiboles ($(X,Y,Z)_7(Al,Si)_2Si_6O_{22}(OH)_2$) (Plumlee, 1999; see Table 5-4 for compositions).

Oxides of iron, aluminium and manganese, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), gibbsite ($Al(OH)_3$) and pyrolusite (MnO_2) are common gangue minerals. Carbonate minerals, such as calcite ($CaCO_3$), dolomite ($(Mg,Ca)CO_3$) and magnesite ($MgCO_3$), are commonly present in the host rock of sulphide ores and can thus also be found in the tailings.

7.4 Sulphide and iron oxidation

The oxidation of sulphide minerals will occur in the presence of an electron acceptor such as O_2, NO_3^-, Fe^{3+} or Mn^{4+}. In tailings impoundments, the primary oxidant is usually oxygen or ferric iron. While the rate of sulphide oxidation can be rather high in unsaturated mine tailings that are exposed to the atmosphere, this rate greatly decreases when the availability of oxidants is limited, such as after the installation of a soil or water cover. This section will briefly review the various mechanisms for sulphide oxidation in mine tailings, and discuss the relative role of microbial mediation.

In the literature, two parallel mechanisms have been considered for the oxidation of sulphide mineral, with either aqueous oxygen (reaction 7-1) or ferric iron (reaction 7-2) as oxidants (e.g. Lowson, 1982; Evangelou and Zhang, 1995; Nordstrom and Southam, 1997; Herbert, 1999). These reactions are presented in Table 7-1, and exemplified with the oxidation of pyrite.

Among reactions 7-1 and 7-2, reaction 7-1 is the first to occur. When oxygen is readily available, ferrous iron produced in reaction 7-1 may be oxidised to ferric iron, as shown in reaction 7-3. This ferric iron may then directly oxidise sulphide minerals (reaction 7-2). Appelo and Postma (1993) concludes that the energy yield of oxidation to sulphate is larger than the oxidation of ferrous iron, often resulting in leachate water rich in sulphate and ferrous iron.

Illustration: Ferric iron precipitates in a ditch receiving leachate water.

Detailed studies of the reaction mechanisms show that electrons are transferred from sulfur atoms at the pyrite surface to oxygen atoms from water molecules attached to the sulfur atoms to form sulfoxy species (Rimstidt and Vaughn, 2003). Using isotope labelled water and horizontal attenuated total reflectance infrared spectroscopy, Usher et al. (2004) report results supporting a mechanism where water is the primary source of oxygen in the sulphate produced by pyrite oxidation, while the oxygen atoms in the iron oxyhydroxide product are obtained from dissolved molecular oxygen.

When ferrous iron is oxidised, precipitation of ferric hydroxide may also occur, as exemplified by reaction 7-4. The total oxidation reaction, for both pyrite and ferrous iron, is thus indicated by reaction 7-5. As shown by this reaction, the solubility of ferric iron is pH-dependent, such that at low pH (e.g. < 3), ferric hydroxide will not precipitate and sulphide oxidation will proceed according to reaction 7-2. Although the oxidation of pyrite by solid ferric hydroxides (reaction 7-6), is a subject of debate, it is clear that the low solubility of the ferric hydroxide at neutral and alkaline pH will significantly restrict the rate of this reaction.

Table 7-1: Examples of oxidation reactions and the generation of acidity by each reaction (adopted from Plumlee, 1999)

Mineral **Reaction formula**	**Production moles H^+**	**Reaction Number**
Pyrite		
$FeS_2 + 3.5O_2 + H_2O \xrightarrow{R_{py}} Fe^{2+} + 2SO_4^{2-} + 2H^+$	2	7-1
$FeS_2 + 14Fe^{3+} + 8H_2O \xrightarrow{R_{py,Fe}} 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	16	7-2
$Fe^{2+} + 0.25O_2(aq) + H^+ \rightarrow Fe^{3+} + 0.5H_2O$	-1	7-3
$Fe^{2+} + 0.25O_2(aq) + 2.5H_2O \rightarrow Fe(OH)_3(s) + 2H^+$	2	7-4
$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow 2SO_4^{2-} + 4H^+ + Fe(OH)_3(s)$	4	7-5
$FeS_2(s) + 14\ Fe(OH)_3(s) + 26\ H^+ \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 34\ H_2O$	-26	7-6
Pyrrhotite		
$Fe_{0.9}S + 1.9O_2 + 0.1H_2O \rightarrow 0.9Fe^{2+} + SO_4^{2-} + 0.2H^+$	0.2	7-7
$Fe_{0.9}S + 7.8Fe^{3+} + 4H_2O \rightarrow 8.7Fe^{2+} + SO_4^{2-} + 8H^+$	8	7-8
Arsenopyrite		
$FeAsS + 3.25O_2 + 1.5H_2O \xrightarrow{R_{As}} Fe^{2+} + HAsO_4^{2-} + SO_4^{2-} + 2H^+$	2	7-9
Chalcopyrite		
$CuFeS_2 + 4O_2 \xrightarrow{R_{Cu}} Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$	0	7-10
$CuFeS_2 + 16Fe^{3+} + 8H_2O \xrightarrow{R_{Cu,Fe}} Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+$	16	7-11
Sphalerite, galena and millerite		
$ZnS + 2O_2 \xrightarrow{R_{Zn}} Zn^{2+} + SO_4^{2-}$	0	7-12
$PbS + 2O_2 \xrightarrow{R_{Pb}} Pb^{2+} + SO_4^{2-}$	0	7-13
$NiS + 2O_2 \xrightarrow{R_{Ni}} Ni^{2+} + SO_4^{2-}$	0	7-14

In mine tailings deposits, the oxidation of sulphide minerals and ferrous iron occurs in the presence of microorganisms that are capable of acquiring energy from the mediation of these reactions. Of particular importance in mine waste deposits are iron- and sulphide-oxidizing bacteria such as *Acidithiobacillus ferrooxidans*. The oxidation of sulphide minerals and ferrous iron can thus proceed in presence or absence of bacteria. For iron oxidation, the abiotic reaction (7-3) is rapid at $pH>5$, but is very slow at $pH<3$. Oxidant availability or slow chemical kinetics may limit the rates of this abiotic reaction. For the same reaction (7-3), biological mediation by certain microbes may drastically enhance the rate of oxidation. Generally, O_2 is the dominant electron acceptor for the chemical and biological metal sulphide oxidation in the environment. At low pH below 4, the biological metal sulphide oxidation by acidophilic, chemolithoautotrophic Fe(II)- and/or sulphur compounds oxidizing bacteria and archaea dominates over the chemical oxidation. The role of bacteria in sulphide oxidation reactions will be discussed in more detail in the next section.

Pyrite oxidation is an acidic process with either Fe^{2+} or $Fe(OH)_3$ as a product, as indicated by reactions 7-1, 7- 2 and 7-5 (Table 7-1). This is also true for pyrrhotite oxidation (reactions 7-7, 7-8) when there is an iron deficiency in the mineral lattice, and for arsenopyrite oxidation (reaction 7-9). However, not all sulphide oxidation reactions are acid generating. The oxidation of such sulphide minerals as sphalerite, galena, and millerite (reactions 7-12, 7-13, 7-14) do not consume or produce acidity. It should be noted, however, that these last three minerals are acid soluble, and will dissolve in acidic solutions as follows:

$$ZnS(s) + H^+ \Leftrightarrow Zn^{2+} + HS^- \qquad (7\text{-}15)$$

In the presence of oxygen, hydrogen sulphide (HS^-) is rapidly oxidized to sulphate or elemental sulphur.

The role of bacteria in the impoundment

There are a number of acidophilic bacterial species in the upper horizons of mine waste deposits that are capable of utilizing reduced sulphur species (e.g. sulphide minerals) as electron sources for carbon fixation, while some may also use reduced iron (*e.g. A. ferrooxidans*, *Leptospirillum ferrooxidans*). For the bacterial oxidation of sulphur and iron to occur in these environments, the reactions must be thermodynamically feasible. Although microorganisms cannot change thermodynamic relationships, their action as catalysts increases the rates of chemical reactions. Under conditions of unlimited oxygen availability (e.g. tailings exposed directly to air), the presence of *A. ferrooxidans* and other bacteria can accelerate the rate of Fe^{2+} and sulphide mineral oxidation by O_2 by up to several orders of magnitude. However, the rate of sulphide oxidation will be limited by the availability of oxygen as either a direct oxidant of sulphide (reaction 7-1) or for the oxidation of ferrous iron (reaction 7-3). Under conditions of limited oxygen availability (e.g. under a soil cover), the rate of sulphide oxidation will be determined by the supply of oxygen and the importance of microbial mediation will be less significant. With a limited oxygen supply, there will be no difference between the abiotic and microbially - mediated oxidation rates.

Illustration: Bacteria thrive in the iron- and sulphur-rich waters in the vicinity of sulphic tailing.

The oxidation of sulphide minerals in mine waste deposits can proceed via a number of pathways, as illustrated in Figure 7-6. Solid-phase sulphides may be abiotically oxidized by O_2 (pathway 1, equation 1); this has been a common pathway investigated in laboratory experiments. However, in natural systems, microorganisms are omnipresent mediators in sulphide oxidation reactions (*i.e*. pathways 2 – 5). The role played by iron- and sulphur-oxidizing bacteria is multi-faceted. In systems containing iron, *A. ferrooxidans* may exclusively oxidize Fe^{2+} to Fe^{3+} to gain energy, although reduced S is also a potential source of energy, with O_2 used as an electron acceptor (pathway 2). Ferric iron may oxidize pyrite (equation 4) with or without microbial mediation (Figure 7-6, pathways 4 and 3, respectively). Finally, other oxidants may be present in the mining environment, such as nitrate (pathway 5), and nitrate-reducing bacteria may contribute to pyrite oxidation.

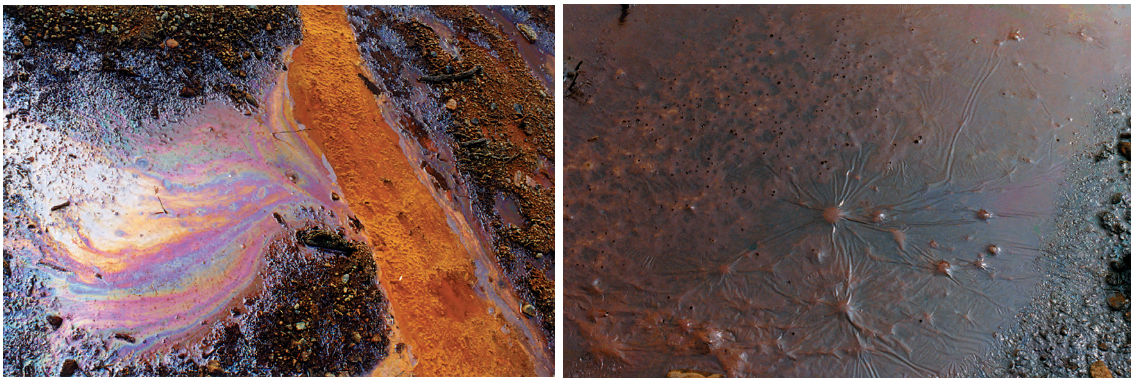


Illustration: Bacteria are omnipresent in sulphidic mine tailings.

There has been a long-standing debate on whether the bacterial oxidation of sulphides proceeds via an indirect or direct mechanism. With the indirect mechanism, ferric iron directly oxidizes the pyrite in a geochemical, abiotic reaction (reaction 7-2, pathway 3). In contrast, the direct contact mechanism requires bacterial adhesion to the pyrite surface. The overall oxidation reaction takes on the form of equation 1, as oxygen is utilized as an oxidant by sulphur-oxidizing bacteria. So far, it has not been shown, how organisms oxidize metal sulphides in a "direct" way. High amounts of Fe bound in a layer of extracellular polymeric substances (EPS) of *Acidithiobacillus ferrooxidans* and of *Leptospirillum ferrooxidans* have been detected (Gehrke et al., 1998; Sand et al., 2001). Recently, Ehrlich (2002) suggested that this EPS bound Fe may serve as an electron shuttle, as Fe also does in the "indirect" way. Following this suggestion, Fe(III) is generally the oxidant for biological metal sulphide dissolution, irrespective if cells are attached ("direct") or not attached ("indirect") to the mineral surface. Rawlings (2002) highlighted the dominant role of EPS bound Fe for bioleaching and stated in his review about the mechanisms of bioleaching, that the mechanism is strictu sensu indirect. A direct contact of a cell to the mineral surface is not essential for bioleaching but increases the rate of bioleaching. He suggested replacing the term "direct leaching" by the term "contact leaching".

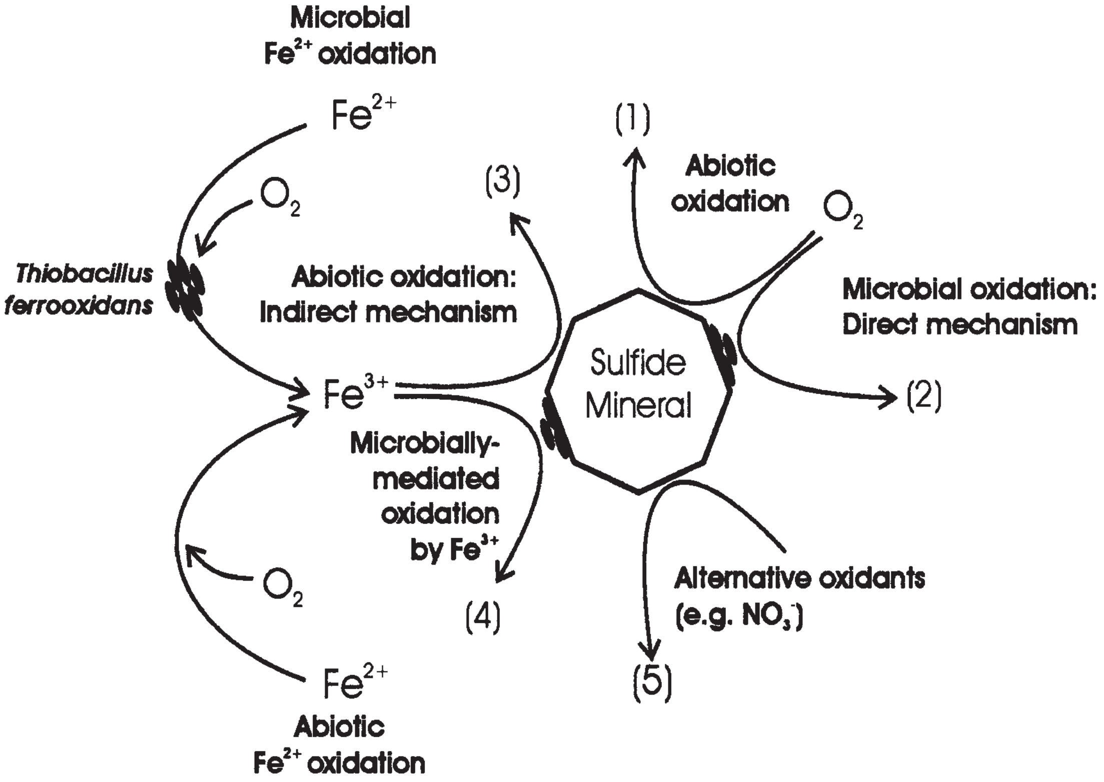


Figure 7-6 Alternative pathways [1] – [5] in the oxidative weathering of sulphide minerals, Herbert (1999).

According to the above discussion, bioleaching of metal sulphides is carried out by acidophilic Fe(II) oxidizing organisms providing Fe(III) to oxidize metal sulphides. As shown by Schippers and Sand (1999), oxidation proceeds via the thiosulphate mechanism or the polysulphide mechanism. The first mentionened mechanism is based on the oxidative attack of Fe(III) on acid-insoluble metal sulphides, such as pyrite. Thiosulphate ($S_2O_3^{2-}$) is produced as an intermediate product of the reaction, but is eventually oxidised to sulphate:

$$FeS_2(s) + 6Fe^{3+} + 3H_2O \rightarrow 7Fe^{2+} + S_2O_3^{2-} + 6H^+ \qquad 7\text{-}16$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \qquad 7\text{-}17$$

The polysulphide mechanism is applicable for acid-soluble sulphides such as sphalerite, galena, and pyrrhotite, where Fe(III) and protons attack the sulphides by oxidative and acidic dissolution, respectively. With this mechanism, the main sulphur intermediates are polysulphide (H_2S_n) and, consequently, elemental sulphur (S_8):

$MS(s) + Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5H_2S_n + Fe^{2+}$ $(n \geq 2)$ 7-18

$0.5H_2S_n + Fe^{3+} \rightarrow 0.125S_8 + Fe^{2+} + H^+$ 7-19

$0.125S_8 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$ 7-20

For the above reactions (7-16 to 7-20), the intermediary sulphur compounds are either oxidized chemically by Fe(III) (7-17, 7-19, 7-20) or biologically by acidophilic sulphur-compound oxidizing organisms (Schippers and Sand, 1999; Sand et al. 2001).

Common iron- and sulphur-oxidising bacteria in mine tailings deposits are acidophiles; organisms that are most active in acidic environments. At neutral to alkaline pH in presence of O_2, which are conditions commonly observed in remediated mine tailings, metal sulphides are predominantly chemically oxidized. Bioleaching organisms cannot live at this pH and Fe is insoluble. Thus, it is not possible that metal sulphides are biologically oxidized in a similar way as described for low pH (see above). It is possible, however, that a microbially–catalyzed dissolution of acid soluble metal sulphides may occur. For example, the dissolution of $Fe_{1-x}S$ at neutral pH has been shown for moderately acidophilic sulphur compound oxidizing organisms such as *Thiomicrospira frisia* (Kuenen et al., 1992; Brinkhoff et al., 1999). These organisms produce protons by sulphur oxidation, which dissolve the acid soluble metal sulphide. According to the polysulphide mechanism, intermediary sulphur compounds like elemental sulphur are formed which are biologically oxidized. In case of the acid insoluble FeS_2, moderately acidophilic sulphur compound oxidizing organisms like *Thiomonas intermedia* only oxidize intermediary sulphur compounds formed by the chemical FeS_2 oxidation and do not increase the chemical FeS_2 dissolution rate (Arkesteyn, 1980; Schippers et al., 1996).

Microbial ecology in tailings impoundments

The implication of acidophilic microorganisms in the production of the environmentally damaging acidic, metal bearing solutions from mines and mine impacted areas is well documented (Ledin and Pedersen, 1996), although several studies have indicated that the phylogenetic richness of AMD affected areas is less than in other environments (Baker and Banfield 2003). Therefore, defining the diversity of natural microbial communities is an important step in studying the microbial ecology of any mining environment. The identification of organisms has traditionally been achieved by cultivation techniques such as plate cultures and most probable number (MPN). However, >99% of naturally occurring microorganisms are un-cultivatable by classical techniques (Amann et al., 1995). An alternative approach that circumvents the need for cultivation is the application of molecular approaches to microbial ecology, and in particular the use of 16S rRNA as a molecular marker (Amann et al., 2000). Molecular phylogenetic techniques include denaturing gradient gel electrophoresis (DGGE), cloning and sequencing and fluorescent in situ hybridization (FISH). The use of DGGE gives an indication of the diversity of the microorganism population, but may only be used semi-quantitatively as changes in band strength may only be used to draw conclusions that a particular species is increasing or decreasing in number (Torsvik et al., 1998). If quantitative results are required then FISH may be used.

Microbial population analysis of Kristineberg mine tailings impoundment

In order to study the microbial population in impoundment 1 of the Kristineberg mine site, groundwater samples were taken from the installed BAT groundwater pipes and tailings samples were collected from cores (Ebenå, 2003). The bacterial diversity in the samples was characterized using both the classical microbiological technique MPN with ferrous iron or solid sulphur as energy sources and the molecular approach of DGGE, cloning and sequencing.

For the solid phase samples, MPN-analysis indicated that the greatest numbers of iron- and sulphur-oxidizing bacteria (probably *Acidithiobacillus ferrooxidans*) are found at the oxidation front (4.7×10^5 cells/g tailings; Ebenå, 2003) compared with the numbers in the oxidized tailings closer to the ground surface (10 cells/g) and deeper in the unoxidized tailings (7 cells/g). These results demonstrate that even though the supply of oxygen is now limited in the tailings, because of the installation of a soil cover in 1996, the activity of Fe- and S-oxidizing bacteria at the oxidation front is still relatively high. The bacteria are capable of utilising the low concentrations of oxygen in the unsaturated tailings for the oxidation of sulphides at the oxidation front and ferrous iron in the pore water.

For the groundwater samples, the MPN-analysis gave a large variation in the bacterial numbers between locations. The highest number of bacteria was found among the iron-oxidizing bacteria, while the sulphur-oxidizing bacteria were more evenly distributed throughout the deposit than the iron-oxidizers (Ebenå, 2003). DGGE analysis identified a total of 7 distinct bands that corresponded to γ-proteobacteria, actinobacteria, firmicutes, and δ-proteobacteria (Athar et al., 2004). These microorganisms possessed 16S rRNA gene sequences similar to moderately thermophilic microorganisms including *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*), an acidophilic reduced inorganic sulphur oxidizer that has been implicated in bioleaching environments (Dopson et al., 1994), a thermal soil bacteria implicated in bioleaching (Dopson and Lindström, 2004), and *Geobacillus tepidamans*, isolated from Yellowstone National Park. Also, three bands relating to un-cultured microorganisms isolated from a sulphate reducing environment, contaminated groundwater, and iron mineral deposits were identified.

This study revealed a broad diversity of bacterial lineages in the microbial community in the Kristineberg tailings impoundment 1. The majority of the organisms detected were either uncultured or recently described species, mostly identified from metal rich environments. The isolation of three moderately thermophilic bacteria suggests that internal zones in the impoundment have raised temperatures, possibly due to the action of microorganisms mediating exothermic processes. As some of the microorganisms present are capable of growing by reducing iron and other heavy metals, they are likely to be the most important organisms at the Kristineberg mine site. Future studies in understanding the microbial role in the bioremediation of the area may be focused on these organisms.

Microbial analysis of a tailings pond

A sediment sample containing black mud and pond water was taken from an acidic (pH 3), metal and sulphur rich pond adjacent to impoundment 1 and a wetland at the Kristineberg field site. Black anaerobic sediments were found ≤5 cm below a hardpan of iron-hydroxide at the bottom of the pond that functioned as an oxygen barrier for the underlying anaerobic community. These samples were analysed by DGGE, cloning and sequencing and the DGGE profile gave 4 prominent bands (Morales et al., 2004). The mud and pond water culture was enriched in sulphate reducing bacteria (SRB) by growth in a column with lactate addition. The total bacterial species identified from the pond mud and water sample showed similarity with *Dechlorosoma sp*. SDGM and *Rhodococcus sp*. although some uncultured β-proteobacteria showing high similarity with *Pseudoxanthomonas brogbernansis* were also retrieved. The initial pond and mud water sample was also analysed by FISH with probes for SRB. In situ hybridization confirmed the presence of SRB with a general SRB probe. Positive results were also found for probes directed towards *Desulfovibrio spp*., *Desulfotalea spp*., *Desulfofusiis sp*., and *Desulfobacterium sp*. These results suggest that the pond water and mud contained anaerobic SRB that will precipitate the metals found in the tailings. Therefore, this culture was used in a column study for the remediation of AMD waters using compost material as an energy source (Morales et al., 2004). The microorganism culture in this column study was also studied using DGGE, cloning and sequencing and the DGGE pattern showed a decrease in the number of bands in column sampled three months after inoculation with pond mud and water. The decrease in the number of bands on the DGGE gel suggests a decrease in bacterial diversity, which may be attributed to the fact that the samples were taken after the depletion of lactate. A good rate of sulphate removal was observed in the column and this may provide a suitable method for remediation of AMD waters.

In principle environmental rRNA sequences can be used to infer some properties of the organism that they represent. One shortcoming in deriving physiological hypotheses from these studies is that many of the sequences are related to uncultivated organisms. However, a combination of qualitative DGGE and a quantitative method such as FISH is a useful step in acquiring a good descriptive tool for microbial community analysis of AMD.

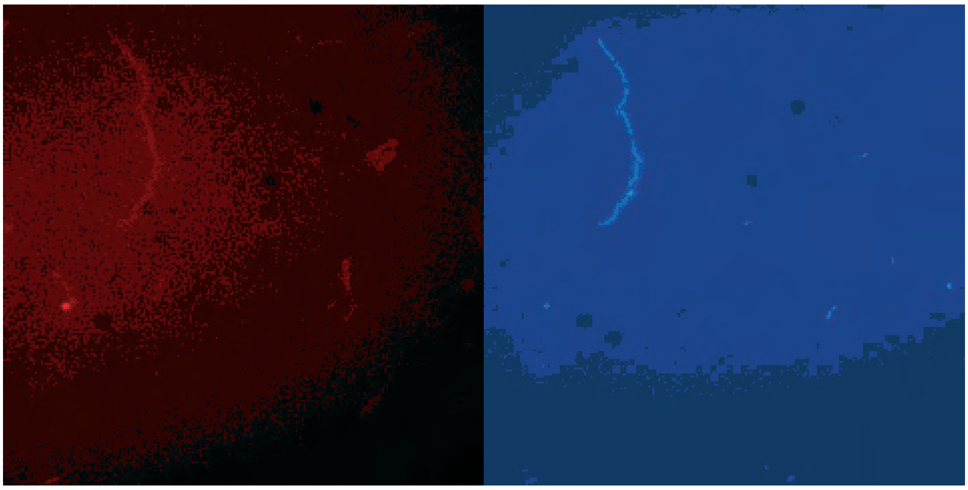


Illustration: DSD 131 probe and DAPI image of sample identifying *Desulfovibrio* spp. (from Morales *et al.* 2004)

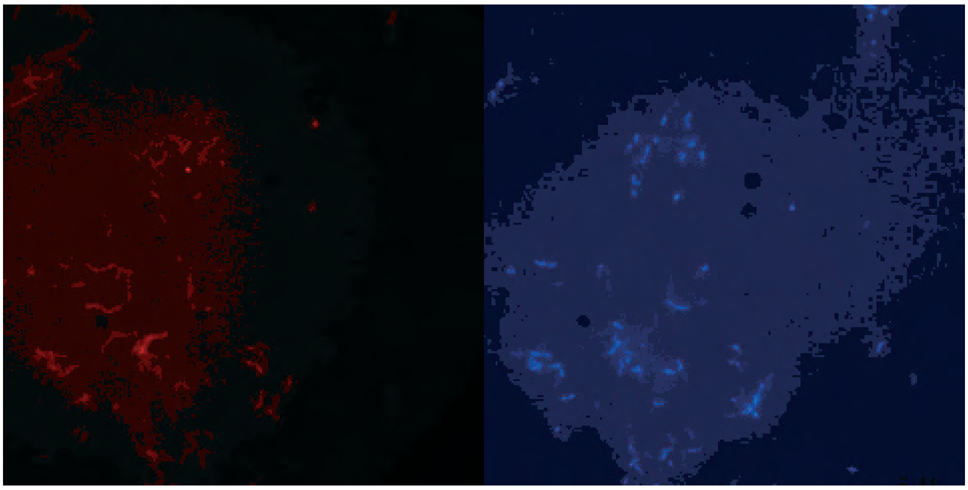


Illustration: SVAL 428 probe and DAPI image of sample showing *Desufotalea* spp. or *Desulfofustis* spp. (from Morales *et al.* 2004)

Biotic versus abiotic sulphide mineral oxidation processes

The rate of pyrite oxidation has been reported to be up to a factor 35 greater in microbiological laboratory experiments than in abiotic controls (e.g. Olson, 1991; Fowler et al., 2001; Yu et al., 2001; see also e.g., review in Nordstrom and Southam, 1997). Microbial mediation has also been reported to accelerate sulphide oxidation on the field or near field scale, though only by a factor 1.5 - 5 (Strömberg and Banwart, 1999a; Edwards et al., 2000; Elberling et al., 2000). In the following, we attempt to quantitatively compare the importance of abiotic and biotic processes for laboratory conditions.

Although a catalytic effect of microbes has often been reported in the literature, systematic, quantitative studies of the oxidation rate are sparse. Furthermore, in many studies of the biotic oxidation of pyrite, the surface area has not been reported which hence limits the quantitative use of these data. Although different ways to quantify the microbial rate of oxidation of pyrite and other sulphide minerals have been presented, experimental data for parameterising such models are thus generally not available in the scientific literature. Commonly, the proposed rate laws take on a Michaelis-Menten like expression. For example, Scharer et al. (1994) proposed the rate law:

$$R_{bio} = b\frac{\mu_m \sigma}{Y_{x/s}} e^{\frac{-E_a}{RT}} \frac{[O_2]}{K_o + [O_2]} \frac{1}{1+10^{2.5-pH}+10^{pH-4}} \qquad (7\text{-}21)$$

where b is a biological scaling factor, E_a is the activation energy, K_o is the half saturation constant for oxygen, $Y_{X/S}$ is the growth yield, μ_m is the specific growth rate, and σ is the specific surface coverage. Equation 7-21 explicitly accounts for the dependence of the biotic oxidation rate on temperature, oxygen concentration, and pH through the terms $e^{\frac{-E_a}{RT}}$ (the Arrhenius' equation), $\frac{[O_2]}{K_o + [O_2]}$ (Michaelis-Menten kinetics), and $\frac{1}{1+10^{2.5-pH}+10^{pH-4}}$, respectively. As the specific growth rate and surface coverage generally is unknown, it seems reasonable to simplify Equation 7-22 to:

$$R_{bio} = b' k_{Bio} \frac{[O_2]}{K_o + [O_2]} \frac{1}{1+10^{2.5-pH}+10^{pH-4}} \qquad (7\text{-}22)$$

where $k_{Bio} = k^0_{Bio} e^{\frac{-E_a}{RT}}$, k^0_{Bio} is a rate constant at a defined standard state, and b' is a scaling factor that accounts for the dependence of R_{bio} on factors not explicitly handled by Equation 7-22. By defining the conditions of the experiments reported in the Table 2 in Scharer et al. (1994) as our standard state (b'=1), their results can be used to estimate $k_{Bio}(T=30^oC)$. For pyrite, chalcopyrite and sphalerite, we estimate k_{Bio} to be 9.4 x 10^{-8}, 9.5 x 10^{-9}, and 1.1-x-10^{-8} mol $m^{-2}s^{-1}$, respectively. Comparison to other available data indicates that it is reasonable to assume 1 x $10^{-6} < K_o <$ 1 x 10^{-5} M.

By combining the abiotic rate expressions for pyrite oxidation by O_2 and by Fe(III) with the biotic expression in Equation 7-22, a tentative fraction diagram was generated for the different pyrite oxidation mechanisms (see Figure 7-7). This preliminary comparison indicates that for a wide range of conditions, the microbially mediated mechanism may dominate. Note, however, that the dominance area is strongly dependent on, for example, the scaling factor b' and the assumed value of K_o. Extrapolation of the results shown in Figure 7-7 may be also indicative for field conditions. However, both biotic and abiotic rates can, to an unknown extent, be expected to be slower than in the laboratory.

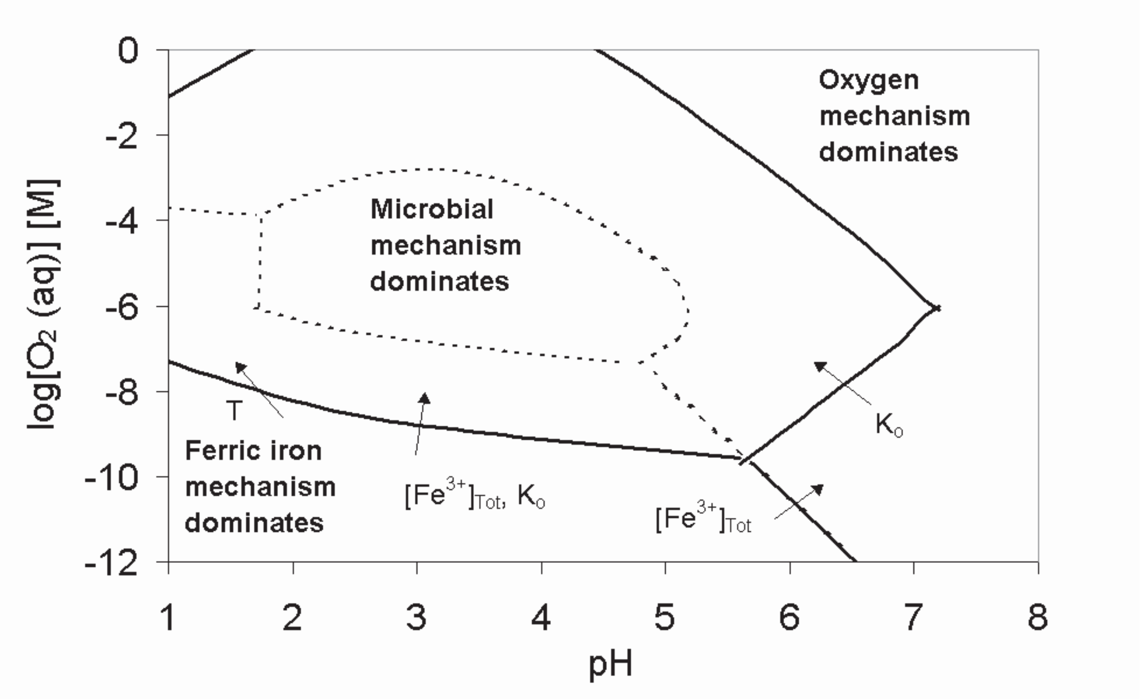


Figure 7-7 Mechanism predominance diagram for pyrite oxidation at T=1°C and $K_o=1 \times 10^{-6}$ M and a total ferric iron concentration of $[Fe(III)]_{tot}=1 \times 10^{-6}$ M. The full and dotted lines denote b'=1 and b'=0.01, respectively. The arrows indicate the response to an increase in the adjacent printed parameter (From Salmon and Malmström, 2002).

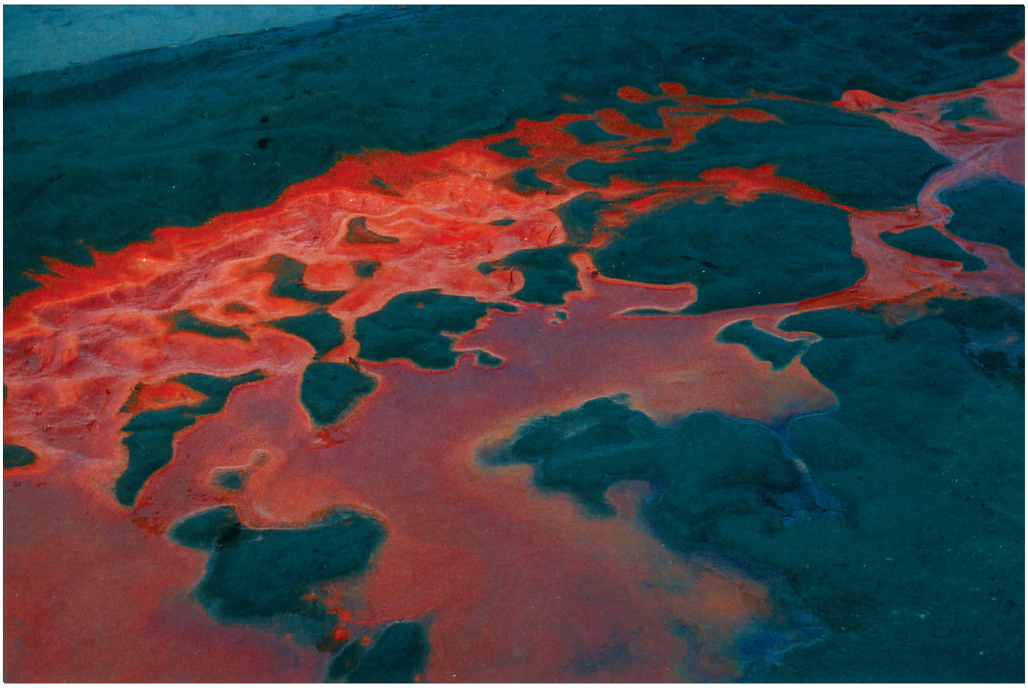


Illustration: Iron sulphides, oxygen, water and microbes initiates the weathering processes.

7.5 pH-buffering reactions

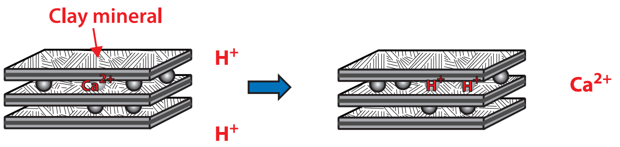
As described in the previous chapter, sulphide oxidation (particularly reactions 7-1 and 7-2) and subsequent oxidation and precipitation of dissolved iron (reaction 7-4) leads to generation of acidity. This acidity may be consumed in the mining waste, by reactions such as ion-exchange, protonation of mineral surface sites (compare Chapter 7.6), and mineral dissolution and alteration reactions (Figure 7-8). The balance between acid producing and acid consuming reactions is of particular importance for the assessment of AMD as the mobility and bioavailability of many metal and metalloid ions are strongly pH dependent.

While ion-exchange and surface protonation reactions on the one hand generally are fast, they have relatively limited capacity, which thus is exhausted soon after deposition of the waste. The mineral dissolution (Table 7-2) and alteration reactions, on the other hand, are generally slower, but have a much larger capacity, and thus constitute the most important pH buffering of the waste material. A succession of precipitation and dissolution reactions has been described in the literature, where high pH, caused by carbonate mineral dissolution (primarily reactions 7-23 and 7-24 in Table 7-2), leads to the precipitation of secondary metal carbonates and hydroxides. As primary carbonate minerals are depleted, the pH drops and is buffered at successively lower levels by the redissolution of these secondary phases (reactions 7-26 to 7-28; see e.g. Blowes and Ptacek, 1994). In parallel, aluminosilicate dissolution (reactions 7-29 to 7-35) also consumes acidity and release base cations (see e.g. Salmon and Malmström, 2004).

Ion-exchange
(clay minerals)

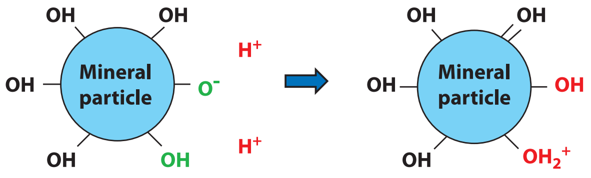
$>SOCa^{+} + 2H^{+} \rightarrow$

$>SOH_2^{+} + Ca^{2+}$



Ion-exchange on permanently charged sites on clay minerals.

Surface protonation



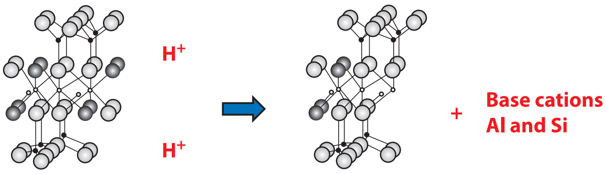
$>SO^{-} + H^{+} \rightarrow >SOH$

and

$>SOH + H^{+} \rightarrow >SOH_2^{+}$

Protonation of variably charged surface sites on carbonates, (oxy)hydroxides, and aluminosilicates.

Mineral dissolution



Reactions in Table 7-2

Dissolution of carbonates, oxy(hydr)oxides, and aluminosilicates

Figure 7-8 Ion-exchange, surface protonation and mineral dissolution serves to consume released acidity.

Table 7-2 Examples of mineral dissolution reactions and the consumption of acidity by each reaction.

Mineral group Mineral Reaction formula	Consump. of acidity moles H^+	Reaction Number
Carbonates		
Calcite		
$CaCO_3(s) + 2H^+ \Leftrightarrow Ca^{2+} + CO_2(g) + H_2O$	2	7-23
Dolomite		
$MgCaCO_3(s) + 4H^+ \Leftrightarrow Mg^{2+} + Ca^{2+} + CO_2(g) + H_2O$	4	7-24
Magnesite		
$MgCO_3(s) + 2H^+ \Leftrightarrow Mg^{2+} + CO_2(g) + H_2O$	2	7-25
Siderite*		
$FeCO_3(s) + 2H^+ \Leftrightarrow Fe^{2+} + CO_2(g) + H_2O$	2*	7-26
Hydroxides		
Fe(III)-hydroxide		
$Fe(OH)_3(s) + H^+ \Leftrightarrow Fe(OH)_2^+ + H_2O$	-**	7-27
Aluminium hydroxide		
$Al(OH)_3(s) + H^+ \Leftrightarrow Al(OH)_2^+ + H_2O$	-**	7-28
Aluminosilicates – tectosilicates		
K-feldspar		
$2KAlSi_3O_8(s) + 2H^+ + 9H_2O \rightarrow 2K^+ + Al_2Si_2O_5(OH)_4(s) + 4H_4SiO_4(aq)$	2***	7-29
Plagioclase (Na/Ca-Feldspar with variable composition)		
$Na_{0.75}Ca_{0.25}Al_{1.25}Si_{2.75}O_8(s) + 1.25H^+ + 1.25H_2O \rightarrow$ $0.75Na^+ + 0.25Ca^{2+} + 1.25Al(OH)_{3(aq)} + 2.75SiO_2(s)$	1.25***	7-30

Mineral group Mineral Reaction formula	Consump. of acidity moles H^+	Reaction Number
Aluminosilicates – phyllosilicates		
Muscovite (Mica)		
$K(Al_2)AlSi_3O_{10}(OH)_2(s) + H^+ + 9H_2O \rightarrow K^+ + 3Al(OH)_{3(s)} + 3H_4SiO_{4(aq)}$	1***	7-31
Biotite (Mica)		
$K(MgFe_2)AlSi_3O_{10}(OH)_2(s) + 7H^+ + 3H_2O \rightarrow$ $K^+ + Mg^{2+} + 2Fe^{2+} + Al(OH)_{3(s)} + 3H_4SiO_{4(aq)}$	7***	7-32
Chlinochlore (Chlorite with variable composition)		
$(Mg_{4.5}Fe^{II}_{0.2}Fe^{III}_{0.2}Al)AlSi_3O_{10}(OH)_8(s) + \frac{47}{5}H^+ + 6H_2O \rightarrow$ $4.5\ Mg^{2+} + 0.2\ Fe^{2+} + 0.2\ Fe(OH)_3(s) + 2\ Al(OH)_3(s) + 3H_4SiO_{4(aq)} + \frac{27}{5}H_2O$	9.4***	7-33
Talc (Clay mineral)		
$Mg_3Si_4O_{10}(OH)_2(s) + 6H^+ + 4H_2O \rightarrow 3Mg^{2+} + 4H_4SiO_{4(aq)}$	6	7-34
Aluminosilicates – Inosilicates		
Hornblende (Amphibole with variable composition)		
$Ca_2(Mg_xFe_yAl_{5\text{-}x\text{-}y})_5\ (Al_{8\text{-}z}\ Si_z)O_{22}(OH)_2 + 2*(2+x+y)H^+ + qH_2O \rightarrow$ $2Ca^{2+} + xMg^{2+} + yFe^{2+} + (13-x-y-z)Al(OH)_{3(s)} + zH_4SiO_{4(aq)}$	4+2x+2y***	7-35

*Transformation of primary carbonate minerals into siderite, eg. $CaCO_3(s) + Fe^{2+} \leftrightarrow FeCO_3(s) + Ca^{2+}$, would if it occurs, attenuate latent acidity as subsequent dissolution of the siderite releases ferrous iron, which may later be oxidised, followed by hydrolysis and be precipitated as Fe(III)-oxy(hydr)oxides (reactions 7-3 and 7-4).

**These reactions, although they do not affect the formal acidity/alkalinity of solution, may alter the actual solution pH, especially at low pH values.

***Formation of secondary kaolinite ($Al_2Si_2O_5(OH)_4(s)$) or aluminium hydroxide ($Al(OH)_{3(s)}$), and similar phases (but not SiO_2 phases) may affect the actual pH that is reached during reaction, but does not affect the formal acidity/alkalinity of the aqueous solution, provided that the secondary phases do not contain alkali or alkaline earth metal ions or ferrous iron.

Implications of relative mineral weathering rates for the evolution of leachate quality and pH

The relative availabilities and rate of dissolution of minerals in the deposit have important implications for the leachate acidity/alkalinity. As seen in Figure 7-9a, the weathering rates (see next section for details) of different mineral groups are very different. Calcite dissolves approximately 3 orders-of-magnitude more quickly than pyrite even at reasonably high oxygen availability. At such conditions, pyrite, in turn, dissolves nearly 3 orders-of-magnitude more quickly than the aluminosilicates. These relative rates of dissolution suggest that if pyrite and calcite are available in similar quantities, calcite weathering will produce alkalinity at a rate that is sufficient to neutralise the acidity produced from pyrite weathering and maintain pH at circumneutral values. If calcite bocomes depleted, then acidic discharges can expected, as the aluminosilicates may dissolve too slowly to consume all acidity (e.g. Banwart and Malmström, 2001). In any case, relatively slow aluminosilicates dissolution will help consuming acidity thereby prolonging the life time of calcite, and increasing the period during which the pH remains at a relatively high level (Salmon and Malmström, 2002; 2004).

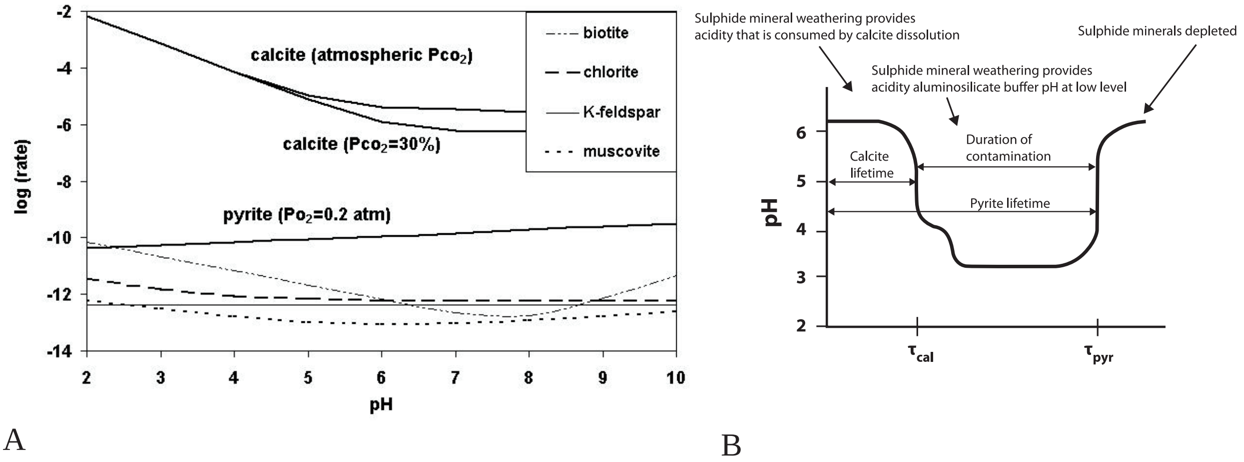


Figure 7-9 Relative mineral weathering rates and their implications for AMD quality. A) Weathering rates of silicates, pyrite and calcite at 5°C (From Salmon and Malmström, 2002)
B) Schematic diagram showing the relationship between pH levels and lifetime of minerals that produce and consume acidity (Modified from Banwart and Malmström, 2001)

During proceeding weathering, a region of tailings that is depleted of pyrite and other sulphides develops. The boundary between the depleted region and that not yet reached by oxygen is observed to be rather narrow, on the order of cm to tens of cm, see Chapter 5. This agrees with simulations using coupled advection, diffusion, and reaction models (Moreno and Neretnieks, 2004). The width of the reaction front is determined by the relative rates of oxygen intrusion and pyrite oxidation, and is larger when the tailings are partially water saturated than when the tailings are fully saturated with water. The protons generated by pyrite oxidation are transported downstream with the seeping water and come in contact with pH buffering minerals, which gets depleted. For circumstances where the amount of pyrite, expressed as proton generation capacity per mass of tailings, is much larger than the neutralising capacity of the carbonate minerals, the pH neutralisation front moves faster than the pyrite oxidation front, thus potentially leading to the release of net acidic water (compare Figure 7-9b). Physical separation of acidity consuming and producing capacity, as may occur as a consequence of liming on top of a partly pyrite depleted deposit, may furthermore lead to less effective pH buffering, as the generation of protons occur after the water has already passed the region of carbonate minerals, and production of low pH leachates.

Because metal ion mobility is linked so strongly to acidic conditions, depletion of calcite and subsequently pyrite also indicate the main periods of contaminant discharge. The lifetime of pyrite, τ_{pyr}, roughly corresponds to the contaminating lifetime of the deposit, but that discharge may remain near-neutral through out this period of time, if the lifetime of calcite, τ_{cal}, is large enough ($\tau_{pyr} < \tau_{cal}$).

For a tailings deposit, the oxidation of pyrite is the primary driving (bio)geochemical process in the system, where molecular oxygen is the dominant oxidant at most conditions (e.g. Salmon, 2000). When there is a sealing cover or in the presence of some other oxygen intrusion barrier, the rate of pyrite oxidation by dissolved molecular oxygen, however, is limited by the intrusion rate of oxygen. For a calcite depleted deposit, the cover must, in order to prevent acidification, essentially slow down the oxygen intrusion, such that the proton release from the pyrite oxidation and the connected release of latent acidity in the form of dissolved ferrous iron becomes equally slow or slower than the acidity consumption by aluminosilicates over the full reaction length. Simulations indicate that aluminosilicate weathering consumes a lot of the protons within tens of cm to some meter at most (Moreno and Neretnieks, 2004) and that the pH may rise from about 3 to 5 in the calcite depleted region, with simultaneous reduction of the acidity by 99 % (Moreno and Neretnieks, 2004) at oxygen limited conditions. Further downstream, where calcite still may be present, calcite dissolution may raise the pH further. Then when the calcite front has moved a corresponding distance, it will slow down in its rate of movement because the aluminosilicates take the largest part of the protons, leaving only a little for the calcite to react with.

Aluminosilicate weathering mechanism and kinetics – Application to tailings deposits

While there is a large capacity for aluminosilicates to consume acidity, the reactions are generally relatively slow. Far from equilibrium between the aqueous phase and the mineral, the empirical rate law for aluminosilicate weathering can often be written as the sum of different parallel processes, each associated with the action of a specific aqueous species

$$r' = \sum_i k_i C_i^{n_i} \qquad [\mathrm{mol\ m^{-2}\ s^{-1}}] \qquad (7\text{-}36)$$

where k_i is the rate constant, C_i is the aqueous concentration, and n_i is the reaction order for the process associated with the aqueous species *i*. Generally, there is a proton promoted and a hydroxyl promoted reaction, where the corresponding rate constants and reaction orders vary between different minerals, often with $0.2 < n_{H^+} < 0.8$ and $0.3 < n_{OH^-} < 1.0$ (e.g., White and Brantley, 1995). The non-integer reaction orders with respect to aqueous species have been attributed to actual kinetic effects from surface species, formed by surface complexation, with a non-linear dependence of surface concentrations on aqueous concentrations (e.g. Furrer and Stumm, 1986; Wieland et al., 1988). At near-neutral pH, there is generally a minimum in the dissolution rate, with a zero-order rate expression governing the overall rate of reaction (see Figure 7-9a).

Other than protons and the hydroxyl ions discussed above, some ligands and multivalent cations have been reported to *accelerate* (particularly organic acids and carbon dioxide; e.g. Zinder et al., 1986; Berg and Banwart, 2000) or *retard* the dissolution (particularly Al^{3+} and oxoanions, such as phosphate; e.g. Chou and Wollast, 1989; Biber et al., 1994) of (hydr)oxide and aluminosilicate minerals. While acceleration has been attributed to the formation of surface species that destabilize bonds of metal ions to the surface, retardation has been attributed formation of multinuclear surface species, bridging two or more metal centres at the surface, making the detachment of metal ions from the surface energetically unfavourable (see e.g. Stumm, 1997, for a review).

For conditions far from equilibrium, Equation 7-36, thus, describes the rate of dissolution, including effects of pH and different cations and ligands. Closer to equilibrium between the aqueous phase and the solid phase, the rate slows down, and has been proposed to follow, for example, the form

$$r = r'(1 - e^{m(\Delta G_r / RT)})^p \; ; \Delta G_r \leq 0 \qquad [\text{mol m}^{-2}\ \text{s}^{-1}] \qquad (7\text{-}37)$$

where ΔG_r is the Gibbs' free energy of reaction, which equals zero at equilibrium, R is the gas constant, and T is the absolute temperature (e.g. Burch et al., 1993; Cama et al., 2000) and where m and p are empirical constants, evaluated from experimental data. For p=m=1, Equation 7-37 can also be written in terms of the saturation index, SI,

$$r = r'(1 - 10^{SI}) \; ; SI \leq 0 \qquad [\text{mol m}^{-2}\ \text{s}^{-1}] \qquad (7\text{-}38)$$

$$SI = \log \frac{IAP}{K_S} \qquad (7\text{-}39)$$

where K_s is the solubility product of the mineral phase, and IAP is the associated ion activity product in the aqueous solution.

Complex aluminosilicates are often observed to dissolve incongruently, with preferential release of one or more of the components. Such apparent incongruent dissolution can be due to stoichiometric release of elements followed by bulk precipitation of secondary mineral phases (see Chapter 7-5), formation of patchy coatings directly on the mineral surface (e.g., Nugent et al., 1998), or interfacial reprecipitation (Hellmann et al., 2003). Alternatively, it can be due to intrinsically non-stoichiometric release of elements, forming a leached or altered layer at the surface of the mineral (e.g., Petit et al., 1990; Hellmann et al., 1997). The formation of patchy coatings or leached layers may slow the rate of element release, such that the dissolution eventually becomes stoichiometric, with a dissolution rate that is determined by the slowest released element, for example by limitations of element release rate through diffusion resistance of the leached layer (e.g. Schnoor, 1990). With regard to AMD generation, the long-term rate effect, along with possible deviations in H^+ consumption compared to congruent dissolution, are the important effects of incongruent dissolution.

Non-stoichiometric release of elements has been attributed to different reactivity between different structural (e.g., Acker and Bricker, 1992) or elemental sites (see recent summary by Oelkers, 2001) at the mineral surface. Oelkers (2001) conceptualise an aluminosilicate as a multi-oxide, the dissolution of which requires the breaking of more than one metal-oxygen bond type. In this conceptual model, the mineral dissolves as a consequence of metal-proton exchange reactions followed by complete destruction of the structure, where the fastest path for breaking the slowest breaking metal-oxygen bond determines the rate of reaction. At acidic conditions and in the absence of high concentrations of dissolved cations, alkali metals, followed by, in the order, Ca, Mg, and Al are expected to be released more rapidly than Si (see Figure 7-10), thereby forming cation depleted surface layers.

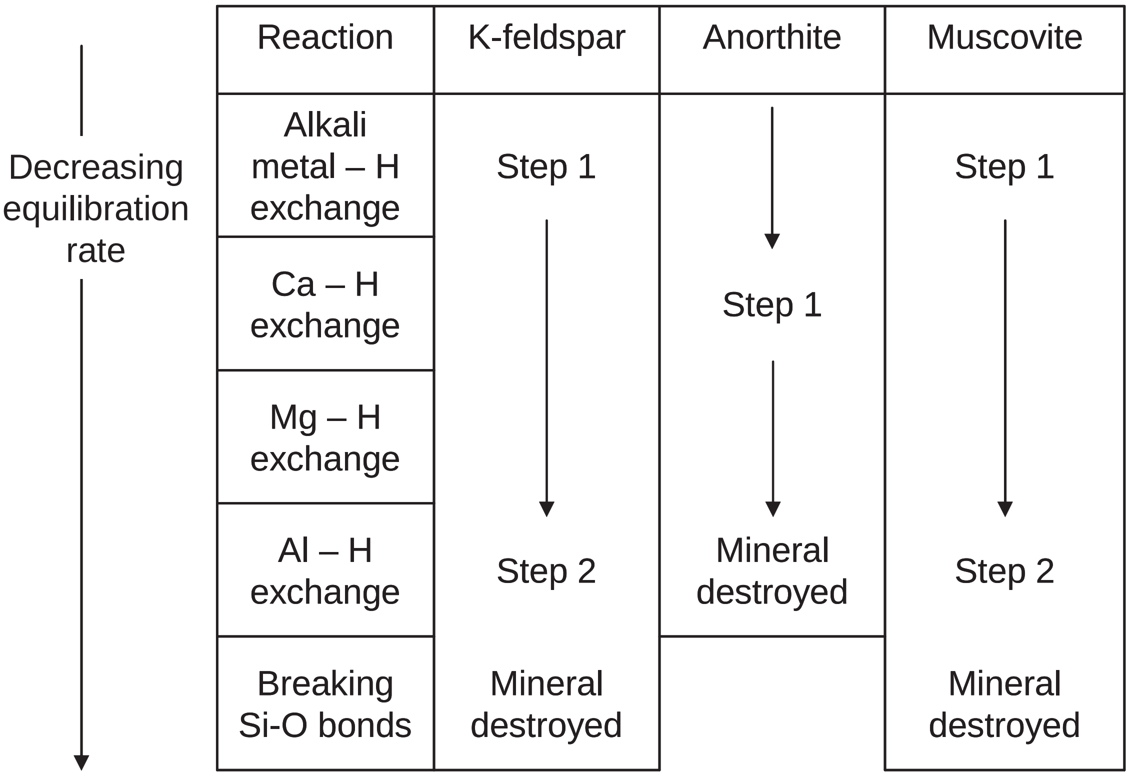


Figure 7-10 Mechanistic model for multioxide silicate dissolution applied to a few minerals of interest for tailings deposits (Modified from Oelkers, 2001).

In addition to differing reactivity of different structural/elemental sites, resulting in formation of chemically altered surface layers, different faces and surface sites of minerals have also been shown to exhibit differing tendency for dissolution. In particular, weathering experiments on phyllosilicate minerals (e.g., mica, chlorite, and clay minerals) have indicated the edge surface to be about two orders of magnitude more reactive than the basal plane (Turpault and Trotignon, 1994; Rufe and Hochella, 1999; Bosbach et al., 2000). For AMD applications, different reactivity between different surfaces constitutes a difficulty in the quantification of the mineral dissolution rate, as the relative abundance and reactivity of different faces and surface sites remain unknown for mining waste. Moreover, studies as to whether rate laws for pure mineral samples apply to complex mineral mixtures, such as tailings and waste rock, are generally not available in the literature.

Salmon (2003) provide first evidence that aluminosilicate weathering rates in the tailings show similar pH dependence as reported in the literature for monomineralic samples, however, absolute rates were found to be up to one order of magnitude lower (see Figure 7-11). This observed discrepancy in weathering rates between experiments on similar laboratory scales is possibly associated with a decrease in surface reactivity with time, rendering freshly crushed samples, normally used in weathering studies, more reactive than minerals in the tailings. The rate was furthermore found to vary between different tailings samples from the same impoundment (Figure 7-11), indicating that mineralogical heterogeneity within a deposit may have important effects on the field scale weathering rates.

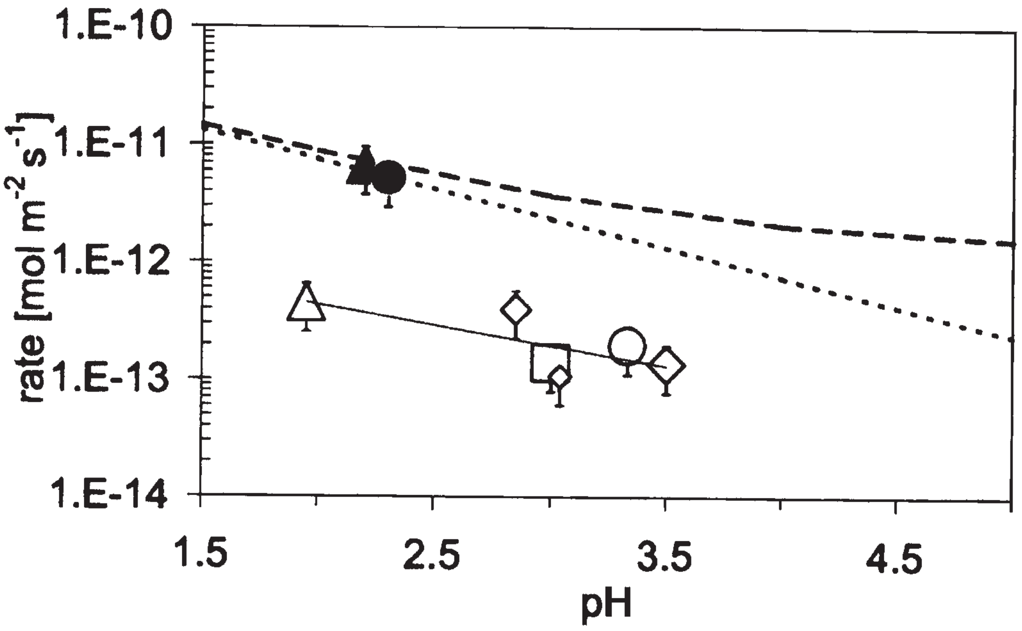


Figure 7-11. Final, surface-area-normalised dissolution rate of chlorite in two tailings samples from impoundment 1, Kristineberg vs. pH in batch reactors at ~25°C in the laboratory. Filled markers – coarse tailings sample; open markers – fine tailings sample. Dashed lines indicate rates from literature rate laws for a pure museum mineral sample (From Salmon, 2003).

Extrapolation of laboratory weathering rates to field applications is associated with further difficulty, as in many cases field scale weathering rates have been observed to be orders of magnitude slower than in corresponding small scale experiments on identical materials (Schnoor, 1990; White and Peterson, 1990; Drever and Clow, 1995; Strömberg and Banwart, 1999a,b). For the Aitik waste rock dump, a scale dependence of up to three orders of magnitude was observed (Strömberg and Banwart, 1994; Malmström et al., 2000). This observed scale-dependence was largely accounted for by a scaling model that took differences in physico-chemical conditions between the observations scales into account:

$$\frac{R_m}{a_{sm}} = \alpha\ k_m \prod \beta_{m,i} \qquad [\text{mol m}^{-2}\ \text{s}^{-1}] \qquad (7\text{-}40)$$

where R_m refers to the scaled weathering rate and a_{sm} is the specific mineral area of mineral m. The factor α is hydrological and accounts for the existence of preferential flow paths and immobile water and the β-factors represent correction of the rate constant, k, obtained from small-scale laboratory experiments, to the field-scale due to the individual differences in temperature, pH, and particle size between the scales (Malmström et al. 2000). In a modelling study of tailings impoundment 1 in Kristineberg, Salmon and Malmström (2004a), after consideration of effects of pH, mineralogical composition, and temperature (compare Equation 7-40), invoked a scaling factor of 0.02 for all pure-mineral, laboratory weathering rate laws in order to explain field observations. The order of magnitude of the remaining scale dependence implied by this calibration factor is at least ten times higher than the observed discrepancy between tailings weathering rates and weathering rates of pure minerals on similar scales (Salmon and Malmström, 2004b; see above).

Reactive surface area of tailings

The tailings consists of fine particles; for example, the tailings in impoundment 1 had 30-45 % of the particles smaller than 50 μm and 5-10 % smaller than 10 μm (Herbert et al., 2003). Associated with the small and highly variable particle size is a variable and relatively large specific surface area. For the impoundment 1 tailings, the area of eight samples from seven locations ranged from 0.2 to 10.1 $m^2\ g^{-1}$, with an average value of 2.96 $m^2\ g^{-1}$ (Salmon and Malmström, 2004a), as determined through nitrogen gas adsorption evaluated through the BET-equation. The geometric surface area of a smooth pyrite particle with diameters 10, 50, and 100 μm can be estimated to 0.12, 0.024, and 0.012 $m^2\ g^{-1}$, respectively, assuming spherical or cubic particles. The higher surface area of the tailings than expected from theory can be attributed to contributions from internal surface areas, if the particle is porous (Moreno and Neretnieks, 2004), from yet smaller particles, including surfaces of other minerals than the sulphides, or surface roughness (see short summary in Malmström, 2003).

There is an ongoing discussion in the scientific literature as to whether the geometric surface area or the BET-surface area is the better for quantifying the reactive surface area (e.g., Lee and Parson, 1995; White et al., 1996; Hodson, 1999, 2002; Gautier et al., 2001). For tailings, which is characterised by a fairly broad particle size distribution and a relatively large mass in the finer fractions, estimation of geometric surface area from the particle size distribution will, in any case, be uncertain, as a large part of the area is associated with the very fine particles, with mass in the tail of the particle size distribution.

For the quantification of kinetic, heterogeneous geochemical processes, such as pyrite oxidation and aluminosilicate weathering, the surface area of individual minerals, rather than a total tailings area is required. Often, the relation

$$A_i = \gamma_i\ A_{s,tot} \tag{7-41}$$

where A_i is the surface area of the i^{th} mineral in a mixture, $A_{s,tot}$ is the total tailings surface area of the sample, as determined from BET or through geometric considerations, and γ_i is the volumetric fraction of the mineral in the mixture, is assumed to apply (e.g. Strömberg and Banwart, 1994; Salmon and Malmström, 2004b). Axelsson (2002) provides evidence that Equation 7-41 is a reasonable first-hand approximation as she determined $A_{s,tot}$ = 0.90 $m^2\ g^{-1}$ for the 75-500 μm particle size fraction (fine fractions removed) of a coarse tailings sample with an estimated pyrite content of 18 vol-%, resulting in an estimated $A_{pyrite}^{est.}$ = 0.16 $m^2\ g^{-1}$ and determined a BET surface area for the associated sulphide concentrate of $A_{sulphide}^{meas.}$ = 0.10 $m^2\ g^{-1}$. The specific surface area of the full tailings sample (including fine particles) was 1.2 $m^2\ g^{-1}$ (Salmon and Malmström, 2004a), thus indicating that in this specific case, the fine fraction did not dominate the specific surface area.

Observed field scale acid neutralisation by aluminosilicates

The capability of aluminosilicate minerals to provide significant buffering to acid mine drainage has been debated in the scientific literature. In the following, we show that for the impoundment 1 in Kristineberg, chlorite weathering likely consumes 50-75% of the acidity produced by sulphide oxidation.

Calculation example:

Let 1 mol of pyrite weather according to Reaction 7-1 in Table 7-1

$$\mathrm{FeS}_{2(s)} + 3.5\mathrm{O}_{2(aq)} + \mathrm{H_2O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{SO}_4^{2-} + 2\mathrm{H}^+ \qquad \text{(A)}$$

and assume that simultaneously 0.1 mol of pyrrhotite is oxidised according to

$$\mathrm{FeS}_{(s)} + 2\mathrm{O}_{2(aq)} \rightarrow \mathrm{Fe}^{2+} + \mathrm{SO}_4^{2-} \qquad \text{(B)}$$

This releases 2 protons which, if consumed by chlorite weathering, release for example Mg^{2+} and Fe^{2+} to solution, where the actual proportion of Mg^{2+} and Fe^{2+} depends on the chlorite composition. One example, using the composition of the "high-Al" chlorite reported to be present in impoundment 1 (Herbert, 2002) is

$$(\mathrm{Mg_3Fe_2Al})\mathrm{AlSi_3O_{10}(OH)_8(s)} + 10\mathrm{H}^+ \rightarrow 3\mathrm{Mg}^{2+} + 2\mathrm{Fe}^{2+} + 2\mathrm{Al(OH)_3(s)} + 3\mathrm{SiO_2(aq)} + 6\mathrm{H_2O}$$

(C)

This reaction formula implies that 3/5 mol Mg^{2+} and 2/5 mol Fe^{2+} is released per 2 moles of protons consumed. According to this simple weathering model, element are released in the following stoichiometry:

Element	Reaction A	0.1 × Reaction B	2/10 × Reaction C	Total
SO_4^{2-}	2	0.1	0	2.1
Fe^{2+}	1	0.1	0.4	1.5
Mg^{2+}	0	0	0.6	0.6

yielding theoretical element ratios of Fe/S = 1.5/2.1 = 0.71 and Mg/S=0.29. The theoretical Fe/S ratio of this model is in excellent agreement with field observations of 0.71, while the Mg/S ratio is about double of that observed in the field, 0.15 (data from Corrége, 2003). Varying the ratio of pyrrhotite (0-0.1 moles) to pyrite weathering (1 mole) and the composition of the chlorite, the model predicts 0.7<Fe/S<0.81 and 0.2<Mg/S<0.3, thus indicating that field release of Mg is around 50-75% of that necessary to buffer pH through chlorite weathering.

7.6 Other chemical processes

Metal ions transferred from solid phase to aqueous solution by sulphide oxidation are exposed to many different substances, ligands, capable of coordinating the ions in aqueous phase. Metal ions may also be associated with solid phases either by precipitation of secondary phases, in which the metal constitutes the dominating cation, by coprecipitation of secondary phases with other metal ions, or by adsorption to surfaces of primary or secondary minerals. This includes association to sulphide minerals under reducing as well as dysoxic conditions. It has been shown that Cu(II) dissolved by oxidation of chalcopyrite ($CuFeS_2$) can be secondarily precipitated in a layer just below the oxidation front by interactions with pyrrhotite under formation of covellite (CuS) (Holmström et al., 1999). Under oxidising conditions (hydr)oxides and hydroxysulphates of iron, aluminium and manganese are stable and can act as scavengers of metals from solution by association of metals to reactive surface groups ($\equiv FeOCu^+$). Also silicates, mainly clay minerals, are capable of removing cationic metals from the porewater.

To illustrate the variety of metal species that may be formed in solution as well as in solid phase, a small selection of possible species of Cu(II) ions released by weathering of chalcopyrite ($CuFeS_2$) is indicated in Figure 7-12. Below, the different types of metal ion species will be discussed in some more detail.

Subsequent sections contain surveys of different types of secondary minerals formed and sorption processes in mine waste and in recipients of drainage discharge.

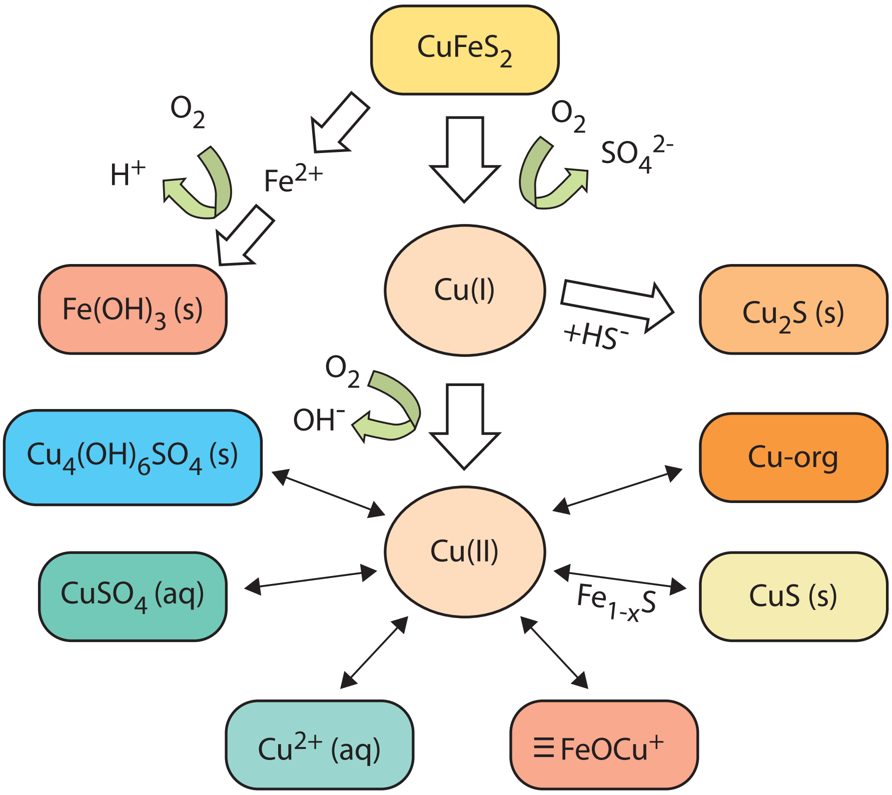


Figure 7-12. Schematic representation of interactions between copper(II)ions released by oxidative weathering of chalcopyrite and various components in the aqueous or solid phases.

Aqueous speciation

At a given point, each element is present as several different species in the solution. The immediate coordination reaction upon mineral dissolution is hydration of the metal ions, i.e. coordination of water molecules. For copper, +II is the dominating oxidation state in water although copper also exists as Cu(I) in important ore minerals, such as chalcocite (Cu_2S), and at mixed valence states (I/II) in several other minerals. A freshly released Cu(II) ion may remain in solution for shorter or longer time periods as a free hydrated ion (Cu^{2+}) but more likely it is complexed by one or several inorganic or organic ligands. Most divalent and higher valent metal ions undergo hydrolysis under neutral and alkaline conditions. Hydrolysis is a process in which one, or several, water molecules in the hydration sphere of the metals is replaced with hydroxide ions (7-42), e.g.

$$Cu^{2+} + OH^- \leftrightarrow CuOH^+ \qquad (7\text{-}42)$$

While ions of alkaline earth metals are hydrolysed only at very high pH, several transition metals may form complexes with hydroxide ions also at circumneutral pH. The tendency among divalent trace metal ions to form hydrolysis complexes increases in the order: $Cd \approx Mn < Zn < Co < Fe < Cu < Pb < Hg$ (Stumm and Morgan, 1996).

Another anion more or less ubiquitous in oxic sulphidic mine waters is sulphate, which can form aqueous complexes with, for instance, Cu(II) and Pb(II) when present in high concentrations. This occurs particularly under weakly acidic conditions where the competition with hydroxide ions is weak.

$$Cu^{2+} + SO_4^{2-} \leftrightarrow CuSO_4(aq) \qquad (7\text{-}43)$$

In well-buffered pore waters in tailings rich in carbonate minerals and in tailings deposited on organic soils the concentration of bicarbonate ions can be in the millimolar range. Under these circumstances also complexation with bicarbonate and carbonate ions is an option for metal speciation that should be considered. The extent to which metal-carbonate complexes are formed is dependent on the partial pressure of CO_2 and pH:

$$Pb^{2+} + CO_2(g) + H_2O \leftrightarrow PbHCO_3^+ + H^+ \qquad (7\text{-}44)$$

By equilibrium model calculations, metal speciation under different geochemical conditions can be calculated. As an example the calculated distribution of Cu(II) between aqueous and solid species is illustrated in Figure 7-13 for a system in equilibium with the partial pressures of oxygen and CO_2 in air, 10 mM of SO_4^{2-} and pH ranging from acidic to alkaline conditions. While the free hydrated Cu^{2+} ion and an aqueous $CuSO_4$ complex is dominating under near neutral and acidic conditions, $Cu_4(SO_4)(OH)_6$ (s) is formed at neutral pH and $Cu_2(CO_3)(OH)_2$ (s) at weakly alkaline pH.

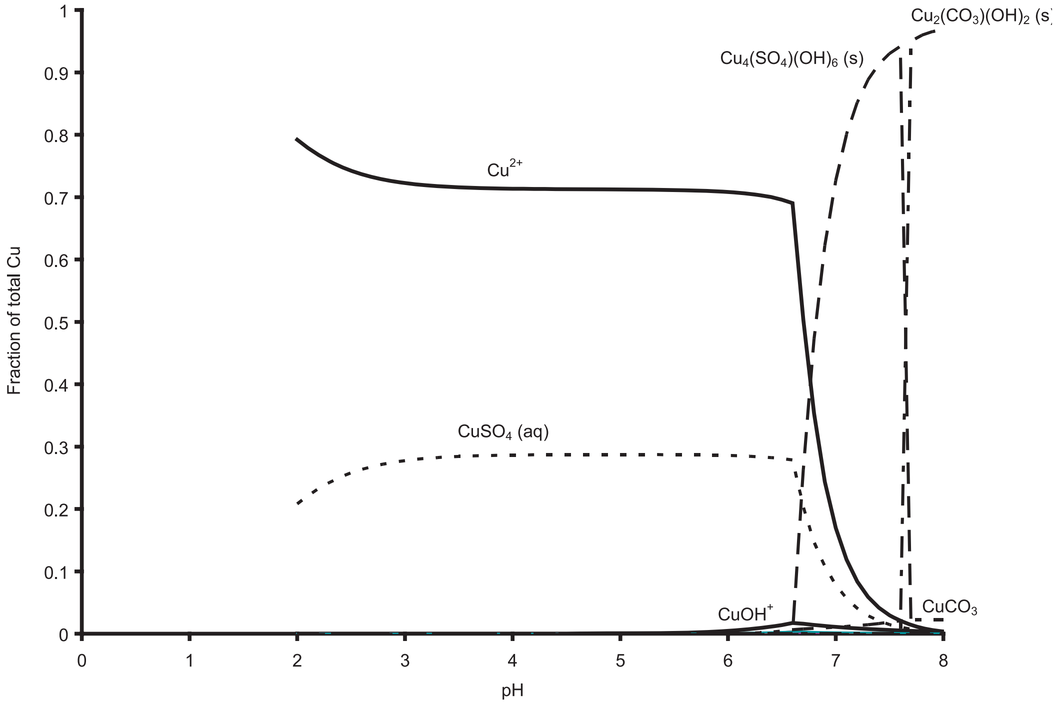


Figure 7-13 Results from speciation calculations of copper using the computer code WinSGW (WinSGW, 2004). $[SO_4^{2-}]_{tot}$ = 10 mM; equilibrium with air (PO_2 = 0.21 atm and PCO_2 = 0.00035 atm).

As described in more detail in following sections, the solubility of ferric iron (Fe(III)) in water is highly limited due to formation of oxyhydroxides and other stable solid phases, except in very acidic and in very alkaline waters. However, ferrous iron (Fe(II)) is much more soluble and behaves quite similar to copper(II). This means that free Fe^{2+}-ions and $FeSO_4$(aq) complexes dominate the speciation at low pH and high sulphate concentrations, i.e. at conditions typical of anoxic porewater in tailings. Also the complexes with e.g. bicarbonate and carbonate ions are quite similar to Cu(II) in strength, and at higher pH the solubility of Fe(II) is limited by precipitation of $Fe(OH)_2$(s).

Under anoxic conditions hydrogen sulphide ions (HS^-) can be present in significant concentrations, which offers possibilities for dissolved metals to form thio (S^{2-}/HS^-) complexes in solution. Thio complexes are particularly important for so called Type B metals, such as Cd(II), Zn(II), Pb(II), Hg(II), and Cu(I), but also Cu(II) and Fe(II) may form thio complexes in solution, e.g.

$$Pb^{2+} + HS^- \leftrightarrow PbHS^+ \qquad (7\text{-}45)$$

and

$$Pb^{2+} + 2\,HS^- \leftrightarrow Pb(HS^+)_2(aq) \qquad (7\text{-}36)$$

Arsenic is an element of special interest in this context. As is a metalloid, which implies that it exhibits properties typical for metals, but also other properties that are typical for non-metals. In the environment, As can exist in three different oxidation states: 0 +III and +V, although As is not found in elemental form in natural waters, irrespective of redox conditions. In natural waters As mainly exists in inorganic species; As(V) as anionic arsenate ($H_nAsO_4^{n-3}$) and As(III) as neutral or anionic arsenite ($As(OH)_3$). Since the chemical transition between these two oxidation states is rather slow, As(III) and As(V) may co-exist at significant concentrations within a wide range of redox conditions. Microorganisms are however known to catalyze the redox-transition of arsenic. Arsenate has a chemical behaviour that strongly resembles that of phosphate. On the other hand, As(III) belongs to the "Type B metals", implying that As(III) can form strong complexes with "Type B ligands", e.g. sulphide ions, under detachment of OH^-. Arsenic is also known for its ability to form organometallic compounds. The speciation of As has implications with respect to both ecotoxic effects and mobility in the environment.

Natural organic matter (NOM) plays a key role in surface water biogeochemistry as well as for processes in soil. Due to the high content of carboxylic groups NOM is capable of both buffering the pH in weakly acidic range and forming complexes with metal ions in solution (Thurman, 1985). Also other functional groups, like hydroxyl, amino and sulfhydryl groups, can contribute to NOM's metal binding ability. Oxalate and citrate are examples of natural low molecular weight acids forming strong complexes with metal ions in solution. This is explained by their ability to coordinate an individual metal ion with two or more functional groups, i.e. forming chelate complexes. For instance, Cu^{2+} is coordinated by oxalic acid and form strong chelate complexes (CuA) (Perrin, 1979). Oxalic acid contains two carboxylic groups which can be deprotonated, and can thus be symbolised H_2A.

$$Cu^{2+} + H_2A \leftrightarrow CuA\,(aq) + 2H^+ \qquad (7\text{-}47)$$

A highly significant component of NOM with respect to pH buffering and metal complexation is humic substances (Tipping, 2002). Humic substances include both residues of decaying organic matter and complex substances that were synthesized during the decay process. Humic substances are highly stable and decompose very slowly. Humic substances are categorized into three distinct groups on the basis of their solubilities: humins, humic acids, and fulvic acids. Humins are not soluble in water at any pH. They have the highest molecular weight, the highest carbon content and the lowest oxygen content of the humic substances. Humic acids are not soluble in water under acidic conditions, but are soluble in alkaline solutions. They are the major extractable component among humic substances. Fulvic acids are soluble in water at all pH values. They have the lowest molecular weight and carbon content of the three humic substances, but contain more oxygen. Although NOM is a heterogeneous mix of different organic substances their acid/base behaviour and metal complexing reactions can be described by models where the organic component is represented by a dicarboxylic acid (H_2L) (Lövgren and Sjöberg, 1989). Accordingly, pH dependent association of Cu(II) to NOM in solution can be formulated:

$$Cu^{2+} + H_2L \leftrightarrow CuL(aq) + 2H^+ \qquad (7\text{-}48)$$

It is known that various bacteria and other microorganisms exude powerful chelate forming substances for the acquisition of iron for metabolic processes (Lewis et al., 1995). These chelators, termed siderophores, will stabilize ferric iron and prevent its precipitation from solution. By definition, siderophores are low molecular weight organic molecules with a high affinity for ferric iron. Various bacteria, fungi and algae have been observed to produce siderophores. These molecules are the products of biosynthesis and supply iron to cells, where ambient iron levels regulate their activity, such that siderophores are synthesized in times of low-iron stress and repressed in high-iron environments. Thus, siderophore production by bacteria would seem rather unlikely in acidic mine wastes, where dissolved ferric iron concentrations are relatively high. However, in near-neutral pH mine tailings where ferric iron solubility is very low siderophore production by bacteria and other microorganisms would be expected.

Precipitation of secondary sulphide minerals

Type B metal ions may be immobilised from anoxic porewater in tailings by forming secondary metal sulphides. This can occur as a result of two different processes: the precipitation of metals with dissolved hydrogen sulphide (H_2S/HS^-), and replacement reactions on existing sulphide phases.

Hydrogen sulphide can be present in tailings porewater as the result of microbial sulphate reduction (see Chapter 9) or the acid dissolution of acid–soluble sulphides such as pyrrhotite and sphalerite:

$$ZnS(s) + 2H^+ \rightarrow Zn^{2+} + H_2S(aq) \qquad (7\text{-}49)$$

Regardless of its origin, dissolved hydrogen sulphide in solution may then precipitate as a metal sulphide (MeS):

$$Me^{2+} + H_2S(aq) \rightarrow MeS(s) + 2H^+ \qquad (7\text{-}50)$$

where Me^{2+} is a divalent metal such as Cu^{2+} or Zn^{2+}.

In addition to the precipitation of metal ions with dissolved H_2S, secondary metal sulphides may also form by the replacement of metal ions in primary sulphides by ion exchange:

$$Cu^{2+} + ZnS(s) \rightarrow Zn^{2+} + CuS(s) \qquad (7\text{-}51)$$

This process occurs with the replacement of a more soluble metal sulphide (e.g. sphalerite, ZnS) with a less soluble phase (e.g. covellite, CuS). This replacement reaction has been implicated for the formation of secondary covellite below the zone of active oxidation in a number of tailings studies (Blowes and Jambor, 1990; Holmström et al., 1999; Holmström et al., 2001).

Arsenic sulphides, like orpiment (As_2S_3), realgar (AsS) and arsenopyrite (FeAsS) have been proposed as secondary minerals in anoxic sediments and other environments with reducing conditions.

$$2As^{3+} + 3FeS \rightarrow As_2S_3(s) + 3Fe^{2+} \qquad (7\text{-}52)$$

There have been a number of studies of mine tailings that have indicated that metal substitution occurs in metal sulphides. Investigations by Holmström et al. (2001) and Müller et al. (2002) have indicated that an enrichment in As, Cd, Cu, Ni and Pb have occurred below the oxidation front, and have attributed this process to either adsorption or solid–solution substitution. Müller et al. (2002) and Al et al. (1997) demonstrate that this enrichment is concentrated to the mineral surface, and is thus a secondary enrichment that can be either attributed to surface complexation or solid–solution substitution.

This substitution reaction has been observed in the Laver impoundment (Holmström et al., 1999). It has also been observed in the Heath Steele (Boorman and Watson, 1976) and Waite Amulet tailings (Blowes and Jambor, 1990) in Canada, where copper substitutes for Fe and Zn in pyrrhotite and sphalerite, respectively. Covellite is a product of the reactions.

It should be noted that the only reported occurrences of metal substitution in sulphides is for Cu substitution in sphalerite and pyrrhotite (confirmed by microscopy), and Ag substitution in pyrite. The retention of other metals in tailings has been attributed to adsorption processes.

Precipitation of secondary iron(III) solid phases

In limited supply, virtually all O_2 available is consumed by the oxidation of the most easily oxidised component, i.e. sulphide/disulphide is oxidised to sulphate. Hence, the ferrous iron remains unoxidised, and the chemical composition of the pore water in tailings is characterised primarily by its high concentrations of Fe^{2+} and SO_4^{2-}. Also, high levels of alkali and alkaline earth metals, i.e. Na^+, K^+ Ca^{2+}, Mg^{2+}, are commonly found as a result of acid consuming weathering of carbonate and silicate minerals. Once exposed to atmospheric conditions the discharging groundwater Fe(II) is oxidised to Fe(III), which is readily hydrolysed and precipitated as oxyhydroxides or hydroxysulphates. In waters with high sulphate concentrations and low pH iron hydroxysulphates are commonly formed of which jarosite $(H,Na,K)Fe_3(OH)_6(SO_4)_2$ and schwertmannite $(Fe_8O_8(OH)_6SO_4)$ are the most frequently reported phases (Bigham and Murad, 1997; Herbert, 1996; Bigham and Nordstrom, 2000). While jarosite is formed under strongly acidic conditions ($pH<\approx 2.5$), schwertmannite precipitates in slightly less acidic waters. Based on laboratory studies Bigham et al. (1996) suggested that there is an optimum pH range for schwertmannite precipitation of $2.8<pH<3.2$.

With increasing pH the sulphate ions are outcompeted by hydroxide ions, and oxyhydroxides are formed, primarily ferrihydrite ($Fe_5O_7OH\cdot 4H_2O$) and goethite (α-FeOOH). More rarely observed secondary Fe(III) oxyhydroxides are lepidocrocite (γ-FeOOH) and hematite (α-Fe_2O_3). It should be noted that there is no sharp borderline between the regions of stability for the different secondary phases (Bigham and Murad, 1997).

Mixtures of the different minerals are often observed, partly due to transformation processes to thermodynamically more stable minerals. During the course of time, the hydrous hydroxides and hydroxysulphates will eventually be transformed into more crystalline phases. For iron it has been shown that goethite is the most common final alteration product for both hydrous hydroxides and hydroxysulphates, c.f Figure 9-1 (Bigham et al, 1992). The transformation is supported by the findings of Peine et al.(2000) for an acidic lake where schwertmannite was suggested to precipitate, sediment and transform to goethite in the sediments. The transformation of schwertmannite is also evident in that goethite is often associated with findings of schwertmannite (Karathanasis and Thompson, 1995; Bigham et al., 1996). Thus, the mineralogy at a particular site is to some extent depending on the time span elapsed since the onset of oxidation. The phase transformation process results in an acid producing replacement of SO_4^{2-} in the solid by OH^- ions according to reaction (7-53).

$$Fe_8O_8(OH)_6(SO_4)\ (s) + 2\ H_2O \rightarrow 8\ FeOOH(s) + SO_4^{2-} + 2\ H^+ \qquad (7\text{-}53)$$

Jönsson (2003) demonstrated by XRD analysis and by following the base consumption that the transformation kinetics is dependent on solution pH. As can be expected from Equation 7-53, the transformation is favoured by an increase in pH. The release of SO_4^{2-} was found to be linear with pH, though time dependent.

Precipitation of oxides, hydroxides, carbonates and sulphates with other metals than Fe(III)

The substantial hydrochemical gradients appearing within deposits of sulphidic mining waste under oxidation as well as in downstream areas do also offer conditions for precipitation of mineral phases containing other metals than iron. Similar to Fe(III), Al(III) forms in acidic environments with high sulphate concentrations hydroxysulphate phases containing a range in Al:SO_4 molar ratio from 1 to 4, e.g. jurbanite ($Al(OH)SO_4\cdot 5H_2O$), alunite ($KAl_3(OH)_6(SO_4)_2$) and basaluminite ($Al_4(OH)_{10}SO_4\cdot 5H_2O$) . Their crystallinity is generally poor and the solubility low. Nordstrom and Alpers (1999) argue that the Al solubilty regulating role of hydroxysulphates is limited to pH values below the first hydrolysis constant of Al^{3+} (pK = 5.0).

Above this value the Al concentration in solution appears to be regulated by microcrystalline gibbsite ($Al(OH)_3$) and amorphous aluminiumhydroxide.

The hydroxides and sulphates of Fe(II) are much more soluble than those of Fe(III). $Fe(OH)_2(s)$ is rarely observed in nature. Ferrous sulphates, such as siderotil ($FeSO_4·5H_2O$) and melanterite ($FeSO_4·7H_2O$), have been observed in small amounts in studies of dried tailings (Blowes and Jambor, 1990). Under certain circumstances melanterite is formed in significant amounts (Frau, 2000). With partial oxidation, the soluble Fe(II) sulphate salts may be converted to hydroxysulphates, e.g. copiapite ($Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2·20H_2O$) (Bigham and Nordstrom, 2000).

When solutions rich in Fe(II) encounters highy alkaline waters under slightly oxidising conditions a fraction of Fe(II) can be oxidized (Nordstrom and Alpers, 1999). The layered Fe(II,III) hydroxide formed under such circumstances has a greenish colour, and is therefore commonly known under the name “green rust”. Green rusts contain water and anions such as CO_3^{-2}, SO_4^{-2}, and Cl^- in the interlayer (references in Williams and Scherer, 2001; Zachara et al., 2002). Since the material has a low stability, and has been only poorly characterised, it has not been recognised as a mineral. In the laboratory green rusts are synthesized by air oxidation of ferrous hydroxide. They have also been reported as biomineralization products of ferrihydrite and lepidocrocite under anoxic conditions. Just as ferrihydrite is a metastable phase to both goethite and hematite, green rusts are metastable to magnetite and siderite. Green rusts are considered to be very strong reductants, presumably due to their high Fe(II) content (Génin et al., 2001).

The generally high concentration of sulphate ions in mine drainage facilitates precipitation of sulphate and hydroxysulphate phases also for other metal ions, such as Cu(II) (Alpers and Nordstrom, 1991; Nordstrom and Alpers, 1999), Pb(II) (Blowes and Jambor, 1990) and Zn(II) (Lin, 1996). Examples of sulphate minerals found in oxidised tailings are anglesite ($PbSO_4$) and chalcanthite ($CuSO_4·5H_2O$) (Ostergren et al., 1999; Dold and Fontbote, 2001). Mixed metal sulphates of melanterite type (Fe^{II},Zn,$Cu(SO_4)·7H_2O$) have also been reported by Alpers et al. (1994). Ostergren et al., (1999) reported that the lead speciation in acidic tailings (pH 2-4) from Leadville was dominated by plumbojarosite ($Pb[Fe_3(SO_4)_2(OH)_6]_2$) with minor contributions from plumboferrite ($PbFe_4O_7$). In contrast, the carbonate-rich Hamms tailings (pH 7-8) was dominated by adsorbed Pb(II) with secondary contributions from pyromorphite ($Pb_5(PO_4)_3Cl$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (Ostergren et al., 1999).

A potentially important secondary mineral is siderite, $FeCO_3(s)$. In a carbonate rich tailings deposit or downstream-situated soil, dissolved Fe^{2+} may, from a thermodynamical point of view, react with carbonate ions to precipitate siderite. This process is of particular interest since it would offer a mechanism for detaining the release of ferrous iron released from the oxidation zone, thus reducing the amount of latent acidity reaching the recipient, at least temporarily. According to http://www.mindat.org/ siderite is often found in sedimentary deposits with a biological component, such as shales, clays and coal beds, which suggests that the siderite is biogenically created under low-oxygen and low-Eh conditions. Siderite is also found e.g. as a gangue mineral in hydrothermal deposits. In natural sediments, siderite is formed under hydrothermal, anoxic conditions in contact with e.g. galena, sphalerite, chalcocite and chlorite, or in organic, anoxic sea sediments. However, siderite formation has been observed in the vicinity of iron ores in the bedrock e.g. in the Mossgruvan mine in Sweden (Spicar, 1995). Modelling studies where siderite may form has been reported in e.g. Wunderly et al. (1996) and Mayer et al. (2003). Field observations within MiMi show that the iron concentrations in the tailings pore water are far higher than what would be expected from equilibrium with siderite when calcite is present. Slow kinetics of precipitation, indicating a rate eight orders of magnitude lower than the corresponding rate for calcite, has been reported (Jimenez-Lopez and Romanek, 2004) which may explain this discrepancy. The formation of siderite should therefore probably not be considered a significant sink for ferrous iron under the conditions observed in mine wastes.

The formation of other secondary carbonates may also be important mechanisms regulating the release of metals from the deposits, e.g. smithsonite ($ZnCO_3$), malachite ($Cu_2(OH)_2CO_3$) and cerrusite ($PbCO_3$). However, the solubility of the carbonate minerals is strongly pH-dependent, and siderite, smithsonite etc. can only potentially regulate the aqueous metal concentrations under neutral and alkaline conditions as illustrated in Figure 7-14.

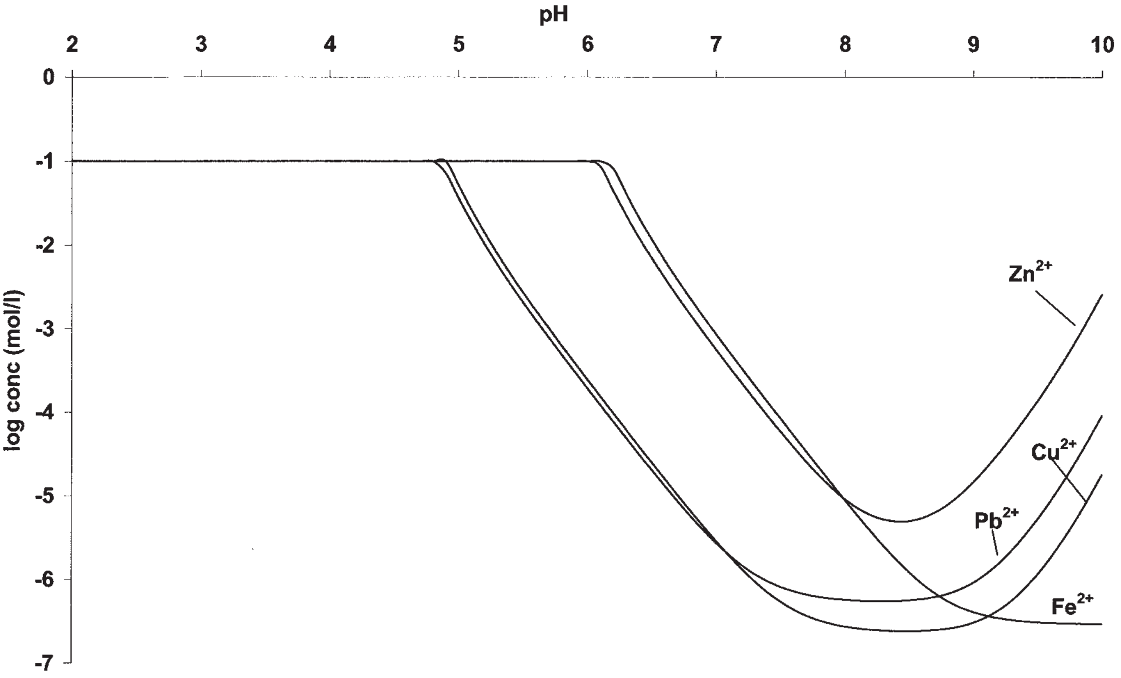


Figure 7-14. Calculated solubility of carbonates of Cu(II), Fe(II), Pb(II) and Zn(II) in equilibrium with 0.4 ppm CO_2 at atmospheric pressure. Calculations are performed using the computer code WinSGW (WinSGW, 2004).

The solubility of solid metal carbonates is strongly coupled to the solution speciation. By forming different complexes in solution the solubility can be enhanced with many orders of magnitude. The increase in metal ion concentration at pH >9 in figure 7-14 is explained by the formation of carbonate complexes in solution. This can be seen in distribution diagrams for Pb(II) and Cu(II) in Figures 7-15 a and b.

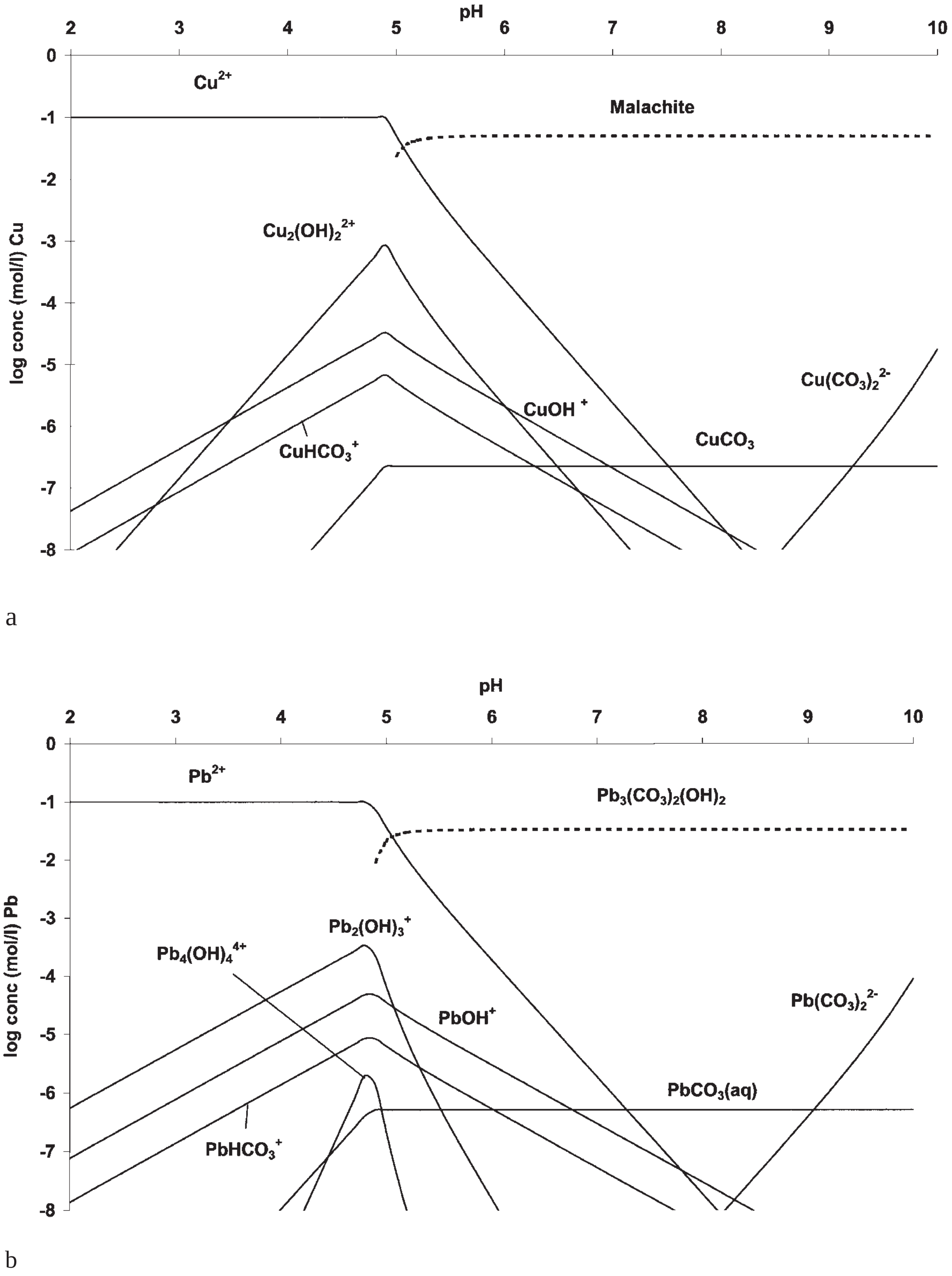


Figure 7-15 Calculated distribution of Cu(II) (a) and Pb(II) (b) calculated for $[Me]_{tot}$ = 0.1 mol dm^{-3}; $[SO_4^{2-}]_{tot}$ = 10 mmol dm^{-3} and PCO_2 = 0.00035 atm.

Concentrations of calcium, magnesium, sodium and potassium are typically in the range of tens to hundreds of milligram per litre (Blowes and Jambor, 1990; Öhlander et al., 2001). Although a major portion of these metals generally escapes the deposits through groundwater discharge, their solubility is in many cases limited by precipitation of secondary salts, e.g. gypsum ($CaSO_4{\cdot}2H_2O$) or by coprecipitation with Fe and Al (Blowes and Jambor, 1990; Nordstrom and

Alpers, 1999). The formation of hexahydrate ($MgSO_4{\cdot}6H_2O$) as an evaporite on bare tailings surface has been determined by XRD (Höglund et al., 2001b).

The solubility of most sulphates is rather high. Metals precipitated as evaporites during dry periods may readily dissolve during rain events and be flushed into the recipients. Their high solubility implies that the concentration of metals remaining in solution is high. Exceptions are sulphates of Ba, Sr and Pb, which have a lower solubility. Hence, their role for attenuation of most metals in a longer term is limited.

Precipitation of secondary phases with metals forming oxyanions

Arsenic is a common constituent of sulphide ores, present at percent levels in e.g. copper and lead ores. As(III) and As(V) exhibit different coordination properties. As(III) is a so called Type B, or “soft”, metal implying that it forms stable compounds with Type B, or “soft”, ligands, e.g. sulphide ions. On the other hand, the chemical properties of As(V) resemble those of P(V), i.e. it forms oxyanions in solution ($H_nAsO_4^{n-3}$). The speciation in solid-phase is of significance for the mobility and bioavailability of arsenic. Both redox states allow adsorption to mineral surfaces to occur, but with different affinities to different types of minerals. Sluggish transformation between As(III) and As(V) often allows both states to be present simultaneously (Fergusson, 1990). The mobility and bioavailability of As in precipitates is generally expected to be lower than for adsorbed arsenic. However, these properties are related to the solubility and stability of the As containing precipitates. The geochemistry of arsenic has attracted a very large interest during the last decade, not only because of its abundance in mine waste discharge but also as it has been identified as a major contaminant of groundwaters in inland or closed basins in arid or semi-arid areas and strongly reducing aquifers often derived from alluvium (Smedley and Kinniburgh, 2002).

Contaminants primarily existing in anionic form in water, such as arsenic, vanadium and chromium(VI), can be removed from the aqueous phase under oxic conditions by formation of solid phases with cationic metals, above all Fe(III), and adsorption to mineral surfaces. Examples of such Fe(III) arsenates are scorodite ($FeAsO_4{\cdot}2H_2O$) and pharmacosiderite ($K_2Fe_4(AsO_4)_3(OH)_5{\cdot}6.3H_2O$) (Smedley and Kinniburgh, 2002). Waychunas et al. (1995) has reported for an arsenical analogue of schwertmannite which contains up to 7 wt-% arsenic. It has also been reported that arsenate can substitute for sulphate in jarosite (Foster et al., 1998).

The high Ca/As ratios commonly found in acid mine drainage can result in Ca containing precipitates under alkaline conditions, like $Ca_4(OH)_2(AsO_2){\cdot}4H_2O$, $Ca_5(AsO_4)_3OH$ (arsenate apatite), and $Ca_3(AsO_4)_2{\cdot}3\frac{2}{3}H_2O$ (Bothe and Brown, 1999). However, the solubility of these phases was found to be rather high. Only at pH > 9 concentrations less than 10 mg/l were obtained. In experiments with $Ca_3(AsO_4)_2{\cdot}3\frac{2}{3}H_2O$, Bothe and Brown (1999) observed As concentrations in the range 490-820 mg/l despite high Ca concentrations (320 – 410 mg/l).

It has also been found that arsenate ions are able to replace up to half of the total sulphate in the structure of schwertmannite (Fukushi et al., 2003). The presence of arsenate significantly inhibited the transformation of schwertmannite to goethite. Gieré et al. (2003) have observed precipitation of As as amorphous non-stoichiometric Fe-sulphoarsenates from acid pore waters in oxidised tailings containing very high levels of sulphate (190 g/l), iron (57 g/l) and arsenic (22 g/l).

In comparison to other oxyanion-forming elements, As has a relative mobility over a wide range of redox conditions (Smedley and Kinniburgh, 2002). Selenium is mobile as selenate (SeO_4^{2-}) under oxidising conditions but is immobilized under reducing conditions either due to the stronger adsorption of its reduced form, selenite (SeO_3^{2-}) or due to reduction to elemental Se. Similarly, chromium is mobile under oxidising condition as Cr(VI) oxyanion species. Under reducing conditions Cr forms cationic Cr(III) species and behaves like other trace cations, i.e. is relatively immobile at near-neutral pH values due to low solubility of its hydroxide and also due to adsorption to mineral surfaces. Other metals that forms oxyanions such as Mo (molybdate) and V (vanadate), also appear to be less mobile under reducing conditions. In sulphur rich, reducing environments, many of the trace metals also form insoluble sulphides. Arsenic is distinctive as it is relatively mobile under reduced conditions.

Sorption processes

Besides by the incorporation of metal ions in solid matter through precipitation of secondary minerals, the solubility and mobility of trace metals are in many natural water bodies regulated by sorption processes at mineral/water-interfaces. In fact, the precipitation of solid matter involves attachment of substances in solution with the particulate phase. Metal ions may be adsorbed to mineral particles under both oxic and anoxic conditions, although the substrate to which they adsorbe may vary. In anoxic tailings sulphide minerals are stable and can attract ions of mainly Type B metals. Under oxic conditions oxides, hydroxides and hydroxysulphates mainly of Fe(III) but also of Al(III) and Mn(III,IV) are present as coatings on parent mineral particles and in some cases also as massive deposits of secondary precipitates. These minerals have a well documented ability to act as adsorbents of ionic compounds. A third group of minerals ubiquitous in natural systems and active sorbents are primary and secondary (alumino)silicates. In surface waters, trace metal solubilities are often regulated by suspended and colloidal matter. In this section, sorption processes at sulphidic and oxidic minerals will be briefly summarised.

Sulphide minerals

Sulphides of other metals than Fe

It is well known from mineral processing that Cu^{2+} is able to substitute Zn^{2+}, Fe^{2+} and Pb^{2+} ions at the surface of sphalerite (ZnS), pyrrhotite ($Fe_{1-x}S$) and galena (PbS), respectively. This phenomenon is widely used to facilitate the adsorption of short-chain thiol collectors to these minerals in flotation (Finkelstein, 1996). The mechanisms behind Cu(II) activation of sulphide minerals is scope for debate. Some researchers have suggested that covellite (CuS) is the activation product, while others have found evidences for formation of chalcocite (Cu_2S) (Finkelstein, 1997). In a study using X-ray Photoelectron Spectroscopy (XPS) coupled to Ar-bombardment etching penetration of Cu into the surface of Cu activated sphalerite was demonstrated (Prestidge et al., 1994). Kartio et al. (1998) suggested that activation at pH 9.2 in absence of oxygen results in a CuS-like product in which the copper is in the Cu(I) state and the formal charge of sulphur is -1. This mechanism can be represented by the following proximary adsorption reaction

$$xCu^{2+} + yZnS \leftrightarrow (y-x)ZnS \cdot Cu^{+}S^{-} + xZn^{2+} \qquad (7\text{-}54)$$

In aerated solutions evidences were found for formation of Cu polysulphides. They also showed that less copper was taken up under oxygenated conditions. Gerson et al. (1999) concluded from spectroscopic studies that adsorbed Cu(II) was reduced to Cu(I) accompanied by the oxidation of three neighbouring sulphide ions to an oxidation state of approximately -1.5.

An important implication of the findings from the above mentioned studies of sulphide activation is that the adsorption of Cu(II) occurs at a surface coverage exceeding a monolayer of metal ions by far and that secondary sulphides may be formed. This in turn leads to a situation where it is difficult to quantify the sorption capacity of sulphide minerals in mine waste for predicitve purposes.

Pyrite (FeS_2) and other sulphides containing Fe

Of the iron containing sulphides, pyrite is the best-studied mineral with respect to metal ion adsorption. In an investigation of divalent metal ion adsorption to pyrite Kornicker and Morse (1991) found that there was a rather small difference in affinity between the different metal ions and the pyrite surface. Adsorption strength increases in the order:
$Zn^{2+}<Ca^{2+}<Ni^{2+}<Mn^{2+}<Cd^{2+}<Co^{2+}$.

The adsorption of Zn(II) was weak even from weakly alkaline solutions. The metal ion sorption shows a pH dependence similar to sorption to Fe, Mn and Al oxyhydroxides (c.f. Dzombak and Morel, 1990). However, the pH range within which metal ions are adsorbed is shifted to higher values in the case of pyrite than for e.g. ferrihydrite. Although their attempt was to establish equilibrium models for surface complexation of the metal ion it was found difficult to attain equilibrium-like conditions with stable metal ion concentrations in the experiments. This may indicate that uptake processes are accompanied by transformation or migration processes. On the other hand, Wang et al. (1989) found that adsorption of Cu^{2+} on pyrite does not involve exchange with lattice cations, which was interpreted as that it was the Cu(II) hydroxide that was adsorbed.

In another study involving pyrite, Voigt et al. (1994) showed that while the adsorption of Cu(I) is independent on pH, Cu(II) is mainly adsorbed at high pH with a peak at pH 9. Also, the adsorption kinetics was found to be faster for Cu(I); it took only 2 minutes for Cu(I) to reach its maximum density at the surface at pH 5. Adsorption at pH 10 was significantly slower.

From electrochemical measurements Nicol (1984) concluded that copper activated pyrrhotite and galena had a covellite-like surface and that Cu(II) adsorbed onto pyrite caused oxidation of disulphide ions at the surface to elemental sulphur.

Arsenic sorption to sulphide minerals

The association of arsenic to sulphide minerals concerns mainly As(III), but also As(V) species may be adsorbed. In a study of sorption of arsenite on pyrite and troilite (FeS) using synchrotron based X-ray absorption spectroscopy (XAS), Bostick and Fendorf (2003) concluded that a FeAsS-like precipitate is formed in slightly sulphidic solutions under consumption of the iron sulphide phase according to reactions (7-55) and (7-56). The authors also suggested that As_2S_3 is formed in highly sulphidic zones.

$$3FeS + As(OH)_3^0 \leftrightarrow FeS_2 + FeAsS + Fe(OH)_3 \qquad (7\text{-}55)$$

$$7FeS_2 + 2As(OH)_3 \leftrightarrow 3FeS_4 + 2\,FeAsS + 2Fe(OH)_3 \qquad (7\text{-}56)$$

The uptake of As(III) showed a pH dependence typical of cation adsorption, i.e. minimal sorption at low pH and increasing uptake with increasing pH. The pH at which half of the As(III) was sorbed was slightly below pH 8 in an experiment where 55 µmol/l of As(III) was adsorbed on 1g/l of FeS. For FeS_2 the corresponding value was between pH 4.5 and 5. The adsorption maximum was found to be 5.6 $\mu mol/m^2$ for pyrite and 4.4 $\mu mol/m^2$ for troilite.

As(III) showed cationic behaviour also when the uptake to galena (PbS) and sphalerite (ZnS) was studied (Bostick et al., 2003). The affinity to both minerals appeared to be rather similar, with half of the arsenite adsorbed at pH close to 6. Based on XAS data the authors suggested formation of polynuclear surface complexes, such as $As_3S_3(SH)_3$, according to e.g. reaction (7-57).

$$3 \equiv MeSH + As(OH)_3 \leftrightarrow 3 \equiv MeOH + \tfrac{1}{3} As_3S_3(SH)_3 + H_2S, \qquad (7\text{-}57)$$

where ≡MeSH is a sulfhydryl group at the mineral surface. In the presence of oxidising agents and synchrotron light the $As_3S_3(SH)_3$ complex was unstable and converted readily into As(V). This phenomenon is a likely explanation of the findings of Farquhar et al. (2002) who reported that both As(III) and As(V) was coordinated to pyrite and mackinawite (FeS) through As-O-S bonds.

As(III) and As(V) sorption to freshly precipitated mackinawite, FeS_{am}, was studied by Wolthers (2003). In the case of arsenate the following sorption reaction was postulated:

$$\equiv FeSH_2^+ + AsO_3(OH)^{2-} \leftrightarrow \equiv FeS\text{-}O\text{-}As(OH)_3^- \qquad (7\text{-}58)$$

Fe(III) oxides, hydroxides and oxyhydroxides

The precipitation of secondary iron solid phases induced by the oxidation of Fe(II) forms basis for sorption processes. Field studies have demonstrated the significance of metal(hydr)oxides for the retention of metals in soils contaminated by acid mine drainage (Herbert, 1996 and Lin, 1996). The regulating role of iron (hydr)oxides in rivers receiving acid mine drainage has been described by, e.g., Johnson (1986), Kimball et al. (1995) and Munk et al. (2002). In some cases, the mobility of contaminants can be enhanced due to adsorption to mobile colloidal particles (McDowell-Boyer, 1992). The large adsorption capacity of Fe(III) oxyhydroxides with respect to both cations and anions is well documented (Stumm, 1992; Cornell and Schwertmann, 1996).

The pH of the water determines the extent to which contaminants are retained. At low pH the tendency for metal cations to be adsorbed is low, while anions like arsenate and sulphate are more strongly associated with mineral surfaces. In heavily limed areas of mining waste deposits with alkaline conditions carbonate minerals may be formed.

Silicates

Silicate and aluminosilicate minerals, such as quartz and feldspars, which are common constituents of gangue minerals are also capable of adsorbing metal ions. Quartz exhibits negatively charged surfaces within a very wide pH-range (Stumm, 1992). The pH_{zpc} is close to 2. This allows cationic metals to be adsorbed, but anions, e.g. arsenate and sulphate are only very weakly adsorbed.

Clay minerals, a group of secondary aluminosilicates with a layered structure, exhibit often a permanent negative charge at the planes as a result of substitution of Si(IV) ions with Al(III) or Al(III) with divalent cations such as Mg(II) in the crystal lattice. This offers possibilities for attachment of metal cations to the mineral surfaces in order to maintain charge-balance.

Surface complexation reactions

The distribution of ions between particle surfaces and the aqueous solution is strongly dependent on solution pH and is also influenced by the presence of complexing ligands in the solution. In general, adsorption of cationic species is favoured by increasing pH (Figure 7-16), whereas anions are more strongly bonded under weakly acidic and acidic conditions.

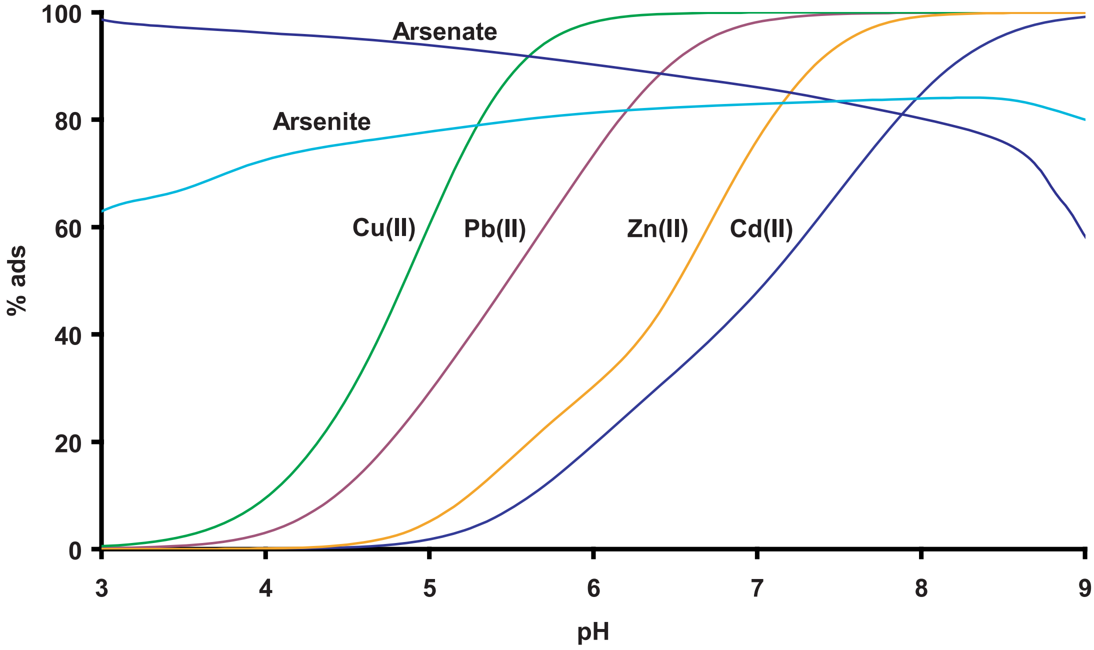


Figure 7-16 Illustration to the pH-dependence of adsorption of some metal ions to Fe oxyhydroxide (goethite). Data for Cu(II), Cd(II), Pb(II) and Zn(II) from Palmqvist et al. (1997) for As(III) from Lützenkirchen and Lövgren (1998) and for As(V) from Lützenkirchen and Lövgren (unpublished results).

Adsorption of ions can be described as complexation reactions taking place at specific binding sites on mineral surfaces. Such sites at metal (hydr)oxide surfaces are often referred to as surface hydroxyl groups, noted as ≡FeOH, where ≡ symbolises the bulk oxide phase, and Fe and OH denotes the metal and hydroxide ions at the surface. The surface sites on e.g. goethite (α-FeOOH) do not only react with metal ions but also protons, showing an amphoteric behaviour, as exemplified with in reactions 7-59 and 7-60

$$\equiv FeOH + H^+ \leftrightarrow \equiv FeOH_2^+ \qquad (7\text{-}59)$$

$$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+ \qquad (7\text{-}60)$$

As follows of reaction (7-61) the adsorption of metal ions involves a competition with hydrogen ions for the binding sites, which implies that cation adsorption is favoured by increasing pH. The rather narrow pH-range within which the vast majority of metal ions are being transferred from the aqueous solution to the particle surface is element specific and also depending on the metal to surface site ratio.

$$\equiv FeOH + Cu^{2+} \leftrightarrow \equiv FeOCu^+ + H^+ \qquad (7\text{-}61)$$

The surface group also provides an atom that can accept electrons, i.e., the metal ion. This enables complexation with donor groups (ligands, L) in the solution, reaction 7-62. Charged species can also be taken up by electrostatic attraction to surface sites of opposite charge, e.g. anions may be adsorbed to surface sites that are positively charged as a result of proton uptake ($\equiv FeOH_2^+$). Hence, anion sorption is favoured by low pH.

$$\equiv FeOH + L + H^+ \leftrightarrow \equiv FeL^+ + H_2O \qquad (7\text{-}62)$$

The aqueous speciation of many transition elements is dominated by interaction with natural organic compounds. Solid organic matter can contribute to the attenuation of metals by sorption. In natural systems, the adsorption of metal ions to mineral surfaces is not only governed by pH and concentrations of adsorbent and adsorbate but also by the presence of natural organic matter (NOM), such as humic substances, as organics can both adsorb to the surface and form soluble complexes with metal ions. Depending on the hydrochemical conditions, high concentrations of NOM can result in increased sorption. However, high NOM concentrations can also result in a decreased sorption due to a pronounced aqueous complexation with metal ions. Enhanced sorption of metal ions under weakly acidic conditions can be explained by electrostatic interactions and/or by formation of Type B ternary surface complexes, in which metal ions (Me) are associated to mineral surfaces (≡S) by coordination to adsorbed organic compounds (≡S-Org-Me). Ternary surfaces complexes of Type A, in which the organic matter adsorbs by binding to metal ions directly coordinated to the mineral surface (≡S-Me-Org) may also contribute to increased adsorption of metal ions.

Specific for Soil Cover

Biogeochemical processes that are specifically related to the presence of a soil cover are associated with the production and degradation of organic matter. It is assumed that a soil cover will behave as a typical soil profile developing in glacial till in northern Sweden. It is intended that lower forms of vegetation will be established on the cover to promote its long-term stability. Organic matter degradation will occur in the soil profile, which is mediated through the aerobic respiration of soil microorganisms. This results in the production of mobile humic substances and CO_2. With the production of humic substances, metals such as ferric iron and aluminium bind to these organic compounds (e.g. humic acids) during their downward transport in the profile. The metals and organic material subsequently precipitate further down in the profile; this is the process of podsolisation. In normal podsol soils, very little organic matter is mobilised below the accumulation zone, so it is unlikely that significant concentrations of organic matter will enter into the underlying tailings.

Carbon dioxide production in the soil profile is the sum of degradation processes and CO_2 production from roots; this production is termed soil respiration. Carbon dioxide levels can reach up to several percent in the soil profile, and oxygen concentrations are consequently less than the normal atmospheric concentration of 21%. Therefore, relative to a tailings deposit without a soil cover, the presence of organic matter in the soil cover will lead to a lower oxygen concentration above the tailings surface and hence a lower oxygen diffusion into the deposit.

Specific for Water Cover

Biogeochemical processes that are specific for a water–covered impoundment are related to the growth of microorganisms and plants in the water column, and to the presence of a calcite–gypsum slurry on the tailings surface.

Microorganisms such as diatoms and blue-green algae will probably flourish in the water–covered impoundment, when pH levels approach near–neutral conditions. As in natural lakes, photosynthesis may be an additional source of oxygen in the upper water layers. In addition, plants will also be established in the water cover. With time, dead organic matter will accumulate on the tailings surface. These sediments will function as a barrier to the diffusion of oxygen to the underlying tailings, by gradually increasing the distance over which oxygen must diffuse, and also by consuming oxygen through the aerobic respiration of microorganisms. In water covers that are exceptionally deep, such as in the case of tailings disposal in pit lakes, anoxia may occur in the deep water when oxygen is consumed by organic matter degradation. In these systems, sulphate reduction may occur and lead to the precipitation of metals present in the water column.

When liming is used to neutralise acidity in the water column, a layer of calcite-gypsum slurry may be present on the surface of the inundated tailings. This is the case with impoundments 3 and 4 in Kristineberg (see Chapter 6). Relatively thick accumulations of this slurry may form, and provide a barrier for the diffusion of oxygen to the underlying tailings. However, the slurry may also constitute a future source of e.g. sulphate due to dissolution of gypsum when the liming operation is halted and the water quality changes in response to this.

7.7 *Mobilisation, transport and attenuation of dissolved substances in tailings*

In this section the mobility of metals within the deposit is discussed. Detailed information on the numerical treatment of these processes is given in Chapter 11.

Specific for tailings covered by soil

Although present in significant amounts as Fe(III) oxyhydroxides in the oxidised layer, the major part of the iron content of pyrite, pyrrhotite and chalcopyrite leaves the deposit transported by the groundwater as Fe(II). Depending on the availability of O_2 and the residence time, fractions of this Fe(II) may be oxidised before the groundwater is exfiltrated and reaches surface waters.

Carbonate minerals may be formed under alkaline conditions, which may occur primarily in heavily limed areas of mining waste deposits. It has been shown that Cu(II) dissolved by oxidation of chalcopyrite ($CuFeS_2$) may be secondarily precipitated in a layer just below the oxidation front by interactions with pyrrhotite under formation of covellite (CuS) (Holmström et al., 1999).

Besides the above described precipitation processes contaminants may be attenuated by sorption onto the secondary phases as well as the parent waste material. Iron(III) oxyhydoxides and clay minerals are recognised to be efficient scavengers of both cationic and anionic compounds in water. It is also known that sulphide minerals can take up trace metals by ion exchange processes and phase transformation. In both cases, the pH of the aqueous phase determines the extent to which contaminants are retained. At low pH, the tendency for metal ions to be adsorbed is low, while anions like arsenate and chromate are more strongly associated with mineral surfaces.

In anoxic tailings, adsorption to sulphide minerals and replacement reactions on present sulphide minerals may play a particularly important role. The relative importance of different mineral phases is largely determined by the affinity of contaminants to the mineral surfaces and by the surface areas available for adsorption. The dominating sulphide mineral in most sulphidic waste deposits is pyrite. Pyrite has a documented ability to adsorb cationic metals, such as Ni(II), Cd(II) and Zn(II) from solution provided pH is in the near neutral range (Kornicker and Morse, 1991). The limiting surface density of adsorbed divalent metal ions on pyrite was approximately 14 µmol/g in their experiments, corresponding to 4.3 $\mu mol/m^2$. In a study of As(III) sorption to pyrite and troilite (FeS), Bostick and Fendorf (2003) observed a maximum As(III) adsorption to pyrite of 5.6 $\mu mol/m^2$ and the maximum adsorption to troilite was 4.4 $\mu mol/m^2$. The specific surface area of tailings from Kristineberg used in column experiments as analysed by N_2-adsorption according to the BET method was found to be 0.90 m^2/g (Axelsson, 2002).

To quantify the capacity of the mineral phases present in tailings to adsorb metal ions detailed information would be required on the mineral composition and on the surface properties of each of these phases. Since such information is largely lacking for most minerals, a rough estimate can be made based on a few simplified model assumptions. Firstly, it is assumed that pyrite can represent metal sorption to sulphides, as being the most significant sulphide mineral. Secondly, it is assumed that silicates can be represented by kaolinite, for which model parameters for surface complexation of trace metals are available. Finally, it is assumed that the tailings consist of silicates active in metal adsorption (73 %), sulphides (25 %) and other minerals (2 %). The surface area of eight tailings samples from seven locations at Kristineberg ranged from 0.2 to 10.1 m^2/g, with an average value of 2.96 m^2/g (Salmon and Malmström, 2004a). For the following estimates we assume the average value to be representative.

Density of wet tailings: 2320 kg/m^3
Density of dry tailings: 1870 kg/m^3
Porosity: 45 % (pores are saturated with H_2O: 450 kg)
Specific surface area of tailings: 3 m^2/g (average 2.96 m^2/g of BET-measurements on eight samples; Salmon and Malmström, 2004a)

Silicates (represented by kaolinite):
Fraction of minerals composed by silicates: 73%
Amount of silicates in 1.0 m^3 of tailings: 0.73 * 1 870 kg = 1 365 kg
Specific surface area of tailings: 3 m^2/g (Salmon and Malmström, 2004a)
Specific surface area of kaolinite: 14.7 m^2/g (Angove et al., 1997)
Density of metal bindning surface sites: 5.5 µmol/m^2 (Angove et al., 1997)
Amount of surface sites: 22 mol/m^3 (based on specific surface area of tailings)
110 mol/m^3 (based on specific surface area of kaolinite)

Sulphides (pyrite):
Fraction of minerals composed by pyrite: 25%
Amount of pyrite in 1.0 m^3 of tailings: 0.25*1 870kg = 467 kg
Specific surface area: 3 m^2/g (Salmon and Malmström, 2004a)
Density of metal binding surface sites: 4.3 µmol/m^2 (Kornicker and Morse, 1991)
Amount of surface sites: 6 mol/m^3

Amount of trace metals in tailings from impoundment 1 (Holmström et al., 2001)
Zn: 0.9 % of 1870 kg/m^3 = 17 kg/m^3 → 259 mol/m^3
Cu: 0.1 % of 1870 kg/m^3 = 1.9 kg/m^3 → 30 mol/m^3
Pb: 0.05 % of 1870 kg/m^3 = 0.9 kg/m^3 → 4.5 mol/m^3

Thus, the adsorption to silicate minerals can contribute to the retainment of trace metals such as Zn Cu, Pb, Cd and As. However, it is not possible at present to determine how much because of lack of information on the competition for sites between the different metals including ferrous iron. Also pyrite can contribute to metal adsorption, but to a smaller extent, according to the simplified calculation above. One should remember that the distribution of metal ions between mineral phases and the solution is strongly influenced by the hydrochemical conditions, above all pH. To fully utilise the metal binding potential of the different minerals residing in the tailings it is therefore critical that the solution chemistry can be maintained at such conditions that metal adsorption is favoured.

Complementary attenuation processes must be considered if the observed uptakes of trace metals from groundwater in tailings are to be fully explained (c.f. Holmström et al, 2001). Formation of secondary sulphide phases is likely to be significant in this context. As is described above, pyrrhotite and sphalerite are considered to contribute more to the latter process than pyrite. The capacity of tailings to form secondary sulphides is largely limited by the access to $Fe_{1-x}S$ and ZnS and also other sulphides with a relatively high solubility. As is reported in Table 5.3 the amount of sphalerite and pyrrhotite present in the tailings deposited in impoundment 1 at the Kristineberg mine is larger than the amount of chalcopyrite, galena and arsenopyrite. Thus, there is, at least a theoretical, possibility that anoxic dissolution and transformation of sulphide minerals can form basis for the observed removal of trace metals (mainly Cu, Pb and As) from the groundwater within the impoundment. However, there are few field evidences of metal sorption in unoxidised tailings, besides observations of covellite formation. Identification of secondary solid phases by X-ray diffraction (XRD) requires that a particular phase constitutes a substantial part of the sample studied. Mumme et al. (1996) report that depending on mineral assemblage, up to eight different minerals in sedimentary rocks can be determined with a detection limit of about 0.5 w-% using the Rietveld method.

During transport through the underlying till and peat, fractions of metals may be scavenged by sorption to silicate minerals and to soil humus. Transport of very small particles in the colloidal range that may act as carrier substances to which contaminants are sorbed must be considered as well. However, considering the often high concentration of dissolved contaminants in this type of system, colloidal transport can be assumed to be of minor importance for metal mobility.

Specific for flooded tailings

There is one important difference compared to the soil cover case. Most of the acidity generated at the oxidation front and the metals released there will diffuse the short distance upward to the water. To avoid forming very acid water in the dam the water turnover in the dam must be large to dilute and neutralise the acidity diffusing upward from the tailings.

The metals released will also diffuse upward into the water in the dam. They will therefore, not form secondary sulphide precipitates in the tailings to the same degree as in the soil cover case. However, if the neutralisation of the primary acidity and the equally large secondary acidity from the oxidation of the ferrous iron takes place in the dam, the ferric oxyhydroxides can adsorb the copper and lead. Zinc and arsenic will also be sorbed but to a lesser degree.

Phytoremediation

During the last decades one has paid a lot of interest in natural attenuation, in which one let the nature taking care of polluted environments. Due to the properties of plants to tolerate tuff environments and handle the metals they can be used in phytoremediation. Phytoremediation is defined as the use of green plants to remove, contain, or render environmental contaminants harmless (Cunningham and Berti, 1993). The most common phytoremediation techniques of heavy metals are: phytoextraction- metal accumulating plants are established on contaminated soil and later harvested in order to remove metals from the soil; rhizofiltration – roots of metal accumulating plants absorb metals from polluted effluents and are later harvested to diminish the metals in the effluent; phytofiltraton –similar to rhizofiltration but the whole plant, mainly submerged plants, accumulates metals: and phytostabilization – metal tolerant plants are used to reduce the mobility of metals, thus, the metals are stabilised in the substrate (Salt et al., 1995). One reason to use plants for remediation is the relatively low cost and maintenance requirements (Cunningham and Berti, 1993).

Phytoextraction is the most investigated method with the aim to clean soils, and high accumulator plants with high translocation of the metal to the shoot are promoting the cleaning (Greger and Landberg, 1999). It is also necessary with high biomass production, since it is a high amount of metals per ha in the harvested parts, mainly the shoot, which make this method effective. However, to be able to clean a highly polluted soil it will take several of hundreds of years and therefore this technique will not be of interest for mine tailings impoundments. On the other hand, a special case of phytoextraction is phytomining, where plants that hyperaccumulate metals, ending up in very high metal concentrations in the shoot are used. This method does not remediate the environment since the biomass of hyperaccumulators is low, but the method can be used to additionally get more metals out of the tailings.

Phytostabilisation may be a successful way to prevent the formation of AMD and stabilise the metals in the tailings (Tordoff et al., 2000). The plant roots should have properties to accumulate metals in the roots or excrete substances which trap free metal ions in the rhizosphere, preventing metal leakage to the surrounding water. In addition, plants with low shoot accumulation should be used to stabilise the elements in the tailings in order to reduce the metal dispersion though grazing animals or at leaf senescence. When plants are established on the water saturated mine tailings, an organic layer will eventually be formed on top of the mine waste. The organic layer would probably consume oxygen (due to the chemical and biological processes) and would contribute to reduce erosion due to wind and waves together with the plants. This may help to reduce the need for a high water table and raised impoundment walls.

Rhizo- and phytofiltration are able to clean already formed polluted water in a wetland system. To use this system efficiently it is necessary to have a high plant biomass to volume of water ratio. When using plants in phytoremediation not only the pollutants as such but also harsh environments, such as cold climate and low pH, could affect the plants. This is the case when dealing with some mining areas in Sweden. Submerged plants with their total plant body in AMD can therefore have problems to survive where the AMD has as low pH as 2.7 and high levels of iron compounds in form of goethite is covering the whole plant. Therefore, rhizofiltration with emergent plants seems to be more suitable in water cleaning of AMD.

Illustration: Wetland plants may grow in tailings and develop extensive root systems.

Synthesis – The fate of different contaminants within tailings deposits

The transport and fate of metals, metalloids, and non-metals in a tailings impoundment is influenced by a wide variety of biogeochemical, microbial, and physical processes. However, the performance assessment conducted within the MiMi programme has addressed this issue, and attempted to minimize the uncertainty in the quantitative significance of these processes. The results of these efforts are provided in detail throughout this report, while a summary of relevant processes, as evaluated by the MiMi programme, is provided below. In this synthesis, only the dominating processes are listed; other processes are considered of marginal importance to the fate of these different contaminants.

Table 7-3 Relevance of different processes for the attenuation of metals and metalloids in tailings deposits.

Process	Trace elements	Estimated relative importance	Cause of uncertainty in estimate
Secondary sulphide formation	Cu and Pb (and Cd?)	High	Amount of pyrrhotite available Front propagation rate
	Zn	Low	Little field evidence for formation. Zinc is released during consumption of sphalerite pH dependence unfavourable
	As	Speculative	Little field evidence. Orpiment seems to have low solubility, whereas realgar seems to be fairly soluble Possibly a surface complexation process (may be important)
	Fe	None	Iron is released – consumption of pyrrhotite
Adsorption to sulphides	Cu, As, Pb	Intermediate	Adsorption to pyrite has been inferred in Kristineberg and from other studies Uncertain if number of available sorption sites is sufficient to accommodate all released trace elements

Process	Trace elements	Estimated relative importance	Cause of uncertainty in estimate
Secondary precipitates	Cu (as sulphates or carbonates mainly)	Low	Carbonate content and pH, competition with secondary sulphide formation No conclusive identification in field
	Pb (as sulphates or carbonates mainly)	Potentially high	No conclusive identification in field
	Zn (as carbonate)	Medium	Carbonate content and pH No conclusive identification in field
	Zn (as hydroxo sulphates)	Low	Too soluble? No field observations
	As (as jarosites, arsenates or arsenites)	Medium – Low?	pH and concentrations of other components Long-term stability
	Fe (forming siderite)	Medium?	No conclusive evidence found in Kristineberg. Reported in literature. Extensive formation not likely since it would contradict the frequently observed high concentrations of iron in tailings pore water Would influence the release rate of latent acidity.
	Fe (forming SIPs)	Medium	Only limited precipitation expected due to oxygen deficiency. Remaining divalent iron constitutes a latent acidity.

Process	**Trace elements**	**Estimated relative importance**	**Cause of uncertainty in estimate**
Adsorption to SIPs	Cu, Pb, Zn, Fe	Low	Weak effect compared to other processes The available amount of SIPs in tailings is limited
	Cd	Low	Adsorption edge at high pH
	As	Medium – high	Strong affinity to SIPs, but the available amount of SIPs in tailings is limited Adsorption is stronger at low pH Possible competition with sulphate, phosphate and carbonate
Adsorption to silicate minerals	Cu, Pb, Fe, Zn	Low – medium	The amount of available adsorption sites may equal a sizeable fraction of the total trace element content of the tailings. Data regarding competition between different chemical elements for the surface sites renders this process uncertain at present
Adsorption to or complexation with NOMs	Cu and Pb	Potentially high	Strong organic ligands, e.g. siderophores, likely in very low concentrations
	Zn, Cd, Fe, As	Low	Fatty acids may occur in up to mM concentrations, but complexation is weak in comparison with sulphate Low TOC concentrations determined in tailings

7.8 Physical processes affecting the long term efficiency

Specific for soil cover

With respect to the efficiency in the long time perspective, it is important that the properties of the sealing layer do not change with time. The short-term efficiency of a dry cover can decrease in the long term as a consequence of different destructive processes that may cause cracks or other discontinuities in barrier layers. Such processes are erosion, frost action, drying, differential settlements, root penetration, digging animals and manmade intrusion.

Frost action

The efficiency of a soil cover can decrease with time as a consequence of different destructive processes that may cause cracks or other discontinuities in barrier layers. One of the most important processes is frost action.

Illustration: The annual average temperature is +0.7°C at Kristineberg. Field sampling during winter is trying.

Within the MiMi programme, the possible impact of frost action on the sealing layer properties has been investigated in terms of the effect from repeated freezing and thawing on the hydraulic conductivity of the till that constitutes the sealing layer. The investigations were performed in the laboratory using a permeameter set-up simulating stress conditions under the load from a protective cover in the field and one-dimensional freezing from above followed by thawing. Eight cycles of freezing and thawing, each followed by measurements of hydraulic conductivity were carried out (Carlsson and Elander, 2001). It was found that for well-compacted samples of the till used in the sealing layer, the hydraulic conductivity increased about ten times after a few cycles of freezing and thawing (from about $1 \cdot 10^{-9}$ m/s to about $1 \cdot 10^{-8}$ m/s). For samples compacted to a somewhat lower compaction rate, the initial hydraulic conductivity was about $1 \cdot 10^{-8}$ m/s and showed only minor changes with freezing and thawing. The difference in compaction rate tested was not very large – the samples with the lower initial hydraulic conductivities were compacted to 100 % and the samples with higher initial hydraulic conductivities were compacted to about 95 % of maximum as determined by Modified Proctor tests. Consequently, it was concluded that freezing and thawing may have a significant effect on the hydraulic conductivity of the sealing layer, but also that it is of utmost importance that the sealing layer is adequately compacted to reach the required low hydraulic conductivity.

A literature survey (Knutsson, 2004) indicated that for most fine-grained soils, the permeability changes during cyclic freezing and thawing appear to increase with increasing plasticity of the soil. However, when dealing with very highly plastic soils, such as sodium-bentonites or their respective bentonite-sand mixes, permeability increases were not encountered during cyclic freezing and thawing.

Experimental studies have also been undertaken to demonstrate whether freezing and thawing cause correspondingly dramatic effects on the water retention characteristics, which is of more concern for the sealing layer as a barrier for oxygen transport. Laboratory investigations show that no distinct effects of frost action can be observed with respect to the water retention characteristics of the sealing layer material. As shown in Figure 7-17, the water retention characteristics are similar for frozen and unfrozen samples. Further, the results imply that the natural heterogeneity of the till material may be of equal or greater importance of the water retention characteristics than the effects of frost. These results may be reasonable from a theoretical point of view, taking into account that the capillary force in a circular pipe is proportional to $1/r^2$ while the flow velocity in a circular pipe is proportional to r^4. Hence, it is probable that the effects of freezing and thawing on water retention characteristics are less expressed than the effects on hydraulic conductivity.

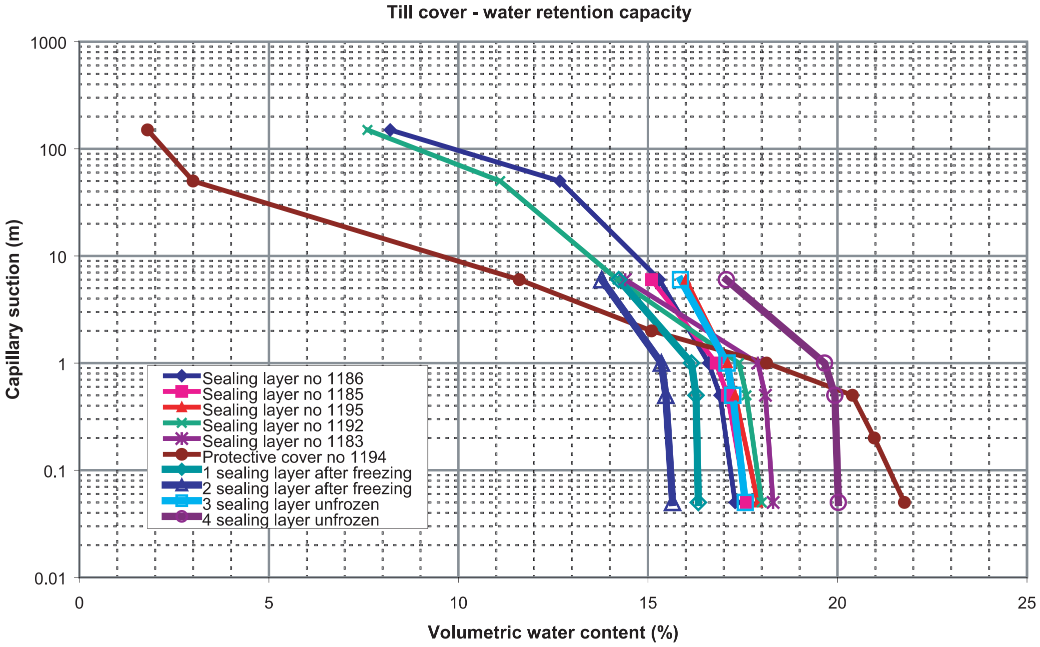


Figure 7-17 Water retention characteristics of the till cover on impoundment 1 in Kristineberg. The figure also shows the results of tests of the impact of frost in the water retention characteristics of the sealing layer.

Root penetration

From a literature survey of root penetration it is clear that roots from certain trees are able to penetrate to depths of up to 6 m below the ground surface (pine), if water is only available at this depth. However, a more “normal maximum depth” is about 2 m below ground surface (Köstler, 1968). To be able to penetrate into a soil, the roots must be able to penetrate into the pore structure. In fine-grained compacted soils, the pores are generally smaller than the root diameter and the roots must be able to induce a deformation in the soil to be able to penetrate. Studies of root penetration into compacted layers showed that roots generally do not penetrate into soils with a higher resistance than 3-5 MPa as measured with a penetrometer or a compaction corresponding to a load of 800 kPa (Eriksson, 1982). This is in accordance with other studies (e.g. Boone et al., 1994). These studies were performed with agricultural plants but are probably valid also for tree roots, as tree roots generally have a larger diameter and thus harder to penetrate into small pores. Consequently, studies on the development of tree roots showed that a compaction according to a load of 400 kPa significantly decreased the intrusion of roots (Wästerlund, 1985). Investigations reported by Ledin (1999), show that root penetration is difficult when the dry bulk density of the soil exceeds 1700 kg/m^3.

With respect to possible effects of processes mentioned above, the sealing layer should be protected primarily against frost action while the compaction that is applied during construction should be appropriate to protect from root intrusion in the sealing layer as long as no other processes (like e.g. frost action) act to decrease the rate of compaction.

Estimation of maximum frost depth

For dimensioning the protective cover thickness, it is essential to estimate the probable maximum frost depth in a long-term perspective. According to Knutsson (2004), the frost depth for bare ground can be estimated with a simplified equation based on a statistical approach:

$$X(t)_B = \alpha \sqrt{F} \qquad (7\text{-}63)$$

where:

$X(t)_B$ = frost depth in bare ground (m)

α = proportionality factor (m· degree day$^{-0.5}$)

F = frost index (degree days)

The proportionality factor depends on soil type and thereby represents the soil properties which influence frost depth, such as thermal conductivity and water content. From a large amount of observations of frost index versus frost depth for different soils, the following proportionality factors have been obtained (Table 7-4).

Table 7-4 Values of the proportionality factor from statistical analyses of observations of frost depth versus frost index.

	Proportionality factor , α (m / degree days$^{0.5}$)		
Soil type	Lower limit	Mean value	Upper limit
Sand	$4.7 \cdot 10^{-2}$	$5.2 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$
Coarse sand and gravel	$5.4 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$	$6.4 \cdot 10^{-2}$
Till	$4.9 \cdot 10^{-2}$	$5.5 \cdot 10^{-2}$	$6.2 \cdot 10^{-2}$
Coarse till (gravely and stony)	$6.8 \cdot 10^{-2}$	$7.3 \cdot 10^{-2}$	$7.8 \cdot 10^{-2}$
Silt (moderately frost heaving)	$4.2 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$	$5.3 \cdot 10^{-2}$
Silt (very frost heaving)	$3.8 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$
Clay	$3.4 \cdot 10^{-2}$	$3.9 \cdot 10^{-2}$	$4.6 \cdot 10^{-2}$
Organic clay (gyttja)	$2.1 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	$2.7 \cdot 10^{-2}$
Peat	$1.7 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$

The till that is used for the protective cover in Kristineberg is relatively fine-grained and classified as a silty-sandy till, with a silt and clay content of about 26 % and a sand content of about 60 %. With respect to the grain size distribution and the above observed values, it is estimated that the proportionality factor does not exceed $5.5 \cdot 10^{-2}$ m/degree days$^{0.5}$.

Frost indices can be calculated from observations of daily temperatures, which for Sweden is performed on a regular basis by SMHI (Swedish Meteorological and Hydrological Institute). From a series of observations comprising at least 100 years, the largest occurring frost indices during this period have been calculated and presented in e.g. *Handboken Bygg* as a function of geographical location. From this presentation, the largest occurring frost index during the observed period for the Kristineberg area is estimated at 1200 degree days.

From the estimates of proportionality factor and using the maximum frost index during the observed 100-year period, the frost depth in bare ground with silty-sandy till in the Kristineberg area can be calculated at 1.9 m below ground surface. However, it is not deemed probable that the maximum frost index will occur during a year without any snow cover, as a snow depth of about one metre normally develops in the area. To correct the calculated frost depth for a snow cover, equation 7-64 (Knutsson, 2004) can be used:

$$X(t)_S = X(t)_B - n \cdot S \qquad (7\text{-}64)$$

where:

$X(t)_B$ = frost depth in bare ground (m)

$X(t)_S$ = frost depth in snow covered ground (m)

n = the relationship between thermal conductivity for frozen ground and snow

S = mean snow depth (m)

The value for n is normally 2.5 but may vary within the interval 1.5-4.0 depending on the density and hardness (i.e. compaction) of the snow (Knutsson, 2004). This means that, during the coldest period, the relationship normally shows a high value as the snow is not compacted, and during the later period of the winter, when melting temporarily occurs, the relationship decreases.

Using equations 7-63 and 7-64 together with possible values for the proportionality factor α, the thermal conductivity relationship between frozen ground and snow and snow depth, frost depths can be calculated for different conditions as shown in Table 7-5.

The probability for the proportionality factor to reach its maximum value at the same time as the relationship between frozen ground and snow thermal conductivity reaches its minimum value is deemed to be small. It is even more unlikely that the snow cover will be thin during a winter when the frost index reaches its maximum value. Provided that the measurements of the frost index maximum can be considered to be representative for a longer period of time, it is considered probable that the frost depth will not exceed 1.5 m into the protective cover.

Table 7-5 Calculated frost depth (m) as a function of varying proportionality factor (α), varying thermal conductivity relationship between frozen soil and snow (n), and varying snow cover. For the calculations, the maximum measured frost index has been used (for a series of 100 years of measurements)

Snow cover (m):	0.0	0.2	0.4	0.6	0.8	1.0
Calculated frost depth for: $\alpha = 6.0 \cdot 10^{-2}$ m/degree day$^{0.5}$ n = 1.5	2.08	1.78	1.48	1.18	0.88	0.58
Calculated frost depth for: $\alpha = 5.5 \cdot 10^{-2}$ m/degree day$^{0.5}$ n = 2.5	1.91	1.41	0.91	0.41	0	0
Calculated frost depth for: $\alpha = 5.0 \cdot 10^{-2}$ m/degree day$^{0.5}$ n = 4.0	1.74	0.94	0.14	0	0	0

Long term stability

Processes like frost action and root intrusion, even if this latter process is less probable, may alter the properties of the constructed cover. For example, these processes may lead to a decrease in the hydraulic conductivity of the sealing layer and may also probably affect the water retention capacity of this layer, even if this effect is probably less pronounced, as described in previous section. However, even if the cover as a consequence of such processes will be less effective, it will still be in place. The impact of other processes like erosion and slope failure may instead lead to partial loss of the cover.

Erosion of the cover may arise if a surface water flow occurs over the covered area. Surface run-off occurs normally during snow-melt when the ground is frozen and during and after heavy rain events when the rain intensity is larger than the infiltration capacity in the soil. Erosion caused by such surface run-off can often be observed when a cover is newly placed, expressed as small rills on the surface. Such erosion is normally stopped once vegetation is established on the surface, provided the slope is not to steep. A rule of thumb that is often used is that the slope should not exceed 1:3 (V:H), based on what is frequently observed in nature (Swedish conditions) for geological formations similar to deposit slopes, which have been stable for thousands of years.

Another reason for erosion, which may be harder to control, is the possible formation of an open water surface (ponding) on the deposit, as indicated in Figure 7-18.

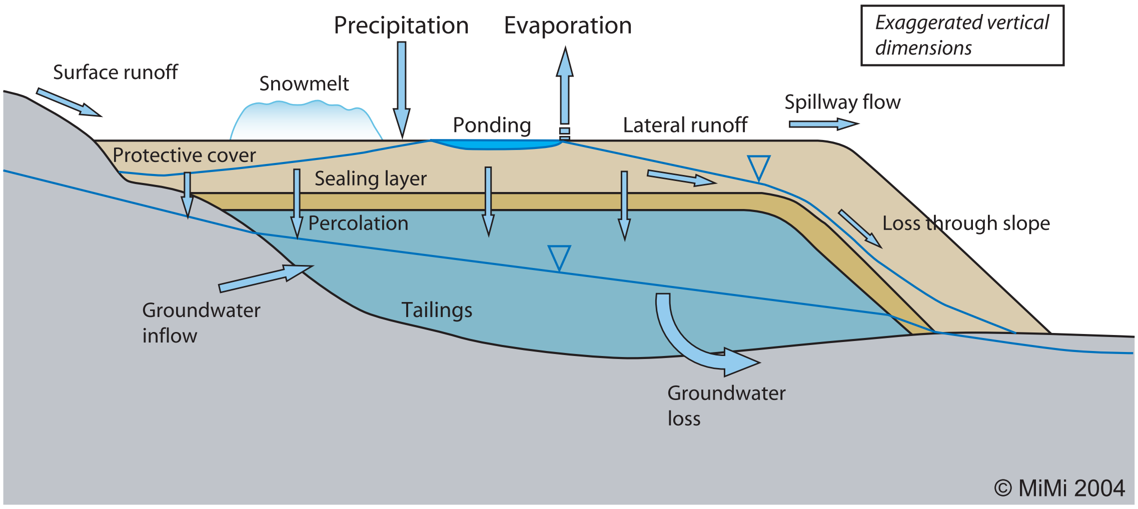


Figure 7-18 Illustration to the water balance of soil covered tailings deposits.

Ponding of water on the surface may occur if the protective cover soil has a low hydraulic conductivity and the slope of the deposit is insufficient to allow for the discharge of the upper ground water. A groundwater table will occur above the sealing layer, as the vertical percolation downward is limited. If ponding occurs over a certain area, larger and more concentrated flow may arise on the surface compared to normal surface run-off at snowmelt and heavy rain events. Such flows of water on the surface will consequently constitute a larger risk for erosion that may imply local damage to the protective cover, and even the sealing layer. This risk should be considered in the dimensioning of the protective cover, which preferably should be designed in such a way that the upper groundwater formed over the sealing layer can be horizontally discharged as groundwater in the protective cover. This can be achieved using levelling and suitable soil materials or combinations of soil materials in the protective cover. However, when using sealing layers with very low hydraulic conductivity on large tailings deposits with flat surfaces, sufficient horizontal discharge may be difficult to achieve. In such cases, discharge must be directed to certain courses by shaping the surface; these courses can be protected against erosion by a coarser soil cover in the upper part.

Slope stability is another essential factor, which is important for the integrity of the deposit and the cover. Slope failures may occur if the shear stresses that are induced along potential slip surfaces in the soil under slopes exceeds the shear strength along one or more of the potential slip surfaces (in cover soil as well as tailings and underlying soil). Analysis of slope stability can be performed using conventional geotechnical analysis of slope stability. For such analyses of long-term stability, so-called effective stress analysis using a Mohr-Coulomb soil model to describe shear strength normally should be appropriate (see e.g. Terzaghi et al., 1968). Shear strength may be determined by investigations in field and laboratory, but empirical values can often be used for describing natural soils like till. Empirical values may also be used to describe the strength characteristics of tailings. However, as there is a large spread in measured values for tailings, as shown in Chapter 5.5, the choice of shear strength characteristics should be performed with caution.

In an effective stress analysis, the pore pressure in the soil has a large influence on the result, as the effective stress is calculated by reducing the total stress in an element in the soil with the pore pressure (in the water filled voids) in the same element. This also implies that the shear strength decreases with increasing pore pressure at unchanged total stress. For this reason, it is essential to also have a good prognosis for pore pressures that may develop in the future. When dealing with covered deposits, it is especially essential to interpret the effect of a low permeable layer in the slope. This may lead to the build up of pore pressures in the tailings below and behind the sealing layer that may considerably reduce the shear strength in the tailings and, if not appropriately accounted for in the dimensioning of the slope, may lead to a slope failure even if the calculated stability factors (using lower pore pressures) show satisfactory values.

It is also essential to investigate the soil underlying the deposit. Presence of cohesion soils like peat and clay may imply a layer with lower shear strength, which must be taken into consideration in the stability analyses. For such soils, the analyses also must account for total stress conditions using undrained shear strength. The undrained shear strength has to be determined by field and laboratory investigations. This is normally performed during the planning when stability analyses are performed for the active period when the tailings impoundment is in operation.

Specific for water cover

In the performance assessment of water covers as a method to limit oxygen intrusion into tailings, it is presumed that the tailings remain covered with water over time. This assumption is true, with a high probability, for formations like natural lakes and pit holes in bedrock. For water covered impoundments where the water balance maintaining the water cover relies on a dam wall (or even a thin core) with low hydraulic conductivity, the long term integrity of the dam wall has to be taken into consideration.

Geotechnical stability for tailings dams is today carefully investigated and analysed for the conditions during the operational phase. For the long term, it may be feasible to use a higher safety factor against a total dam failure, regarding unforeseeable alterations in load conditions or shear strength that may occur. High safety factors against a total dam failure can often easily be achieved using e.g. waste rock as stabilizing fill outside the dam. It is also essential to construct the dam in such a way that overflow over the crest that may cause erosion is avoided; by creating ways for the discharge of water in such a manner that they are protected against erosion and large enough to be practically impossible to be blocked.

To construct a dam so that dam failures can be avoided is a delicate mission, not least showed by the large number of dam failures that have occurred in the past. From statistics, the probability for a failure is 10^{-4} per year and dam (Bartsch, 1995). In the statistical data, there is also a trend showing that the probability factor for dam failures has decreased for dams constructed during the latest decades. However, statistical analyses of dam failures and damage on earth dams also show that failures and damage more frequently occur relatively soon after the construction; about 70 % of reported dam failures occurred within 10 years after construction (ICOLD, 1995). Consequently, there is no evidence that the probability for a dam failure for a specific dam increases with time. It shall be noticed though, that these studies are performed on dams in operation and consequently are objects under supervision and maintenance.

In the long term, a more probable event than a total dam failure may be internal erosion in the dam wall, which will lead to increasing leakage and loss of water from the dam and in the end exposure of the tailings to oxygen. Internal erosion is among the most common reasons for damages and failures for earth dams (Bartsch, 1995). This shows that the design and construction of successive filters between the sealing core and the stabilizing fill inside and outside the dam wall is of utmost importance, and have maybe not been shown appropriate care in the past.

Agrell (2002) has studied natural lakes in Sweden that are impounded by soil formations similar to earth dams, as analogues to constructed dams. He did not find any soil formation of geological origin with a higher hydraulic gradient than 0.05 (5 %). This may lead to the conclusion that this is the upper limit for what is possible to maintain without maintenance in the long term. However, naturally deposited soils with a morphology that can form a dam wall also show relatively high hydraulic conductivity (eskers and superficial moraines) and this can also be a reason why higher hydraulic gradients are not found in nature. The hydraulic gradients in a constructed dam are usually much higher than 5 %. This gradient corresponds to a homogeneous dam with 10 m height from the base to the water surface and a width of 200 m.

In Sweden, the practice in dam construction has been to accept a design when the phreatic surface corresponds to a "normal high" hydraulic gradient, which is said to be fulfilled when

$$\tan\alpha \leq \frac{1}{2}\tan\phi \qquad (7\text{-}65)$$

where

α is the inclination of the phreatic surface and ϕ is the friction angle of the material (Bjelkevik, 2004). A friction angle for soils used in dam constructions is often conservatively estimated at 35°, which results in a hydraulic gradient of $\tan\alpha \leq 0.35$ or 35 %. Comparing this value with the observed hydraulic gradients for natural analogues gives a value of the highest acceptable gradient within the interval 0.05 - 0.35 m/m.

8 Description of Far Field

The *far field* comprises the area outside the constructed deposits that receives drainage water from the deposits. It is important to understand and describe the far field in order to address and quantify different natural attenuation processes and their importance for the environmental impact. The far field conditions relevant for the Kristineberg mine site are described as a part of the MiMi performance assessment analysis.

8.1 General for the Kristineberg site

Mining of metals has been carried out in Sweden for more than 1000 years, primarily in three mineralised provinces, where ore bodies are concentrated: the Norrbotten and Skellefte fields in the north, and Bergslagen in the middle of the country. In addition, other separate ore bodies are spread throughout the country (see Figure 8-1). Whereas historically mining has occurred over the entire country, the Kristineberg site, in common with most mining sites of today, is situated in northern Sweden, and is thus expected to show similar climatic, vegetational, and soil characteristics as other major Swedish mining sites.

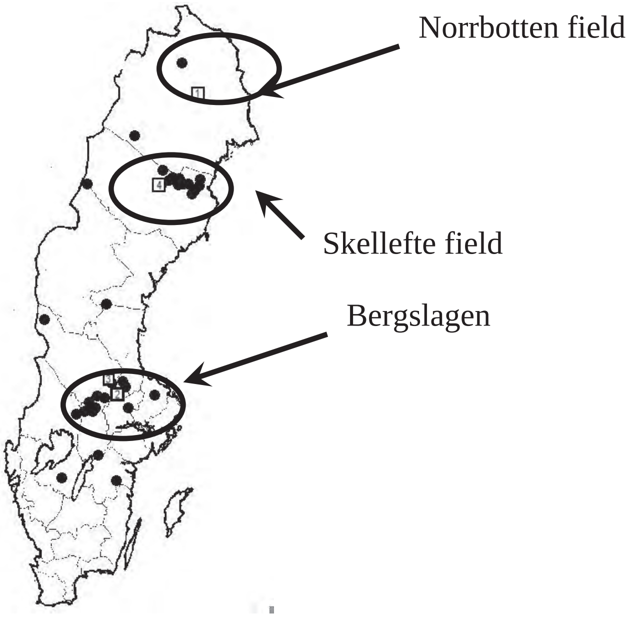


Figure 8-1 Approximate location of 42 of the 50 mining sites that were classified by the Swedish Environmental Protection Agency as high to medium risk to the environment (Modified from SEPA, 1995).

The far field is divided in two distinct parts. In the surface part we consider the processes that mainly take place above ground. In the sub-surface part those that take place below ground. The water and solute transport in these regions takes place in parallel and is governed by partly different mechanisms. The present day far field surrounding the Kristineberg mining site is complex. The water from impoundment 1, which has been the main study object within MiMi, flows in an easterly direction and passes impoundments 3 and 4 before leaving the area (see Figure 8-2). At present, we wish to study the transport processes in the far field in a general way and for times that extend far longer into the future than the present day operations. For this purpose, we consider a far field that extends from impoundment 1 to Vormbäcken and Vormbäcken itself as if there were no impoundments downstream. This simplification will permit us to highlight processes that are expected to be more generally applicable to future deposits.

Figure 8-2 Map of the mine area at Kristineberg and the location of the tailings impoundments 1, 1B, 2, 3 and 4.

8.2 *Natural geography*

Lapland is the vast interior region of the northernmost part of Sweden, 109 702 km^2 land area, almost all wilderness. East of and bordering Lapland are the two regions Västerbotten, 15 093 km^2, and Norrbotten, 26 671 km^2. These two regions comprise the coast along the northernmost part of the Baltic, the Gulf of Bothnia, and a short part along the Kvarken straits. The total land area of the three regions, 151 466 km^2, is about 37 % of the land area of Sweden, 410 930 km^2. Together they constitute only two administrative provinces, the County of Västerbotten and the County of Norrbotten, Lapland is divided between these two.

The Kristineberg mine is situated in the Laplandic part of the County of Västerbotten at 65^{o}5'N; 18^{o}35'E (Swedish map 23I Malå, 1: 100 000). It is at the NW border of an upland area between the large rivers Skellefte älv to the north and Ume älv southwards (see insert to Figure 8-2). To the north the area reaches the small town of Malå 15 km NNE of the mine and the highest peak, Hornberget, 561 m above sea level, is close to and north of the mine (Lidmar-Bergström, 1994). The relief is relatively even but may be said generally to vary between 300 and 500 m above sea level. The area is an eroded hilly but relatively flat upland with the peaks and hills being remnants of the original bedrock, sometimes covered by younger rock. In Swedish the terrain is called ”bergkullterräng”.

To the west the height above sea level decreases a little before the Scandinavian mountains, which may be defined as mountains being higher than 800 m (Lidmar-Bergström, 1994). Scandinavian mountains may also be defined as mountains without closed forest, even if not without trees. This border between the northern boreal and the alpine region vary between about 900 m in the south and 500 m farthest to the north. Accordingly, what is called Scandinavian mountains in the north may be lower than in the south. To the east the height decreases, sometimes stepwise, to the narrow coastal plain along the Gulf of Bothnia.

The northern part of Sweden is characterized by large river valleys and rivers running from NW to SE and discharging into the Baltic. The Skellefte River and the Ume River are examples of that. The scant farming of northernmost Sweden occurs in these valleys and on the coastal plains.

The Scandinavian landscapes and nature is marked by: 1) ice ages and large continental ices covering the whole peninsula. The latest one started to retreat about 14 000 years ago and it left the landmass depressed into the earth crust. 2) The sea level also rose when the ice melted and parts of Sweden were covered by sea during the early developmental stages of the present Baltic. However, until about 9 000 years ago so much water was tied up in ice that the southernmost tip of Scandinavia was connected by land bridges via Denmark to the European continent (National atlas of Sweden, 1996).

When the ice melted, the sea level rose and the bridges were broken by the straits separating the Danish islands and Sweden from each other. Old coastlines often are visible at varying heights above the present sea level and partly the land still rises. In the Province of Ångermanland, where the land rise has been fastest, the highest shoreline is 280 – 285 m above the present sea level (Fredén, 1994). Today, the land rises fastest along the coast of the Province of Västerbotten, 9.2 mm per year. Towards north and south it rises slower and at the southernmost part of Sweden the land rise has ceased (Björck and Svensson, 1994).

This history has affected the Swedish nature in several ways: land forms, soils and therefore vegetation, the occurrence of lakes and distribution of lake types, immigration and distribution of animals and plants. The origin of present nature cannot be understood without taking the ice and its consequences into account together with the developmental stages of the Baltic. The nature of the Nordic countries still is young and changing because of the ice.

8.3 The biogeographical regions

Schematically Sweden comprises a number of biogeographical regions from south to north (Sjörs, 1999), corresponding to vegetation zones. In the south there is a nemoral region followed by a boreonemoral one limited in the north by *limes norrlandicus*, the biological border to the north of Sweden (Angelstam and Svensson 1996, Sjörs 1999). The nemoral region originally was dominated by forests of deciduous hardwood (ädellövskog) as oak, ash, linden, elm etc. Spruce was absent. Today forestry has introduced it there. The boreo-nemoral is dominated by coniferous trees mixed with deciduous hardwood species.

Limes norrlandicus is a distinct biological border, north of which deciduous hardwood species are rare. At least they do not form closed and large stands and in the high north, approximately north of the province of Ångermanland, they do not occur naturally. There the only deciduous trees are birches, aspen, grey alder, rowan and bird-cherry. The region from limes up to the forest limit and the alpine regions in the Scandinavian mountains is the vast boreal region, the western-most part of the enormous Eurasian taiga. Kristineberg is situated in this region.

However, in the central–north Sweden this north - south pattern is complicated by the mountains and the varying height above sea level in east - west direction, besides the vast extension in south- north direction. It is usual to distinguish three subzones, southern, middle and northern boreal. Usually, Kristineberg is regarded as belonging the middle boreal (Gustafson, 1996, p 27; Fig. 7 in Sjörs, 1999). However, in southern Lapland the middle boreal is below 300m (Sjörs, 1999). Since Kristineberg is situated in an upland area 300 – 500m above sea level, it would ecologically belong to northern boreal. However, the limits of the middle and northern boreal are complicated and difficult to define. No part of Västerbotten and southern Lapland is regarded as southern boreal.

The boreal forest

The biogeographical region called the boreal forest or taiga covers more than 50% of Sweden. It comprises a number of different types of nature, sometimes equivalent with vegetation types. There is a common type classification for the Nordic countries (Nordiska ministerrådet). There is also a regional Swedish survey of biogeography and regional ecology, National Atlas of Sweden (1996).

The type concept is used for giving regional overviews and it is not a detailed one equivalent to ecosystem or plant and animal community. Most of the boreal region is characterized by a macro-mosaic of conifer forests, mires and lakes with rivers and streams as important ecological corridors (Nilsson, 1999). Lakes, rivers and wetlands, such as mires, are types that may be of interest for the mining industry as recipients of mine water, drainage water from mine waste deposit; and mires even as sites for deposits. The conifer forest proper is of course locally affected but not used in a way implying large-scale regional problems.

The Swedish taiga is of course characterized by coniferous tree species although the deciduous mountain birch (*Betula pubescens ssp. czerepanovii*, Swedish ”fjällbjörk”), forms the forest border upwards in the mountains. It is included in the northern boreal region as a subalpine belt (Carlsson et. al., 1999; Gustafsson, 1996).

Most of the coniferous forests in the middle and northern boreal may be regarded as species poor, compared especially to deciduous forests in the south, but also compared to the boreo – nemoral conifer forests. There are only two important and dominating conifer species in Sweden, Scots pine (*Pinus sylvestris*) and Norwegian spruce (*Picea abies*), although the North American *Pinus contorta* has been planted over large areas. Therefore conifer forests are classified as pine and / or spruce forests. However, the understory vegetation and its species richness may differ much and is used for differentiating communities.

The communities, and also species constituting them, may be ordered in a system of two gradients in environmental factors 1) wet – moist – mesic – dry and 2) low alkalinity and nutrient availability – high alkalinity and nutrient availability (Engelmark and Hytteborn, 1999; Gerell et al., 1996).

Ordered in this two-dimensional system, we get conifer forest plant communities as *Pinus – Vaccinium vitis-idaea* and *Picea – Vaccinum myrtillus*. The first is pine forest with the dwarf shrub lingonberry dominating in the field layer (Swedish: lingontallskog). The second is spruce forest with bilberry dominating in the field layer (blåbärsgranskog). Swedish coniferous forests is divided into about ten such communities from dry, species and nutrient poor Pinus – lichen to wet, species and nutrient rich *Picea* – herb – rich swamp forest (Engelmark and Hytteborn, 1999; Sjörs, 1971). These communities are recognized over most of Sweden.

Illustration: Lingonberry shrubs and a mushroom (Fly agaric, *Amanita muscaria*).

Most of them also occur in Västerbotten and southern Lapland (Malmström, 1949; Engelmark & Hytteborn, 1999). Since the investigation is old, the results would be more valid for a situation less affected by forestry, air pollution, and acidification than today. It does not seem possible to state the area covered by different communities. However, over Sweden at large, *Picea* – *Vaccinum myrtillus* is the community covering the largest area. Malmström (1949) estimated species numbers of vascular plants in plots measuring 10 x 10 m in the various communities. The *Picea* – tall herb community was richest with a mean of 52 species and *Pinus* - lichen poorest with eight per plot. *Picea* – tall herb is especially characteristic of northern Sweden and the mountains there with richer bedrock. Around Kristineberg and in ”Skelleftefältet” species numbers are probably usually low.

It is much more difficult to differentiate deciduous forest into stable communities (Sjörs, 1971). It is maybe too species rich, being much more species rich than coniferous forest, especially in the south, and too variable. The few deciduous species occurring in the middle and northern boreal are mentioned above. Only birches (*Betula pendula* and *pubescens ssp pubescens*), aspen (*Populus tremula*) and grey alder (*Alnus incana*) may be regarded as important below the subalpine belt. They can form more or less pure stands, as swamp forests or successional stages after forest fires (*Betula ssp*, *P. tremula*).

Ecological disturbances as fires can start successions with stages deviating from, but developing into, the more stable, mature communities. Spruce is counteracted by fires. Pine is much more fire resistant and is favoured at the expense of spruce. *Betula ssp* and aspen have good dispersal powers and are early colonizers on burnt ground. Pine behaves in a similar way, besides better enduring the fire. Browsing by moose may affect both tree and bush species composition and dominance. Speed and direction of ecological successions may also be affected. Since moose prefer deciduous trees and bushes before conifer ones and pine before spruce, spruce is favoured at the expense of other species. Reindeer may also affect and disturb vegetation. Engelmark and Hytteborn (1999) summarizes coniferous forest disturbances. Accordingly, the unaffected natural boreal conifer forest, albeit comparatively species poor, is much more dynamic and variable than maybe often believed. From the point of view of nature conservation it may also be more valuable than usually believed. However, human activities hinder natural dynamics by affecting almost all coniferous forest except nature reserves. Forestry can determine the composition of the vegetation, at least which tree species that grow there. By combating forest fires and promoting a dense moose population, spruce is favoured over pine and deciduous trees and bushes. Most forests therefore are not natural.

Illustration: Reindeer are frequent visitors on the flat and open tailings impoundments.

The largest area with unaffected and older coniferous forest is situated east of and along the mountains (Gustafsson, 1996, p 48). It comprises about 15 000 km^2 and is very valuable for nature conservation and most of the *Picea* – tall herb community probably is found there. It is difficult to exploit commercially, and the majority of Sweden’s coniferous forest reserves are situated there, in total about 5 000 km^2. In spite of that, the area to a large extent is affected by forestry. The exploitation has been heatedly debated.

Most of the middle and northern boreal coniferous forests grow on podzols (soil map in Lundmark, 1986, p 94 – 95). The humus type is mor, with some possible exceptions. Under *Picea* – low herb community, there may be mor / mull, maybe moder. Under *Picea* – tall herb there is mull and probably brown forest soil (cambisol). In the mors, the mean pH value (Malmström, 1949) was usually 4 or below, with a lowest mean of 3.7 for *Picea* – *Vaccinum myrtillus*. For *Picea* – low and tall herb communities, the average pH varied between 4.4 and 5.9. These are common and expected values. However, Västerbotten and the interior of southern Lapland clearly have been acidified since then.

There are a number of different podzols (Troedsson and Nykvist, 1973). The extent to which soil is podzolised usually is estimated by measuring the extent of the E – horizon, which indicates that the Laplandic podzols are leached to much varying extents. There are also large areas with gleyic soils affected by ground water and of course peat. The different types seem to be rather irregularly distributed over the region. Podzols do not extend into the alpine regions. There the soils mainly are azonal.

The wetlands

Second only to forests of all types, wetlands may be stated to cover more than 25% of the Swedish land mass. The extent partly depends upon the definition of wetlands. One common definition used by the Swedish Environmental Protection Agency (Löfroth, 1991) is: *Wetland is land where water during a large part of the year stands near, under, at or just above soil surface and water whose surface is covered by vegetation*. Accordingly, anaerobic conditions often are important in such soils/sediments. The definition cited is common in other countries too (Landin, 2002).

At least three large series of wetlands may be distinguished. Mires (Swedish ”myrar”, Rydin et al., 1999) produce peat because of the anaerobic conditions in the soil. Shores and littorals, both freshwater and marine ones, are regarded as wetlands, since at least part of the year the soils are anaerobic, even above the mean water level, because of flooding. ”Other” wetlands, the third category, are moist meadows, forests etc, which do not form peat or are situated on shores. Of course the borders between them are blurred. Further, the three categories are subdivided into a lot of types.

The vegetation should consist of ”wetland plants” to at least 50%. Next question is what a wetland plant is, and it may simply be defined as any plant growing in soil which at least periodically is anaerobic, including emergent, submerged, floating –leaved and floating species. Shallow water is usually regarded as wetland as long as the surface is dominated by vegetation.

Wetlands often get large attention in conservation work. Especially in Southern Sweden, they have been subjected to drainage, sometimes to almost total destruction, which is the reason for the large interest. Mires comprise almost 5 million ha and swamps or wet forests 5.1 million ha of the Swedish area (Naturmiljön i siffror, 1996 and 2000). To this marine and freshwater shores are to be added. Accordingly, more than 25% of the Swedish area must be classified as wetlands in spite of the extensive destruction.

Forslund et al. (1993) describe the classification used in the wetland inventory of the County of Västerbotten and the human influence on the wetlands. In the coastal region of Västerbotten more than 30% of the wetland area has been influenced to such a degree that the hydrology has changed. Near the Scandinavian mountains the figure is about 6%. Human destructive influence on wetlands usually decreases northward in Sweden.

The area of the County of Västerbotten is 55 190 km^2, that is 5 519 000 ha. About 14% of this is stated to be wetland, dominated by mires, 12% or about 570 000 ha (Forslund et al., 1993). The areas certainly are underestimated since they are estimated from aerial photographs. Only objects larger than 50 ha therefore are included.

The difficulties in estimating and perhaps defining wetland areas, maybe areas of other types of nature too, are well illustrated by Forslund et al. (1993). Using other inventories (Hånell, 1989; Löfroth, 1991) they reach the conclusion that the area is 28%. This probably is closer to the truth.

Illustration: Wetland surrounding the river Vormbäcken downstream the Kristineberg mine.

Most of the wetlands of Västerbotten are mires, 89% (Forslund et al., 1993). Mires are subdivided in several types (Rydin et al., 1999). There is a gradient in nutrient availability from the poor raised bogs to rich fens and they differ in abundance between north and south Sweden. For example there is a bog type called ”flat bog of northern type” (Rydin et al., 1999). In Västerbotten this comprises 97% of the bog area. The raised bogs (Swedish ”högmossar”), common in southern half of Sweden, are not common in the north. In the north there are more flat bogs and fens (Swedish ”kärr”) and also sloping ones, which means moving water, contributing to nutrient richness. Fens comprise 75% of the mires in Västerbotten.

During the last ten years, wetlands are eagerly studied in Sweden and constructed or restored. The aim is generally to withhold and/or remove plant nutrients from water leaking into lakes and rivers and finally the sea (Tonderski et al., 2002). However, metal retention seems to be studied only little compared with retention of plant nutrients (Kadlec and Knight, 1996) and much remains to be learned. But Sobolewski (1999, cited after Sjöblom, 2003) state that there are a number of studies dispersed through the scientific and technical literature.

Sjöblom (2003) summarizes literature on wetlands for acid mine drainage treatment. The wetlands were natural and constructed and the studies included laboratory experiments and field observations. The wetlands seem to always have positive effects from an environmental point of view in one way or another. However, the results vary much, seemingly in an unpredictable way.

Using wetlands in combination with mining industry may have other advantages and drawbacks. Biodiversity certainly will be promoted by favouring aquatic organisms. However, new ways of dispersing metals to organisms may be established. Terrestrial organisms as large herbivores may browse metal contaminated wetland plants and accumulate the metals. Insectivorous birds may do the same by feeding on water insects or terrestrial adult stages hatching from the wet-lands.

As outlined by MiMi (1998) (Programme plan, 1999-2000) and judging from the literature review and the results presented by Sjöblom (2003), wetlands can serve as a valuable treatment, but only complementary to source treatments at and in the impoundments and mine. It is not possible to divert mine water and untreated tailings drainage directly into wetlands and get good, sustainable effects. Wetlands have only been used by the mining industry for about 20 years and no wetland seems to have functioned without additional measures for more than three or four years (Sjöblom, 2003). Accordingly, their sustainability may be questioned.

Mining is not a large threat to wetlands or other nature types by exploiting ground since the industry uses relatively small areas compared with for example forestry. Forslund et al. (1993) do not mention mining as a threat in Västerbotten, and in the vicinity of the Kristineberg mine there seem to be no wetland of high conservation value. However, in the inlands and near the Scandinavian mountains there are large undisturbed wetland areas and also areas of high conservation value. Therefore, caution when searching and exploiting both old and new deposits is advisable.

At least parts of the impoundments at Kristineberg are situated on peat, accordingly former wetland, in the bottom of the valley. There are also large areas of mire along the brook Vormbäcken and its tributaries. They receive water from the Kristineberg area and Vormbäcken is the recipient of the impoundments. Vormbäcken including downstream wetlands have been studied by Sjöblom (2003) as a part of MiMi.

8.4 Climate

Climate is the major determinant of the distribution of the biogeographical regions (see for example Krebs, 2001). On a worldwide scale, the boreal forest occurs in continental interiors between 50 and 70° N almost completely around the northern hemisphere. The mean annual temperatures vary between approximately +4 and –5° C and precipitation between ca 500 and 1 500 mm per year. Taking the enormous area into account, the environment may still be regarded as homogenous, perhaps making it possible to generalize concerning environmental consequences of mining and mine waste over the whole northern hemisphere.

From the west, the climate of the Scandinavian peninsula is affected by the Atlantic. From the east, it is influenced by the Eurasian continent. These opposite influences lead to a highly unpredictable weather and variable climate, especially in the north. In the westernmost parts of the Swedish mountains, a temperature index incorporating differences between January and June and between day and night during June generally is 25 – 30 °C. In most of Northern Sweden, that is in the boreal forest, the difference is 35 – 40 °C, or even exceeding 40 °C (Vedin, 1995). Mean annual temperatures in the forest, away from the Baltic coast, vary between +2 and – 2° C. At Kristineberg the mean annual temperature is 0.7 ° C.

The Scandinavian mountains and the dominating westerly winds give rise to orographic precipitation comprising as much as 2 000 mm per year, or even more in the western parts of the Swedish mountains. However, eastward it decreases and in most of the provinces of Västerbotten and Norrbotten, the annual precipitation is on average between 600 and 700 mm (corrected for common measuring errors). Since the potential evaporation is 300 – 500 mm, there is still generally an excess of precipitation, comprising almost half the yearly precipitation (Bringfelt and Forsman, 1995; Alexandersson and Andersson, 1995; Nordiska Ministerrådet, 1994). For the Kristineberg site in particular, the corrected annual precipitation is 660-670 mm/a (Axelsson et al., 1991), and impoundment 1 at the site, as an example, had an estimated effective infiltration of 243 mm/year prior to remediation; surrounding moraine areas contributed recharge with up to similar quantities (see summary in Malmström et al., 2001).

8.5 *Geology*

Bedrock

The bedrock in the Kristineberg area consists of c. 1.9 Ga metamorphosed ore bearing volcanic rock overlain by metasedimentary rocks. Pyrite-rich massive sulphide ores are intercalated within a stratigraphic unit consisting of mainly basic volcanics and redeposited volcano-clastic rocks (Carlsson, 2000). Figure 8-3 shows the geology of the Kristineberg area.

Results from geophysical investigations show indications of fracture zones at the Kristineberg mining site. In the underlying bedrock, two fracture zones in the Northwest-Southeast direction were identified being in hydraulic contact with impoundment 1.

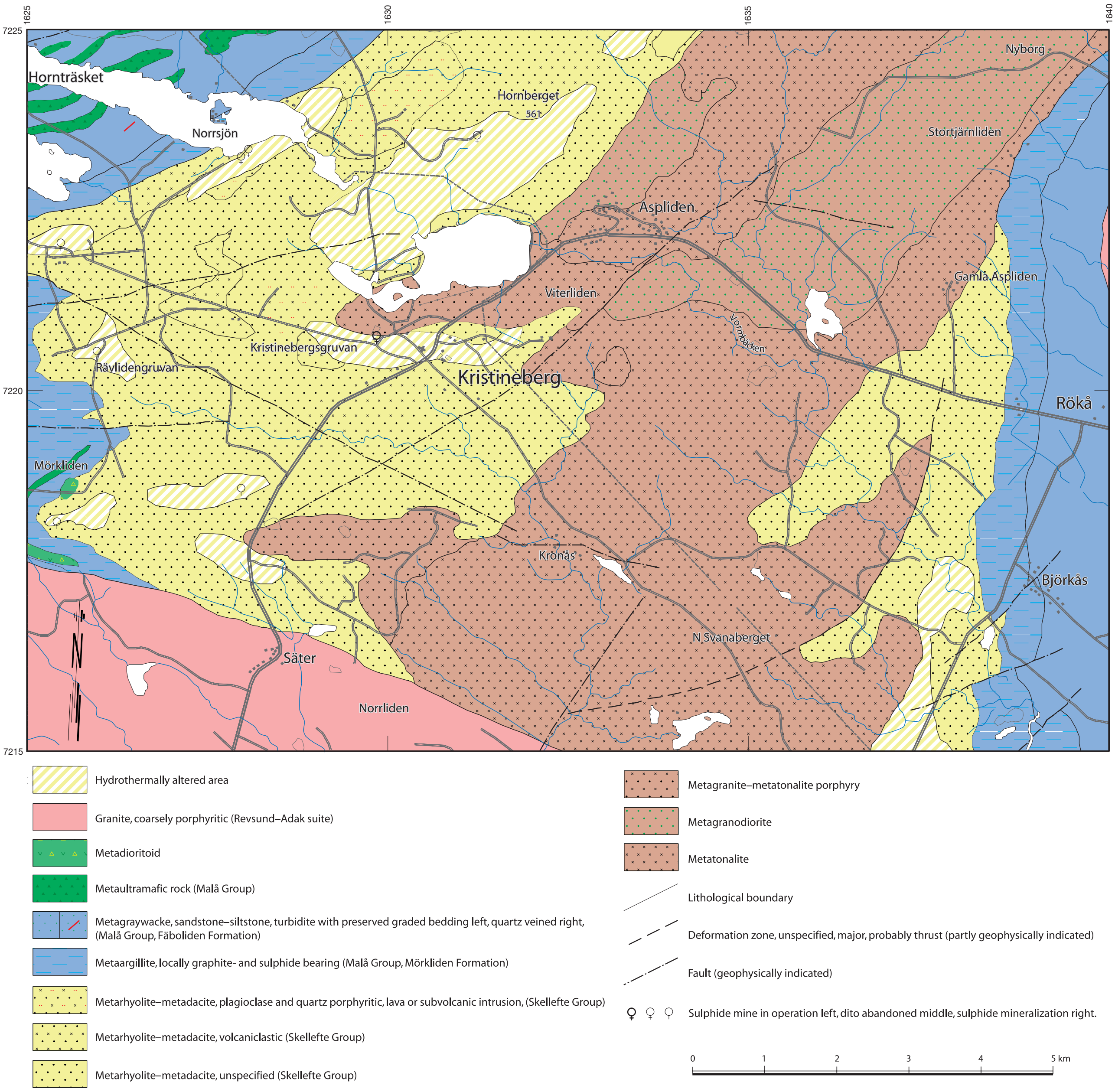


Figure 8-3 Geology of the Kristineberg area, modified from SGU Serie Ai, no. 117.

Quaternary deposits

The dominating overburden is till. The till mainly consists of sand and fine sand material. In the depressions of the terrain, the till overburden is generally covered by a thin layer of peat. In the lower parts of the valley field investigations also indicates that there are elements consisting of thick layers of fluvial deposits (see Figure 8-4). The thicknesses of the overburden vary from a few meters on the hillsides, or sometimes even no overburden at all, to more than 15 meters in the valleys (Axelsson et al., 1986).

For the construction of the protective cover, till from the local area were used. Large amount of data have been collected for the characterisation of the till cover and some of these data can consequently be applied for the description of the natural till overburden, see section 6.5. From the grain size distribution the till used for constructing the protective till cover is characterized as a sandy/silty till. Rock fragments dominate the till. Major minerals are quartz, plagioclase and microcline-perthite. Biotite and hornblende are rather common. The biotite is often altered to chlorite, and the feldspars are often sericitized. Clay minerals, probably as alteration products of feldspars, have been observed, but not identified. Primary chlorite also occurs. Trace amounts of pyroxenes, tremolite-actinolite, olivine, serpentine, epidote, zircon, apatite, calcite, titanite, garnet, iddingsite and tourmaline occur. The content of opaque minerals is generally 1-2%, dominated by magnetite and ilmenite. Small amounts of sulphides, dominated by pyrite and pyrrhotite occur, mainly as inclusions in silicates. Free grains are strongly altered to Fe-oxyhydroxides. Hematite, rutile, and a few grains of chalcopyrite have been observed (Öhlander et al., 2004).

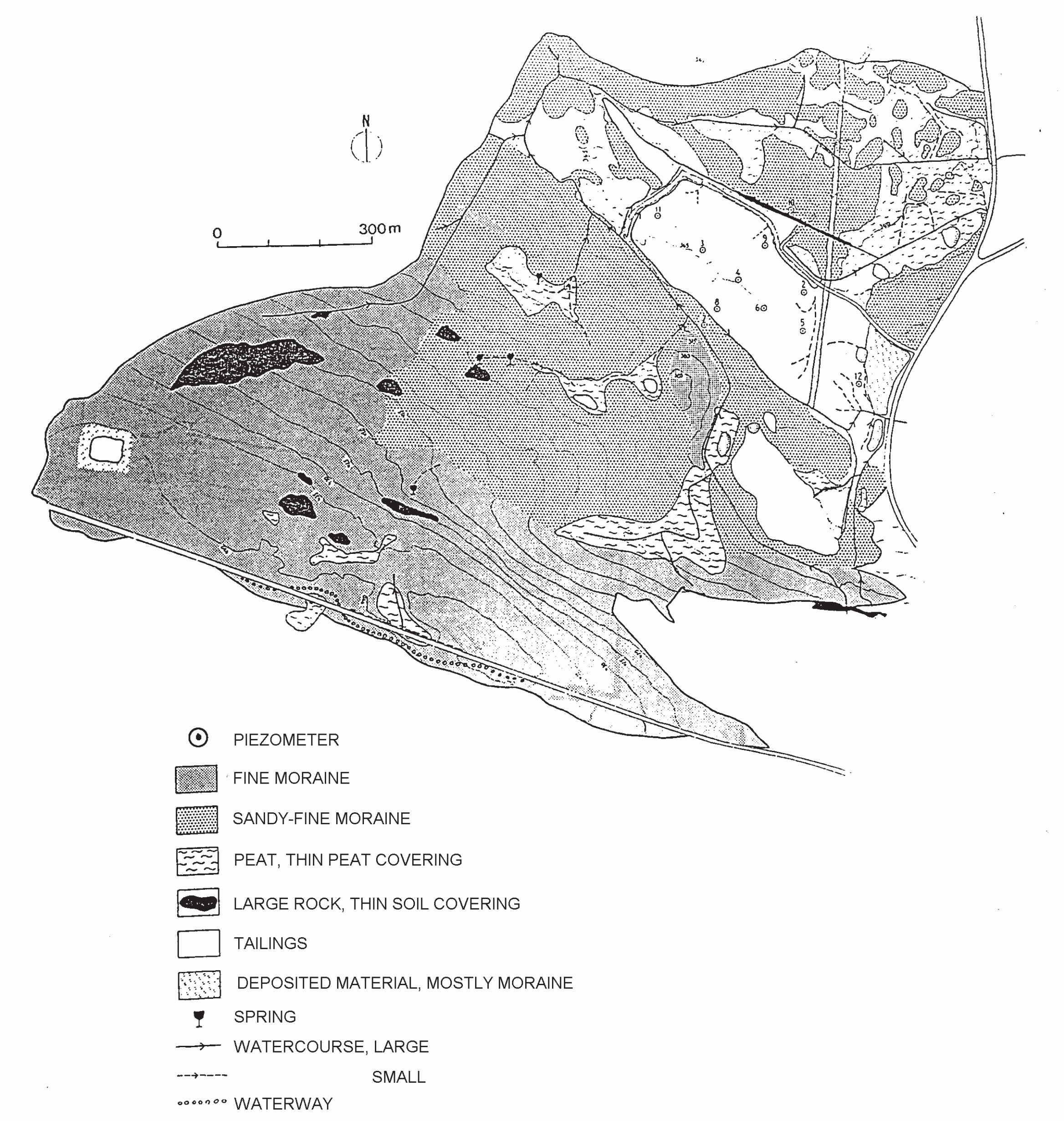


Figure 8-4 Map of surficial deposits in the Kristineberg area (Malmström et al., 2001; modified from Axelsson et al., 1984).

Soils

In the County of Västerbotten, the bedrock east of the mountains to a large extent comprises weathering resistant and rocks poor in plant nutrients (Lundqvist, 1994; Sjörs, 1999). The overlying soils are thin (<25 cm deep), mostly coarse and nutrient poor moraines, which, according to FAO Unesco system of soil classification (Driessen and Dudal, 1989), would be classified as leptosols. They are situated above the level of the highest coast (Fredén, 1994), implying a lack of fine, nutrient rich sediments. There are also ”patches” of unconnected peat, thin soils, or exposed bedrock all over the landscape and sediment bands from ice rivers running NW to SE, partly along the present rivers. Floodings and sediments in the present river valleys have made the nature there richer and agricultural conditions better than in most of the landscape. For the Kristineberg area, the major soil type is a podzol produced from weathered glacial till (Granlund and Wennerholm, 1935; Granlund, 1943). The composition of the local till is discussed in Chapter 6.5.

Illustration: Section through podzolised till.

8.6 Hydrology

The impoundment area is situated in a valley surrounded by steep slopes, the surrounding hills are up to 440 m.a.s.l. (metres above sea level). The natural bottom of the valley were the impoundment and the primary recipients are situated is between 340 to 350 m.a.s.l.. The catchment area of the five impoundments is approximately 2.64 km^2 (Axelsson et al., 1991). Different local catchment areas in Kristineberg have been estimated by Svensson and Höglund (2004), see Figure 8-5.

The regional monthly average of precipitation is quite evenly distributed over the year. The annual average of the precipitation in the Kristineberg area varies between 400-800 mm/a (Axelsson et al., 1986). Groundwater level fluctuations follow a normal seasonal trend for the region with groundwater recharge in connection with the snowmelt period in April-May and in connection to autumn rains in August-September (Malmström et al., 2001). In groundwater modelling studies of the actual area, a value of 200 mm/year for the groundwater recharge on natural ground have been used (Jarsjö et al., 2000).

Based on the observed hydraulic gradient between impoundment 1 and the underlying moraine, Axelsson et al. (1986) concluded that there may be a peat layer with lower hydraulic conductivity than both the tailings material and the underlying moraine. Some hydrological information on impoundment 1 and the surrounding geological formations is summarized in Tables 8-1 and 8-2.

Table 8-1 Average vertical and horizontal hydraulic gradients (m/m) in impoundment 1 and the surrounding moraine estimated from field data (from Axelsson et al., 1986).

Component	Gradient (m/m)
Vertical (impoundment/moraine)	0.09-0.13
Horizontal (moraine, west of impoundment 1)	0.08

The lower and upper limits are for periods of low and high groundwater level, respectively.

In the bedrock underlying impoundment 1, two potential fracture zones with possible hydraulic contact with the impoundment were identified *Axelsson et al.* (1986). The hydraulic properties of the potential fracture zones were summarised by Malmström et al. (2001) (see Table 8-2).

Table 8-2 Estimated hydraulic conductivities and infiltration capacities (m/s) for impoundment 1 and surrounding geological formations (data from Axelsson et al., 1986; see Malmström et al., 2001, for details).

Formation	Hydraulic conductivity K (m/s)	Infiltration conductivity K_i (m/s)
Organic sediment (peat)	$10^{-9} – 10^{-8}$	
Moraine	8.10^{-6}	5.10^{-5}
Bedrock	$3{\cdot}10^{-7} – 5{\cdot}10^{-5}$	

8.7 Recipients

The water leaving impoundment 4 enters the small river Vormbäcken (Figure 8-5). Vormbäcken starts downstream from the lake system Sörsjön-Holmträsket-Norrsjön, almost 2.5 km upstream from the outlet from the mine area at Kristineberg, and flows for approximately 40 km before joining the river Vindelälven at Vormsele. Vindelälven is a primary tributary to the river Umeälven, which in turn enters the Bothnian Sea at Umeå.

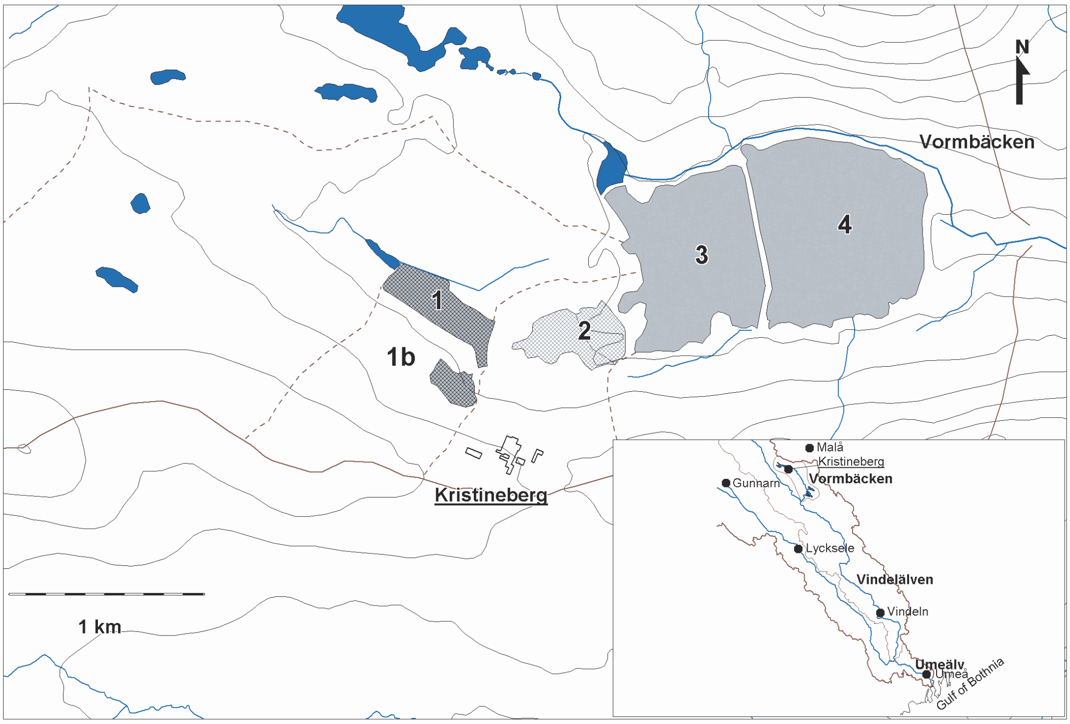


Figure 8-5 Local water catchment area at Kristineberg (Svensson and Höglund, 2004). The dashed lines mark identified sub-catchment areas.

The major tributaries to Vormbäcken are drainage from the lake Holmtjärn, and the rivers Kimbäcken, Svältamyrbäcken, Svartbäcken, and Rökån. Approximately 14 km downstream from the Kristineberg mine, there is a bifurcation, which allows water from Vormbäcken to join Rökån. Before entering Vindelälven, Vormbäcken flows through the 8-km^2 lake Vormträsket. The difference in elevation between Sörsjön-Holmträsket-Norrsjön and Vormsele is about 130 m.

The catchment area of Vormbäcken is approximately 370 km^2. In the catchment, the vegetation is dominated by coniferous forests and mires. The soil is moraine, and the bedrock is mainly composed of granite (Brånin et al., 1976). Mining activities have taken place at several locations in the uppermost part of the catchment area since the 1940's. The Kristineberg mine is the only mine in the area that is still active. The mines at Rävliden, Hornträsket, and Kimheden have all been reclaimed.

In the case of Vormbäcken, the water quality at Vormsele is to a large extent the result of mixing the original river water with the water leaving impoundment 4, surface water from the tributaries, and groundwater from the rest of the catchment area.

In this part of Sweden, the flow of water in running waters exhibits a distinct peak during snowmelt, which typically occurs in May (SMHI, 1979). At the sampling station Storkalven (immediately downstream from Hornträsket), the flow of water in Vormbäcken usually varies between 0.06 and 4 m3/s (Brånin et al., 1976). The average flow is 0.4 m^3/s (ibid.). At Vormsele, the flows have increased to 0.9-25 and 4 m^3/s, respectively (ibid.). The discharge from impoundment 4 is also greatest during snowmelt. Widerlund et al. (2001) report discharges of 0.37 m^3/s in May 1999 and 0.25 m^3/s in September the same year. The mixing ratio between the river water and the water leaving impoundment 4 was greater during high flow events (12:1 in May 1999) than during periods of low flow (3:1) (Sjöblom et al., 2003b). This probably reflects that the catchment area of impoundment 4 is small in comparison to that of the river upstream from the spillway.

Upstream from the Kristineberg mine, the river water has a low ionic strength (40 μS/cm; Sjöblom et al., unpublished data) and low alkalinity (Table 8-3). The pH is close to 6, and the water contains approximately 6 mg DOC/l and 0.2 mg Fe/l (Sjöblom et al., 2004). A substantial part of the Fe has been found to occur in particles of 1 kDa – 0.2 μm size (Forsberg, 2002). At present, the concentrations of Cd, Cu, and Zn in the river water are elevated already upstream from the outlet from the mining area at Kristineberg (Sjöblom et al., 2001). This is probably due to a combination of earlier mining activities and the local geology (cf. Runnells et al., 1992). During normal operation of the water treatment facilities at Kristineberg, the treated water actually dilutes the river water with respect to the trace metals mentioned above (Sjöblom et al., 2001). However, the treated drainage is a significant source of Ca to the river water (ibid.). To some extent, mixing of the river water with the treated drainage resembles the situation encountered in estuaries. The increase in ionic strength may lead to flocculation of dissolved organic matter and coagulation of smaller particles, which is also suggested by results presented by Forsberg (2002), Sjöblom and Håkansson (2003), and Sjöblom et al. (2004). The treated drainage often has a comparatively high pH (>9 according to Sjöblom et al., 2003b), which probably favours trace metal association to particles (Sjöblom et al., 2004).

Significant contributions of Fe are made from the groundwater (Sjöblom et al., 2003b). Since the solubility of Fe in near neutral, oxygenated water is low, this translates into increasing concentrations of particulate Fe along certain stretches of the river. It has been suggested that this phenomenon favours trace metal association to particles (Sjöblom et al, 2004). The influence of Fe is less pronounced during high flow events, presumably due to dilution (Sjöblom et al., 2003b). Furthermore, it is clear that the groundwater makes significant contributions of As to the river water (ibid.). High concentrations of As have also been found elsewhere in the Skellefte mining district (Rönnblom-Person and Ljungberg, 2001).

Table 8-3 Water chemistry along Vormbäcken illustrated by data from a sampling campaign conducted in June 2000 (Sjöblom et al., 2001 and 2003b).

	Storkalven (S, at 0 km)	Spillway (U)	Aspliden (S+U [1)], at 3 km)	Svältamyr-bäcken (tributary)	Brännfors (at 26 km)
pH	5.3	9.3	5.8	5.6	6.1
Alkalinity (mg HCO_3^-/l) [2)]	2.49	n.d. [3)]	4.98	3.07	5.56
Conductivity (mS/m)	4.0	145	36	3.0	10
TOC (mg/l)	6.4	1.2	5.5	10.4	9.7
Sulphate (mg/l)	12	839	166	5	33
Ca (mg/l)	4	355	66	3	15
Fe (µg/l)	206	165	554	351	552
Zn (µg/l)	505	33	383	27	116
Cu (µg/l)	116	8	84	5	19
As (µg/l)	0.8	0.7	1.0	0.7	2.3
Pb (µg/l)	1.10	0.27	1.24	0.08	0.40
Cd (µg/l)	1.4	0.09	1.1	0.04	0.3

1) This sampling station is situated where the river water and the treated drainage from the mine area can be assumed to be totally mixed. It also reflects contributions made by other sources in this part of the catchment area (e.g. As, Fe, and Pb).
2) Herbert (unpublished data).
3) n.d.=not determined.

The concentration of Cd, Cu, and Zn in the natural tributaries investigated in 2000 was much lower than those encountered in Vormbäcken (Sjöblom et al., 2001). The trace metal contributions made by Svältamyrbäcken, the natural tributary that exhibited the highest concentrations, were still larger than those made by the Kristineberg mine (ibid.).

8.8 Transport pathways

Water that infiltrates the impoundment will leave it through the cover on the lowest slopes and by flow downward into the underlying till and rock. The water that leaves through the cover will emerge into a drainage ditch adjacent to the impoundment and flow as surface water to some larger stream. This water will immediately be exposed to air and will contact flora and fauna in the stream.

The water that flows downward will eventually emerge to the surface. The paths can vary considerably in length and have very different residence times. Underway the water may come in contact with different reactive materials that can attenuate the solutes. The attenuation processes are described in Chapter 9. The pathways are schematically illustrated in Figure 8-6. The far field transport pathways are much more heterogeneous than those in the near field. Their hydraulic, chemical and biochemical properties are also not as well characterised.

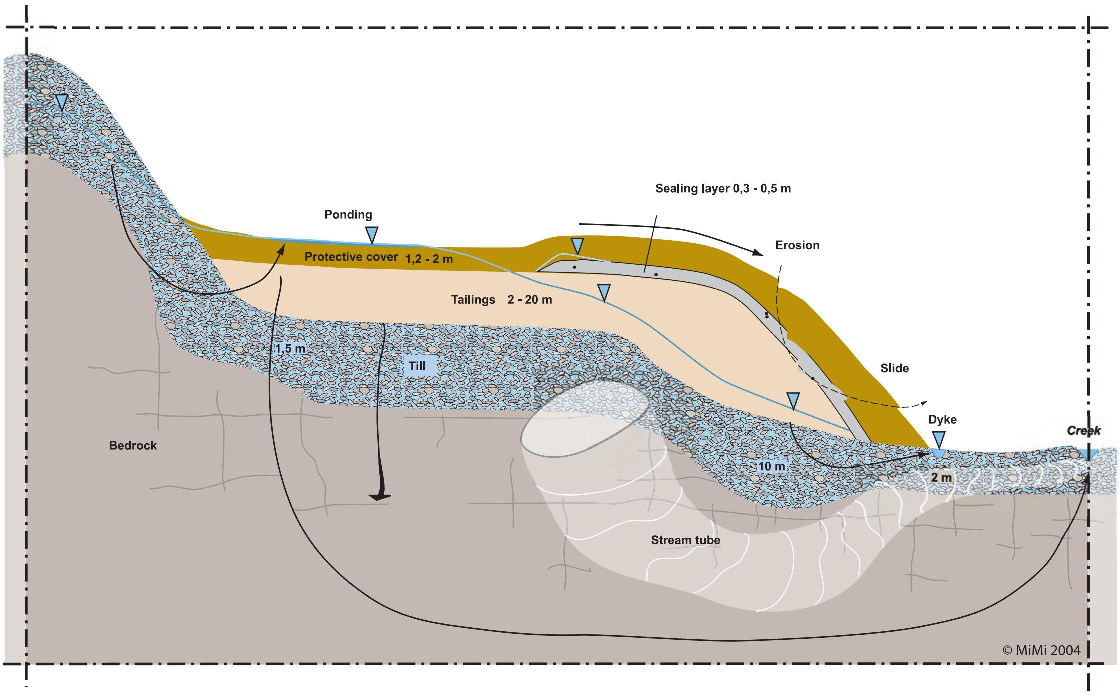


Figure 8-6 Schematic illustration of the transport pathways in the far field.

9 Natural Attenuation Processes in the Far Field

The MiMi programme has proposed that natural attenuation may be utilised as a final polishing step in an integrated system of remediation measures implemented at a mine site (MiMi, 2001). Since the overall objective of the MiMi programme has been to contribute to a solution of the environmental concerns of mine waste on a long-term basis, focus has been put on passive systems which require a minimum of maintenance. Such a system may be part of a natural drainage system (streams, lakes and wetlands), or may consist of constructed ponds and/or wetlands. This chapter contains a summary of the key factors controlling natural attenuation of metals, and a brief discussion of engineering aspects that should be considered when natural attenuation systems are planned and designed.

9.1 Introduction

As is decribed in Chapter 7, significant fractions of the trace metals released by oxidation of sulphide minerals may be retarded by various geochemical processes within the waste impoundment (near field attenuation). Dissolved metals in groundwater leaving the tailings through underlying soil may also be immobilised by sorption to mineral particles and to peat below the waste. The sequence of possible attenuation processes then extends to the region of exfiltration of the contaminated groundwater and to ditches, ponds and other surface waters in the closest vicinity of tailings impoundments. Also, processes in nearby creeks, lakes and wetlands may remove shares of residual contaminants before the water finally reaches the Bothnian Sea via rivers.

Suspended particles play a significant role in the natural attenuation of metals taking place in surface drainage waters within mine sites, as well as in recipients located downstream of such sites. Particulate matter in general is a mixture of particles composed of:

- detrital (primary minerogenic) material (silicates, carbonates and primary ore minerals from ore/ore concentrates and waste rocks)
- secondary precipitates (mainly Fe, Al and Mn oxyhydroxides, calcite and gypsum)
- organic matter (living biota, dead organic matter (detritus) and humic substances)

Contaminant attenuation in the far field involves formation of secondary solid phases and sorption processes under both anoxic and oxic conditions. This holds for metals existing in cationic form, e.g. Pb(II), Zn(II), Cu(II) and Cd(II), as well as, anionic contaminants, such as sulphate, As (arsenate/arsenite), Mo (molybdate) and V (vanadate). Considering the very large amounts of iron generally present in mine waste leachates, iron-containing phases have the potential to play a particularly important role in this context.

Active sorbents can be both primary and secondary mineral phases and particulate organic matter. In addition to oxyhydroxides, calcite and gypsum may precipitate from mine waste leachates and form suspended particles. Sorption of trace metals into calcite through coprecipitation appears to be common (e.g., Rimstidt et al., 1998).

A significant attenuation of contaminants requires efficient removal of the particulate phase from the flowing water by filtration (groundwater) or sedimentation (surface water). Aggregation of colloidal particles facilitates filtration and sedimentation. Presence of dissolved organic matter, as well as, inorganic compounds can be expected to influence both the uptake of contaminants and the fate of the particles. For instance, the mixing of waste leachates with high salinity and natural surface waters containing considerable amounts of dissolved organic matter may strongly affect the particle dynamics in this type of environments.

Long-term alterations of the particulate phases leading to virtually irreversible immobilisation of metals are important for natural attenuation in the long-term perspective. This includes phase-transformation resulting in formation of less soluble mineral phases. Incorporation of metals, originally adsorbed onto mineral surfaces, into the solids would result in a decreased tendency for remobilisation. Metals associated with particles formed under oxic conditions, which are retained in environments where reducing conditions are prevailing, can be transferred into sulphide phases with low solubility. Such processes are facilitated by sulphate reducing bacteria in e.g. wetlands and organic-rich sediments.

Natural attenuation processes can be utilised in active as well as passive treatment systems. Wetlands are being used for passive treatment of leachate discharge at many locations, but with varying success. While there are several examples of well functioning wetland treatment systems, in other cases loads of metals have been too high to maintain an operating ecosystem. For instance, high levels of Fe and Al have resulted in such extensive precipitation of secondary iron/aluminium solid phases that even resistant plants have not survived.

To summarise, metals discharged from mine waste can be attenuated in the far field according to a sequence:

- Particle formation
- Association of metals to particles by co-precipitation or adsorption
- Aggregation of colloids to larger particles
- Particle removal by sedimentation or deposition on plants or debris in wetlands
- Phase transformation of poorly crystalline phases with time

9.2 Abiotic processes

Particle formation

Iron(II) contained in anoxic discharge is a primary source for formation of particulate phases in recipients of AMD, but AMD may also contain significant amounts of Mn(II) and Al(III) . While exposed to atmospheric oxygen, Fe(II) and Mn(II) is are oxidised to Fe(III) and Mn(III,IV), respectively although rates can be slow for acidic conditions. Hydroxides, and in the case of Fe and Al also hydroxysulphates, will be readily precipitated with a sulphate content that is dependent on the Fe/Al to SO_4^{2-} molar ratios in the drainage. In the following discussion focus will be put on secondary iron phases. As is discussed in section 7-6 and summarised in Figure 9-1 jarosites are formed at very low pH and high sulphate concentrations. Schwertmannite is the phase commonly observed in slightly less acidic environments (c.f. reaction 9-1), and ferrihydrite and goethite are commonly precipitated at pH >5 (reaction 9-2).

$$8\ Fe^{2+} + 2O_2 + 10\ H_2O + SO_4^{2-} \rightarrow Fe_8O_8(OH)_6(SO_4)(s) + 14\ H^+ \qquad (9\text{-}1)$$

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \qquad (9\text{-}2)$$

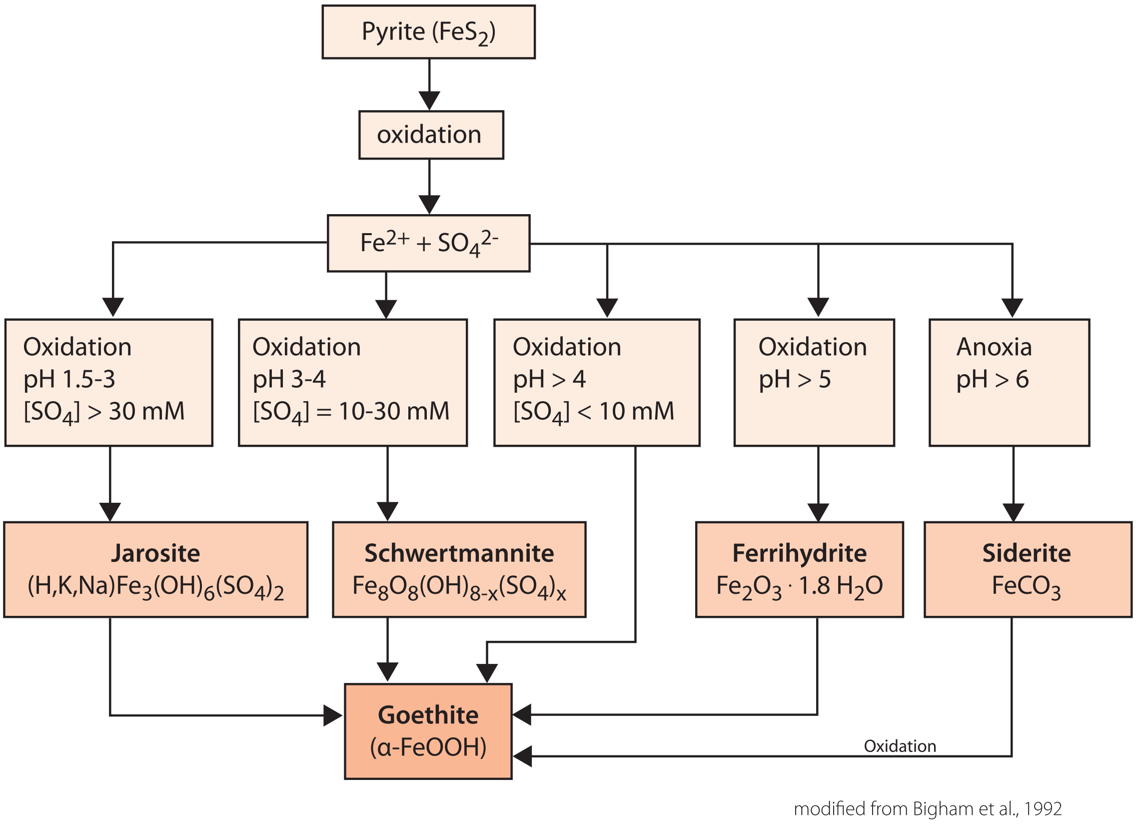


Figure 9-1. Biogeochemical model for precipitation and transformation of secondary iron solid phases from mine waste leachates, modified from Bigham et al. (1992).

In acidic drainage the concentrations of dissolved Al(III) are likely to be high. This aluminium forms weakly soluble (hydr)oxides and hydroxysulphates when the acid water is neutralised by receiving surface water or discharge of less acidic groundwater. On the other hand, the solubility minimum of Al hydroxides at pH ca. 6 results in low Al concentrations in near neutral and neutral drainage waters. Since precipitation of secondary phases commonly involves association of metal ions to anions of weak acids, e.g. OH^- and HCO_3^-/CO_3^{2-}, these reactions are acid producing processes.

Effects of geochemical conditions

The oxidation kinetics of ferrous iron is strongly related to solution pH. As shown by Stumm and Morgan (1996) the oxidation kinetics of Fe(II) in dilute water is increased with two orders of magnitude per pH unit. On the other hand, the oxidation and the subsequent hydroxide precipitation is less pH dependent in presence of high sulphate concentrations even if sulphate not is coprecipitated (Jönsson, 2003). This was shown in laboratory experiments with groundwater from Kristineberg impoundment 1 containing 34 mmol dm^{-3} (2 g dm^{-3}) of Fe and 52 mmol dm^{-3} (5 g dm^{-3}) of sulphate. The oxidation and preciptation reactions proceeded ca. 3 times faster at pH 7 than at pH 5.5 at 25°C. In another series of experiments Fe(II) oxidation was studied at 10°C. While the oxidation kinetics at pH 7 appeared to be virtually unaffected by temperature, the reaction was 35-50 % slower at 10°C than at 25°C and pH 5.5. The solid phase formed at pH 7 was lepidocrocite. At pH 5.5 a mixture of different Fe oxyhydroxides and schwertmannite was formed. The kinetics of Fe(II) oxidation may in these systems be significantly influenced by the presence of sulphate at high concentrations in the solution.

As an example of slow oxidation kinetics at low pH, the acidic (pH 3.0) pore water of schwertmannite sampled at Kristineberg in June 1998 by Jönsson (2003) contained Fe concentrations much above the calculated solubility of Fe(III) (hydr-)oxides, Tables 9-1 and 9-2. This was likely due to presence of unoxidised Fe(II), although the solution was in direct contact with air.

Table 9-1. Characterisation of schwertmannite. Elements in μmol g^{-1}, H_2O and LOI in weight-% of dry weight (Jönsson et al., 2004).

Fe	8 700	Na	29	Zn	0.15	Zr	0.034	Mn	<0.46	Nb	<0.06
S	1 600	Mg	11	Ba	0.12	Co	0.006	W	<0.32	Mo	<0.06
C	580	P	6.8	La	0.094	Ni	0.004	Cr	<0.19	Sc	<0.02
Si	340	As	2.8	Pb	0.081	Cd	0.0002	Sn	<0.17	Hg	<0.0002
Al	56	V	0.74	Sr	0.068	N	<35	Cu	<0.16	LOI	35.6
K	37	Ti	0.53	Y	0.056	Ca	<18	Be	<0.07	H_2O	20.7

Table 9-2. Elemental composition of pore water from the schwertmannite sample (Jönsson et al., 2004). Concentrations in µM, besides Hg which is in nM. pH = 3.0.

S	25 800	Al	960	Fe	130	Sr	12	Cd	0.16	As	0.012
Ca	13 000	Si	950	K	100	Ni	7.6	Ba	0.067	Pb	0.008
Mg	10 700	Mn	670	Zn	29	Cu	1.5	Mo	0.047	Hg	0.045
Na	1 050	C	470	Co	15	P	0.97	Cr	0.026		

Association of contaminants

The precipitation of secondary iron solid phases induced by the oxidation of Fe(II) forms the basis for sorption processes in the far field. Field studies have demonstrated the significance of metal(hydr)oxides for the retention of metals in soils contaminated by acid mine drainage (Herbert, 1996 and Lin, 1996). The regulating role of iron (hydr)oxides in rivers receiving acid mine drainage has been described by, e.g., Johnson (1986), Kimball et al (1995) and Munk et al. (2002). In some cases, the mobility of contaminants can be enhanced due to adsorption to mobile colloidal particles (McDowell-Boyer, 1992). The large adsorption capacity of Fe(III) oxyhydroxides with respect to both cations and anions is well documented (Stumm, 1992; Cornell and Schwertmann, 1996).

In a study of element transport within the mining area at Kristineberg, Öhlander et al. (2004) found that a large fraction of many trace metals, e.g. Cu, Pb and As, was associated to suspended matter in the inlet of impoundment 2, Table 9-3. The corresponding values for the metals leaving impoundment 2 were in many cases significantly lower. This is likely explained by the lower pH in the outlet (pH 3.25 ± 0.35) than in the inlet (pH 4.6 ±1.3).

Table 9-3. Total transport and the contribution of suspended particulate material in % of total transport at the inlet and outlet of impoundment 2, Kristineberg during the period 990525–991020 (Öhlander et al, 2004).

Element	**Inlet impoundment 2**		**Outlet impoundment 2**	
	Total transport (kg)	% susp. mtr. of total transport	Total transport (kg)	% susp. mtr. of total transport
Ca	597 000	0.025 %	423 000	0.023%
Fe	38 800	2.5%	54 700	1.3%
K	18 500	0.042%	12 300	0.053%
Mg	51 500	0.10%	61 300	0.029%
Na	20 700	0.026%	14 300	0.031%
S	584 000	0.89%	543 000	0.052%
Si	2580	2.5%	6520	0.46%
Al	3800	4.1%	21 900	0.085%
As	7.98	60%	1.39	55%
Ba	16.7	1.5%	15.7	1.6%
Cd	14.5	46%	60.5	0.043%
Co	36.0	41%	98.2	0.037%
Cr	4.55	83%	5.61	1.7%
Cu	1710	81%	2680	0.051%
Hg	0.0235	77%	0.00919	81%
Mn	898	9.5%	1970	0.37%
Mo	1.12	85%	1.15	1.9%
Ni	14.7	34%	45.4	0.061%
Pb	16.8	76%	34.6	1.2%
Sr	613	0.040%	438	0.031%
Zn	6330	61%	27 000	0.032%

The pH of the groundwater determines the extent to which contaminants are retained. At low pH the tendency for metal cations to be adsorbed is low, while anions like arsenate and cromate are more strongly associated with mineral surfaces. In heavily limed areas of mine waste deposits with alkaline conditions carbonate minerals may be formed.

The distribution of ions between particle surfaces and the aqueous solution is strongly dependent on solution pH and is also influenced by the presence of complexing ligands in the solution. In general, adsorption of cationic species is favoured by increasing pH (Figure 9-2), whereas anions are more strongly bonded under weakly acidic and acidic conditions. Adsorption of ions can be described as complexation reactions taking place at specific binding sites on mineral surfaces.

All of the studied metals except Cd(II) have a higher affinity for schwertmannite than goethite (Figure 9-2). The higher affinity for the schwertmannite surface could potentially be explained by the formation of surface complexes involving surface sites, SO_4^{2-} and metal ions.

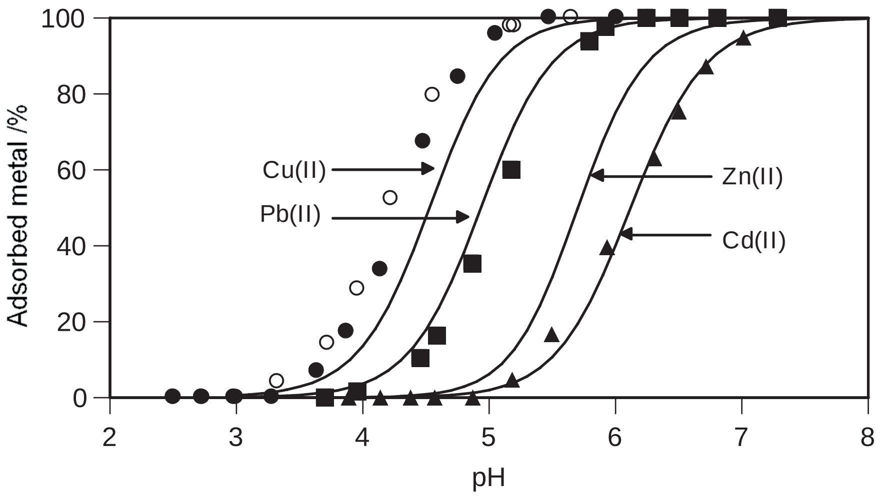


Figure 9-2 Adsorption of Cu(II) (○), Pb(II) (●), Zn(II) (■) and Cd(II) (▲) to schwertmannite as a function of pH with metal/mineral ratios of 0.06 µmol m^{-2}, a solid concentration of 1 g dm^{-3} and a specific surface area of 200 m^2 g^{-1}. The solid lines represent the calculated adsorption to goethite at corresponding metal solid ratios. Model parameters from Palmqvist et al. (1997).

By the introduction of surface complexation theories it is now possible to describe adsorption and desorption processes in terms of equilibrium reactions involving specific functional groups, commonly symbolised ≡FeOH, at mineral surfaces. By applying electric double layer theories, effects of surface charge can be adjusted for. These theories are described in more detail in Chapter 11.2. Due to the poor stability of schwertmannite it is not possible to show that adsorption/desorption processes involving schwertmannite are truly reversible, which is a requirement for equilibrium modelling. Instead, partitioning coefficients, K_d, can be derived based on empirical data for adsorption processes. K_d is defined as:

$$K_d = \frac{C_S}{C_L} \qquad (9\text{-}3)$$

where C_S is the amount associated with the solid (mol g^{-1}) and C_L is the concentration in solution (mol dm^{-3}). K_d is widely used in geochemical modelling to quantify retention by solid phases. Unfortunately, K_d is conditional and the value determined is often valid at the specific conditions under which it was determined. Adsorption of metal ions to mineral surfaces is strongly pH dependent and a range of K_d values for Cu(II), Pb(II) and Cd(II) adsorption to schwertmannite have therefore been calculated, Table 9-4. As the adsorption edges for Cu(II) and Pb(II) are very similar, the K_d values are set to be identical for the two metals. For Zn(II) the agreement between data sets was not as good as for the other metal ions. The K_d values have therefore been separated in Table 9-4 where values for “Zn(II) low” are estimated from the data of Figure 9-2 and “Zn(II) high” from data obtained from experiments at higher surface coverage of Zn(II). The reason for blank fields in Table 9-3 is that K_d cannot be estimated in the pH ranges where the metal ions are adsorbed to 0 or 100%.

Table 9-4. log K_d for metal partitioning by schwertmannite calculated from adsorption experiments performed at a surface coverage of metal ions corresponding to 0.057 μmol/m^2 and 0.52 μmol/m^2 (Jönsson, 2003).

	Log Kd				
pH	Cu(II)	Pb(II)	Cd(II)	Zn(II) low	Zn(II) high
3.5	-1.04	-1.04			
4.0	-0.34	-0.34		-1.71	
4.5	0.42	0.42		-0.85	-1.12
5.0	1.06	1.06	-1.79	-0.01	-0.63
5.5	2.14	2.14	-0.79	0.61	-0.24
6.0			-0.20	2.05	0.14
6.5			0.38		0.74
7.0			1.11		1.52
7.5			1.28		
8.0			2.00		

Thus, two important pH-effects can be noted regarding the natural attenuation of metals in AMD. 1) The formation of secondary Fe, Al and Mn precipitates occurs over different pH ranges, and the composition of the solid phases formed is largely determined by solution pH. 2) Sorption processes are strongy pH dependent with cationic species adsorbed mainly at neutral and high pH, while and adsorption of anionic species is favoured by low pH.

The chemical composition of the aqueous phase strongly influences sorption processes but also dominating pathways for phase transformation. Long-term alterations leading to virtually irreversible immobilisation of metals by adsorption/ transformation or co-precipitation, substitution etc. are important for the long-term performance of remediation actions.

The effect of natural organic matter on metal sorption

The aqueous speciation of many transition elements is dominated by interaction with natural organic compounds. Solid organic matter can contribute to the attenuation of metals by sorption. On the other hand, NOM in the aqueous phase may significantly influence the degree of sorption of metals onto mineral surfaces. Depending on the hydrochemical conditions, presence of high concentrations of NOM can increase sorption as a result of formation of so called ternary surface complexes. However, high NOM concentrations can also result in a decreased sorption due to a pronounced aqueous complexation with metal ions.

The effect of NOM on the Cu(II) adsorption to schwertmannite and goethite was investigated by Jönsson (2003). There was a difference between Cu(II) adsorption in the Cu(II)-goethite and NOM-Cu(II)-goethite systems. As the NOM-concentration increases, the adsorption edge for Cu(II) was shifted towards lower pH. This effect has been observed in previous studies and may be explained by considering that negatively charged organic molecules adsorbed to the mineral surface lowers the positive charge at the protonated surface and thereby favours the binding of cationic metals to the surface. Increased metal uptake in presence of complexing ligands may also be explained by the formation of ternary surface complexes involving metal ions, complexing ligands and surface functional groups. As pH increases and NOM desorbs, Cu(II) can potentially be mobilised if associated with NOM. It is well documented that Cu(II) and several other trace metal ions form complexes with natural organic molecules in solution. In an EXAFS study of Cu(II) coordination in complexes with goethite and humic acids (HA), Alcacio et al. (2001) suggested that Cu(II) predominantly adsorbs to goethite by forming type A ternary surface complexes, i.e. complexes of the type ≡FeOCuA, at moderate surface loading of HA. At higher levels of adsorbed HA, type B ternary surfaces complexes were suggested to form, i.e. complexes in which Cu(II) coordinated to adsorbed HA. These observations resemble those reported by Tipping et al. (1981) and Xu et al. (1989).

As SO_4^{2-} is an anion it can be expected to have an effect on adsorption similar to NOM, i.e. lowering the surface charge and thereby attracting cations at low pH and forming ternary surface complexes. Sulphate is not only part of the bulk structure of schwertmannite but also present in significant amounts adsorbed at the surface.

Quantitative considerations

Since Fe-containing secondary phases play a dominating role in the trace metal attenuation in the far field, the capacity of these secondary phases to attenuate contaminants is limited by the amount of iron available in the deposited mine waste. In experiments carried out to quantify the metal uptake capacity of schwertmannite, Jönsson (2003) found that one Cd(II) or Zn(II) ion could be adsorbed per sixteen Fe atoms residing in the solid phase. However, it should be noted that freshly precipitated secondary iron phases are generally poorly crystalline. Upon ageing these solids are transformed into more ordered structures. Phase transformation can be expected to result in altered sorption properties and hence affecting the solubility of metals. While incorporation of metals into the solids would result in a decreased tendency for remobilisation, decreased surface areas imply reduced sorption capacity. The long-term attenuating capacity of the secondary Fe phases is yet to be quantified. Not to forget, the degree of association of metals to solid matter is strongly dependent on the hydrochemical conditions, above all pH.

The potential of metal attenuation by secondary iron phases can be estimated from the molar ratio between trace metals and iron and on the above mentioned observation of one trace metal ion adsorbed per sixteen Fe atoms in schwertmannite. An estimate based on the average composition of unweathered tailings in Kristineberg, impoundment 1 (Holmström et al., 2001) indicates sufficient amounts of Fe for significant retainment of Cu(II), Pb(II) and Cd(II) (Table 9-5). Although this kind of arithmetics cannot be applied directly for anionic species, like arsenite and arsenate, the Fe/As ratio in the tailings seems favorable for significant attenuation. This would be true irrespective if As is associated to particulate phases by adsorption or by (co-)precipitation with Fe. Also for Zn the Fe/Me molar ratio is high enough for removal of most of the metal from the drainage water. However, considering the rather weak sorption of Zn(II) and the possibility of loss of sorption sites due to phase transformation during aging, a large fraction of this metal can be assumed to remain in solution.

The potential for significant natural attenuation in the far field is further accentuated when considering that the trace metals are preferentially removed from the pore water of the tailings (c.f. Chapter 7). Thus, the Fe/Me molar ratio is for most trace metals much larger in the discharging groundwater than in the waste material itself (Table 9-5).

Table 9-5. Molar ratios Fe/Me in tailings from Kristineberg, impoundment 1 (Holmström et al., 2001) and in discharging groundwater from the same impoundment (Jönsson, 2003).

	Tailings		**Discharge water**	
	mass-%	Fe/Me molar ratio	µmol/dm^3	Fe/Me molar ratio
Fe	16.8	-	34 200	-
S	14	0.69	52 100	0.66
Zn	0.9	22.1	28	1 200
Cu	0.1	200	0.12	285 000
Pb	0.05	1 350	0.025	1 370 000
Cd	0.002	16 900	0.004	8 600 000
As	0.02	1 230	0.035	980 00

Aggregation and sedimentation

Relatively large particles can be expected to settle rather shortly after precipitation. They may be resuspended and transported further downstream by convection in running waters. On the other hand, very small particles of colloidal size may exist suspended also after a long time period in slowly moving or stationary surface waters. Colloids are characterized by their flocculation at increasing salinity (van Olphen, 1963). Electrostatic repulsion between particles with equally charged surfaces is important in maintaining a stable colloidal phase. The surface charge is strongly related to the hydrochemical conditions (Stumm, 1982). pH and ionic strength are master variables in this context. High concentrations of ions may shield charges at surfaces and in this way reduce the electrostatic repulsion. Aggregation of colloids into larger particles will increase settling and, hence, the removal of solid matter from the flowing water. The mixing of a saline mine waste leachate and natural fresh water thus may cause flocculation of colloidal matter carried by the fresh water, for example humic substances. Among the dissolved main elements in mine waste leachates, Ca^{2+} ions are most effective in coagulating colloidal humic matter, both in terms of the Ca^{2+} concentration required and the amount of humic matter flocculated (Eckert and Sholkovitz, 1976).

Organic matter in natural waters is often expressed as total organic carbon (TOC), a collective term for dissolved, colloidal and particulate organic carbon. Literature data suggest that the effects of organic matter on flocculation processes may be quite variable. For example, Ali et al. (1984) found that salt flocculation was retarded by organic matter, possibly due to the stabilization of flocs by organic polymers present on particle surfaces. On the other hand, particle attachment may be enhanced if organic polymers form bridges between particles. It is also well known that organisms present in natural waters can cause flocculation of suspended matter.

If the reclamation activities at the Kristineberg mine area work as planned, future liming may not be needed in order to improve the quality of the drainage from the mine area before it is released into the recipient. However, it is possible that a reduction in the ionic strength of the stream water (at present often > 300 µS/cm a couple of hundred meters downstream of the outlet; Sjöblom et al., unpublished data) will have a negative influence on natural attenuation processes coupled to aggregation of colloids (cf. Sjöblom and Håkansson, 2003).

Laboratory mixing experiment at the Kristineberg site, northern Sweden

A laboratory experiment simulating flocculation processes in a flooded tailings impoundment was performed at the Kristineberg mine (Widerlund et al., 2004a). Water from impoundment 4 (pH = 8.0) was mixed with natural stream water (pH = 7.0; dissolved Ca = 380–740 mg l^{-1}). The proportion of water from the impoundment was 0, 25, 50, 75 and 100 vol% in the five mixing bottles. After completion of the experiment, the flocculants that had formed and settled in the mixing bottles were retrieved by centrifugation.

Total organic C and dissolved Fe, Mn and Al – Iron was rapidly flocculated. Fe was almost completely removed from solution within 24 h of mixing. In the range of 50–75 vol% of water from impoundment 4, the degree of removal amounted to 93–97% of the dissolved concentration expected for a theoretical, conservative mixing behaviour shown by the straight mixing line between the two end-member components.

The removal of manganese from the solution was initially small. Dissolved Mn showed an essentially conservative behaviour for at least 48 h after mixing, while removal of dissolved Mn was detected in the mixing bottles 13–98 days after mixing. This removal was most pronounced at 25–50 vol% of water from impoundment 4, where 95–98 % of the dissolved Mn was removed. The mixing curves for dissolved Al initially (24–48 h after mixing) indicated significant, but far from complete, removal of dissolved Al. At 25–50 vol-% of water from impoundment 4, 13–50% of the dissolved Al was removed from solution. The pronounced decrease of Al concentration 13–98 days after mixing occurred in all bottles and is interpreted as a storage artefact (sorption to bottle walls).

Removal of flocculated TOC appeared to be of little or no significance in the mixing experiment.

Dissolved, Cd, Cu and Zn – Cu and Zn were added to the dissolved phase during the experiment. The only reasonable explanation for such a non-conservative mixing behaviour is that Cu and Zn were transferred from the particulate to the dissolved phase, most probably due to dissolution of suspended calcite and gypsum particles present in the unfiltered water from impoundment 4. Addition of Cd, Cu and Zn from dissolving calcite/gypsum particles is also necessary to explain the enrichment of these metals in the flocculants that formed during the mixing experiment. For Cd, some scatter in the data was evident, and a slightly non-conservative mixing behaviour of Cd (addition to or removal from solution) could not be excluded.

Formation and settling of flocculants – Brown flocculants formed and settled within 24 h of mixing in all bottles containing fresh water, either pure fresh water or a mixture of fresh water and water from impoundment 4. The concentrations of total C (18 wt-%) and acid-leacheable Fe (14–19 wt-%) in the flocculants suggest that organic matter and Fe oxyhydroxides formed substantial fractions of the flocculants. In addition, based on the acid-leacheable concentrations of Mn and Al, Mn and Al oxyhydroxides probably also were present in the flocculants (Widerlund et al., 2004a).

The total amount of flocculants that had formed and settled after completion of the experiment varied from 2.8 to 6.2 mg l^{-1} of fresh water. The amount of flocculants was linearly correlated to the ionic strength, i.e., the proportion of water from impoundment 4 in the mixing bottles. By subtracting the amount of particulate matter that settled in pure fresh water (2.8 mg l^{-1} of fresh water), the amount of settled particulate matter formed due to the increasing electrolyte concentration was calculated to be 1.7–3.4 mg l^{-1} of fresh water. If stream water is diverted through tailings ponds as part of a remediation programme, flocculation processes are likely to contribute to natural sedimentation in the pond. However, based on the amount of flocs formed in the study, significant contributions from flocculation processes can therefore only be expected when streams with average suspended matter concentrations < 10–15 mg l^{-1} are diverted into an impoundment (Widerlund et al., 2004a).

Trace metal uptake in flocculants – The high concentrations of Cd, Cu and Zn found in the flocculants formed in the presence of water from impoundment 4 suggest that these metals were sorbed to the settling flocculants. However, the fact that unfiltered water from impoundment 4 was used in the experiment may have affected this metal sorption in two ways:
1) metals may have been supplied from dissolving suspended calcite/gypsum particles, and
2) suspended Fe oxyhydroxides (with high concentrations of Cd, Cu and Zn) to some extent may have been incorporated into the settled flocs.

Based on the contents of Cd, Cu and Zn found in two floc samples, the transfer of these metals into settling flocculants has been calculated (Table 9-6).

Table 9-6. Transfer of Cd, Cu and Zn from the dissolved phase into flocculants.

	Cd	Cu	Zn
Floc sample 1			
Metal content in flocs (µg)	0.045	5.6	47
Transferred from dissolved phase (µg l^{-1})	0.028	3.5	29
Floc sample 2			
Metal content in flocs (µg)	0.077	5.7	48
Transferred from dissolved phase (µg l^{-1})	0.024	1.8	15

The Cd uptake in the flocculants (Table 9-6) was within the data scatter for the dissolved phase, and was therefore not detectable in this phase. However, a mass balance calculation suggested that the amount of Cd found in the flocs slightly exceeded the loss from solution. Thus, a small amount of Cd (0.007–0.048 µg) was probably supplied from 1) dissolving suspended calcite/gypsum particles, and/or 2) by incorporation of suspended Fe oxyhydroxides. For Cu and Zn, a similar mass balance calculation showed that these elements must have been supplied by one or both of these processes. Due to the possible incorporation of suspended Fe oxyhydroxides into flocs, the metal transfer into flocculants reported in Table 9-6 must be regarded as an estimate of the upper limit for sorption of dissolved forms of these metals into flocculants. Relative to the dissolved concentrations of Cd, Cu and Zn in water from impoundment 4, the trace metal uptake in the flocculants exceeded 50% of these concentrations only for Cu and Zn.

Phase transformation

A changed composition of the drainage water may lead to an increased adsorption or to a situation where adsorbed metal ions will be mobilised. For an immobilisation on a long-term perspective it is important that the sedimented solids are consolidated into forms where the contaminants are not readily re-mobilised. Phase transformation is a key-word in this context. Under oxidising conditions metals originally adsorbed to freshly precipitated solids may be incorporated in more crystalline phases, and can by this be expected to be less disposed for rapid re-mobilisation. Dissolved or precipitated sulphate ions present in organic-rich sediments may under anoxic conditions be transformed into sulphide, which in turn can form weakly soluble solid phases with metals, such as Cu(II), Zn(II), Cd(II) and Pb(II). On the other hand, reductive dissolution of Fe(III) (hydr-)oxides and hydroxysulphates initially leads to a situation where adsorbed metals are remobilised and may leave the sediments by diffusion.

The hydrous hydroxides will eventually be transformed into more crystalline phases. It has been shown that goethite (α-FeOOH) is the most common final alteration product for both hydrous hydroxides and hydroxysulphates of Fe(III), Figure 9-1 . Thus, the mineralogy at a particular site is to some extent depending on the time span elapsed since the onset of oxidation.

The transformation of schwertmannite to goethite involves release of sulphate ions to the solution, Equation 9-4.

$$Fe_8O_8(OH)_6(SO_4)_{(s)} + 2\ H_2O \rightarrow 8\ FeOOH(s) + SO_4^{2-} + 2\ H^+ \qquad (9\text{-}4)$$

Samples of schwertmannite sampled on top of the till covered impoundment 2 at Kristineberg have been extensively studied with respect to phase transformation (Jönsson et al, 2004). It was shown that the release of SO_4^{2-} is accompanied by a 5-fold increase in surface area after only 6 h. The low surface area of the original sample seems to arise from adsorbed SO_4^{2-} as the surface area increases as the SO_4^{2-} is released from the solid. The stability of the Kristineberg schwertmannite was studied at two pH values, 6 and 9 at 25°C. Two samples were also left in the original pore water at 4 and 25°C. XRD analysis showed a gradual transformation of schwertmannite into goethite.

The phase transformation was favoured by an increase in pH. According to the OH^- consumption 98 % of the sample was transformed after 6 months at pH 9, at pH 6 the consumption of OH^- continued for the entire period. Goethite and possibly traces of H-jarosite were detected in the sample that was left in the original pore water and stored at 25°C during 45 months, although the transformation did not seem to be complete. For a sample stored at 4°C, no transformation was detected even after 58 months. Thus, schwertmannite appears to be relatively stable at low pH and temperature and high SO_4^{2-} concentrations. The temperature dependence is supported by the fact that autoclaving schwertmannite is suggested to complete the transformation in 20 min (Regenspurg et al., 2002). Even at the sub-arctic climatic conditions prevailing at Kristineberg, with an annual average temperature slightly above 0ºC , temperature dependent phase transformations may be significant during summer.

9.3 Physical aspects of natural attenuation systems

Temperature

An important effect of cold temperatures is that the reaction rate of many chemical and biological reactions decreases. For this, the decreased rate of schwertmannite transformation described in the preceding section is a good example. This temperature effect is usually described by the Arrhenius equation:

$$\ln(\frac{k_1}{k_2}) = \frac{E_a}{\ln 10 \cdot R} \cdot \frac{T_1 - T_2}{T_1 \cdot T_2} \qquad (9\text{-}5)$$

where k_1 and k_2 are reaction rates at temperatures T_1 and T_2, Ea is the activation energy of the reaction and R is the gas constant. Equation (9-4) indicates that if the temperature decreases from T_1 to T_2, the reaction rate also will decrease in a non-linear manner. Although temperature effects in general are complex under field conditions, several studies confirm that Eq. (9-5) is a valid approximation for chemical and microbiological oxidation rates (e.g., Dawson and Morin, 1996). In a laboratory experiment, Jönsson et al. (2003a) also found that the oxidation and precipitation of Fe from AMD was more rapid at 25°C than at 10°C.

Water discharge

In cold climates with seasonal snow covers, large seasonal variations in streamwater discharge can be expected. These discharge variations, in turn, can have profound influences on streamwater transport and concentrations of dissolved substances, the latter through dilution and wash-out effects. In addition, streamwater concentrations of suspended particulate matter (SPM) are often positively correlated to the water discharge according to an equation of the type:

$$SPM = A \cdot Q^{B} \qquad (9\text{-}6)$$

where A and B are empirical constants and Q is the streamwater discharge (e.g., Morehead et al., 2003). Streamwater discharge will also affect the residence time of water in lakes and constructed ponds.

Replacement time and residence time – For lakes and ponds receiving most of their water from streamflow, the replacement time for water (τ_w) can be calculated as:

$$\tau_w = \frac{V}{Q_i} \qquad (9\text{-}7)$$

where V is the water volume in the lake/pond and Q_i is the streamwater inflow. The replacement time of a dissolved substance in the lake/pond (τ_r) is defined as:

$$\tau_r = \frac{M}{C_i \cdot Q_i} \qquad (9\text{-}8)$$

where M is the total mass of the dissolved substance in the lake/pond, C_i is the dissolved concentration of this substance in inflowing streamwater and Q_i is the rate of streamwater inflow. If the lake/pond is at a steady state with respect to water and the dissolved substance of interest, τ_w and τ_r can be viewed as residence times as well as replacement times.

Relative residence time (Stumm and Morgan, 1981) is an additional concept which gives an indication of the type of behaviour to be expected for a given substance. The relative residence time (τ_{rel}) is calculated as:

$$\tau_{rel} = \frac{\tau_r}{\tau_w} \qquad (9\text{-}9)$$

A relative residence time of 1 indicates that the substance does not react chemically in a lake, and simply accompanies water as it passes through a lake. If τ_{rel} is less than 1, the substance tends to be removed via sorption and sedimentation in a lake, a behavior found for particle-reactive substances. If τ_{rel} is greater than 1, the substance tends to be trapped in a lake while the water transporting the substance into the lake discharges from the lake. This behaviour is found for elements that are cycled within lakes, that is, they are precipitated/sorbed and settle to the lake bed where they redissolve, which is followed by a new cycle of sorption/settling/redissolution. This type of behaviour is characteristic of elements involved in biological processes.

Stratification of water columns

A stable density stratification of the water column of a lake or a constructed pond may influence the natural attenuation sequence in different ways. The presence of a pycnocline (i.e. a layer of water where the water density changes rapidly) would tend to reduce the settling of suspended particulate matter in lakes/ponds, which would result in a rather inefficient entrapment of metal-enriched particulate matter. In relatively deep lakes/ponds, a stable density stratification would also reduce the wind mixing of the water column, possibly resulting in anoxic bottom water conditions, at least during part of the year (e.g., Wetzel, 2001).

Anoxic bottom water conditions would, in turn, result in a redissolution of redox-sensitive sorbents such as Fe and Mn oxyhydroxides at the sediment – water interface. Metals sorbed to Fe and Mn oxyhydroxides could thus be released back into the water column in dissolved forms.

Characteristics of suspended particulate matter

Two important physical factors can be noted regarding suspended particulate matter in natural attenuation systems: 1) the size distribution of the suspended particles and 2) the suspended matter concentration. Particle size distributions in natural waters normally span a size range of several orders of magnitude. The differential settling of particles occurring in such a system will enhance the number of particle collisions and thus also the rate of flocculation. This implies that larger, suspended detrital particles present in a natural attenuation system should be capable of enhancing flocculation through differential settling, which is the dominant collision mechanism for larger particles. Particle settling velocities are also related to the suspended matter concentration, and increase with increasing suspended concentrations.

9.4 Biotic processes

Metal accumulation by microorganisms

Several different kinds of mechanisms can be involved in the accumulation of metals by microorganisms, *e.g.* adsorption, precipitation, complexation and transport (Gadd, 1992b). The amounts accumulated can be large and many studies focus on how to use these processes for remediation purposes. The passive part of microbial metal accumulation can, in principle, be influenced by: (i) surface properties, such as charge and orientation of the metal binding functional groups on the cell surface, and (ii) metal speciation in the aqueous phase.

Metal accumulation by microorganisms is influenced by the surface characteristics of microorganisms, but can also themselves lead to changes in the surface properties. Bacteria may produce macromolecules outside their proper cell wall. These can be firmly retained by the cells (*i.e.* capsules) or slough off from the cell into the surrounding medium, i.e. slime (Geesey and Jang, 1990). Most capsule and slime exopolymers described to date are composed of polysaccharides, but also protein, DNA and RNA can be found (Geesey and Jang, 1990). The amount and composition of the polymers can be greatly influenced by the growth conditions. Such polymers can influence metal accumulation.

Primary production of phytoplankton and metal attenuation

Several studies have indicated that biogenic particulate matter appears to be a major carrier of trace metals in natural waters (e. g., Landing and Feely, 1981; Sigg, 1987). The association of metals to organic matter may be caused by metal sorption to algal surfaces (Xue et al., 1988) as well as active biological uptake of metals into living biota. It has been proposed that the

Redfield model for the biological control of nitrogen and phosphorus could be extended to several bioreactive trace elements, among them Cu and Zn (Morel and Hudson, 1985; Sigg, 1985). Thus, trace metals would be assimilated by biota in stoichiometric proportions relative to C, N and P, and the removal of dissolved metals from surface waters should vary with the mean primary production. A tentative estimate of the biological sorption and/or active uptake of metals in phytoplankton, B_{Me} (mol m^{-2} yr^{-1}), thus can be obtained from the equation:

$$B_{Me} = PP \cdot \frac{Me}{C} \qquad (9\text{-}10)$$

where PP represents the primary production (mol C m^{-2} yr^{-1}) of phytoplankton in the euphotic zone and Me/C is the metal : organic C mole ratio of this organic matter. As a first approximation, B_{Me} can be estimated by using primary production data and Me/C ratios from the literature. Primary production in lakes is relatively well known, and ranges from < 10 to > 500 g C m^{-2} yr^{-1} depending on whether the lake is oligotrophic or eutrophic (e.g., Wetzel, 2001). In contrast, data for trace metal : C ratios are less well known, and some natural variability in these ratios can also be expected. For biota of Lake Constance, Sigg (1985) tentatively proposed Cu/C and Zn/C mole ratios of about $7 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$, respectively. Using these Me/C ratios, estimates of the biological uptake of Cu and Zn in oligotrophic, mesotrophic and eutrophic lakes are presented in Table 9-7. For comparison, the annual transport of these metals in a stream with a water discharge of 200 l s^{-1} and dissolved Cu and Zn concentrations of 10 and 100 µg l^{-1}, respectively, would be 63 kg yr^{-1} of Cu and 630 kg yr^{-1} of Zn.

Table 9-7. Potential biological uptake of Cu and Zn in lakes of different trophic status.

Trophic Status	Primary prod. (g C m^{-2} yr^{-1})	Cu/C (mole ratio)	Zn/C (mole ratio)	Cu uptake (kg ha^{-1} yr^{-1})	Zn uptake (kg ha^{-1} yr^{-1})
Oligotrophic	< 10–100	$7 \cdot 10^{-5}$	$5 \cdot 10^{-4}$	< 0.037–0.37	< 0.27–2.7
Mesotrophic	100–300	$7 \cdot 10^{-5}$	$5 \cdot 10^{-4}$	0.37–1.1	2.7–8.2
Eutrophic	300– > 500	$7 \cdot 10^{-5}$	$5 \cdot 10^{-4}$	1.1– > 1.8	8.2– > 14

Cu/C and Zn/C represent metal/C ratios in plankton.
The uptake of Cu and Zn is calculated using equation (9-10).

The data in Table 9-7 suggest that biological uptake of Cu and Zn potentially may be significant (> 10% of the hypothetical transport of these metals in a minor stream) if the lake size exceeds tens to hundreds of hectares (oligotrophic – mesotrophic lakes). However, in oxic waters, plankton-associated metals to a large extent are likely to be remineralized in the water column or in the surface sediment (e.g., Landing and Feely, 1981; Widerlund, 1996). Thus, permanent burial of plankton-associated metals in sediments may be relatively minor.

Sulphate reduction

In anoxic environments with an abundance of sulphate and readily degradable organic matter, sulphate-reducing bacteria (SRB) such as *Desulfovibrio* and *Desulfotomaculum* can use sulphate as terminal electron acceptor in the oxidation of either organic matter or molecular hydrogen (reviewed in Perry, 1995):

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow 2CO_2 + 2H_2O + H_2S \qquad (9\text{-}11)$$

$$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow 4H_2O + H_2S \qquad (9\text{-}12)$$

The hydrogen sulphide can react with soluble metal ions, e.g. from acid mine drainage, to form an insoluble metal sulphide and thus serve as a metal trap (9-13).

$$H_2S + Zn^{2+} \rightarrow ZnS(s) + 2\ H^+ \qquad (9\text{-}13)$$

The H_2S generated is readily oxidised, which consumes oxygen.

Sulphate reducing bacteria are frequently found in a wide range of ecological systems where the requirements of organic substrates and dissolved sulphate are fulfilled. The organisms are found in greatest numbers in anaerobic environments, although the absence of oxygen is no longer considered necessary for sulphate reduction (Perry, 1995). The use of SRB in the treatment of acid mine drainage is favourable in many respects: sulphate reduction can result in increased pH and metals are precipitated. Continuous supply of a suitable nutrient source is, however, needed to establish and maintain sulphate reduction. Systems which have previously been employed using sulphate-reducing bacteria are of three types: artificial wetlands, fixed-bed anaerobic filters, and sludge reactors (White and Gadd, 1996b).

Biofilms

Bacteria preferentially adhere to solid surfaces where nutrients tend to concentrate. This biofilm mode of growth also gives the microorganisms other advantages: protection from short-term pH-fluctuations, salt- and biocide concentrations, dehydration, pool and preservation of genetical information and feasibility of gene transfer (Flemming, 1993). The majority of microorganisms on earth is considered to be living in biofilms (Flemming, 1993). In natural water systems, as well as other environments, biofilms occur to a greater or lesser extent (Flemming, 1995). The biofilm consists of microorganisms embedded in extracellular polymers produced by the microorganisms and will cover the underlying material at least partially, thereby changing its properties.

Biofilms from a wide range of environments have been demonstrated to bind metals (Brown, et al., 1994). The biofilms contained a variety of morphotypes held together by an organic extracellular matrix. Nutrient levels of the groundwater were low, but yet several elements were immobilised in the biofilms. Some of these elements were concentrated from extremely dilute concentrations. All elements were chemically complexed together to form amorphous or crystalline fine-grained minerals, associated both with the bacterial surfaces and scattered throughout the extracellular matrix.

Mineral formation

High concentrations of metals may develop on bacterial surfaces and be a subject to mineral formation and diagenesis. The morphology of the minerals can differ substantially. Microbially mediated Fe mineral formation has been found in several environments. Epiphytic and episammic bacteria from the solute-rich waters of the Rio Solimões, Brazil, provided major sites for Fe deposition (Konhauser, et al., 1993). Once bound to the bacteria, the Fe served as nucleation sites for the formation and growth of fine-grained authigenic mineral phases. The precipitates showed a wide range of morphologies, from amorphous gel-like to crystalline structures. In contrast, bacteria collected from the solute-deficient waters of Rio Negro remained unmineralised. This could reflect the low availability of dissolved metals in the water as well as the high concentrations of dissolved humic materials, which would compete with the bacteria for metal binding. All bacterial populations, regardless of physiology, consistently formed identical mineral phases (Konhauser, et al., 1993).

Phytoremediation

Phytoremediation is defined as the use of green plants to remove, contain, or render environmental contaminants harmless (Cunningham and Berti, 1993). Phytoremediation of heavy metals can be divided into three groups: I) phytoextraction: metal accumulating plants are established on contaminated soil and later harvested in order to remove metals from the soil; II) rhizofiltration: roots of metal accumulating plants absorb metals from polluted effluents and are later harvested to diminish the metals in the effluent; and III) phytostabilization: metal tolerant plants are used to reduce the mobility of metals, thus, the metals are stabilised in the substrate (Salt et al., 1995). One reason to use plants for remediation is the relatively low cost and maintenance requirements (Cunningham and Berti, 1993).

Phytostabilisation may be a successful way to prevent the formation of AMD and stabilise the metals in the tailings (Tordoff et al., 2000). Plants with low shoot accumulation should be used to stabilise the elements in the tailings in order to reduce the metal dispersion though grazing animals or at leaf senescence. When plants are established on water saturated mine tailings, an organic layer will eventually be formed on top of the mine waste. The layer would probably consume oxygen (due to the chemical and biological processes) and together with the plants also reduce wind and wave erosion. Additionally, a high water table and impoundment walls are not needed.

Plant biology and bioaccumulation

Mine tailings impoundments are harsh areas where plants have problems to be established and survive. This is not due to the high metal concentration, but to the very low nutrient level and the absence of organic material. However, specific ecotypes of plants can sometimes be found growing, slowly, on the tailings.

It is known that plants growing in old metal rich environments have high metal accumulation and use tolerance mechanisms to take care of the metals to make them harmless. Such plants are common on soils where the bedrocks naturally have high metal levels, such as in serpentine soils with high Ni and Cu concentrations. Plants that hyperaccumulate metals are found in such places, e.g. New Caledonia and Cyprus. Hyperaccumulators are endemic and have low biomass production, due to that the energy is used for the mechanisms to cope with the high metal level. On the metal rich soils these plants survive while other plants do not and it is thus not necessary in such environments to have high biomass production to compete for the space. Hyperaccumulators have high metal concentrations in their leaves, e.g. the concentration (%) is shown to be >0.1 for Cu and Ni and > 1 for Mn and Zn (Baker et al., 2000). However, also non-accumulator plants can have elevated metal levels in naturally metal rich environments, such as spruce trees in the vicinity of mining areas, species that normally have a very low metal concentration in their tree trunks (Sunnerdahl, 2000; Österås et al., 2000).

The most common strategy on polluted areas, such as mine tailings impoundments is to have low metal accumulation, thus to avoid uptake and toxic effects. These plants probably use excretion products from roots in the rhizosphere to trap metals and make them less available. Mycorrhiza can also be involved preventing the metals to enter the plant roots and mycorrhiza is found in mine tailings (Khan et al, 2000).

Plants grown on mine tailings are mostly wetland plants, especially emerged plants. The reason is that the tailings are water-saturated and is oxygen deficient with very low redox potential. Since plant roots need oxygen to survive plants living in water logged soil have evolved mechanisms where oxygen from the air taken up via leaves, or oxygen from the photosynthesis, is translocated through a lacunar system of intercellular airspaces or through aerenchyma to the roots (Armstrong et al., 1992, Brix, 1993). Plants without this mechanism will thus not survive in water-saturated mine tailings. The oxygenising of the rhizosphere could, however, be a threat increasing the weathering of the tailings and thus release metals and sulphuric acid. *Typha latifolia* showed slightly decreased pH and increased soluble Zn concentrations near the roots (Wright and Otte, 1999). In pyrite rich tailings, however, *Europhorum spp*. kept the pH around 6 and prevented the release of heavy metals (Stoltz and Greger, 2002; Stoltz, 2004).

Illustration: Spontaneously established wetland environment in a tailings impoundment.

The outlet of the leakage water from the mine tailings is ending up in the recipient, commonly some kind of wetland system. In this wetland systems both emerged and submerged plants are found. The flow of particle-bound metals are retarded by plants, thus increasing the sedimentation. Plants also take up metals from the water, in the case of submerged plants also by the shoot. Further, organic matter originating from plants acts as traps for metals in the water. In addition, during their photosynthesis the submerged plants increase the pH of the water due to the change in equilibration of the carbonic acid system. This increase in pH may precipitate the soluble metals in the water. During the growing season a gradient in metal concentration in the sediment from upstream to down stream appears, where the highest concentration was found upstream and the plants followed the same pattern (St-Cyr et al., 1994). During the winter season the metals associated with the upper plant parts are exported further on in the system. High metal level in the plant litter may decrease the decomposition rate.

9.5 Natural wetlands

In a wetland, one or more of the abiotic and biotic processes outlined in the preceding sections may act to attenuate pollutants in leachate from mining waste. It is important to bear in mind that improvements in water quality, which appear to be the result of metal immobilisation in a wetland, may also be the result of dilution with uncontaminated water (Hedin and Nairn, 1993).

Natural wetlands can be divided into two broad categories; ”peatlands” and ”marshes”. In a peatland-type wetland, a substantial fraction of the water flows through the peat, and association with the organic material (sorption) may act as an important mechanism of metal retention (Wieder and Lang, 1986; Eger and Lapakko, 1988; Eger et al., 1994). In a marsh-type wetland, most of the water flows across the substrate. The presence of plants in this kind of system will improve the conditions for sedimentation (Boto and Patrick, 1978; Brooks, 1989).

In AMD-contexts, metal uptake by plants often accounts for an insignificant part of the total amount of metals accumulated in the wetland (Eger and Lapakko, 1988; Spratt and Wieder, 1988; Fennessy and Mitsch, 1989; Eger et al., 1994; Mitsch and Wise, 1998; Mays and Edwards, 2001). However, algae and cyanobacteria may improve the conditions for metal immobilisation by producing O_2 and increasing pH during photosynthesis (Wieder, 1994; Jones et al., 1995). Furthermore, aquatic plants can transport oxygen to their roots, thereby favouring aerobic attenuation processes, such as the formation of Fe(III)(oxy)hydroxides, in the sediments (Armstrong et al., 1990; Peverly et al., 1995; Doyle and Otte, 1997). In general, wetland sediments are anaerobic due to slow diffusion of O_2 in water and consumption of O_2 during breakdown of organic material (Giblin, 1985; Faulkner and Richardson, 1989; Gambrell, 1994). Such an environment is favourable for sulphate reduction.

There is clear evidence that the geochemical conditions in natural wetland environments are sometimes highly favourable for metal accumulation. Well-known examples from mineral exploitation and exploration include bog iron (limonite), as well as copper and uranium bogs (Brooks, 1983; Nationalencyklopedin, 1992; Owen and Otton, 1995; Sobolewski, 1997 and 1999). However, the fact that large amounts of metals have gradually accumulated in a wetland, perhaps over several thousand years, does not necessarily imply that the water flowing through the wetland would have been considered to have received an adequate treatment.

The performance of natural wetlands that receive AMD from mines and mining waste has been investigated in a number of studies. Cases where the water quality improved upon passing through the wetland have been reported by e.g. Eger and Lapakko (1988), Stark (1990), Kwong and Van Stempvoort (1994), Beining and Otte (1996), Sobolewski (1997); Wildeman and Pavlik (2000), and Räisänen et al. (2001). To some extent, the positive influence on water chemistry ascribed to natural wetlands may actually originate from neutralisation of the drainage during mixing with other sources of water.

In some cases, it was found, or suspected, that the treatment efficiency varied over the year. This may be due to pollutant loads overwhelming the processes that act to immobilise the metals during periods of high flow (Kwong and Van Stempvoort, 1994). An alternative explanation is that temporal variation in the proportions of the acidity carried by AMD and the acid neutralising capacity of the surface water results in inadequate neutralisation (Räisänen et al., 2001), or simply that the temperatures during autumn and winter are too low to allow for an efficient immobilisation of metals (P. Lane and Associates Limited, 1990).

It is sometimes suspected that higher treatment efficiency would have been obtained if the flow patterns within the investigated wetlands had been less channelised, and if the contact between the water and the anoxic sediments had been more intense (P. Lane and Associates Limited, 1990). In one case it was reported that it was difficult to make more AMD move through peat that was already saturated with water (Emerick et al., 1988). Brinson (1988) stresses, that the capacity of a wetland to purify water is heavily influenced by its hydrology and location in the landscape.

Illustration: Field sampling in wetland area downstream the Kristineberg mine.

The studies of metal immobilisation in natural wetlands conducted within the MiMi-programme indicated little or no immobilisation of priority pollutants (such as Cd, Cu, and Zn) in the wetlands situated along a stream receiving treated AMD (Vormbäcken) (Sjöblom et al., 2003b). Thus, the decreasing concentrations of a number of trace metals along the river are best explained by dilution with unpolluted waters, Figure 9-3.

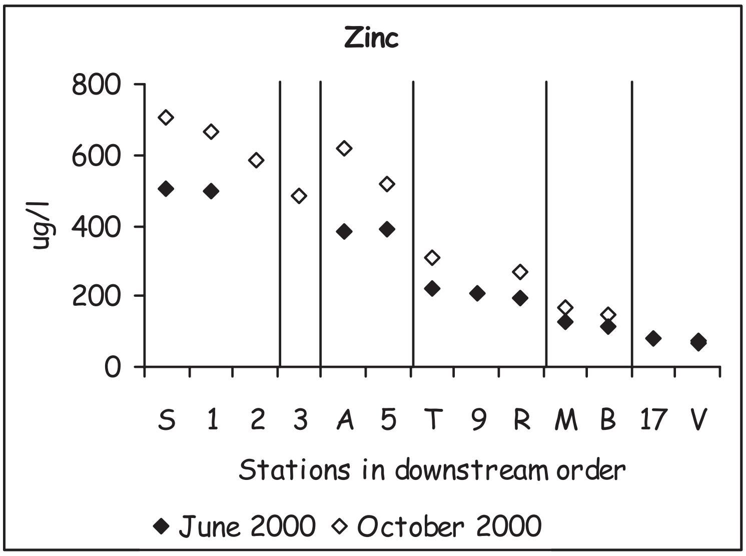


Figure 9-3. The total concentrations of Zn in surface water samples collected from Vormbäcken in June and October 2000. The sampling stations are given in downstream order. Vertical lines mark entry of important tributaries. From Sjöblom (2003).

Possible explanations for the low treatment efficiency of the wetlands include limited contact with the bottom substrates, channelised flow, short growing season, and saturation of the metal accumulation capacity (Sjöblom, 2003). It was also observed that the bottom of one of the wetlands can be frozen during snowmelt, Figure 9-4. If this phenomenon prevents exchange between the stream water and the bottom substrates, it would lead to reduced treatment efficiency during a critical time period.

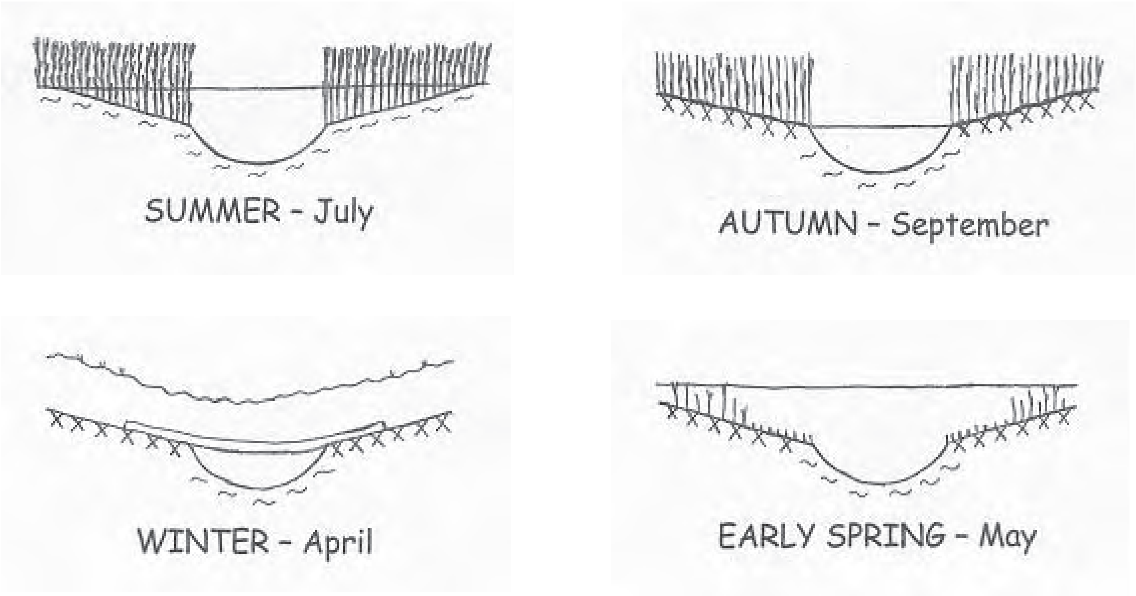


Figure 9-4. An illustration of a hypothesis regarding the hydrology of the wetland downstream of the sampling station Rökå (at 14 km). During autumn, the wetland vegetation dies back, and the wetlands dry up. This allows the ground/sediments to freeze (X). In winter, the central channel through the wetland is covered with ice. The movements of the ice cut off the surficial parts of the wetland vegetation. The whole system is covered with snow. When spring comes, the frozen ground/sediment is inundated by water from the snowmelt. From Sjöblom (2003).

9.6 Stimulated attenuation processes

Reactive Barriers

Background

The installation of a soil cover or the flooding of a tailings deposit are generally successful in reducing oxygen diffusion to tailings, but the lag-time between tailings deposition and reclamation may be several years to tens of years. During this time, sulphide minerals in the mine wastes may partially oxidise. Even though later reclamation efforts may lead to a significant decrease in sulphide oxidation and leachate production, many years may be required before the accumulated sulphide oxidation products are flushed from the tailings pore space. During this interval, reactive barriers may be constructed to intercept and treat the leachate water. This sequence of events is illustrated in Figure 9-5, below.

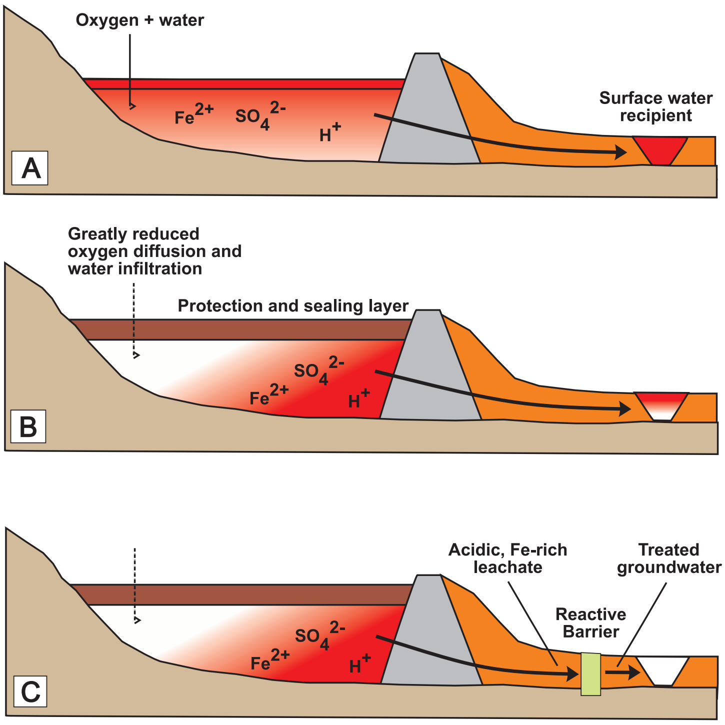


Figure 9-5 Schematic diagram illustrating sequence of events where the installation of a permeable reactive barrier may be necessary. (A) A tailings impoundment is exposed to the atmosphere for an extended period of time, and sulphide oxidation commences; (B) a sealing layer with protective cover are later installed on the deposit, but the discharge of leachate to adjacent water bodies will continue for many years; (C) a reactive barrier is installed to treat the leachate discharging from the impoundment. Treatment continues until leachate quality has improved.

A permeable reactive barrier is a passive, in-situ technique: groundwater treatment proceeds within the aquifer and long-term maintenance of the installation is unnecessary. This method consists of installing an appropriate reactive material into the aquifer, so that contaminated water flows through the material (see Figure 9-5). The reactive material induces chemical reactions that remove the contaminants from the water or otherwise cause a change that decreases the toxicity of the contaminated water (Herbert et al., 1998). For the treatment of water contaminated with acid mine drainage, a number of studies have shown the effectiveness of this method (Blowes et al., 1994; Benner et al., 1999; Benner et al., 2000; Herbert et al., 2000; Benner et al., 2002). Other in-situ techniques are available for the treatment of contaminated groundwater, such as the barrier system installed by the MiMi programme (see Morales, 2001), but the reactive barrier technology is the most well documented and successful of these methods and is therefore the chosen remediation method for this study.

Important biogeochemical processes in reactive barriers

In a reactive barrier for the treatment of mine drainage - contaminated groundwater, organic matter is emplaced in the subsurface as the reactive substance. The decomposition of the organic matter in the reactive barrier consumes oxygen, creating an anaerobic zone of low redox potential in the wall. The anaerobic conditions promote the growth of sulphate-reducing bacteria, which obtain energy and nutrients by oxidizing low molecular weight organic compounds (e.g. lactate, acetate) or hydrogen (reaction 9-14), using sulphate as an external electron acceptor.

$$\underset{\textit{lactate}}{2\,CH_3CHOHCOO^-} + SO_4^{2-} \Rightarrow \underset{\textit{acetate}}{2CH_3COO^-} + 2HCO_3^- + H_2S \qquad (9\text{-}14)$$

Bicarbonate (HCO_3^-) and hydrogen sulphide (H_2S) are reaction products. As previously discussed in section 9.4, reaction 9-14 may also be written as an acid-consuming reaction with CO_2 as a reaction product (reaction 9-11). Aqueous hydrogen sulphide (or bisulphide) and aqueous divalent metals (e.g. Cu, Pb, Zn) may then react and precipitate as amorphous metal sulphide (reaction 9-13). Thus, sulphate reduction in the reactive wall generates alkalinity and may lead to the formation of metal sulphides with relatively low solubility. In the case of the formation of FeS, ferrous iron is removed from the flow system and the groundwater is altered from having an acid generating potential (latent acidity) to possessing an acid *consuming* potential. See section 7-5 for a discussion of acidity and alkalinity in drainage waters.

Besides the precipitation of metal sulphides in the barrier, other solid phases may form as well. The production of bicarbonate via sulphate reduction may lead to oversaturation with respect to a variety of carbonates, such as siderite ($FeCO_3$). Results from Herbert et al. (2000) suggest that a relatively small amount of siderite may have precipitated in the Nickel Rim barrier. If limestone has been added to the barrier material to enhance acid neutralisation, then calcite ($CaCO_3$), dolomite [$(Ca,Mg)CO_3$], and gypsum ($CaSO_4 \cdot 2H_2O$) may potentially precipitate. The formation of other carbonates such as lead or zinc carbonate is not likely, since the corresponding metal sulphides have very low solubility products. In addition to precipitation processes, solutes may also be retained within the barrier by either specific adsorption or ion-exchange (see Chapter 7) on the organic substrate. While adsorption may provide a relatively permanent sink for various ions (e.g. heavy metals), ion exchange would only lead to a temporary reduction in the flux of specific metals from a tailings impoundment.

The performance of the reactive barrier is dependent on the availability of reactive organic carbon for an energy and carbon source of heterotrophic sulphate – reducing bacteria. Although the rate of sulphate reduction in a reactive barrier is controlled by a number of factors (e.g. hydraulic residence time, solution chemistry, temperature), the composition of the organic substrate is of critical importance. Previous studies (Herbert et al., 2000; Benner et al., 2002) have shown that the rate of sulphide accumulation and sulphate reduction decreases with time in such barriers. This observation is probably related to the consumption of labile low molecular weight organic compounds (LMWOC; e.g. fatty acids), so that the concentration of more recalcitrant compounds increase with time. These compounds are less available to SRB as an energy source, and the rate of sulphate reduction hence declines.

A key to predicting the long-term performance of a reactive barrier is to understand the balance between the production and consumption of LMWOCs in the barrier. In the anaerobic environment of the barrier's organic substrate, organic compounds are degraded through the processes of either sulphate reduction or fermentation. With the process of fermentation, there are no external electron acceptors such as sulphate in sulphate reduction and nitrate in nitrate reduction. Instead, fermentation is an internally balanced oxidation – reduction process in which carbon from the same external organic compound is partially oxidized and partially reduced (Brock et al., 1994). For example, alcoholic fermentation of glucose ($C_6H_{12}O_6$; carbon's oxidation state is zero) results in the production of carbon dioxide (oxidized carbon, C(+IV)) and ethanol (CH_3CH_2OH; reduced carbon C(-II)). In a number of fermentation reactions, the electron balance is maintained by the production of molecular hydrogen (H_2) from the reduction of protons in water. Other common fermentation products are the fatty acids formate, acetate, lactate, and propionate. Molecular hydrogen and fatty acids are considered are the preferred energy sources for a variety of SRBs. Therefore, the fermentative degradation of complex organic molecules results in the production of LMWOCs, which can be degraded further via fermentation or sulphate reduction. Fermentative bacteria and SRBs therefore coexist in the barrier substrate. However, the production rate of fermentation products will partially control the rate of sulphate reduction, since labile LMWOCs are generally the preferred electron donors for sulphate reduction. This interrelationship between SRBs, fermentative bacteria, and methanogens is illustrated in Figure 9-6.

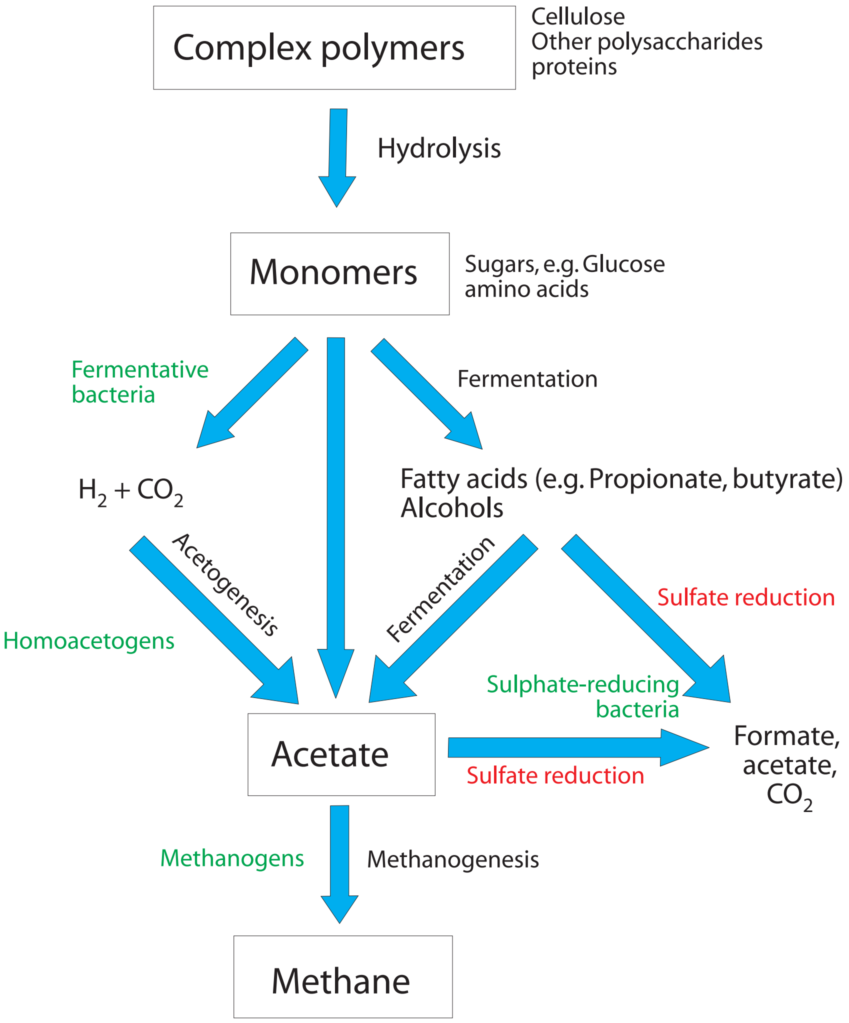


Figure 9-6. Degradation pathways of organic compounds in anaerobic environments, where the processes sulphate reduction, fermentation, and methanogenesis are considered (adapted from Brock et al., 1994).

Rate of sulphate reduction in a reactive barrier

Since the precipitation of metal sulphides in a barrier system is commonly the goal of the remediation activity, the rate of sulphate reduction / hydrogen sulphide production is critical for the effectiveness of the system (Herbert et al., 2000; Benner et al., 2002). Studies have shown (Boudreau and Westrich, 1984; Benner et al., 2002) that the rate of sulphate reduction follows a Monod rate law (Monod, 1949) and is directly related to the sulphate concentration in solution:

$$\mathrm{Rate} = k \frac{[\mathrm{SO_4}]}{K_s + [\mathrm{SO_4}]} \tag{9-15}$$

where K_s is the saturation constant (1.62 mM; Boudreau and Westrich, 1984), the concentration at which Rate = k/2. The value k is the rate constant, in units of concentration/time. Equation 9-15 is an empirical hyperbolic relation, and indicates that when the sulphate concentration is much greater than the saturation constant (K_s), then the term $[SO_4]/(K_s + [SO_4])$ approaches unity and the rate is zero-order. Although the sulphate concentration explicitly determines the rate of sulphate reduction (cf. equation 9-15), other environmental factors such as temperature, organic carbon availability, and the intensity of master variables (pH, redox potential) control the rate constant and are equally important in determining the overall reaction rate. In addition, the rate of groundwater flow through the barrier is also an important variable, since this determines the groundwater residence in the barrier; groundwater must remain in the barrier long enough for a sufficient amount of H_2S to be produced and precipitate metals.

Reactive barrier composition and construction

A reactive barrier for leachate treatment is designed to promote the growth of SRB, which require anaerobic and relatively pH - neutral conditions. These conditions are best achieved by constructing a barrier with organic material. The rate of sulphate reduction is intimately linked to the reactivity of this organic substrate (Boudreau and Westrich, 1984; Westrich and Berner, 1984), with low molecular weight (LMW) organic compounds (e.g. lactate, acetate) being most reactive and thus more accessible to SRB. Studies by Westrich and Berner (1984) have demonstrated that the rate of sulphate reduction is a function of both the concentration of ”decomposable” organic matter and OM reactivity. In the case of the Nickel Rim reactive barrier, the first reactive barrier installed for the treatment of AMD, a mixture of leaf and municipal compost and wood chips was chosen as a reactive material (Benner et al., 1997). Leaf compost has shown to be an appropriate substrate for later studies as well (e.g. Ludwig et al., 2002), probably because of the abundance of labile LMWOCs in the material. In addition to concentration and reactivity of the labile organic matter, it is also important that labile OM is available to SRB over relatively long periods of time. The long-term capacity of the material to produce LMW OM, via fermentation reactions, must also be considered.

A reactive barrier for groundwater treatment must be emplaced in the subsurface so that groundwater must flow through the barrier, and not around it. This implies that the hydraulic conductivity of the barrier material must be greater than that of the surrounding aquifer. This requires the evaluation of the hydraulic conductivity of the reactive material and the aquifer material prior to barrier construction. In Nickel Rim, the organic components were mixed at a 1:1 ratio with pea-sized gravel to increase the hydraulic conductivity.

A reactive barrier is designed to treat the entire contaminated plume down-gradient from a tailings impoundment, and may therefore encompass the entire breadth of the impoundment. The barrier should be installed to a depth so that all the contaminated groundwater is intercepted by the barrier. The required breadth or flow-path length (L) of the barrier is calculated from the desired residence time (T_r) and groundwater velocity (v):

$$L = T_r \times v \tag{9-16}$$

The linear groundwater velocity (v) is calculated as the hydraulic conductivity multiplied by the hydraulic gradient, divided by the aquifer porosity (see Chapter 10 for examples of these values). The residence time used to dimension the barrier should be determined from empirical data on sulphate reduction rates, which is the limiting design factor. Metal sulphide precipitation (reaction 9-13) is relatively rapid and will not impact the design parameters. For the Nickel Rim reactive barrier (Benner et al., 2000), a residence time of ca. 4 months was sufficient to reduce 74% of sulphate in solution and remove >85% of the dissolved Fe and >90% of the dissolved Ni. Iron and Ni are primarily retained as monosulphide mineral phases (Herbert et al., 2000).

Reactive barriers are often constructed by simply excavating the soil to below the water table, and filling with reactive material. To avoid the sides of the excavation from collapsing in poorly consolidated soils and for barriers installed far below the water table, the excavation may be filled with a liquid that is denser than water, such as guar gum (Day et al., 1999; Ludwig et al., 2002). A critical issue when filling a barrier excavation is the homogeneity of the reactive barrier material. Since the reactive material may consist of several components, such as compost, gravel, and limestone (cf. Benner et al., 1997), it is vital that the material is well – mixed prior to filling the excavation. Experience from the Nickel Rim Barrier suggests that regions of preferential flow occur in the barrier because of the presence of sections will relatively high hydraulic conductivity, which may be the result of inadequate mixing (Benner et al., 2002). The results of the aqueous and solid phase sampling within the reactive barrier (Herbert et al., 2000) indicate that there has been a channeling of flow within the barrier, such that the greatest flow occurs at a depth of about 1 to 2 m. In this region, there is a greater accumulation of iron sulphides relative to other depths in the barrier, since the flux of H_2S and Fe^{2+} through this region is greatest. Because of this vertical heterogeneity in the barrier, the lifetime of the reactive material may be less than calculated from the column experiments.

Longevity

Reactive organic matter such as fatty acids will be rapidly consumed by heterotrophic bacteria (e.g. sulphate reducing and fermentative bacteria; see above), leaving less reactive material as a carbon and energy source for subsequent reactions. This decrease in reactivity has been noted in the Nickel Rim barrier (Herbert et al., 2000; Benner et al., 2002). Eventually, the barrier material will need to be replaced. According to column experiments and estimates of the groundwater flux through the Nickel Rim barrier, it is expected that the barrier will continue to satisfactorily treat groundwater for at least 12 - 15 years, at which point it is predicted that the supply of reactive carbon will have declined to such a degree that the rate of sulphate reduction will decrease and there will be a breakthrough of ferrous iron.

In addition to the depletion in labile organic matter, barrier clogging may potentially lead to a decrease in porosity and hydraulic conductivity of the barrier material, and hence a decrease in performance. However, organic matter is consumed with time (cf. reaction 9-11) and replaced with metal sulphide precipitates (reaction 9-13) that have a greater density than of organic matter; thus, a decrease in porosity due to metal sulphide precipitation is not expected. Decreases in porosity and hydraulic conductivity may potentially occur, however, because of the precipitation of gypsum and carbonates in the barrier. However, this has not been a problem in organic matter – based reactive barriers that are currently in operation.

Constructed Wetlands

Constructed wetlands offer a number of advantages in comparison to natural wetlands. Perhaps most importantly, the use of natural wetlands for treatment purposes is strictly regulated by law in many countries (e.g. Hedin, 1989), which may make constructed wetlands the only legally and environmentally acceptable alternative. Ecosystem damages have also been reported from a natural wetland exposed to AMD for treatment purposes (Wheeler et al., 1991). Since constructed wetlands are designed and built by man, they may also offer increased treatment efficiency (cf. Herbert and Ekström, 2003) and better control of the water flow paths. For instance, treatment of non-target water and groundwater contamination can be avoided by incorporating liners (Hellier, 1999; Figure 9-7). Furthermore, constructed wetlands can be prepared for maintenance, such as periodic removal of accumulated precipitates, already when they are being built.

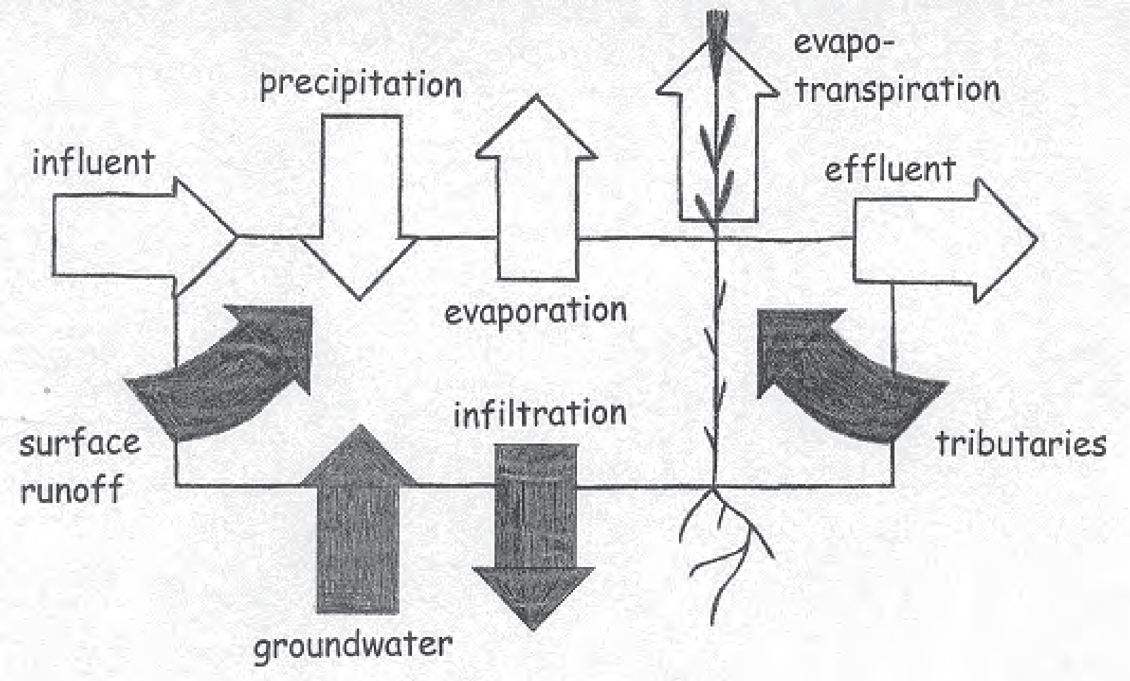


Figure 9-7. The hydrology of a wetland. The importance of the various processes varies between different kinds of wetlands. Dark arrows mark pathways that can be restricted in constructed wetlands, without affecting the true treatment efficiency. From Sjöblom (2003).

The higher treatment efficiency in constructed, or modified natural, wetlands is usually due to improvements in hydrology, or addition of materials that improve the chemical conditions for metal immobilisation. Improvements in hydrology include creating vertical, rather than horizontal flow, through the solid substrates (Hedin et al., 1988; Lapakko and Eger, 1988; McIntire and Edenborn, 1989; Eger, 1994; Eger et al., 1994), and increasing the retention time of the water by creating serpentine flow in natural wetlands (Eger et al., 1993), or by constructing a wetland in the first place (Hedin et al., 1993). The incorporation of buffering materials, such as limestone, in the wetland substrates will favour the formation of Fe, Mn, and Al (oxy)hydroxides and counteract the resulting acidification. Addition of organic material provides sites for metal sorption (Howard et al., 1989; Eger et al., 1993). It also provides nutrients for the microbial community (Stark et al., 1991; Wheeler et al., 1991; Eger et al., 1993; Gross et al., 1993; Fyson et al., 1994), and helps to create anoxic conditions in the wetland sediments, both of which are favourable for sulphate reduction.

A pre-treatment system, such as an anoxic limestone drain (ALD) (Brodie et al., 1993; Hedin et al., 1993; Faulkner and Skousen, 1994; Hedin and Watzlaf, 1994; Hedin et al., 1994), may also improve the conditions for metal removal in wetland treatment systems. As the name suggests, an ALD adds alkalinity to AMD through the dissolution of limestone under anoxic conditions. In this way the pH of the drainage can be increased without the formation of Fe(III) hydroxides, which otherwise would armour the limestone, inhibiting further dissolution. A prerequisite for the proper functioning of an ALD is that the AMD does not contain > 1 mg/l Fe^{3+}, Al^{3+} or dissolved O_2 (Hedin et al., 1993; Kepler and McCleary, 1994).

In order to achieve successful treatment, the design of a constructed wetland has to be adapted to the quality of the drainage to be treated. Usually, a distinction is made between aerobic, anaerobic, and vertical flow wetlands (also called successive alkalinity producing systems/reducing and alkalinity producing systems – SAPS/RAPS) (Kepler and McCleary, 1994; Brown et al., 2002; Ziemkiewicz et al., 2003). The various types can also be used in combination. The choice between different kinds of wetlands is facilitated by decision making charts presented in Hedin et al. (1993), Hellier (1999), and Brown et al. (2002). In brief, aerobic wetlands are used to remove Al, As, Fe, Hg, and Mn from net alkaline waters, while anaerobic and vertical flow wetlands are used to treat net acidic waters, and to remove metals such as Al, Cd, Cu, Fe, Hg, Pb, U, and Zn (Hedin et al., 1993; Eger, 1994; Gusek, 1995; Ziemkiewicz et al., 2003). If the water contains large quantities of Fe, one usually tries to remove it early in the treatment sequence.

In the ideal passive, maintenance-free treatment wetland, the processes that act to immobilise metals balance the rate at which the drainage is produced, for as long as polluted drainage is generated. The metals must not be re-mobilised to any significant extent, neither during nor following treatment. The costs for wetland treatment should also be less than for conventional treatment systems. The first of these criteria has certainly been fulfilled at the constructed wetlands that have exhibited successful treatment (e.g. Stark et al., 1994b). To some extent, this is a question of proper sizing. A recent compilation of sizing criteria is given in Brown et al. (2002). Sizing criteria are often based on empirical data rather than the rates of specific processes (Sobolewski, 1999).

It still remains to be shown for how long successful treatment of AMD in wetlands can be maintained. Without maintenance, several mechanisms of metal immobilisation in wetlands exhibit definite limits (Table 9-8). For instance, accumulation of precipitates in settling ponds and wetlands will eventually fill up the whole basins. Sediment accumulation rates of 3.8 cm/year have been reported by Demko and Pesavento (1988) and Stark et al. (1994b). The amount of metals that can be removed by sorption processes is limited by the number of available sites. New sorption sites may be generated through the formation of peat. However, in the study by Eger et al. (1994) it was found that, in order to balance the input of metals and the formation of new removal sites, the input flow would need to be reduced by an order of magnitude. In order to achieve long-term treatment of net acidic water, buffering capacity has to be generated within the wetland. This is generally accomplished by sulphate reducing bacteria who needs a constant supply of suitable organic carbon (cf. Tarutis and Unz, 1994; Eger and Wagner, 1995). Plants could act as a long-term source of organic carbon. However, plants need nutrients, and a gradual loss of nutrient base cations from the substrate of wetlands exposed to AMD has been noticed (Wieder et al., 1990; Wieder, 1993). The recycling of nutrients from decaying plant material can also be affected by decreasing decomposition rates in AMD environments (Kittle et al., 1995). Thus, the key to achieve long-term treatment of AMD in a wetland is probably to calculate its total metal accumulating capacity (e.g. Wieder, 1988; Wieder et al., 1990; Beining and Otte, 1997), and to make sure that it is not exceeded by the total anticipated metal load.

Table 9-8. Factors affecting the long-term functioning of different mechanisms of metal immobilisation in wetlands.

Mechanism	**Limits to long-term immobilisation**	**Factors that can lead to remobilisation**
Sedimentation	Sediment accumulation in basin may lead to shorter residence times	Resuspension of particles during high flow events Failure of dikes
Adsorption	Saturation of adsorption sites Restricted flow through adsorbent due to hardpan formation	Changes in water chemistry Decomposition, reduction or other change of adsorbent
Biological uptake (plants)	Depletion of nutrients Gradual poisoning Metal accumulating plants are replaced by native species	Decomposition of plant material upon senescence and death
Precipitation as oxyhydroxides	Gradual acidification Accumulation of precipitates (cf. sedimentation)	Development of anoxic conditions in the sediments Ageing of precipitates may release co-precipitated metals
Precipitation as sulphides	Gradual acidification Depletion of suitable small organic molecules	Exposure of sediments to oxidizing agents, such as O_2 and Fe^{3+}, or acidic drainage

Metals may be re-mobilised from wetland sediments by re-suspension during periods of high flow. Metals can be leached from decaying plant material to the surrounding water (Rice and Windom, 1982). Metals that have been immobilised by sorption may be liberated if the sorbent is exposed to changes in water quality, such as decreases in pH, and increases in salinity or dissolved organic carbon (Lapakko and Eger, 1988). Decomposition of peat (Henrot and Wieder, 1990) and ageing of Fe hydroxides (Martínez and McBride, 1998) can also lead to a decrease in the number of sorption sites available. Furthermore, Fe(III)(oxy)hydroxides may dissolve if they are exposed to reducing conditions, which often occur in wetland sediments (Vile and Wieder, 1993; Stark et al., 1994a; Tarutis and Unz, 1995; Olivie-Lauquet et al., 2001). Metals accumulated as sulphides may be re-mobilised if the wetland sediments are exposed to oxygen during periods of drought, or failure of structures that serve to maintain an adequate water level (Sobolewski, 1997 and 1999; Martin et al., 2001). Acid volatile sulphides (AVS) are also susceptible to re-mobilisation if exposed to acidic waters (Hedin et al., 1989).

One of the most frequently cited benefits of constructed treatment wetlands is that they are comparatively inexpensive. This is because wetlands typically require less input of chemicals and less maintenance than more conventional treatment systems. Thus, typically, the costs for AMD treatment in wetlands are dominated by the construction costs (Brodie et al., 1988 and 1989; Brodie 1993; Sanders et al., 1999). These may vary substantially depending on factors such as wetland design. In general, aerobic wetlands are cheaper than anaerobic and vertical flow wetlands (Gusek, 1995; Ziemkiewicz et al., 2003).

The time that satisfactory treatment can be maintained in constructed wetlands is a key factor when comparing the costs for different treatment options. In some cases, the costs for wetland treatment break even with the costs for conventional treatment already during the first year (Brodie et al., 1988; Hedin, 1989; Kleinmann et al., 1991), while in some cases the wetland has to work for at least 7 years in order to pay back the initial investment (Demchak et al., 2001). Other key factors are the quality of the drainage and the desired level of treatment. For instance, it may be expensive to treat low strength AMD from coal mines, since that would require larger wetlands (Baker et al., 1991). Similarly, it may be expensive to achieve high removal efficiencies (ibid.).

A recent evaluation of passive treatment systems used to treat AMD from coal mines in the Appalachia shows that limestone leach beds, ALDs, and open limestone channels provide a high level of reliability (success versus failure), high acid load removals, and low treatment costs (Ziemkiewicz et al., 2003). 75% of the ALD-wetland combinations and 47% of the vertical flow wetlands in the study showed treatment success, that is, removed acid at a cost below that estimated for chemical treatment. 44% of the aerobic wetlands and 28% of the anaerobic wetlands showed treatment success (ibid.).

In many cases, it is better to prevent the formation of the AMD in the first place, rather than to treat it. Thus, when comparing different methods to reduce the environmental impact of mining waste, it is probably most appropriate to compare wetland treatment with other treatment methods. Some of the problems with AMD treatment, such as the generation of large amounts of precipitates, are common to more or less all treatment methods. An advantage of treatment wetlands is that they may reduce the amount of chemicals and energy used at a site, which is beneficial from an overall resource perspective. Furthermore, wetlands at least offer the potential for long-term maintenance-free treatment, which active treatment systems certainly do not. This is especially the case if reclamation activities further upstream have reduced the metal load to the wetland (cf. Younger, 1997).

9.7 Engineering aspects of systems for utilising natural attenuation processes

A remediation programme implemented at a mine site should be planned and designed with the aim of achieving optimal conditions for natural attenuation processes. Some of the experiences gained at various mine sites are described in the references summarized in Table 9-9, although engineering aspects may not be specifically addressed in these references.

Table 9-9. Summary of references describing effects of natural attenuation processes observed at mine sites.

Natural attenuation process	References
Particle formation: Includes chemical precipitation of secondary minerals and primary production of phytoplankton.	Schemel et al. (2000) Dinelli and Tateo (2002) Lee et al. (2002) Jönsson et al. (2003a)
Sorption: Any process capable of removing metals in solution into particulate matter. Includes adsorption, coprecipitation and active biological uptake into living biota.	Kimball and Wetherbee (1989) Ranville et al. (1989) Smith et al. (1989) Schemel et al. (2000) Jönsson and Lövgren (2000, 2001) Dinelli et al. (2001) Lee et al. (2002) Jönsson et al. (2003b, 2003c) Sjöblom et al. (2003a) Sjöblom and Håkansson (2003)
Flocculation: Aggregation of colloids and small particles into larger particle aggregates (flocs).	Dinelli et al. (2001) Sullivan and Drever (2001) Forsberg (2002) Widerlund et al. (2004a)
Sedimentation: Settling of particulate matter (flocs and/or individual particles) to stream and lake beds.	Kimball et al. (1995) Schemel et al. (2000) Kimball et al. (2001, 2002) Widerlund et al. (2004a)

Particle formation

Formation of secondary precipitates acting as metal sorbents (Fe, Al and Mn oxyhydroxides) can be achieved by mixing AMD with natural waters of higher alkalinity and pH (Lee et al., 2002). This mixing should take place under oxic conditions (e.g., in streams) to ensure an efficient oxidation and formation of Fe and Mn precipitates. Approximate pH values required for precipitation and theoretical estimates of the maximum amount of precipitates that may form are given in Table 9-10.

Table 9-10. Gravimetric factors as estimates of maximum amount of Fe, Al and Mn precipitates forming due to oxidation of dissolved Fe, Al and Mn in AMD.

	Fe	Al	Mn
Approximate pH required for precipitation	3–5	~ 5	~ 8
Amount of precipitate formed per 100 mg of dissolved Fe, Al and Mn in AMD	159*	289*	160*

*Amount of precipitate formed if the following species are assumed to precipitate: FeOOH, $Al(OH)_3$ and MnOOH.

To maximize the precipitation of secondary Fe and Al phases, a pH of ≥ 5 is required after mixing. Considering that dissolved Mn concentrations in AMD in general are considerably lower than those of Fe and the insignificant precipitation of Mn oxyhydroxides at $pH < 7$ (Table 9-10), Mn oxyhydroxides should play a relatively minor role as a scavenger of trace metals in mining-affected waters.

To increase the amount of dissolved Fe(II) entering a natural attenuation system (and thus the potential for formation of Fe precipitates), diversion of groundwater into oxic surface waters may be considered where possible (e.g., where minor, localised groundwater outflows occur). However, this measure may be possible only when the alkalinity of the receiving water is sufficient to neutralize the acidity produced by Fe precipitation. Furthermore, possible clogging of the drainage system (streams and ditches) with secondary Fe precipitates should be considered. This implies that active measures to enhance the formation of secondary precipitates may be feasible only in systems with low to moderately high dissolved Fe and Al concentrations.

An important practical implication of phase transformation of Fe and Al hydroxysulphates, when present in large quantities, is that these phases must be regarded as stored acidity since the transformation processes are net acid producing, c.f. reaction 9-4. Catalan et al. (2002) reported that using aqueous acidity to estimate the amount of lime needed in lime treatment of oxidised sulphidic mine tailings can underestimate the amount needed by more than 50% due to the inherent acidity of jarosite and schwertmannite as these minerals form goethite and gypsum. The current study has shown that the amount of lime needed to neutralise schwertmannite can be directly calculated from the SO_4^{2-} content of the mineral.

Sorption of contaminants

A natural attenuation system should be designed so that secondary precipitates are formed in the presence of the trace metals to be sorbed. This will increase the possibilities for coprecipitation of trace metals into the precipitating sorbents (e.g., Lee et al., 2002; Sjöblom et al., 2003a).

The degree of metal attenuation may depend on the mixing ratio between AMD and natural waters, as well as on the rate of mixing. Slow mixing and a low AMD : natural water ratio may allow a progressive evolution of the streamwater composition, with a sequential formation of near-equilibrium precipitates concentrating only phase-forming elements (Fe and Al). If mixing occurs rapidly at a higher AMD : natural water ratio, a rapid formation of mixed precipitates containing Fe, Al and trace metals may occur, resulting in a more efficient attenuation of trace metals (Dinelli and Tateo, 2002).

To maximize pH-dependent sorption of trace metals onto suspended particles, pH in the mixed AMD – natural water should be above the sorption edges for the trace metals of interest (e.g., Jönsson and Lövgren, 2001; Jönsson et al., 2003b, 2003c).

In general, pH-dependent adsorption is a fairly rapid process with a time scale in the order of hours, i. e., considerably shorter than the time scale for flocculation, which may exceed tens of days (e.g., Vezina and Cornett, 1990). Thus, although adsorption and flocculation processes may be initiated simultaneously when AMD is mixed with a natural water, adsorption can be expected to occur before the total surface area of suspended particles is significantly reduced due to flocculation.

Flocculation

Due to the relatively slow flocculation of colloids into larger particles, the residence time for particulate matter in lakes/ponds should exceed tens of days to allow flocculation and formation of larger, settling particle aggregates to occur. In general, flocculation of suspended particulate matter is facilitated by:

- High concentrations of suspended particulate matter spanning a large size range resulting in differential settling.

- Presence of natural organic matter enhancing particle-particle attachment, although salt flocculation of colloids may counteracted by organic matter.

- Increasing salinity, in particular dissolved Ca^{2+}, resulting in flocculation of colloids.

Thus, to enhance the attenuation of metals, the following engineering aspects may be considered at mine waste sites:

- Streamwater with high concentrations of suspended particulate matter may be diverted into lakes/ponds containing mixed AMD – natural waters.

- Acid mine drainage with high dissolved Ca^{2+} concentrations can be mixed with natural fresh waters with high concentrations of dissolved/colloidal/particulate organic matter.

However, it should be pointed out that the effects of organic matter on the attenuation of metals appear not to be fully resolved, and contradictory results have been reported regarding sorption of metals in the presence of natural organic matter (e.g., Jönsson et al., 2003c; Sjöblom et al., 2003a).

Sedimentation

The following engineering aspects regarding sedimentation of particulate matter may be pointed out:

- Settling of particulate matter increases if the suspended particles partly are composed of organic matter and with increasing suspended matter concentration.

- Thus, settling of particulate matter may be enhanced if streamwater with high concentrations of suspended, organic particulate matter is diverted into lakes/ponds.

- Particle settling rates should be predicted using empirical formulas rather than Stokes' law, which may underestimate the settling rates by up to an order of magnitude.

- Constructed settling ponds should be designed so that the residence time for particles exceeds the time for settling predicted by appropriate formulas. Settling of particulate matter can be promoted if inlet and outlet structures are constructed as full length inlet and outlet weirs or multiple pipe inlet/oulet systems. Such systems tend to spread the flow evenly across a pond, which reduces the risk for channeling and short-circuiting of the free flow. Constructions of various types of meandering systems can also be considered.

- Stable density stratifications should be avoided in the water columns of basins where settling of particulate matter is intended to occur. Density stratifications can be expected to reduce the attenuation of metals if the settling of particulate matter is retarded, and if anoxic bottom water conditions develop. The latter would facilitate reductive dissolution of redox-sensitive metal sorbents (Fe and Mn oxyhydroxides), resulting in early diagenetic remobilisation of metals (e.g. Sakata, 1985). In cold climates where lakes and ponds are ice covered during the winter, particularly stable density stratifications can be expected beneath the ice.

- Resuspension of settled particles should also be considered, and lakes and ponds intended as settling basins should be deep enough to minimize the risk for resuspension. For lakes, a diagram has been developed where the effective fetch is used for prediction of water depths where resuspension may occur (Håkansson, 1981). A laboratory study of resuspension of pyrrhotite tailings showed that the rate of oxidation increased with the degree of turbulence-induced mixing of the water column (Yanful et al., 2000). This stresses the importance of avoiding resuspension of sediments where sulphide-rich tailings may occur.

10 Definition of a Base Case

To highlight the most important mechanisms determining the behaviour of a tailings deposit, the performance assessment is applied to a simplified case, here referred to as the “Base Case”. The emphasis is on the assumptions used in the model, namely, for the source term, the cases with soil cover and water cover and finally the reactive barriers. The source term is described where the assumed composition and physical properties of the tailings are given. In Section 10-2, the case of a deposit with soil cover is discussed. The properties of the material used in the cover, the mechanisms for water and oxygen transport, and the definition of the stream tube concept are given. In Section 10-3, similar information is given for the case with a water cover. The Model Database is presented in the last section. A schematic picture of the modelled system is shown in Figure 10-1 for the soil cover. The data for the Base Case is mainly based on the conditions at Kristineberg.

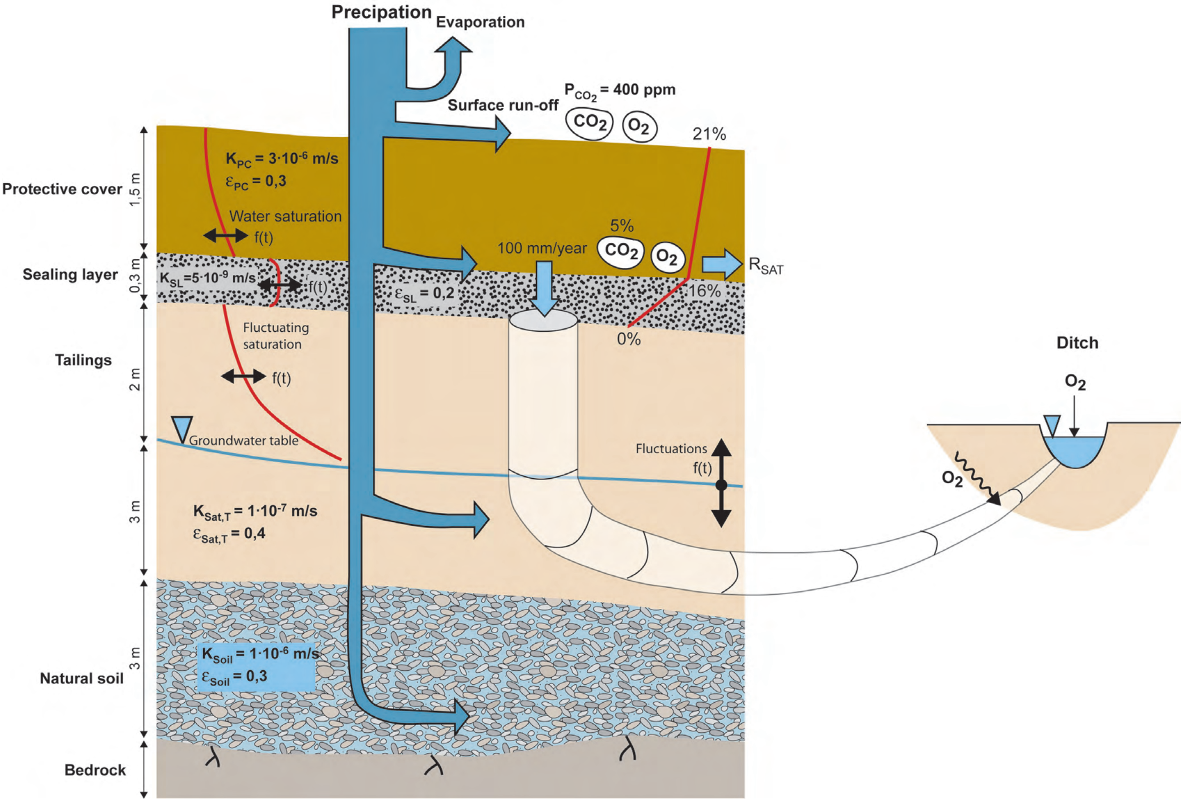


Figure 10-1. Schematic picture of the deposits and the stream tube concept used in the modelling of the soil cover case.

10.1 Source term – waste

In impoundment 1 at Kristineberg, the content of sulphide minerals ranges from 10 % to more than 30 % in the unoxidized tailings (Öhlander et al., 2001). For impoundment 1B the content is about 20 %. Pyrite is by far the most common sulphide mineral. Other sulphide minerals, in order of occurrence, are pyrrhotite, sphalerite, chalcopyrite, galena, covellite and arsenopyrite. Most of the gangue minerals are quartz, K-feldspar, Mg-chlorite, plagioclase, muscovite, amfiboles/pyroxenes and biotite. Calcite is present in trace amounts.

Acid Base Accounting (ABA) tests of the tailings show a large Acidity Potential (AP). The unoxidized tailings are rich in pyrite and contain only minor amounts of carbonates. The acidity potentials of the tailings are 302 and 307 kg of calcite per tonne mineral for impoundment 1 and 1B respectively. The Neutralisation Potential (NP) of the tailings is negligible in comparison. This results in a negative Net Neutralisation Potential (NNP). For example for impoundment 1 the net neutralisation potential is –301 kg calcite per tonne mineral.

The Humidity Cells Tests (the mineral is contacted alternatively with dry and wet air) confirm these results. The pH is lower than that obtained by carbonate buffering. Other minerals could work as buffers but at lower pH. Al-oxyhydroxides buffer in the pH range 3.7 – 4.4 and Fe-oxyhydroxides in the range 3.3 – 3.7. Aluminosilicate buffering is important because of their abundance. Different aluminosilicates may buffer at different pH values in a range about 3-7. 75 % of the particles have a size less than 0.1 mm and that about 25 % have a size less than 0.01 mm. The particles are so small that their inner reactive surfaces are immediately accessible to reactants such as oxygen and protons.

In the Base Case, it is assumed that the tailings are unoxidized initially. The mineralogical composition and properties of the tailings used in the Base Case are shown in Table 10-1. The sulphide minerals are represented by pyrite, which is the dominant sulphide in the tailings. The presence of other sulphides has little or no influence on the consumption of oxygen and acidity generation in the tailings. However, the metals forming these sulphides, for example, lead, zinc, copper may have an important impact on the environment and their release will be considered.

Calcite and chlorite are used as pH-buffer minerals in the model. The reaction of calcite with the protons generated from the pyrite oxidation is assumed to be fast. Chlorite is the dominant aluminosilicate in the tailings and its neutralisation reaction rate is slow compared to calcite.

Table 10-1. Mineralogical composition of the unweathered tailings used in the Base Case.

Mineral	Composition, wt-%
Pyrite, pyrrhotite	25
Quartz (50 %)	50
Chlorite (20 %)	20
Calcite	2
Talc, K-feldspar, Plagioclase	3

Based on data from Kristineberg, a porosity of 0.45 is used for the Base Case. The thickness of the tailings is taken to be 5 m, with 2 m above the water table. The water saturation for the partially saturated tailings has been estimated to 0.85. For the tailings below the water table, a hydraulic conductivity of $1 \cdot 10^{-7}$ m/s is used. Other geometry data and physical properties may be found in the Model Database (Section 10.5).

The oxidation of the pyrite and the neutralisation of the acidity by calcite are assumed to be instantaneous. The acid neutralisation by chlorite is kinetically controlled.

10.2 Soil Cover

The tailings are covered by a sealing layer overlain by a protective cover. The protective cover primarily serves to protect the sealing layer and the tailings. The sealing layer acts as a barrier to intrusion of oxygen and infiltrating water. On the protective cover, vegetation may be established, which may contribute to reduce the amount of oxygen and water intruding into the deposit due to root respiration and increased evapotranspiration. However, vegetation may potentially have a negative effect on the sealing layer due to root penetration.

The geometry and physical properties of these layers are simplified to concentrate upon the most important mechanisms. Variations from these simplified values will be discussed later. The protective cover is formed by an unspecified till with a thickness of 1.5 m. The porosity of the protective cover is 0.23 and the hydraulic conductivity is $6 \cdot 10^{-7}$ m/s.

The sealing layer consists of compacted clayey till with a hydraulic conductivity of $5 \cdot 10^{-9}$ m/s . It is 0.3 m thick and has a porosity of 0.18. The clayey till has particles with sizes up to 20 mm. However, about 75 wt-% of the particles have a size less than 1 mm and 20 wt-% less than 0.01 mm.

For comparison, Table 10-2 shows values of hydraulic conductivity for other natural materials. The hydraulic conductivities of these materials cover a wide interval of values, several orders of magnitude.

Table 10-2. Hydraulic conductivity of natural materials (Values taken from Schnoor, 1996)

Material	Hydraulic conductivity, m/s
Unconsolidated deposits	
Gravel	– 1.0
Sand	$10^{-6} – 10^{-3}$
Silt	$10^{-8} – 10^{-6}$
Clay	$10^{-11} – 10^{-8}$
Consolidated material	
Sandstone	$10^{-9} – 10^{-6}$
Crystalline rock	
Fractured	$10^{-8} – 10^{-6}$
Unfractured	$10^{-13} – 10^{-11}$

It is assumed that the water flow is vertical through the protective cover, sealing layer, and the partially water saturated tailings. In the sections of the deposit located below the water table and in the underlying till, horizontal water flow may exist.

The water influx into the tailings is 100 litres/m^2,year. The oxygen intrusion into the tailings is controlled by the diffusion in the sealing layer. The protective cover only protects the sealing layer from drying and from erosion and other mechanical effects. However, due to the presence of vegetation, the concentration of oxygen is decreased and the concentration of CO_2 increased during the summer as a consequence of organic matter degradation in the soil.

The technique applied to model the chemical evolution in the system in space and time is based on the streamtube concept. An imaginary “tube”, which starts at the top of the deposit and continues through the covers and tailings to the discharge point is defined. No water flow is allowed through the tube walls. The same water volume entering the tube at the inlet leaves the tube at the outlet. The cross section of the stream tube varies depending on the local water velocity. Multiple, parallel streamtubes can be used to study the contribution from different parts of the deposit to the total contaminant discharge.

The oxygen may intrude the deposit dissolved in the infiltrating water and by diffusion in the air and water filled pores. The transport of oxygen with the infiltrating water is very small due to the small oxygen solubility in water, 10 mg/l. Oxygen diffuses faster in the air-filled pores than in the water-filled pores because diffusion of oxygen in air is about four orders of magnitude larger than the diffusion in water.

The diffusion through a partially water-saturated porous medium decreases strongly with the increase of the water saturation (See Figure 7-2). Therefore the diffusion through the sealing layer will be small for a sealing layer that has a high degree of water saturation.

10.3 Water Cover

The Base Case for the water cover uses the same data for the tailings as the soil cover case. One difference between the two cases is that there is a dam that always maintains a water table height of 2 m above the top of the tailings. The following assumptions are made: -The design is such that wave action will not influence the tailings. -The tailings will always be maintained as originally deposited. -Negligible resuspension will take place. -The water covering the tailings is fully saturated with oxygen. -There will be a water inflow to the dam that is sufficient to maintain the water table at all times.

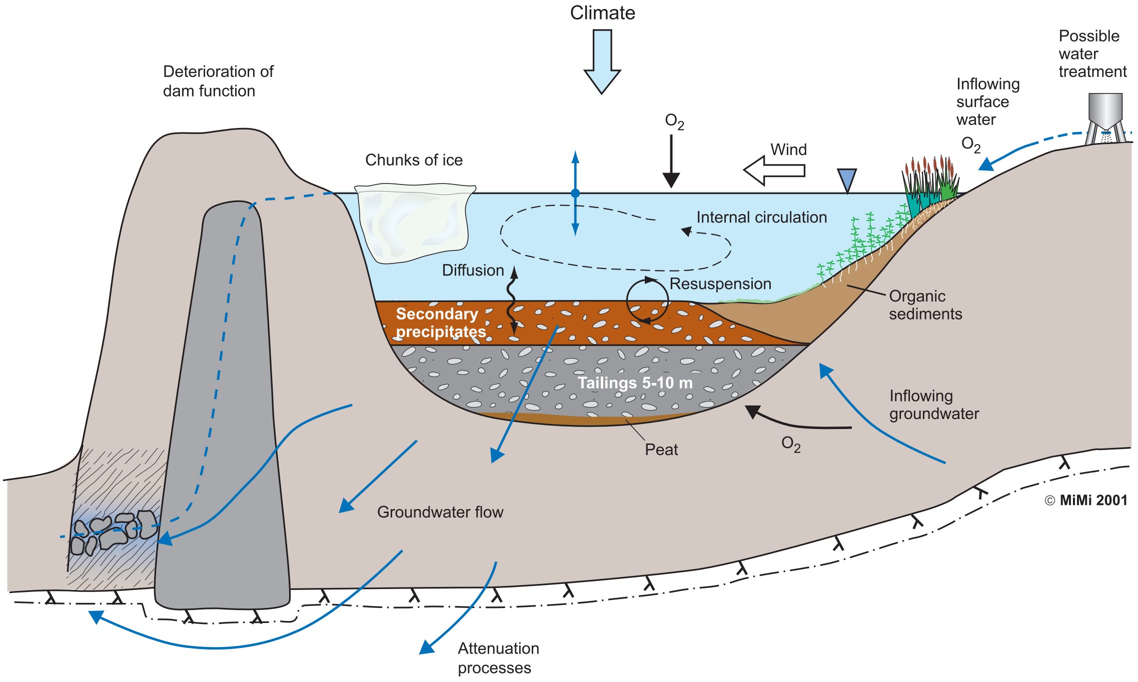


Figure 10-2. Principles of and processes in a water cover case.

In the Base Case for the water cover the same infiltration rate of water is used as for the soil cover case. Oxygenated water is constantly in contact with the tailings and oxygen can intrude by molecular diffusion as well as by infiltration with the seeping water. There are no sediments that cover the tailings in the Base Case. The impact of sediments is explored in variation cases. Water flows into the dam and also leaves the dam, exchanging the water at a certain rate. The inflowing water has an alkalinity that may neutralize some of the acidity that diffuses up from the tailings to the water in the dam. The rate of water exchange as well as the alkalinity of the incoming water is varied over a range of values.

10.4 Data needs for PA calculations.

Some data for the PA calculations are central and essential and must be based on the site-specific conditions. These data can often have a strong impact on the results. Other data are also used as input to the models but do not have so large impact on the final results. We call these secondary data. They may be site specific but are often bounded by practical constraints. Finally, some data may be estimated from general knowledge or assumed without loss of accuracy.

The release of contamination from a tailings deposit is determined primarily by the oxygen intrusion into the tailings. Therefore the parameters that have influence on the oxygen intrusion are of highest importance. In order to systematise the discussion the data are classified in:

- Data essential for the calculations. In most cases they are site-specific. They are based on laboratory and/or field measurements.

- Secondary data are supplemented from information on other similar sites.

- Data of general knowledge that is required in the calculations.

Table 10-3 Data essential for the calculations.

Entities	**Comments**
Geometric data	▪ Volume of the deposit ▪ Surface area of the deposit ▪ Thickness of the different sections (protective cover, sealing layer, partially water-saturated tailing, and water-saturated tailings. It may also include till under the tailings.
Water percolation in the sealing layer	▪ Hydraulic conductivity of the sealing layer. Water percolation determines transport of the dissolved species.
Oxygen intrusion into the tailings	▪ Capillary properties of the sealing layer (e.g., van Genuchten parameters). To calculate the water saturation of the sealing layer (water retention). ▪ Capillary properties of the protective cover and tailings may also be needed. ▪ Oxygen diffusion in a partially water saturated medium (sealing layer) to determine oxygen intrusion into the tailings.
Tailings mineral compositions	▪ Types and amount of major metal sulphides (pyrite, pyrrhotite). ▪ Types and amount of pH-buffer minerals (calcite; silicates, feldspars). ▪ Types and amount of other metal sulphides (e.g., sphalerite, chalcopyrite, covellite, galena, and arsenopyrite).
Sulphide oxidation and acidity neutralisation. Equilibrium case	▪ Oxidation of pyrite and other sulphides. For the Base Case the kinetics of the pyrite oxidation is fast (instantaneous) ▪ The dissolution of the other metal sulphides is assumed to be congruent with pyrite oxidation.
Sulphide oxidation and acidity neutralisation. Kinetics case	▪ Kinetic rates for neutralisation kinetics with pH-buffer minerals. To determine time and spatial extent of the neutralisation. Important for buffer minerals with slow neutralisation kinetics (e.g., silicates, feldspars). ▪ For buffer minerals with fast kinetics, equilibrium may be assumed, e.g., for calcite.
Dilution at the discharge zone	▪ Percolating water flowrate ▪ Water run-off flowrate ▪ Recharge flowrate upstream of the deposit ▪ Total recharge flowrate

Table 10-4 Secondary data.

Entities	Comments
Hydrological and meteorological data	▪ Precipitation, average and seasonal variation. ▪ Temperature, average and seasonal variation.
Oxygen intrusion into the tailings	▪ Hydraulic conductivity of the protective cover. For estimating the water infiltration and water run-off. ▪ Porosity (and tortuosity) of the sealing layer (protective cover). For estimating effective oxygen diffusivity in the sealing layer for water saturation =0.
Sulphide oxidation and acidity neutralisation. Equilibrium case	▪ Secondary minerals from neutralisation reactions. To determine the neutralisation pH. Information from field observations could be used. ▪ Water saturation in the partially water saturated tailings. To determine oxygen diffusion into the tailings. In general, oxygen transport is limited by the diffusion in the sealing layer. ▪ Carbon dioxide concentration in the air-filled pores in the protective cover. Determine the carbon dioxide dissolved in the infiltrating water. ▪ Tailing density, particle density.
Sulphide oxidation and acidity neutralisation. Kinetics case	▪ Pyrite oxidation rate. Only needed for cases with severely damaged sealing layer. For the Base Case equilibrium may be assumed. ▪ Calcite neutralisation rate. Calcite reaction rate is sufficiently fast, equilibrium may be assumed.

Table 10-5 General Data.

Entities	Comments
Oxygen into the tailings	▪ Oxygen diffusivity in air and water ▪ Oxygen concentration in air and dissolved oxygen in water ▪ Oxygen diffusion in a partially water saturated medium
Pyrite oxidation, chemical reactions	▪ Pyrite oxidation ▪ Fe^{3+} precipitation ▪ Fe^{2+} oxidation -> Fe^{3+}
Neutralisation reactions	▪ Neutralisation with calcite ▪ Neutralisation with chlorite ▪ Neutralisation with other silicates and feldspars

10.5 Model data base

Geometrical and physical data

Table 10-6 Geometrical and physical data.

Notation	Entity, unit	Value	Reference
<u>General data</u>			
D_a^o	Oxygen diffusion in free air (m^2/s)	$1.8.10^{-5}$	Perry et al., (1997)
D_{Rel}	Relative oxygen diffusion as a function of water saturation	Fig 7-2 in this report	Collin, (1987)
D_w^o	Oxygen diffusion in free water, m^2/s	$2.5.10^{-9}$	Perry et al., (1997)
$C_{O_2}^o$	Oxygen concentration in air, vol-%	20.94	Weast and Astle, (1980)
$C_{CO_2}^o$	Carbon dioxide concentration in air, vol-%	0.033	Weast and Astle, (1980)
W_{Prec}	Precipitation (seasonal variation), mm/year	400-800	Axelsson et al., (1991)
T_{ave}	Annual mean temperature, ^oC	0.7	Axelsson et al., (1986)
W_{Perc}	Percolation, mm/year	100	Base Case definition
$C_{CO_2}^s$	Carbon dioxide at the surface, pressure, Pa (equivalent value in ppm)	40 (400)	Base Case definition
<u>Protective cover</u>			
L_{Prot}	Thickness, m	1.50	Base Case definition
ε_{Prot}	Porosity (-)	0.23	Öhlander et al., (2004)
S_{Prot}	Water saturation (-)	Unsaturated	Base Case definition
K_{Prot}	Hydraulic conductivity (saturated), m/s	6.10^{-7}	Öhlander et al., (2004)
<u>Sealing layer</u>			
L_{Seal}	Thickness, m	0.30	Base Case definition
ε_{Seal}	Porosity (-)	0.18	Öhlander et al., (2004)
S_{Seal}	Water saturation, (-)	0.95	Öhlander et al., (2004)
K_{Seal}	Hydraulic conductivity at full water saturation, m/s (range of values)	5.10^{-9} $(10^{-9} – 10^{-8})$	Öhlander et al., (2004)

Table 10-6 Continuation. Geometrical and physical data.

Notation	**Entity, unit**	**Value**	**Reference**
Tailings			
ε_{sand}	Porosity (-)	0.45	Öhlander et al., (2004)
ρ_{sand}	Particle density in tailings, kg/m^3	3400	Öhlander et., al (2004)
ρ_{bulk}	Bulk dry density of the tailings, kg/m^3	1870	Calculated
$a_{tailing}$	Specific surface (BET), m^2/g	0.1-10	Base Case definition
PWST	Partially water saturated tailings		
L_{PST}	PWST-Thickness, m	2.0	Base Case definition
S_{PST}	PWST-Water saturation (-)	0.85	Öhlander et al., (2004)
i_{PST}	PWST-Hydraulic gradient	1.0	Base Case definition
WST	Water saturated tailings,		
L_{ST}	WST-Thickness, m	3.0	Base Case definition
K_{ST}	WST-Hydraulic conductivity, m/s	1.10^{-7}	Öhlander et al., (2004)
i_{ST}	WST-Hydraulic gradient, m/m	0.02	Öhlander et al., (2004)
Underlying till			
L_{Till}	Thickness, m	3.0	Base Case definition
ε_{Till}	Porosity (-)	0.23	Öhlander et al., (2004)
K_{Till}	Hydraulic conductivity, m/s	1.10^{-7}	Base Case definition
i_{Till}	Hydraulic gradient, m/m	0.02	Base Case definition
a_{Till}	Specific surface (BET), m^2/g	0.1 – 10	Base Case definition

Thermodynamic and kinetic data

Table 10-7 Kinetic data used in the calculations for pyrite oxidation.

Kinetic Data for iron oxidation	Rate expression	Reference
Pyrite + Oxygen At 25 ^{o}C	$r = 6.5 \cdot 10^{-9} \dfrac{m_{DO}^{0.5}}{m_{H+}^{0.11}}$ $r = \text{rate, mol } FeS_2 / m^2 / s$ $m = mol / kg$	At 25 ^{o}C Williamson and Rimstidt, (1994)
Pyrite + Oxygen Correction at 1 ^{o}C	$r = 8.7 \cdot 10^{-10} \dfrac{(m_{DO})^{0.5}}{(m_{H+})^{0.11}}$ $r = \text{rate, mol } FeS_2 / m^2 / s$ $m = mol / kg$	Salmon and Malmström (2002)
$Fe^{3+} + \text{Pyrite}$ Expressed as Fe^{3+} at 25 ^{o}C	$r = 3 \cdot 10^{-5} \cdot (m_{Fe^{3+}})^{0.62}$ $r = \text{rate, mol } Fe^{3+} / m^2 / s$ $m = mol / kg$	Rimstidt and Newcombe, (1993)
$Fe^{3+} + \text{Pyrite}$ Expressed as FeS_2 at 25 ^{o}C	$r = 2.1 \cdot 10^{-6} \cdot (m_{Fe^{3+}})^{0.62}$ $r = \text{rate, mol } FeS_2 / m^2 / s$ $m = mol / kg$	
$Fe^{3+} + \text{Pyrite}$ Correction at 1 ^{o}C	$r = 8.1 \cdot 10^{-8} \cdot (m_{Fe^{3+}})^{0.62}$ $r = \text{rate, mol } FeS_2 / m^2 / s$ $m = mol / kg$	Salmon and Malmström, (2002)
$Fe^{2+} \Rightarrow Fe^{3+}$ At 20 ^{o}C	$R_{hom} = k_2 \dfrac{[Fe^{2+}]}{[H^+]^2} [O_2(aq)]$ $k_2 = 5 \cdot 10^{-14} \text{ mol/l/s}$ $R_{hom} = \text{mol/l/s}$ $[\;] = \text{mol/l}, \; pH > 5$	Stumm and Morgan, (1996)
$Fe^{2+} \Rightarrow Fe^{3+}$ Approximate correction at 1 ^{o}C	$R_{hom} = k_2 \dfrac{[Fe^{2+}]}{[H^+]^2} [O_2(aq)]$ $k_2 = 0.3 \cdot 10^{-14} \text{ mol/l/s}$ $R_{hom} = \text{mol/l/s}$ $[\;] = \text{mol/l},$	Stumm and Morgan, (1996)

Table 10-8 Kinetic data used in the calculations for neutralisation with buffering minerals.

Kinetic Data for buffer minerals	**Rate expression**	**Reference**
Chlorite At 1 ^{o}C	$r = k_{Ch1}\left[H^{+}\right]^{0.5} + k_{Ch2}$ $k_{Ch1} = 2.6 \cdot 10^{-11}$ $k_{Ch2} = 4.6 \cdot 10^{-13}$ $r = \text{mol chlorite/m}^{2}\text{/s}$ $[\ ] = \text{mol/l}$	Salmon and Malmström, (2002)
Muscovite At 1 ^{o}C	$r = k_{mu1}\left[H^{+}\right]^{0.4} + k_{mu2}$ $k_{Ch1} = 2.9 \cdot 10^{-12}$ $k_{Ch2} = 3.6 \cdot 10^{-14}$ $r = \text{mol muscovite/m}^{2}\text{/s}$ $[\ ] = \text{mol/l}$	Salmon and Malmström, (2002)

Thermodynamic data were, in general, taken from databases MINTEQ and PHREEQC, which are included in PHREEQC version 2.8.

Table 10-9 Other data.

Unoxidised tailings	**Formula**		**wt-%**	**Reference**
Chemical composition	SiO_2		42.8	Öhlander et al., (2004)
	Al_2O_3		9.35	
	CaO		1.01	
	Fe_2O_3		24.0	
	K_2O		0.81	
	MgO		7.73	
	MnO_2		0.12	
	Na_2O		0.46	
	P_2O_5		0.07	
	TiO_2		0.30	
	S		14.4	
Mineral composition	Pyrite	FeS_2	25.0	Base Case definition
	Quartz	SiO_2	50.0	
	Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	20.0	
	Calcite	$CaCO_3$	2.0	

11 Process modelling

This chapter outlines the modelling concepts, the main ideas underlying the models and how the models are used in the performance assessment calculations. A large number of models have been used for background calculations not directly used to generate results for the performance assessment. This section describes the most important models. Some of the models that are within well-established areas where there are many textbooks that can be referred to are described briefly and references given to the literature. One area has been given more space, namely modelling of sorption processes. This is a strongly evolving field that has not yet reached the maturity of many of the other fields but that is deemed to be important in practice in the future. It has not been possible to fully utilise this knowledge in the present performance assessment work because there is not yet sufficient data available for all the main minerals present in mine tailings.

Within the MiMi programme a lot of modelling has been made that that has been aimed at process and mechanism understanding. Much of that modelling has not been used directly in this report. It has, however, given insights and information on what processes and mechanisms are essential to include in the performance assessment modelling and which can be toned down or even omitted.

The available space has only permitted a very brief description of the models used in the performance assessment calculations. The actual modelling using data for a case based on the Kristineberg site is found primarily in Moreno and Neretnieks (2004).

11.1 Conceptualisation

In this chapter the concepts and scope of the models are described first in words and then the main parts of the mathematical models are outlined. Only what is deemed the most important processes are included. Details are referred to in background reports. A systematic methodology for judgement and documentation of processes deemed to be of importance and which can be omitted in the performance assessment is described in Chapter 14.

Physical processes

Hydrology

The covered waste deposit is exposed to wind, precipitation, freezing and thawing, drying during dry, warm and windy periods and a number of other processes. The rain that falls on the deposit will partly run off as surface water, partly evaporate and a part will intrude into the waste through the cover. The rate of intrusion can be controlled by the appropriate selection of material properties and design of the cover layer. Water will also enter the deposit by lateral water flow coming from the adjacent elevated areas. We model the rate of water intrusion from above by a simple model that accounts for the hydraulic conductivity of the sealing layer and its thickness and assume that there is water above the sealing layer. This defines the hydraulic head that drives the water through the layer. The rate of water infiltration is also estimated using data on annual rainfall, runoff and evapotranspiration for comparison. The various chemical and biochemical reactions are followed that occur along the flow paths. In this way account is also taken of the impact of different lengths of flow paths.

For the water cover case similar estimates of the water balance are made. Account is taken of precipitation, upstream infiltration and outflow through the spillways, as well as leakage through and under the dam.

Intrusion of oxygen

The infiltrating water contains dissolved oxygen that can be brought into the waste. Oxygen can also intrude by molecular diffusion through the cover layer(s). The rate of diffusion of oxygen is controlled by the design of the cover and by its diffusive properties but also by the rate of reaction of oxygen in the cover itself and in the waste below it. The overall rate of oxygen intrusion can be governed by the diffusion resistance in an effective diffusion barrier or, if this is less effective, by the chemical and biochemical reaction rates. The relative importance of the transport mechanisms can vary over time. The oxygen diffusion through the sealing layer is determined by the concentration difference over the layer and by the effective diffusivity of oxygen in the layer. The diffusivity is very dependent on the degree of water saturation. This may vary over time depending on rainfall and periods of drought.

If the sealing layer should degrade or lose its integrity the rate of oxygen intrusion will be limited by the rate at which it can react in the waste.

The models account for oxygen intrusion by flow with the water and diffusion in the gas and/or liquid filled pores in the protective and sealing layers as well as in the tailings themselves. The same basic principles apply to the soil and the water covered cases. Account is taken of variable transport properties in the system in space as well as over time. The rate of depletion of oxygen by reactions influences the rate of intrusion and these processes are strongly coupled. They must therefore be accounted for simultaneously using coupled models.

The models have been developed over several years in the MiMi project and details can be found in Werner, (2000), Werner et al. (2001), Werner and Berglund, (2001, 2003), Moreno and Neretnieks, (2004).

Biogeochemical processes

The reactions between oxygen and the minerals in the tailings are influenced by chemical and biogeochemical processes. The former are fairly well investigated and quantified whereas the latter are not. However, as biochemical processes speed up the reaction rate their potential influence has been assessed by assuming that they are very fast. It may already here be stated that the increase in reaction rate due to microbial activity does not influence the overall rate because other processes are found to be limiting.

Abiotic reactions

The rate of reaction depends on several entities. The magnitude of the surface area of the reactive mineral grains, the oxygen concentration, pH, temperature, the possible presence of microbial activity are the most important.

When the pyrite in the waste is oxidised acidity is generated by the oxidation of the sulphur. Additional acidity is generated if and when the iron is oxidised from divalent to trivalent state and when the latter precipitates as ferric oxy-hydroxide. This may not take place in the waste if the dissolved ferrous iron is carried away by the seeping water quickly enough. The acidity produced can react with pH buffering minerals in the waste and the acidity can partly be neutralised. Other metal sulphides are also oxidised and their metal content can be dissolved into the seeping pore water. They may also partly precipitate e.g. as carbonates or sulphates if the conditions permit. The mineral surfaces of the waste material can adsorb the metals and retard their rate of migration in relation to the rate of water movement.

The pH will be influenced by the rate of depletion of the acidity by the neutralisation reactions. The minerals in the system will bring the pH back to circum neutral if the reactions are rapid.

Biomediated reactions

The rates of several of the chemical reactions of interest here can be increased by microbial catalysis. For low concentrations, the rate of reaction is proportional to the concentration of the reactants and to the number of microbes in the system. When one or both of the reactants have a high concentration the microbes cannot digest the reactants fast enough and a maximum reaction rate is approached. Microbial reaction rates strongly decrease with a decrease in temperature, much more than abiotic reactions. The rate can also be influenced by a number of other factors. The range of possible rate constants can be quite large. The microbes utilise the energy released by the chemical reaction to sustain their life and to derive energy to increase the population. A part of the microbial population is attached to the mineral surfaces and another part is floating around in the water. There is an exchange between the immobilised microbes and those in the water. Those in the water will be carried by the seeping water and can carry adsorbed metals along. The microbes also generate organic molecules that can increase the solubility of many of the metals of interest. In the modelling concept both the microbes and their exudates are treated as any other complexing agents.

Attenuation processes

The attenuation of inorganic contaminants from mining waste leachates implies that these substances are transferred from the flowing water to stationary solid phases. Different types of solid phases control the solubilities of metals depending on pH and redox conditions. In tailings downstream the oxidation front, molecular oxygen is depleted and mainly sulphidic minerals, silicates and potentially also carbonates can be assumed to be responsible for metal attenuation. This is likely to occur by adsorption processes and by formation of secondary sulphide minerals that remain in the tailings.

Iron containing phases are particularly important in this context. Iron bearing sulphide minerals, such as pyrite and pyrrhotite are commonly major constituents of mining waste. Primary oxidation of the iron sulphides leads to oxidation of sulphide sulphur to sulphate. In the absence of excess oxygen, iron remains in the divalent oxidation state with a generally high solubility. In presence of excess oxygen, Fe(II) is oxidised and can precipitate as oxyhydroxides, which have a well documented ability to scavenge both metals in cationic form and anionic compounds, such as sulphate and arsenate.

The acid formed by sulphide oxidation can react with acid neutralizing minerals such as calcite and aluminosilicates. The association of metal ions to mineral phases and organic matter is largely determined by solution pH and the relative amounts of metal ions and solid matter. Presence of complexing ligands can strongly affect the degree to which contaminants are associated to particulate phases. Depending on the hydrochemical conditions organic matter may both increase and decrease metal uptake.

Contaminants can also be retained in surrounding soils and in the sediments of leachate recipients. Active sorbents can be both primary and secondary mineral phases and particulate organic matter. Furthermore, metals can be accumulated by plants and by bacteria and fungae.

The above-mentioned processes are well understood qualitatively but in some areas there is a lack of data to quantify them in detail. When this is the case simplifying assumptions are made and data chosen so that the results will be as reasonable as possible but leaning to the conservative, which means that metal and acidity release rates will be overestimated and residence times underestimated.

Coupling of the processes and computational approaches

The above processes and many individual reactions are coupled in a complex manner and can usually not be treated separately. One simplification used is to follow a water package along its path through the system. This simplifies the computations significantly as the model essentially becomes one-dimensional in space. It also makes it possible to account for the chemical reactions in a very detailed manner, which would not be feasible if fully three-dimensional flow paths were modelled. The transport along the shortest possible flow paths is also simulated as these will have the shortest residence times and may not allow all attenuation to have occurred.

We can follow the water package along the streamtube (or streamline) and the changes in water and mineral composition along the path. The mass of every species dissolved into the water or precipitated from the water will change the composition of the solid phases in the streamtube. Reaction fronts develop and can be tracked. One such front is that between the upstream region where all the pyrite has been exhausted and that where there still is unreacted pyrite. Another front is that where a pH buffering mineral exists and where it is gone.

In many cases we need not to account for the short term variations in concentrations. This permits us to neglect the instationary nature of the system. The model can then be used to simulate the system as if it evolves as a series of steady states. This approach can be visualised by an analogy to a movie. The movie has captured a continuous movement on a set of frames. Each frame has frozen the movement and depicts the state of the object at an instant. The next frame does the same for a short time interval later. If the movement of the object is not jerky or jittery with a frequency faster than the time between the pictures are taken the film, when played, will show a reasonable similarity to the continuous movement. In the Pseudo Steady State (PSS) a similar procedure is applied. This makes it possible to follow the movement of the fronts by using a limited number “of frames”. The method can be used for slowly changing systems even when there are fast reactions locally.

In other cases, e.g. where we study the wetting and drying of the sealing layer, the evolution over time must be modelled with a higher resolution in time because the rate of change, as in seasonal variations, is fast.

11.2 Description of the models

Physical processes

Hydrology

The water flow in a saturated porous medium is usually calculated using Darcy’s law

$$q = K \cdot i \qquad (11\text{-}1)$$

where q is the specific water flow (m^3/m^2,s), K is the hydraulic conductivity (m/s) and i the hydraulic gradient (m/m).

For a partially water-saturated medium the conductivity and the gradient can vary strongly in space and over time and this is then accounted for in the calculations.

Often it is not necessary to use the complex relations to calculate the water flow through the protective cover, since due to its large hydraulic conductivity the water flow rate is determined by the water availability (precipitation). Equation 11-1 may directly be used to determine the water flow rate through the sealing layer and the water-saturated regions at the bottom of the waste deposit.

Intrusion of oxygen

In partially water-saturated media, oxygen is transported by diffusion through the air and water phases in the pores of the material. Moreover it may also be transported with the percolating water as oxygen dissolved in water. The transport of oxygen may mathematically be described by a differential mass balance.

$$\frac{\partial C}{\partial t} = D_e \cdot \frac{\partial^2 C}{\partial z^2} - q\frac{\partial C}{\partial z} - r \qquad (11\text{-}2)$$

The first term is the accumulation of oxygen in the system. The second term describes the diffusion of oxygen, where the effective diffusion coefficient, D_e, depends strongly on the water saturation. The third term describes the oxygen transported with the percolating water, where q is the water flux. Finally r represents the oxygen consumption rate by reaction. Reaction rate expressions are described below.

This relationship may be applied to any cover, but the dominant processes depend on where the equation is applied. In the protective cover, for example, the transport by diffusion is important. Moreover, the reaction term may also be significant if there is organic material that may react with and scavenge the oxygen already before it reaches the tailings.

Another important observation is that in most of the cases the accumulation term is not important. The oxygen concentration changes very slow in the waste deposit. This permits the use of a PSS approach in the solution of the equations of transport. This leads to considerable simplifications computationally. The PSS approach has been used frequently in the modelling. It has frequently been supplemented by specific studies of the short-term effects, which may be important before PSS has been reached. This combination of methods gives valuable insights in the processes and highlights when a particular process is important and when it is not.

Biogeochemical processes

The models used account for a variety of chemical reactions, different species and chemical complexes, mineral phases, sorption phenomena and activity relations. The models are long established and the databases needed are also reliable for the systems of interest here. There is however, still lack of sorption data for several of the minerals in the tailings. Also data for mineral dissolution and precipitation reaction rates are not available for some of the minerals.

In the application of the models, often assumptions need to be made of data and processes. Such assumption are based on analogues to other minerals, general chemical principles etc. The impact of the assumptions is subsequently tested. Often it is found that the results are insensitive to the assumptions. When not, sensitivity analysis is made.

Abiotic reactions

By abiotic reactions, we mean reactions that are not mediated by biological processes. These occur in parallel to those that are. We distinguish homogeneous reactions and heterogeneous reactions. The former takes place between solutes dissolved in the water and the latter between a dissolved solute and a solid phase. The rate of reaction r_i of a reactant generally increases with the concentration of the reactant, not always in direct proportion. As at least two reactants are needed for a reaction the rate of reaction will depend on the concentrations of both reactants. A general formula for the reaction rate can be written

$$r_i = kc_i^a c_j^b \tag{11-3}$$

r_i is the rate of reaction of component i in mol l^{-1} s^{-1}.

c is the concentration of components i and j respectively. a and b are exponents and often between 0.5 and 2. Very commonly the value is unity. The reaction rate constant k actually can depend on the concentrations of other components, especially the proton concentration, i.e., pH can have a considerable influence. One example of a reaction of large importance for our system is the oxidation of ferrous iron by dissolved oxygen. For this reaction the constants a and b are unity. This reaction is extremely sensitive to the pH. The reaction rate increases hundredfold for an increase in pH of one unit. In acid waters, it is practically negligible whereas in neutral and slightly alkaline waters it is very fast.

In heterogeneous reactions, the magnitude of the surface on which the reaction takes place has the same effect as the other component in the homogeneous reaction. It can be written

$$r_i = kA_i c_j^b \tag{11-4}$$

A_i is the “concentration” of surface in the water, m^2 l^{-1}, the other entities have the same meaning as for the homogeneous case.

Biomediated reactions

Biomediated reactions commonly have a maximum rate per microbe. This is because the metabolism of the microbe cannot digest faster than a certain rate irrespective of how much reactant is offered. At low concentrations of the reactants, the biomediated reaction can be described by Equation 11-3 with the difference that the reaction rate constant k now would denote the rate per microbe. If we know the number of microbes per litre water or per surface area, the rate of reaction per litre water can be assessed. For not so low concentrations of the reactants the rate is modified as follows

$$r_i = kc_m \frac{c_i}{c_i + k_i} \frac{c_j}{c_j + k_j} \tag{11-5}$$

The constants k_i can be seen as the concentration at which the rate of reaction is half that of the maximum. The equation reduces to 11-3 for small concentrations and it also shows that the reaction rate will become constant and maximum when the concentrations are much larger than the k_i’s. c_m here denotes the concentration of microbes. It changes over time and can be very different in different locations, because the population density varies.

For every reacted mol of a component, there will be some increase of the number of microbes. Very simplistically one can visualize the process in the following way. Part of the energy released from the reaction is used to synthesise one molecule of the microbial substance. We can think of it as CH_2O, part of the building material of the microbial body. For this one molecule of carbon is used. In our system where sulphides are oxidised by oxygen the carbon is taken from inorganic carbonate. To synthesise organic matter from carbonate there is a large demand for energy and therefore many more molecules of the components are needed to supply the energy for one molecule of CH_2O.

The maximum efficiency for building organic matter is if all released energy can be used for the synthesis. This can be estimated. Then the maximum rate of growth of the biomass can be assessed. However, in practice several other substances or lack of substances will be limiting factors for microbial growth and reactions. It is seldom possible to quantify all important factors in practical systems outside the laboratory.

Some of the microbes will attach to the surfaces of the grains and some will remain in the water and can thus be swept away carried downstream by the seeping water.

Geochemical processes and models for attenuation

For predictive purposes it is important that the different chemical processes that take place in aqueous systems can be represented by quantitative model parameters. Equilibrium models can be applied to all kinds of reversible reactions occurring in aqueous solution, such as acid/base reactions, redox reactions, metal complexation by dissolved ligands and precipitation/-dissolution of solid phases (Stumm and Morgan, 1996). Exchange of gases between a liquid phase and its surrounding atmosphere can also be represented in equilibrium modelling by applying Henry's law. Compilations of model parameters in terms of stoichiometric composition and stability of species formed are available in both electronic (e.g. NIST, 2003; Pettit and Pettit, 2002) and printed form (e.g. Smith and Martell, 1989). Electronic databases are also included in several of the most commonly used computer programs for equilibrium modelling, such as WATEQ4 (Ball and Nordstrom, 1991), MINTEQ (Allison et al., 1991) and PHREEQC (Parkhurst and Appelo, 1999).

Precipitation of secondary solid phases

The solubility of solid phases in water is at equilibrium defined by their solubility products, i.e. the constant relationship between the aqueous concentrations of all components of the solid. An important difference in the numerical treatment of equilibria in homogeneous solution and precipitation/dissolution reactions is related to the choice of standard state. While the activity of a dissolved species is given by its concentration adjusted for ionic strength effects by multiplying with the activity coefficient, the activity of a solid phase is equal to 1 if the solid phase exists (Stumm and Morgan, 1996). A calculated activity less than 1 implies that the solid phase is thermodynamically unstable, and will tend to dissolve.

Sorption processes

Modelling of exchange of substances between particles and aqueous solutions is not equally straightforward. Traditionally, sorption processes were quantified by applying empirical representations like distribution coefficients, K_d, or adsorption isotherms when nonlinearities must be accounted for. The distribution coefficient postulates a constant relationship between the amount of substance associated with solids (C_s) and amount of the substance present in the aqueous phase (C_w) according to equation (11-6) (Stumm and Morgan, 1996).

$$K_d = \frac{C_s \ (\mathrm{mol \cdot kg^{-1}})}{C_w \ (\mathrm{mol \cdot dm^{-3}})} \qquad (11\text{-}6)$$

Distribution coefficients are particularly useful in cases where the sorbent is highly heterogeneous and when dealing with sorption of hydrophobic substances on organic particles or mineral particles coated with organic matter, i.e., an absorption process rather than adsorption.

Adsorption isotherms, such as *Langmuir* and *Freundlich* isotherms are frequently used to describe adsorption equilibria. These can be visualised by plotting the amount of adsorbate A adsorbed per mass of adsorbent (Γ_A; mol/g or mol/m^2) vs. the equilibrium concentration of A in the solution (mol/dm^3).

$$\Gamma_A = f([A]) \quad (\text{or } \log\Gamma_A = f(\log[A]) \qquad (11\text{-}7)$$

The Langmuir isotherm is valid up to the formation of a surface coverage corresponding to a monolayer, which means that each surface site is occupied by one sorbing molecule. The Freundlich isotherm is applied mainly for energetically heterogeneous solid surfaces.

By applying concepts of solution coordination chemistry to the description of the interaction of metal ions and inorganic/organic ligands at the particle/solution interface it is possible to include adsorption processes in thermodynamic modelling (Stumm, 1992).

The concept of surface complexation is based on the assumption that adsorption takes place at specific coordination sites and that adsorption processes are reversible. Such sites at metal (hydr)oxide surfaces are often referred to as surface hydroxyl groups, noted as $\equiv$MeOH, where $\equiv$ symbolises the bulk oxide phase, and Me and OH denotes the metal and hydroxide ions at the surface. It should be noted that this notation is a simplification of the coordination environment of the hydroxyl groups. As pointed out by Hiemstra et al. (1989a,b) the (hydr-)oxide surfaces exhibit a range of structurally different functional groups.

The surface hydroxyl groups can take up and release protons and metal ions from the solution in the same way as ligands in the aqueous solution can, e.g. reactions (11-8 to 11-11). The adsorption of metal ions involves a competition with hydrogen ions for the binding sites, which implies that adsorption is favoured by increasing pH. The rather narrow pH-range within which the vast majority of metal ions are being transferred from the aqueous solution to the particle surface is element specific and also depends on the metal to surface site ratio.

The surface group also provides an atom that can accept electrons, i.e., the metal ion. This enables complexation with donor groups (ligands, L) in the solution, reaction 11-10. Charged species can also be taken up by electrostatic attraction to surface sites of opposite charge, e.g. anions may be adsorbed to surface sites which are positively charged as a result of proton uptake ($\equiv$MeOH$_2^+$). Hence, anion sorption is favoured by low pH. While strongly sorbed anions such as phosphate (PO_4^{3-}) (Persson et al, 1996) and arsenate (AsO_4^{3-}) are directly coordinated by the metal ion, the more weakly bonded sulphate ions are mainly adsorbed by electrostatic attraction (Persson and Lövgren, 1996).

$$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+ \qquad (11\text{-}8)$$

$$\equiv FeOH + Me^{z+} \leftrightarrow \equiv FeOMe^{(z-1)} + H^+ \qquad (11\text{-}9)$$

$$\equiv FeOH + L + H^+ \leftrightarrow \equiv FeL^+ + H_2O \qquad (11\text{-}10)$$

$$\equiv FeOH + H^+ + L^- \leftrightarrow \equiv FeOH_2^+, L^- \qquad (11\text{-}11)$$

Adsorption of metal ions from the solution can also be a result of ternary complexation, which means that the metal ion is bound indirectly to the surface by complexation with an adsorbed anion forming a so called Type A ternary surface complex, ($\equiv$FeOMeL). Correspondingly, anion adsorption may under certain circumstances be enhanced by adsorption to adsorbed metal ions under formation of a Type B ternary surface complex ($\equiv$FeLMe).

With regard to coordination chemistry, the mechanisms behind site specific adsorption to iron(hydr-)oxide surfaces can be distinguished between formation of outer-sphere and inner-sphere complexes (Stumm, 1982). By definition, an inner-sphere surface complex is formed when there is a direct chemical bond between the adsorbing ion and the metal ion at the surface. In outer-sphere complexes hydroxyl groups or water molecules separate the adsorbed ions and the surface metal ion centre or hydroxyl group. The dominating driving force for the adsorption is the attraction of opposite charges, with the surface waters and hydroxyls possibly acting as proton donors in hydrogen bond arrangements. Outer-sphere complexes are often considered to be weaker than inner-sphere.

Thermodynamic modelling

The surface equilibria can be described by mass law equations. A complication in this respect is that, due to the density of surface hydroxyl groups, adsorption of charged species from the solution results in the development of an electric charge. The surface charge affects the stability of the surface complexes by electrostatic attraction or repulsion. From a thermodynamic point of view, the total Gibbs free energy for a given reaction consists of both a chemical and a coulombic term (Stumm, 1982).

$$\Delta G^0_{tot} = \Delta G^0_{chem} + \Delta G^0_{coul} \qquad (11\text{-}12)$$

ΔG^0_{chem} represents the direct chemical interaction between the donor/acceptor atom of the surface and the sorbing ion/molecule, or in other terms, the charge independent (intrinsic) function of the stability constant. ΔG^0_{coul} represents the electrostatic interactions at the charged surface. To correct for the electrostatic effects resulting from the build up of surface charge a handful of electric double layer (EDL) models have been developed. The different EDL's differ with respect to the number of planes of specifically adsorbed ions and to what extent a diffuse layer of counter ions in solution is considered.

For speciation modelling of surface complexation equilibria it is critical that the EDL model parameters are consistent since the density of active surface sites, specific capacitances and intrinsic equilibrium constants are interrelated. As an example, the protonation and deprotonation of surface hydroxyl groups at the surface of goethite (α-FeOOH) can be described by the two reactions:

$$\equiv FeOH + H^+ \leftrightarrow \equiv FeOH_2^+ ; \qquad \beta_{1,1,0} \qquad (11\text{-}13)$$

$$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+ ; \qquad \beta_{-1,1,0} \qquad (11\text{-}14)$$

Applying the Constant Capacitance Model (CCM, the intrinsic equilibrium constants for these reactions was determined by Lövgren et al (1990) to be $\log\beta_{1,1,0\ (intr)} = 7.47$ and $\log\beta_{-1,1,0(intr)} = -9.51$. The electrostatic forces at the charged surfaces was accounted for by the specific capacitance 1.28 $C\ V^{-1}\ m^{-2}$ and a density of proton active sites of 1.68 nm^{-2}, corresponding to 2.79 $\mu mol/m^2$ (Lövgren et al., 1990). In a series of studies metal ion complexation to goethite Lövgren and co-workers have determined model parameters (inner-sphere) based on the above mentioned model, Table 11-1.

Outer-sphere complexation is commonly modelled using Triple Layer Model (Yates et al. 1974; Davis et al. 1978). A more recent development in surface complexation modelling is the Charge-distribution Multisite Surface Complexation Model (CD-MUSIC), which describes the proton affinity of various types of surface hydroxyl groups on a mineral surface and accounts for spatial distribution of charge at the mineral surface (Hiemstra and Van Riemsdijk, 1996).

Although the above described models for surface complexation of protons, metal ions and sulphate to goethite is consistent, and can be combined in a model calculation of a multi-component system, it is clear that the different surface complexation models available in the literature are not as generally applicable as models for equilibria in homogeneous solution. The most ambitious attempt to provide a set of consistent thermodynamic data for sorption of inorganic compounds for hydrous oxide minerals was presented 1990 by Dzombak and Morel. Based on a *generalized two-layer model* the authors reinterpreted published experimental data for adsorption of cations and anions to hydrous ferric oxide (HFO), also called amorphous ferric hydroxide (Dzombak and Morel, 1990). HFO material is the solid formed by rapid hydrolysis of ferric iron at 20°C to 30°C. Based on a compilation of results from earlier studies, two different types of active surface sites were distinguished: strongly complexing sites ($\equiv Fe^{s}OH$) and weakly complexing sites ($\equiv Fe^{w}OH$). The density of $\equiv Fe^{s}OH$ was fixed to a value corresponding to one site per 200 Fe atoms in the solid, and the corresponding number for $\equiv Fe^{w}OH$ was one site per five Fe atoms. In other terms, for 1.0 g/l of HFO with a specific surface area of 600 m^2/g the total concentration of $\equiv Fe^{s}OH$ is $5.5 \cdot 10^{-5}$ mol dm^{-3} and $\equiv Fe^{w}OH$ is $2.2 \cdot 10^{-3}$ mol dm^{-3}. For further details about the model parameters for the fundamental properties of the material the reader is referred to Dzombak and Morel (1990). The database for cation sorption covers 12 metal ions and models for anion sorption is presented for 10 inorganic anions, e.g. sulphate, arsenate, arsenite and vanadate. Since HFO is a material of relevance for many different natural environments, and the database is the largest known set of consistent models for surface complexation it is often included in computer programs for geochemical calculations, such as PHREEQC (Parkhurst and Appelo, 1999) and MINTEQA2 (Allison et al., 1990).

Table 11-1 Results from previous studies of surface complexation of Pb(II), Cu(II), Zn(II), Cd(II) and Hg(II) at the goethite/water interface. (I = 0.1 M $NaNO_3$; t = 25°C).

Acid/base reactions (Lövgren et al, 1990):	**Eq. nr**	**Stability constants**
$\equiv FeOH + H^+ \leftrightarrow \equiv FeOH_2^+$	11-15	log $\beta_{1,1(intr)}$ = 7.47
$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+$	11-16	log $\beta_{1,1(intr)}$ = -9.51
Specific capacitance: 1.28 C V^{-1} m^2; Density of hydroxyl groups: 1.68 sites/nm2 ; 2.79 µmol sites/m^2		
Pb(II) (Gunneriusson et al,. 1994):		
$\equiv FeOH + Pb^{2+} \leftrightarrow \equiv FeOHPb^{2+}$	11-17	log $\beta_{0,1,1(intr)}$ = 8.2
$\equiv FeOH + Pb^{2+} \leftrightarrow \equiv FeOPb^+ + H^+$	11-18	log $\beta_{1,1,1(intr)}$ = 0.17
$\equiv FeOH + Pb^{2+} + H_2O \leftrightarrow \equiv FeOPbOH + 2 H^+$	11-19	log $\beta_{2,1,1(intr)}$ = -8.85
Cu(II) (Palmqvist et al., 1997):		
$\equiv FeOH + Zn^{2+} \leftrightarrow \equiv FeOZn^+ + H^+$	11-23	log (0,2,1(intr) = 10.67
$\equiv FeOH + Zn^{2+} + 2 H_2O \leftrightarrow \equiv FeOZn(OH)_2^- + 3 H^+$	11-24	log $\beta_{-1,1,1(intr)}$ = -2.0
	11-25	log $\beta_{-2,1,1(intr)}$ = -18.2
Cd(II) (Gunneriusson, 1994):		
$\equiv FeOH + Cd^{2+} \leftrightarrow \equiv FeOHCd^{2+}$	11-26	log (0,1,1(intr) = 6.4
$\equiv FeOH + Cd^{2+} \leftrightarrow \equiv FeOCd^+ + H^+$	11-27	log $\beta_{-1,1,1(intr)}$ = -2.2
$\equiv FeOH + Cd^{2+} + H_2O \leftrightarrow \equiv FeOCdOH + 2 H^+$	11-28	log $\beta_{-2,1,1(intr)}$ = -12.0
Hg(II) (Gunneriusson and Sjöberg, 1993):		
$\equiv FeOH + Hg^{2+} \leftrightarrow \equiv FeOHg^+ + H^+$	11-29	log $\beta_{-1,1,1(intr)}$ = 4.45
$\equiv FeOH + Hg^{2+} + H_2O \leftrightarrow \equiv FeOHgOH + 2 H^+$	11-30	log $\beta_{-2,1,1(intr)}$ = -2.77

Phyllosilicates, i.e. aluminosilicates with a layer structure are expected to show surface properties that differ from those of simple oxides and oxyhydroxides of several reasons. Surfaces of aluminium silicates exhibit both oxygen atoms coordinating to Al(III) atoms and oxygens coordinating to Si(IV) atoms. Phyllosilicates, such as kaolinite, consist of tetrahedral silica sheets and octahedral alumina sheets bonded together by the sharing of oxygen atoms between the silicon and aluminium atoms in adjacent sheets. In kaolinite, the O-Al-O-Si-O layers are attached to each other in the crystal lattice by hydrogen bonding. Resulting from isomorphic substitution of Si(IV) by Al(III) atoms the crystals carry negatively charged sites at all pH. For particularly 2:1 minerals (O-Si-O-Al-O-Si-O), e.g. smectites, the net negative charge of each 2:1 layer is neutralised by cations in the interlayer region. Since the charge density of these surfaces is low the interlayer metal ions are rather weakly bonded and may be exchanged with other metal ions. The edges of layer silicates contain both ≡AlOH and ≡SiOH sites, which may be considered as one common type of surface site (≡SOH) which can exhibit amphoteric properties, i.e. they can both take up and give away protons. (Angove et al., 1997). Consequently, metal ions may be attached to layer silicates in three different ways: ion exchange at layers with a permanently negative surface charge, ion-exchange in the interlayer region and formation of surface complexes at the ≡SOH sites.

In the case of kaolinite, exchange in the interlayer region does not occur. Thus, metal ions may be adsorbed to kaolinite by ion exchange and also form surface complexes with ≡SOH groups. Angove et al. (1997) propose that the sorption of Cd(II) by kaolinite involves bidentate ion exchange onto permanent negatively-charged sites on the silanol faces (≡XH), and formation of bidentate inner sphere complexes on pH-dependent surface hydroxyl groups (≡SOH).

11.3 Coupling of the processes

Some of the processes described earlier are weakly coupled and can be treated separately. Other processes are so intimately coupled that they must be considered simultaneously because they influence each other. Examples of the first are that water flow rates in and through the deposit are not much influenced by the chemical reactions inside. The water flowrate and pathways can therefore be calculated independently of the processes inside. This is a simplification because mineral dissolution and precipitation of secondary minerals may change the hydraulic properties of the system. In practice this is handled by separate calculations of the hydraulics with different values of the permeability.

The chemical and biochemical reactions on the other hand can be very dependent on the residence time of the water and the time the water is contact with the minerals. Some of the reactions e.g. speciation reactions in the liquid phase are so fast that it is permissible to treat them as if they are in equilibrium. Other reactions e.g. the redox reaction when pyrite and other sulphides are oxidised by the primary oxidant oxygen can under some conditions be slow compared to other processes. These must be treated explicitly in the models and account must be taken of how the other reactions influence the reaction rates. Another example is the oxidation of ferrous iron by oxygen which is very slow at low pH but fast at neutral and higher pH values. In this process acidity is generated and could slow down the reaction if it were not that the acidity is partly neutralised by reactions with minerals. The rates are then competitive and must be handled simultaneously.

Another example is the competition between a physical process, namely in-diffusion of oxygen and the chemical reaction of the oxygen with the minerals. Here the rate of reaction can be the dominating mechanism when the supply of oxygen is large, e.g. when the cover is damaged, but is of negligible importance when the cover functions as intended and limits the supply of oxygen. The models are set up in such a way that they automatically account for these effects.

However, it should be realised that some processes are very well understood and quantified. Other processes can be well understood in principle but can be influenced by some less well-understood processes. This is true for some of the biochemical processes. For these the general form of the reaction rate, see e.g. 11-5 is usually applicable but if there is lack of some trace, but essential nutrient, the rate constant k would seem to decrease considerably. In such cases one must rely more on field measurements of the specific reaction. Another approach in such cases is to try to assess if the process is essential to include. One can e.g. assume that the reaction is infinitely fast. If it then is found that other processes sufficiently limit the reaction anyway no further effort need be spent to obtained better data. For very complicated systems this approach is often necessary.

There is a large number of chemical components in the system. Many of them react with each other and therefore one must account for their presence simultaneously in all parts of the system in order to determine how they evolve in time and space. In a simple way, this can be visualised as “book keeping” of the mass of the components. In words it can be stated in the following way: What goes into a (control) volume and does not go out must accumulate. Accumulation designates both negative and positive change in this case. This is called keeping the mass balance. By choosing to make the book keeping on what we call components (basic building stones), chemical reactions are readily accounted for. When two components A and B react to form a new compound, AB, the components are still retained but now as part of AB.

Equation 11-31 states this in mathematical terms. It can be interpreted in the following way. Term by term it means:

$$\left[\text{Accumulation}\right] = \begin{bmatrix}\text{Net in by} \\ \text{Diffusion}\end{bmatrix} + \begin{bmatrix}\text{Net in by} \\ \text{Flow}\end{bmatrix} + \begin{bmatrix}\text{Depletion} \\ \text{by reaction}\end{bmatrix} \qquad (11\text{-}31)$$

This mass balance is made for every component in the system. The system of equations, typically 10 – 20 equations in the present applications, is then solved simultaneously all along a streamtube.

For illustration purposes, one may think of the techniques for solving the equations in the following way. The stream tube is divided into a set of compartments. These are in essence chemical reactors with inflow and in-diffusion at one end and outflow and out-diffusion at the other end. Fresh water and oxygen enters the first reactor. Reactions take place there during a predetermined time and the effluent from this reactor goes to the next reactor downstream. There the procedure is repeated. After a number of exchanges of water in each reactor the chemical and mineral composition in the reactors and thus along the stream tube is obtained.

The rate of net in-diffusion is determined by the diffusivities of the components. The difference in concentration at the inlet and the outlet plus the volume of the reactor will determine the accumulation. The net rate of outflow is obtained in a similar way but now from the information on water flowrate obtained earlier from the hydraulic calculations.

The generation by reaction is obtained from the sum of all reactions where the specific component is involved, be they abiotic or biotic. In principle the fate of every component influences the fate of every other component.

In applications of these models, it is often found that if all components are accounted for at the same time the results become difficult to interpret. An experienced user of these type of models will therefore try to simplify the system in order to capture the main traits of the system. Another bonus of simplification is that computations are speedier and reasonable size computers can be used. Scoping calculation often precede full-scale calculations. One example is that the maximum rate of intrusion of oxygen can be estimated by the diffusion equation applied to the cover and assuming that all intruding oxygen is immediately consumed. Then the maximum rate of oxidation of the minerals can be assessed. This will later help to verify that the full-scale calculations give reasonable results.

Scoping calculations are also used for simple sensitivity studies. This may in an early stage indicate if a specific process may have a large impact on the final results or not. If the latter is found, one need not assign a large effort to obtain additional and firm information on that process.

12 Model calculations for the Base Case and sensitivity analysis

12.1 Introduction and outline of chapter

This chapter describes the results of the calculations for the Base Case and the most important variation cases. The processes that are considered in the modelling are described in Chapters 7 and 9. The Base Case is described in Chapter 10 and the modelling in Chapter 11. Detailed calculations are found in Moreno and Neretnieks (2004), which is the main reference to this chapter unless otherwise noted.

The key processes that drive all subsequent reactions are the intruding water and oxygen: The oxygen reacts swiftly with the metal sulphides, mainly the pyrite, and generates an acid water with dissolved metals. The amount of sulphides oxidised is directly proportional to the amount of oxygen that intrudes. Therefore the calculations first concentrate on the rate of oxygen intrusion for the soil cover scenario. Later in this chapter oxygen intrusion rates in a water cover case are presented.

In the soil cover case the acid solution with the dissolved metals flows downstream. The acid reacts with acid buffering materials in the tailings. Two main questions are addressed. The first is: Which and how much buffering minerals are present in the tailings. This will determine how much acid they could neutralise if they were to react. The second question is whether they react sufficiently fast to have time to neutralise the water before the water has passed out of the tailings deposit.

The fate of the other metals such as Cu, Pb and Zn, as well as As, dissolved by the mineral oxidation is also studied and the formation of secondary sulphide minerals is specifically addressed as well as sorption processes that may retard the movement of these metals.

The influence of the rates of the chemical reaction of pyrite with intruding oxygen and rates of acid neutralisation by the buffering minerals is studied specifically.

Further, deliberations of a number of other mechanisms and processes are discussed that have been considered but were not found to have the same impact as those described previously.

Finally a number of variation cases are presented that illustrate the sensitivity of the results to uncertainties in data and assumptions.

12.2 Results for the Base Case

Oxygen intrusion for the soil cover case

The oxygen may intrude into the deposit by molecular diffusion through the protective cover and sealing layer. It may also be transported dissolved in the infiltrating/percolating water. In a partially water-saturated porous medium, most of the oxygen transport occurs by diffusion through the air-filled pores. For water-saturated porous media, diffusion occurs through the water-filed pores. Since diffusion in water is several orders of magnitude less than in air, transport by diffusion in a water-saturated medium is very small. This has been described in more detail in Chapter 7.

Figure 12-1 shows how the system is modelled for the soil cover. A column with a cross section area at the top of 1.0 m^2 and with no transport through the vertical walls is used as a basis for the calculations. This very simple case captures the essentials of the transport modelling. Water flow, oxygen transport and the transport and reaction of a large number of chemical species is modelled in the column.

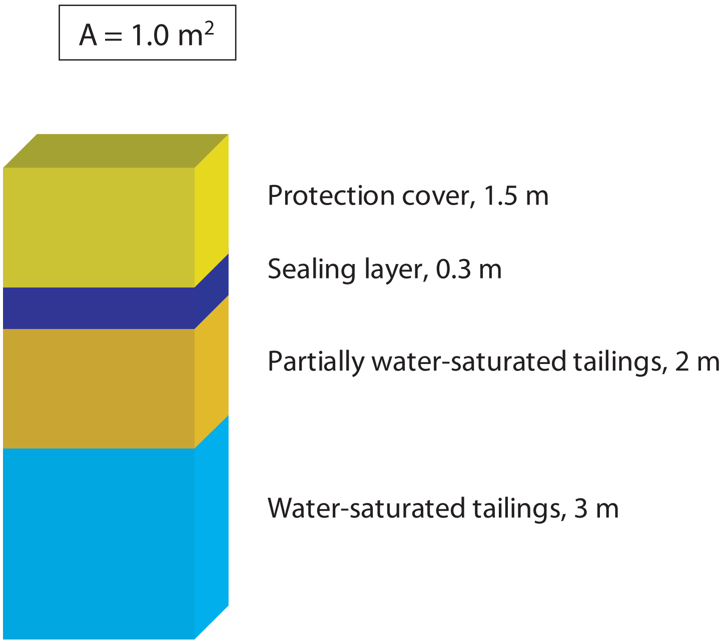


Figure 12-1 Schematic picture of the modelled cover system.

Detailed data for the Base Case are given in Chapter 10. For a cover system formed by various sub-layers in series, as shown in Figure 12-1 the sub-layer with the higher diffusion resistance controls the oxygen transport by diffusion. In the case discussed here, the diffusivity in the sealing layer that has high water content is much smaller than that of the protective cover. The oxygen intrusion into the tailings is controlled essentially by the diffusion in the sealing layer.

For the case that no oxygen is consumed as it diffuses through the cover and sealing layers, the rate of oxygen intrusion is obtained from Equation (12-1).

$$N_{oxygen} = D_{eff} \cdot \frac{(C_0 - C_b)}{\Delta L} \qquad (12\text{-}1)$$

N is the oxygen flux (mol/m^2,s), D_{eff}, is the effective diffusion coefficient (m^2/s), C_o and C_b are the oxygen concentration (mol/m^3) at the top and bottom of the sealing layer respectively.

An estimate of the rate of intrusion of oxygen is made assuming that the oxygen is consumed quickly as it reaches the tailings. It will later be shown that this assumption is valid. With a diffusion coefficient $D_{eff}=1.0\cdot10^{-9}$ m^2/s, which applies to a water saturation of about 95 %, a sealing layer thickness of 0.3 m and the oxygen concentration difference derived from oxygen concentration in air at the top and zero at the sealing layer/tailings interface, the rate of oxygen intrusion is about 1 mol/m^2,year. Oxygen will also intrude with the inflowing oxygen saturated water, 100 litres per year and m^2. This adds 0.03 mol/m^2,year.

An oxygen intrusion rate of 1 mol/m^2,year will be used in the following for the Base Case. This is a fairly realistic value for a well-constructed and intact sealing layer.

Oxidation of pyrite – unbuffered conditions

The oxygen reacts with the pyrite generating ferrous ions, sulphate, and protons (Reaction 7-1). 1 mol of O_2 will generate 4/7 mol of H^+ that dissolves in the 100 litres of water. This would give a pH of 2.2 if no neutralisation or buffering would occur. The concentration of ferrous iron will be nearly 3 mmol/l and that of sulphate 6 mmol/l.

The water that leaves the pyrite reaction front will react with minerals downstream. The acid water will be neutralised by buffering minerals and the dissolved metals will react in various ways with the minerals and at least partly be retained in the tailings.

Neutralisation of the acidity by the pH-buffer minerals

There are several minerals that may act as buffer for acidity. They are, for example, calcite and some silicates (e.g., K-feldspar ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$) and chlorite ($Mg_5Al_2Si_3O_{10}(OH)_8$).

Neutralisation of the acidity by calcite

Calcite reacts very quickly and can be assumed to react instantaneously in these calculations. There is much less calcite than pyrite in the tailings. This leads to the development of two reaction fronts that move downward in the tailings. The pyrite oxidation front moves slowly downward as more and more oxygen intrudes and reacts with the pyrite. With the pyrite concentration 25 % in the tailings in the Base Case the rate of front movement is 0.07 mm/year. If no other neutralisation agent were present the calcite reaction front would move with a velocity of 0.7 mm/year for a calcite concentration of 2 % by weight. It would take 30 000 years to deplete the pyrite in a 2 m high layer of tailings. The neutralisation capacity of the calcite will be exhausted in the same volume in 3 000 years. The pH of the water downstream of the calcite front will be near neutral.

However, potential acidity is still carried by the water in the form of ferrous iron, i. e. a latent acidity, which can be oxidised when the water eventually leaves the deposit and comes in contact with air. The released ferrous iron is oxidised followed by hydrolysis of ferric iron. Then an additional release of 2 H^+ will occur (Reaction 7-4). Thus, even for a drainage buffered by calcite to near neutral conditions, the final drainage after the second stage of oxidation may be acidic. The released amount of H^+ would theoretically restore the pH to about 2.2, not taking into consideration the possible buffering by remaining hydrogen carbonate in the drainage water.

It is already here pointed out that the content of ferrous iron in the effluent water could cause some concern. Therefore, also processes that might retain iron in the tailings are explored.

Neutralisation of the acidity by using silicates as pH-buffer

There is much less buffering capacity due to calcite than acid generating capacity in the tailings and the calcite might be used up long before all the pyrite is oxidised. Therefore the potential neutralisation by other minerals is explored.

Several silicates present in the tailings can act as pH-buffer minerals: K-feldspar, albite, anorthite, and chlorite. In general it is observed that the choice of the secondary minerals that may precipitate influences the outlet pH. For example, when kaolinite is allowed to precipitate, the pH is somewhat higher than when only $SiO_2(a)$ is precipitated.

Chlorite is a strong buffer mineral and the resulting pH is almost neutral or slightly basic. K-feldspar is a weaker pH buffer mineral. Depending on which buffering mineral is used and which secondary phase is precipitated, the calculated downstream pH will lie between 4.5 and 8.4. In practice all the minerals will react simultaneously but to different extent. To begin with, in these calculations it is assumed that equilibrium is reached between the protons and the pH-buffer minerals. There are comparable amounts of acid neutralising aluminosilicate minerals as there is acid generating capacity per mass of tailings. This implies that if the reactions were fast most acid could be neutralised by these minerals. The system is rather robust and the most plausible reactions will all neutralise the water to above pH 5.

However, it is known that neutralization with these pH-buffer minerals is a slow reaction compared to the sulphide oxidation. Therefore, the neutralisation front will not be as sharp as for calcite but can extend over tens of cm to meters. If the reaction region extends over a very long distance the water may not have time to be neutralised before it exits the impoundment. In the next section, the impact of the kinetics on pyrite oxidation and on the pH neutralisation is addressed.

Figure 12-2 illustrate how the three reaction fronts move over time and also that the fronts have a certain extent.

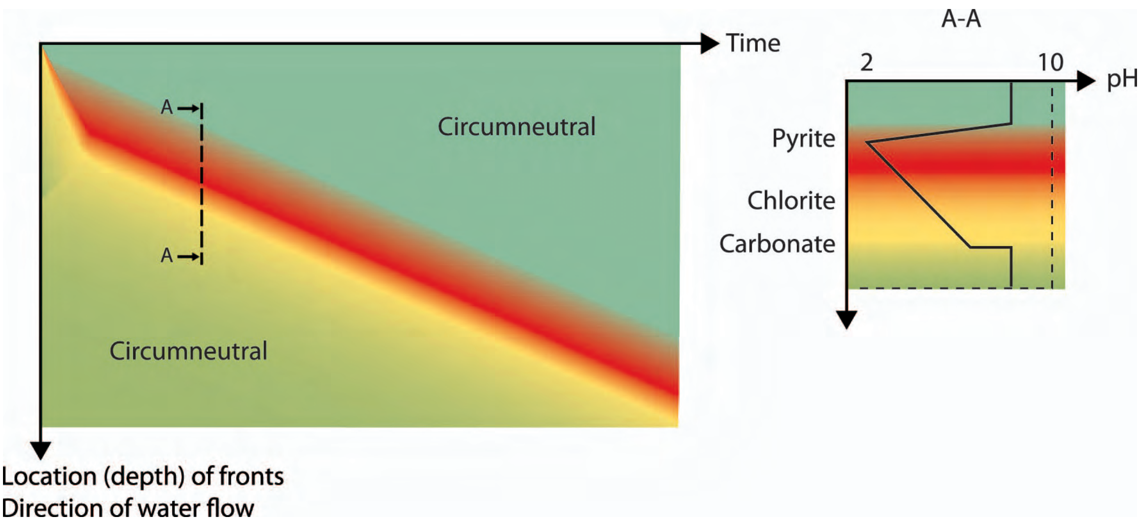


Figure 12-2 Illustration of the redox and neutralisation front movements and approximate pH upstream, between and downstream of fronts. The small right hand figure illustrates the pH profile over the fronts.

Influence of chemical reaction rates on the rates of acid generation and neutralisation

In the above sections it was assumed that the reactions were fast. This simplifies the problem considerably and allows the use of simple mass balance calculations. For the pyrite oxidation this leads to a possible overestimation of the rate of pyrite reaction. If the reaction rate between pyrite and oxygen were slow compared to the possible oxygen intrusion rate then this could become the rate limiting process and all intruding oxygen could not be consumed rapidly. It was found in the calculations, when reaction kinetics were considered, that it is not probable that the chemical and biochemical reaction rates can be credibly shown to decrease the rate of pyrite oxidation and so limit the overall rate of pyrite oxidation. The diffusion limited influx of 1 mol/ m^2,year of oxygen by diffusion will be the rate determining step. However, if the sealing layer was severely damaged, the chemical/biochemical oxidation rate could become limiting. This will be discussed later.

There is, however, another important consequence of a limited pyrite oxidation rate. In the above it was assumed that only the sulphur part of the pyrite is oxidised leaving the ferrous iron in solution. This is reasonable from the thermodynamic point of view and in accordance with many observations. The sulphur is more readily oxidised and there will be no oxygen left to oxidise the ferrous iron to ferric iron before it has flown away into the lower regions where the oxygen has not yet penetrated. Also, at low pH the abiotic reaction rate of ferrous iron is very slow. Microbial activity can, however, increase the rate at low pH.

When the pyrite oxidation rate is slow compared to the rate of transport of oxygen within the tailings a situation can occur where oxygen may persist over a large depth and the pyrite reaction extends over a long distance instead of taking place at a “sharp” front. In such a case there will be oxygen in regions where there is also ferrous iron present. Then, if the ferrous iron oxidation rate is “fast” it can be oxidised to ferric iron. When the acidity is neutralised further downstream the ferric iron will oxidise pyrite or precipitate as a hydroxide. If ferric hydroxide precipitation occurs it releases further protons that need to be neutralised.

This leads to two interesting consequences. The first is that the effluent water from the impoundment could contain less ferrous iron. The other is that the ferric hydroxide could act as a sorbent for trace elements.

It is thus of some interest to account for the various competing reaction rates in the modelling. This will be explored further in the sensitivity analysis below.

Heavy metal release at the pyrite reaction front

The concentrations of the other metals in the water are assumed to be in the same proportion to iron as they are in the tailings. These are shown in Table 12-1 below. The data are based on the mineral composition in Table 5-3 and are meant to be indicative at this stage of the report.

Table 12-1 Metal concentrations in water leaving the pyrite reaction front for the Base Case.

Metal	Relative mole concentration in tailings and water	Concentration in water (μmol/l)
Fe	1	2860
Zn	0.061	175
Cu	0.0082	23.5
Pb	0.00097	2.8
As	0.0011	3.1

Sorption processes

For sorption on mineral surfaces an important factor is the number of sorption sites that may be found. If the number of sites is not large enough, the sites may be totally occupied after a while and no more net sorption will take place. Also, metals that exist in large concentrations (ferrous ions) may compete with and displace and remove the metals initially sorbed on the mineral surfaces.

There are sorption data in the literature for some of the metals on some of the minerals in the tailings. However, data are sparse for ferrous iron sorption on the full assembly of minerals relevant for tailings. Some data exists, e. g. for surface complexation of ferrous iron on hydrous ferric oxides (Appelo et al., 2002; Liger et al., 1999). Ferrous iron is present in much higher concentration in the water than the other metals and As. It may therefore possibly compete strongly for the sorption sites. Only very rough estimates of the sorption of the metals and As can therefore be made. The calculations suggest that ferrous iron could sorb on mineral surfaces downstream the redox front and therefore initially be retarded in relation to the water velocity by one or at most two orders of magnitude. Copper and lead could be retarded more, but zinc and arsenic retardation is difficult to assess.

It is therefore not possible to invoke sorption as a major retardation mechanism for ferrous iron and the other metals with a high degree of probability.

Secondary mineral formation and sorption on ferric hydroxides

The metals that have been released by oxidation of metal sulphides will flow downstream into unoxidised tailings containing pyrite and pyrrhotite ($Fe_{1-x}S$). The metals that form sulphides with a lower solubility than the pyrrhotite may acquire its sulphide ion and precipitate as a new sulphide. Several secondary sulphides can form. Sulphides considered potentially forming secondary minerals are sphalerite, covellite, galena, and realgar for zinc, copper, lead, and arsenic respectively. Precipitation of orpiment has also been considered as the possible arsenic sulphide mineral to be formed. In these calculations the concentration of arsenic decreases to negligible levels. However, the formation of orpiment does not seem to find support in the literature (Smedley and Kinniburgh, 2002; Cleverley et al., 2003; Craw et al., 2003; Jaüimovi et al., 2002; Ruy et al., 2002; Fukushi et al., 2003; Nicholas et al., 2003). Most of literature indicate the precipitation of both orpiment and realgar, which would indicate that the precipitation of orpiment is retarded in the field. Based on this the calculations were done using realgar as secondary sulphide mineral. For realgar the concentration of arsenic was only slightly reduced, independent of the pH used (within the range 5-7).

Results from computations are presented for different pHs in the tailings (5, 6, and 7) in Figure 12-3. Large reductions of the concentration for zinc, copper, and lead are found to take place. Copper, lead and zinc concentrations are reduced by more than four orders of magnitude in the pH range 5-7. Arsenic is hardly affected at all.

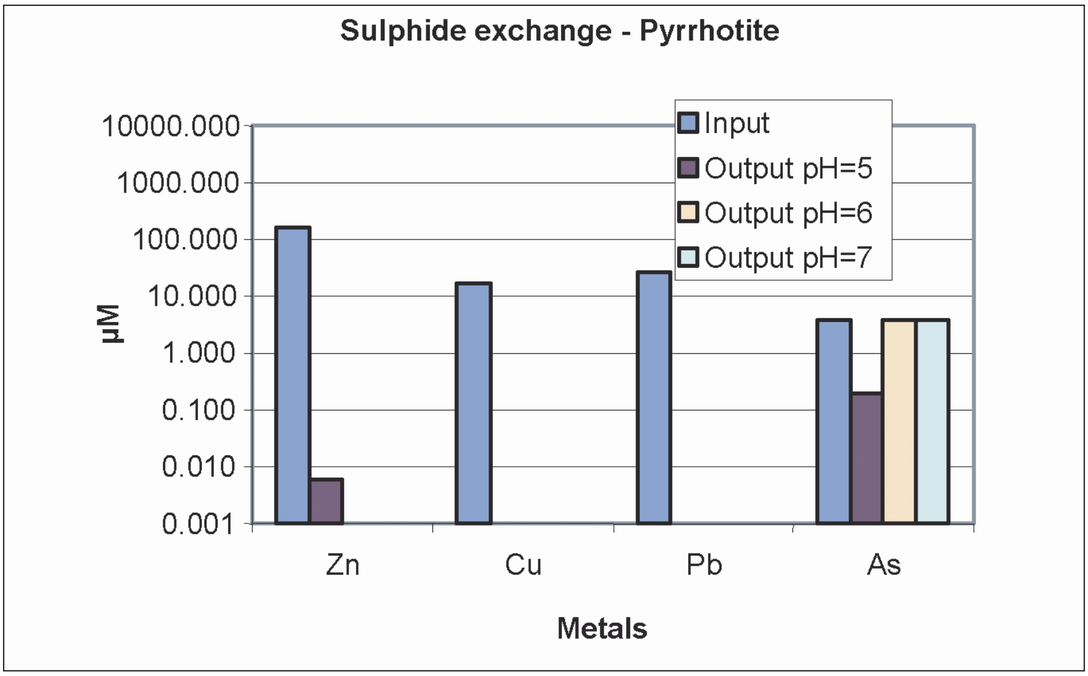


Figure 12-3 Attenuation by formation of secondary sulphides.

Sorption on precipitated Ferric oxy-hydroxides in the tailings

Precipitates of $Fe(OH)_3$ are excellent sorbents, since they present very large surfaces where dissolved metals (cations) may be sorbed. But, as indicated above the formation and precipitation of $Fe(OH)_3$ within the deposits is not obvious and is not ensured although some precipitation is expected.

As discussed earlier in this chapter, ferric hydroxides may form in the tailings is the pyrite oxidation is lower than the oxygen intrusion rate. The ferric hydroxide strongly sorbs other metal ions and could potentially help to keep also the concentration of these at a low level in the effluent water.

Composition of water leaving the deposit

Table 12-2 shows the expected composition of the water that leaves the deposit. It applies to the Base Case where 1 mol O_2/m^2,year enters the deposit and for a water infiltration rate of 100 l/m^2,year.

It may be noted that some of the entities (the first three in the table), will be marginally influenced by even a major increase of oxygen influx rate whereas some, the last five marked as *italic*, will be directly proportional to oxygen influx rate (for a given water flux).

Table 12-2 Expected composition of the water that leaves the deposit for the Base Case.

pH	acidic to circumneutral (pH 4.5-8)
$CO_2(g)$	0.0004 bar
Cu, Pb, Zn	<0.1 μmol/l
Fe(II)	*3 mmol/l*
SO_4^{2-}	*6 mmol/l*
Mg+Ca+2K+2Na	*3 mmol/l*
As	*3 μmol/l*
Latent acidity from Fe(II)	*6 mmol/l*

This water composition is used later as input for the calculations of processes that occur outside the deposit when the water encounters air, is oxygenated and diluted in waters outside the deposit.

The above water composition, especially the ratios of Fe(II)/SO_4^{2-} and SO_4^{2-}/(Mg+Ca+2K+2Na) can be used to compare with the water compositions observed in the Kristineberg site. The concentration of Fe(II) and SO_4^{2-} is directly related to the oxygen intrusion rate/water flowrate. The SO_4^{2-}/(Mg+Ca+2K+2Na) indicates to what extent the aluminosilicates have participated in the acid neutralisation. Major deviations can indicate that mixing processes have occurred or that other reactions have been active that are not accounted for in the models. A high sulphate or iron concentration indicates that much oxygen has intruded or that less water has infiltrated in relation to the oxygen.

12.3 Sensitivity of Base Case to some processes and to uncertainties in data

The intrusion rate of oxygen depends strongly on the water content of the sealing layer. The dependence is shown in Figure 7-2. It may be noted that in the region of high moisture content the diffusivity is strongly influenced by the moisture content. A change from 95 % to 90 % can lead to an increase in diffusivity by an order of magnitude or more. The impact of the drying effects on the oxygen transport is of crucial importance.

The influence of the chemical reaction rate of pyrite oxidation on the overall oxidation rate is explored. The combined effect of rate of oxidation of dissolved ferrous iron by oxygen and neutralisation rate of the acid on the formation of ferric hydroxide precipitate is also discussed.

Oxygen intrusion for different drying conditions of the sealing layer

The influence of a dry period on the oxygen intrusion is explored by the following example. During most of the year the sealing layer has high moisture content (95 %) but during a few dry and warm months the sealing layer slowly gives off moisture by diffusion and can attain lower moisture. The oxygen transport rate will be higher during this period.

Loss of moisture is calculated from vapour pressure data as a function of temperature and diffusion rate of water vapour through the cover layer up to the air above. The influence on the rate of diffusion is then obtained from Figure 7-2.

Pastor (2003) studied the variation of the water saturation in the sealing layer considering evaporation and moisture transport by diffusion and by capillarity effects. The water saturation was calculated for meteorological conditions for that part of Sweden during a period of 8 years. The sealing layer showed high water saturations over all the period. Variations in water saturation were observed only in the protective cover.

To simulate an extremely dry year, a typical year was chosen and the precipitation from May to August was removed. The results calculated for six consecutive dry years, show that the water content in the sealing layer is still close to saturation. Noticeable variations are observed only in the upper part of the protective cover, but these variations decrease with depth.

The results are shown in Table 12-3. It is seen that even two months drying at high temperature would only marginally change the oxygen influx.

However, some processes that could increase the water evaporation have not been possible to quantify, for example the effects of root suction by vegetation. Another process that is not accounted for is the wind effect. The higher permeability of the protective cover could allow some airflow in the protective cover during windy periods, which would enhance evaporation.

Table 12-2. Amount of water evaporated from the sealing layer during an extremely dry period and resulting average water saturation.

Temperature at top sealing layer	5^{o}C	10^{o}C	15^{o}C
Water vapour pressure, kPa	0.87	1.23	1.71
Mole fraction	0.009	0.012	0.017
Concentration, mol/m^3	0.39	0.55	0.76
Mass flux mol/m^2/month	2.7	3.8	5.3
Resulting water saturation after 2 months drying, %	0.95	0.95	0.95

The water saturation of the tailings is not influenced much even by a long dry period. During the dry period, the water saturation of the upper part of the protective cover reaches values of about 10 % (protective cover almost totally dry) for three months. Water saturation is reached during the rain period. This variation decreases with depth. At a depth of about 1.0 m, the water saturation is over 80 % at all times. For the sealing layer, the water saturation is close to the saturation during all the period. Small oscillations are observed in the water saturation but these variations are less than 1 %.

The presence of vegetation that builds up a bed of organic material on top of the protective cover may significantly reduce the intrusion of oxygen. During the warm period of the year, oxygen may be consumed by reaction with decaying organic material. However, in dry periods the plants may extend their roots deep into the protective cover to reach water. This may cause an extra loss of water of the protective cover and even from the sealing layer. In extreme cases roots may reach the sealing layer and go through it. It has not been possible to quantify this.

Influence of reaction kinetics on pyrite oxidation, neutralisation and ferric iron hydroxide precipitation

Pyrite oxidation and ferric hydroxide precipitation

Once that oxygen reaches the tailings, it reacts with the pyrite present in the tailings producing protons, and dissolved sulphate and ferrous iron (Reaction 7-1). The water flows downward into the region where the oxygen has not yet penetrated. However, if the pyrite reaction is slow there may be oxygen present in the locations where there is water with ferrous iron.

We consider the partially saturated upper part of the tailings where the oxygen can diffuse more rapidly in the air filled pores than the dissolved oxygen is carried by the water that seeps downward.

In presence of oxygen, Fe^{2+} may be oxidised to Fe^{3+}. At pH above 4 to 5 the ferric ions may precipitate as $Fe(OH)_3$.

In a system with infiltrating oxygenated water the extent of the oxidation of the ferrous ions to ferric ions depends on the relative kinetics of the pyrite oxidation in relation to the oxidation of the ferrous ions. If the pyrite oxidation is much faster, the oxygen is mainly consumed by this reaction and the infiltrating water washes out an important fraction of the ferrous ions in the solution. On the other hand, a faster reaction of oxidation of the ferrous ions causes a greater fraction of the ferrous to be oxidised to ferric ions, which precipitates as $Fe(OH)_3$(a) and is immobilised in the deposit. However, if the ferric ions formed by oxidation of the ferrous ions remain in solution they may oxidise the pyrite, again forming ferrous ions.

This is a very important issue to account for, since the solubility of many heavy metals is increased under oxidising conditions and low pH. Also the metals sorb strongly on the precipitated $Fe(OH)_3$(a) and they can be retained in the tailings.

For the calculation results presented below the amount for the different minerals is not crucial, since we are interested mainly in the pH level reached at the outlet of the tailings when these buffer minerals are present and the possible formation of ferric hydroxide precipitates.

Kinetics for the pyrite oxidation

Several expressions based on experimentally determined rates may be found in the literature (Salmon and Malmström, 2002). A commonly used expression is that given in Williamson and Rimstidt (1994). This applies to the oxidation of pyrite with oxygen

$$\mathrm{Rate} = k_{oxy} \frac{\left[O_2(aq)\right]^{0.5}}{\left[H^+\right]^{0.11}} \qquad (12\text{-}2)$$

This relationship is valid for a pH interval of 2-10. Salmon and Malmström (2002) compared several expressions for reaction rate and they found that the reaction rates may differ by up two orders of magnitude. At atmospheric conditions they are in the interval $10^{-9} – 10^{-10}$ mol/m^2,s. It is found that the microbially mediated oxidation rates are greater than those caused by abiotic oxidation (Herbert, 1999).

Salmon and Malmström (2002) have made a number of detailed calculations on the rates of pyrite oxidation under conditions closely resembling those found at the Kristieneberg site. The model they used does not permit the spacial resolution of the reactions and thus does not show whether ferric hydroxide would precipitate but they show that for a well functioning sealing layer the rate will be limited by the rate of oxygen intrusion by diffusion. They also include the effects of microbially catalysed increases in the rates. When the availability of oxygen is not limiting, the pyrite oxidation is governed by reaction kinetics. Much higher pyrite oxidation rates, one to nearly two orders of magnitude higher, are found when the sealing layer is not functioning properly.

pH neutralisation

The main neutralisation reactions are presented below.

Neutralisation with calcite. The protons react with calcite according the following reactions

$$\begin{aligned} &CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \\ &CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad (12\text{-}3) \\ &HCO_3^- + H^+ \rightarrow CO_2(aq) + H_2O \end{aligned}$$

One mole of calcite consumes one or two moles of protons depending on the resulting pH. The calcite reaction is fast compared to the oxidation reactions and is considered to be "instantaneous" in any practical aspect.

Neutralisation by silicates.

There are a number of different aluminosilicates in the tailings. They buffer at different pH's and form different secondary minerals that are left behind. The resulting pH will depend on both the mineral(s) that react and the secondary minerals that form. It may be noted that all these reactions release alkali or alkaline earth metals in proportion to the protons consumed. This has been used as an indicator of the extent of acidity neutralised by aluminosilicates in the field studies.

12.4 Oxygen intrusion in water cover case

In the Base Case, the tailings are initially in direct contact with the pond water. With time, sediments may constitute a layer on the top the tailings. A schematic picture of the system to be modelled is shown in Figure 12-4**.**

Initially the oxygen intrusion is high because the tailings are in direct contact with oxygen-saturated pond water. Wind causes the oxygen saturated water to be mixed with water from the bottom. The concentration equals the concentration of dissolved oxygen in equilibrium with atmospheric oxygen (about 10 mg/l). Oxygen diffuses into the tailings and reacts with sulphide minerals. Additional oxygen intrudes with the inflowing water. The water infiltration through the bottom and walls around the impoundment is estimated to be on the order of 100 l/m^2/year. During early times the unreacted tailings are in direct contact with the oxygenated pond water and the oxidation rate is determined by the reaction kinetics between pyrite and oxygen.

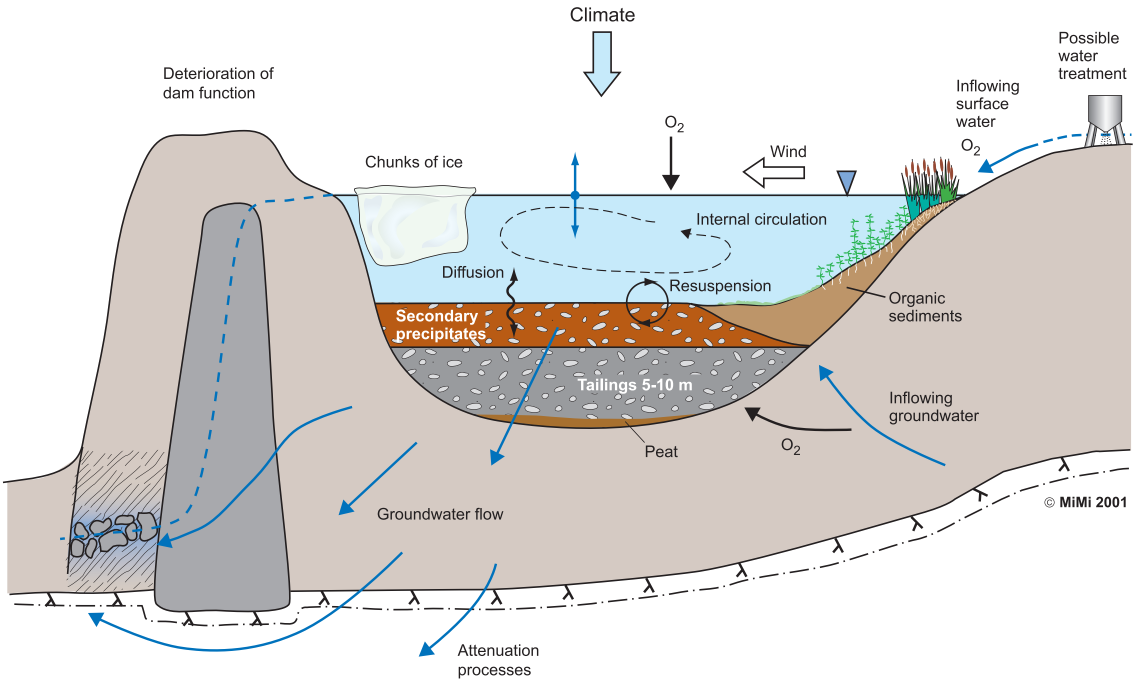


Figure 12-4 Schematic illustration of processes of interest for the water cover case.

The tailings nearest the pond water are gradually depleted of pyrite and a depleted layer forms and grows with time. The interface between the depleted layer and that not yet reached by the oxygen is called a redox front. The front has a thickness on the order of cm and is thus rather sharp. The oxygen then has to diffuse through the (nearly) stagnant pore water in the pyrite depleted layer and the intrusion rate slows down as this layer grows. Because the diffusion of oxygen in water is slow, even a thin depleted layer can offer a strong resistance to oxygen diffusion. Calculations show that the intrusion rate of oxygen with the inflowing water is very small in comparison with that due to diffusion until the depleted layer has become quite extensive.

Even a thin layer of sediments can substantially alter the influx of oxygen as can be seen in Figures 12-5 and 12-6 below. Already a few cm of sediments, artificial or natural, can limit the oxygen intrusion to less than 1 mol/O_2/m^2,year but that if there are no sediments then quite high oxidation rates can be expected during the first decades.

The further reactions and chemical composition of the water flowing deeper into the tailings will be very similar to those described for the soil cover case.

There is one important difference compared to the soil cover case. Most of the acidity generated at the oxidation front and the metals released there will diffuse the short distance upward to the pond water. To avoid forming very acid water in the pond, the water turnover in the pond must be large to dilute and neutralise the acidity diffusing upward from the tailings.

The metals released will also diffuse upward into the pond water. They will not form secondary sulphide precipitates in the tailings as in the soil cover case. However, if the neutralisation of the primary acidity and the equally large latent acidity from the oxidation and hydrolysis of the ferrous iron takes place in the pond, the ferric oxyhydroxides can adsorb the copper and lead. Zinc and arsenic will also be adsorbed but to a lesser degree.

It is thus essential in the water cover case to ensure sufficient dilution and neutralisation by water that flows through the pond.

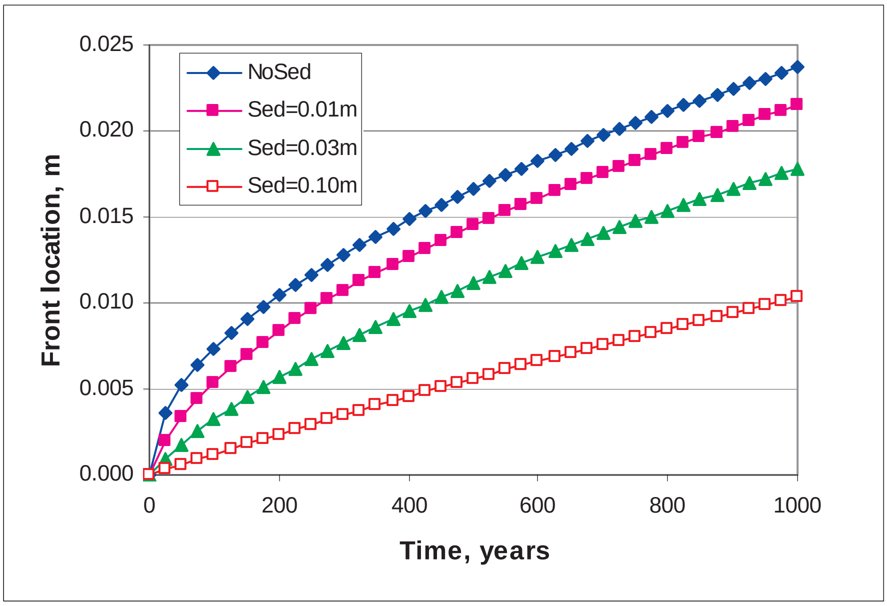


Figure 12-5 Penetration depth of redox front as a function of time; for no sediments, 1 cm, 3 cm and 10 cm sediments.

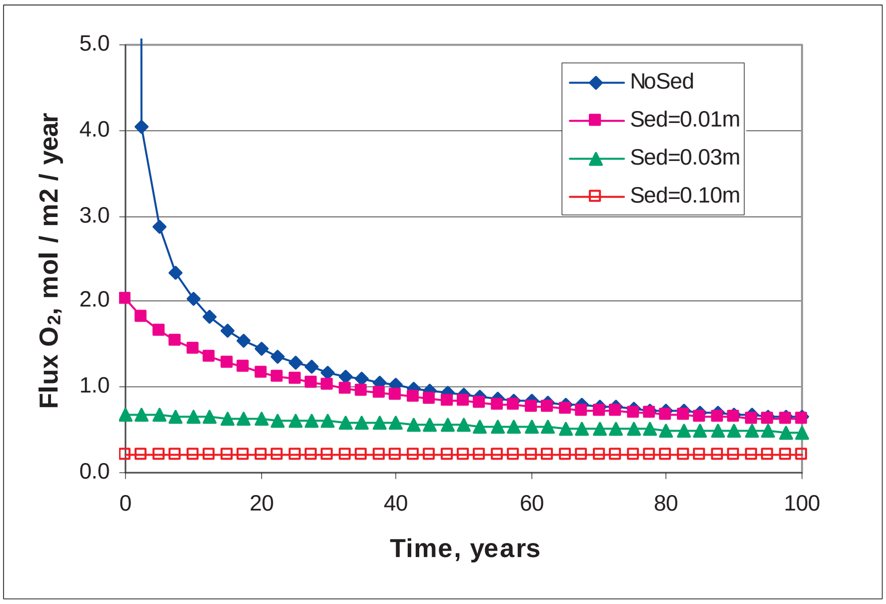


Figure 12-6 Oxygen flux as a function of time for different thicknesses of sediments; for 1 cm, 3 cm and 10 cm.

12.5 Processes outside of deposit

Oxidation of ferrous iron and ferrihydrite formation

The water that exits from the deposit, either through the underlying rock and gravel, or through the bounding slopes or dams of the deposit, will be oxidised generating acid.

Partly the acid can be neutralised by CO_2 degassing if the intruding rainwater has taken up much CO_2 during its passage through the root zone in the recharge area. This is illustrated in Figure 12-7 below. For details see Moreno and Neretnieks (2004).

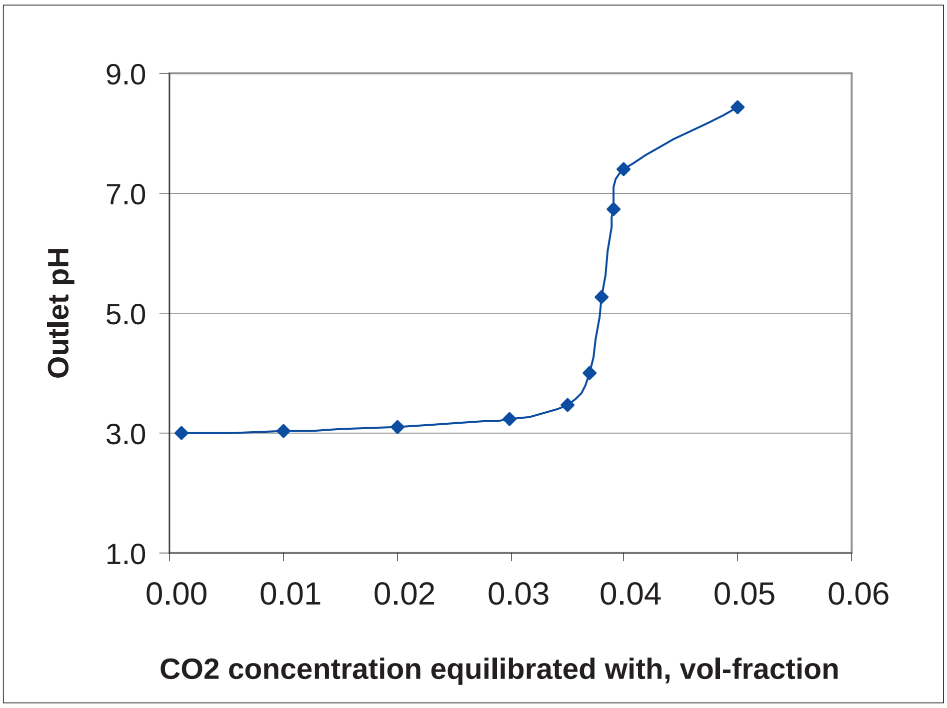


Figure 12-7 The pH after equilibrium with CO_2 and oxygen at the recharge zone as a function of the CO_2 concentration equilibrated with the infiltrating water.

In an active root zone the CO_2 volume fraction in the air can be 2-5 vol-%. Under favourable circumstances the effluent water could become circumneutral. The ferric iron would form amorphous ferric oxy-hydroxides that either flow with the water as colloids or precipitate.

In the Base Case where a deposit with an area of 1.5 km^2 is considered, 46 tonnes per year of ferric hydroxides form in the 150 000 m^3/year effluent water from the deposit.

Dilution in a stream

If the effluent water contains only little carbonate that can de-gas, the oxidation may still take place, but with no neutralisation or buffering the pH would become as low as 2.2. No ferric oxy-hydroxides form at this low pH and the water must be neutralised either by mixing with other streams that contain alkalinity or just by dilution.

The hydraulic conditions in Kristineberg are such that effluent water is released to and mixed with the river Vormbäcken. Vormbäcken has a flowrate of 0.5 m^3/s, corresponding to $15 \cdot 10^6$ m^3/year. Vormbäcken is taken to have an alkalinity 0.1 mmol/l in the calculations below.

When mixed, the effluent water it will both be neutralised and diluted. Figure 12-8 shows the resulting acidity for a generic case where the effluent stream is mixed with another stream "SR" times larger.

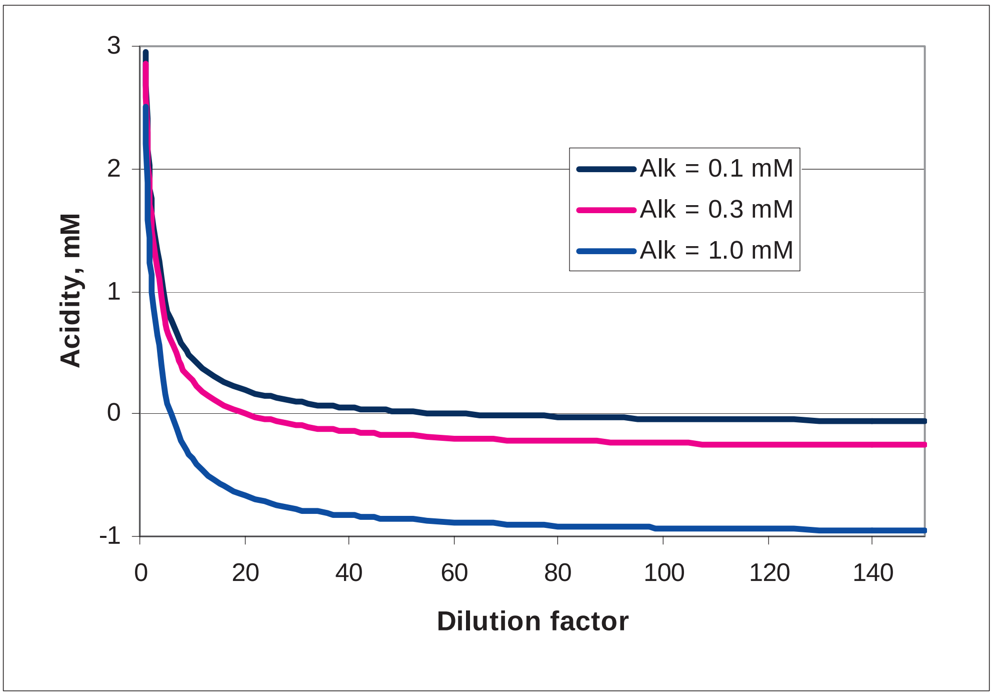


Figure 12-8 Resulting acidity when an effluent stream with an acidity of 6 mmol/ mixes with another stream SR times larger that contains 0.1, 0.3 and 1 mmol/l alkalinity.

For a mixing ratio of one hundred, which is the Base Case mixing ratio and an alkalinity of 0.1 mmol/l the mixed water is fully neutralised. Vormbäcken has an alkalinity sufficient for the mixed water to maintain a net-alkalinity in the Base Case. The concentration of $Fe(OH)_3(a)$, as colloids, would be about 3 g/m^3 if no settling of precipitates takes place.

Illustration: Mixing-point of spillwater and the recipient, river Vormbäcken, at Kristineberg.

12.6 Discussion of Base Case computations and results and sensitivity analysis

Sealing layer properties and oxygen intrusion rates

The sealing layer is the main resistor to oxygen intrusion. Should it be damaged or become dryer the oxygen intrusion rates can increase considerably. Even a small change in water content may change the diffusivity markedly, thus allowing a higher oxygen flux. A damaged or drier sealing layer can allow one to perhaps two orders of magnitude larger oxygen intrusion rates. However, then the chemical reaction rate will be the limiting factor for the overall oxidation rate of the tailings.

It is not probable that long dry yearly periods will have a seriously detrimental influence on the sealing layer.

It is deemed probable that a sealing layer can be constructed and that its sealing properties can be maintained over very long times.

Acidity and pH in and outside the deposit

Aluminosilicates and carbonates will neutralise the primary acidity formed in the deposit and the waters will become circumneutral. There is enough pH buffering capacity in the tailings to ensure this for very long times, i. e. as long as there is still acid generation capacity left in the tailings.

However, the ferrous iron in the effluent waters has a considerable acid generation capacity (latent acidity) when the water leaves and is oxidised outside the deposit. For the Base Case the corresponding pH outside the deposit could be as low as 2.2. For higher oxygen intrusion rates it may be even lower.

Dilution of the effluent waters by mixing with a stream outside the deposit will dilute and neutralise the acidity present for the Base Case as shown earlier in Figure 12-8. However, for a 10 times higher oxygen intrusion rate this will not be the case as is shown in Figure 12-9.

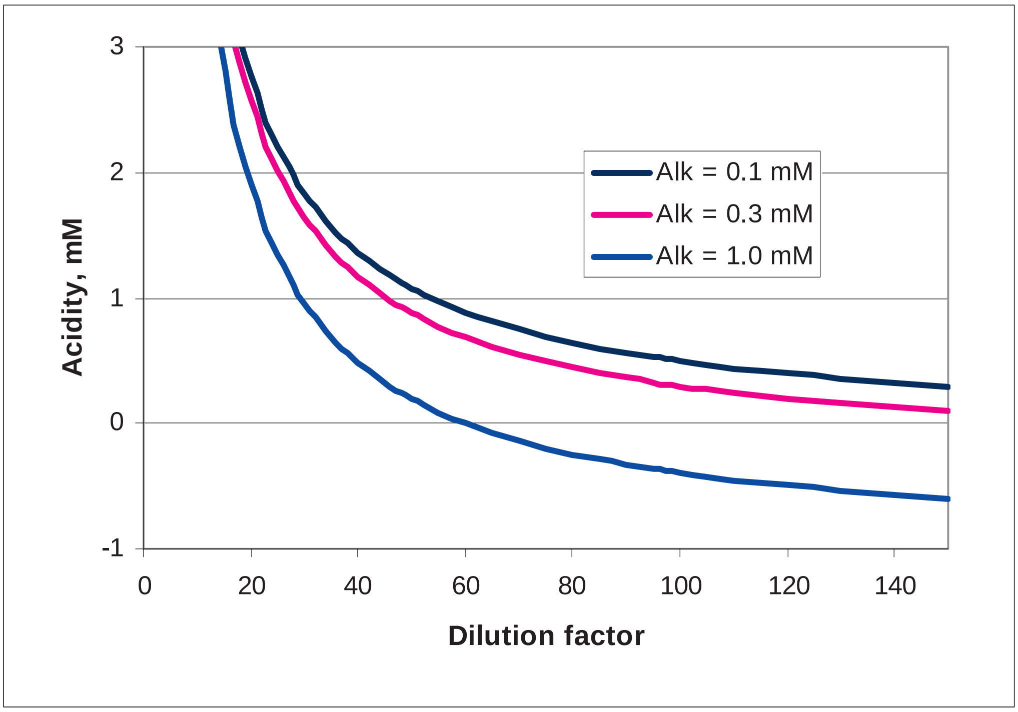


Figure 12-9 Alkalinity of the mixed waters when an effluent stream with an acidity of 60 mmol/l (corresponding to 10 times increased oxygen transport compared with the Base case) mixes with another stream SR times larger that contains 0.1, 0.3 and 1 mmol/l alkalinity.

Metal retention

The retention of copper, lead and zinc, is caused by precipitation of secondary sulphide minerals and this retention is not, per se, influenced by the oxygen intrusion rates. The modelling suggests that irrespective of oxygen intrusion rates the concentrations of these metals will be very low. This does not apply to arsenic, see discussion in section 12.2. Its concentration is directly proportional to its primary release rate from the sulphide minerals and thus to oxygen intrusion rate.

Soil Cover-Water cover

In both cases the metal and acidity releases are governed by the oxygen intrusion rate. In the Base Case this is lower for the soil cover case initially but over time the water cover will have less long-term oxygen intrusion. The water cover is sensitive to the loss of water cover as is the soil cover case to the decrease of the sealing layer resistance to oxygen intrusion.

Reaction rates and reactive surfaces

Reported in the literature and measured within the MiMi programme, the abiotic chemical reaction rates for pyrite oxidation vary within a range of approximately two orders of magnitude. A similar uncertainty is also reported for the reactive surface of the minerals (Salmon and Malmström, 2004). Adding to the uncertainty is that especially the rates of oxidation reactions of the sulphide minerals and the dissolved ferrous iron in the water can be considerably enhanced by microbial activity. This is commonly observed in the field but it has been found difficult to obtain reliable data for quantitatively modelling these processes.

In the present setting these uncertainties have little influence on the overall rates of oxidation of the sulphides in the deposits. The overall rate is governed by the transport resistance of oxygen in the sealing layer in the soil cover case and in the sulphide depleted layer in the water cover case.

Larger chemical reaction rates would only lead to a narrower reaction (redox) front. The reaction front is rather narrow, on the order of cm’s, in the Base Case setting anyway. A slower reaction rate would widen the reaction front but this would have a marginal influence on the overall oxidation rate.

The same applies for the acid neutralisation reactions. Even the relatively speaking lower reaction rates for aluminosilicate reactions compared to those for the pyrite oxidation are fast enough to neutralise most of the primary acidity that is generated by the pyrite oxidation before the water exits the deposit. The neutralisation is expected to occur within a few metres from the redox front. This reaction is equally fast in the partially saturated upper region of the tailings where the water flow is vertical as in the deeper, water saturated region, below the groundwater table where the water flow turns practically in a horizontal direction.

The water will thus have a long way to flow before it exits the deposit and will have time to be neutralised except perhaps in locations very near the edges of the deposit.

13 Impact of release on the recipient

This chapter introduces the reader to some criteria for evaluation and classification of the environmental quality of surface waters, sediments and biota presented by the Swedish Environmental Protection Agency. In some cases, complementary criteria used in other countries are given for comparison.

Some historic data for the past environmental load on the recipient, based on information provided by Boliden AB, are briefly discussed.

Data from the MiMi research on the present day environmental conditions in the recipient at the MiMi field site at Kristineberg are also summarised.

13.1 Water quality criteria

Trace elements

The Swedish Environmental Protection Agency´s environmental quality criteria for lakes and water courses.

The Swedish EPA (SEPA) has given two sets of criteria for the assessment of the quality of freshwaters in their environmental quality criteria for lakes and water courses (SEPA, 1999 and 2000):

Criteria for the classification of the current water quality status. These criteria are related to biological effects in freshwater ecosystems.

Criteria for assessing the influence of point sources of pollutants. These criteria are a classification of the deviation of contaminant concentrations from naturally occurring concentrations (water unaffected by point sources).

These two sets of criteria are discussed below and are shown in Tables 13-1 and 13-3.

Water quality status

Freshwater is classified into five classes on the basis of the total trace element concentration in water. The classes are described as follows:

Class	Represents:
1	No or very low risk of biological effects. The concentration represents an estimate of the concentration in water which is unaffected by human activities. The upper boundary represents the 75th percentile of three groups of water bodies in N. Sweden, small and large water courses and lakes. For Cd and Pb, the upper boundary is adjusted to half the value of the 75th percentile, as the concentration of these metals has already been increased by pollution (fallout).
2	Low risk of biological effects. The water is affected by long distance dispersal of trace elements or by releases from point-sources. However, some water bodies can have concentrations in this class because of geological conditions, i.e. high background concentrations. Measurable biological effects can generally not be registered.
3	Biological effects can occur. The risk for effects is greatest in soft-, nutrient-poor and humus-poor water, as well as in acidic waters. By biological effects is meant the reproduction of a species or group of species, or the survival of early stages of the life-cycle, which result in a decrease in the number of individuals of a species. The reduced number of individuals can result in a changes at the level of the community or ecosystem.
4	Increasing risk for biological effects
5	Survival of aquatic organisms is affected even after short exposure.

The values given for the trace elements copper, zinc, cadmium, lead, chromium, nickel and arsenic are shown below.

Table 13-1 Classification of water quality status (SEPA, 4913).

	Metal concentration in water (µg/l)						
Class	Cu	Zn	Cd	Pb	Cr	Ni	As
1	<0.5	<5	<0.01	<0.2	<0.3	<0.7	<0.4
2	0.5-3	5-20	0.01-0.1	0.2-1	0.3-5	0.7-15	0.4-5
3	3-9	20-60	0.1-0.3	1-3	5-15	15-45	5-15
4	9-45	60-300	0.3-1.5	3-15	15-75	45-225	15-75
5	>45	>300	>1.5	>15	>75	>225	>75

A complete assessment of the risks for biological effects should also take into account the chemical form and bioavailability of the metals, which is dependent to a large extent on other water quality parameters, e.g. pH, hardness, organic matter concentration. The most sensitive waters are soft-waters, nutrient poor, humus poor and low pH. Because of this, SEPA recommends that classification should also take into account the deviation from natural background concentrations (see below). If high natural concentrations occur in a water body, it is likely that the ecosystem in that water has adapted to the prevailing metal concentrations. This would be the case if metal concentrations were classified in class 3 or above in the classification of water quality status, but only in the lower classes according to the deviation from the reference value.

The background reports to the classification shown in Table 13-1 above does not give details about how these boundaries were derived. As a complement, it is possible to use other water quality criteria which have been based on compilations of ecotoxicological data, e.g. Canada's water quality criteria for the protection of aquatic life (CCME), or the Netherlands suggested maximum permissible concentrations (RIVM, 2001).

Influence of point sources of pollution

The classification of the influence of point sources is based on comparison with a reference value, which indicates the background conditions in rivers/lakes not influenced by point sources.

Again, freshwater is classified into five classes on the basis of the total trace element concentration in water. The classes are described as follows:

Class	Represents
1	Little or no effect of anthropogenic sources
2	↓
3	Increasing effect of local or more diffuse sources
4	↓
5	Clear effect of local sources.

The class boundaries are calculated by multiplying the reference value by a number of factors. These factors are based on the distribution of measured concentrations in Swedish lakes and rivers and are shown in Table 13-2 below. For example, the boundary between class 4 and 5 is based on the 95th percentile for lakes and water courses that are not affected by local sources.

Table 13-2 Factors applied to reference value to derive class boundaries for classification of influence of point sources (SEPA, 4913).

Class	Cu	Zn	Cd	Pb	Cr	Ni	As	Co	V
1	1	1	1	1	1	1	1	1	1
2	2	3	8	8	2	2	2	8	3
3	4	8	15	15	6	4	5	15	8
4	7	13	30	30	11	8	9	30	13
5	>7	>13	>30	>30	>11	>8	>9	>30	>13

A series of reference values is then given by SEPA; for larger water courses, smaller water courses and lakes in different parts of Sweden. For all metals, the reference value for northern Sweden is lower than that for southern Sweden. For most metals, the background value for larger water courses is slightly higher than for small water courses, especially for copper and zinc. The upper boundaries of each class calculated with these reference values are shown in the Table 13-3. The upper boundary of class 1 is the reference value.

Table 13-3 The upper boundaries of each class for classification of influence of point sources (based on reference values for larger water courses in N. Sweden).

	Upper boundary of class (metal concentration in water (μg/l))								
Class	Cu	Zn	Cd	Pb	Cr	Ni	As	Co	V
1 (ref. value)	1.3	2.9	0.005	0.12	0.2	0.5	0.2	0.05	0.1
2	2.6	8.7	0.04	0.96	0.4	1	0.4	0.4	0.3
3	5.2	23.2	0.075	1.8	1.2	2	1	0.75	0.8
4	9.1	37.7	0.15	3.6	2.2	4	1.8	1.5	1.3
5	>9.1	>37.7	>0.15	>3.6	>2.2	>4	>1.8	>1.5	>1.3

SEPA's background report (4920) to the classification shown in Table 13-3 also includes a summary of the trace element concentrations measured as part of the national environmental monitoring programme. These concentrations can be used as an estimate of regional background concentrations. The distribution of trace element concentrations is summarised for mountain rivers, forest rivers, and streams in N. Sweden, see Table 13-4.

Table 13-4 The distribution of trace element concentrations measured in rivers in N. Sweden (SEPA, 4920).

	Metal concentration (μg/l)								
Percentile	Cu	Zn	Cd	Pb	Cr	Ni	As	Co	V
Mountain rivers									
10	0.4	1.3	0.003	0.06	0.05	0.25	0.08	0.02	0.03
20					0.06	0.34	0.11	0.02	0.05
25	0.6	2.1	0.003	0.08					
30					0.14	0.51	0.16	0.04	0.08
40					0.26	0.7	0.23	0.06	0.13
50	0.9	3.3	0.005	0.13	0.46	1	0.4	0.13	0.2
75	1.6	5.3	0.009	0.26					
90	3	8.9	0.017	0.52					
Forest rivers									
10	0.4	1.2	0.003	0.06	0.05	0.21	0.12	0.02	0.06
20					0.08	0.3	0.14	0.04	0.14
25	0.5	1.8	0.004	0.08					
30					0.21	0.59	0.19	0.07	0.24
40					0.37	0.76	0.33	0.12	0.32
50	0.8	2.7	0.006	0.13	0.68	1.04	0.57	0.2	0.52
75	1.3	4.4	0.01	0.22					
90	2.2	7	0.019	0.44					
Streams									
10	0.2	0.5	0.003	0.02	0.05	0.11	0.03	0.02	0.03
20					0.05	0.19	0.04	0.02	0.04
25	0.3	0.8	0.003	0.02					
30					0.14	0.32	0.07	0.03	0.07
40					0.35	0.52	0.13	0.08	0.13
50	0.4	1.3	0.003	0.04	0.66	1.27	0.38	0.31	0.38
75	0.6	2.3	0.005	0.15					
90	0.9	3.8	0.021	0.28					

Sediment

Quality criteria for sediment have been derived in a similar way to the criteria for surface water. Table 13-5 summarises the values given by SEPA (4913) for sediment quality status (based on the risk for biological effects) and influence of point sources (based on comparison factors given in SEPA 4913 applied to reference values representing background concentrations in N. Sweden.

Table 13-5 Classification of sediment quality status and influence of point sources (SEPA, 4913).

		Upper boundary of class Trace element concentration in sediment mg/kg dry-wt							
		As	Cd	Cr	Cu	Hg	Pb	Zn	Ni
Sediment quality status									
Class	Description of water concentration								
1	very low	5	0.8	10	15	0.15	50	150	5
2	low	10	2	20	25	0.3	150	300	15
3	moderate	30	7	100	100	1	400	1000	50
4	high	150	35	500	500	5	2000	5000	250
5	very high	>150	>35	>500	>500	5	2000	5000	>250
Influence of point source									
Class	Comparison with reference value								
Class1	reference value	10	0.8	15	15	0.13	50	150	10
Class2	small increase	20	4	30	30	0.39	750	300	20
Class3	significant increase	30	10.4	90	60	1.04	2250	750	40
Class4	large increase	40	18.4	165	105	1.69	4000	1500	80
Class5	very large increase	>40	>18.4	>165	>105	>1.69	>4000	>1500	>80

Acidification

Assessment of the acidification of freshwaters can be based on SEPAs environmental quality criteria for lakes and water courses. Assessment can be based either on the buffer capacity of the water or its pH-value. The buffer capacity of the water indicates the sensitivity of the aquatic system for acidification, while the pH-value indicates the actual acidification status. Buffer capacity can be expressed as alkalinity or as the acid neutralising capacity (ANC). The pH-value can show large variation during the year, though alkalinity is usually more stable.

Alkalinity

Alkalinity is usually expressed as the bicarbonate concentration of the water in meq/l. Water quality classes based on alkalinity are shown in Table 13-6:

Table 13-6. Classification of freshwater based on alkalinity (SEPA, 4913).

Class	Description	Alkalinity (meq/l)
1	Very good buffer capacity	>0.2
2	Good buffer capacity	0.1 – 0.2
3	Weakly buffering	0.05 – 0.1
4	Very weakly buffering	0.02 – 0.05
5	Insignificant or no buffer capacity	<0.02

Acid neutralising capacity

An alternative measure of buffer capacity is the acid neutralising capacity (ANC). The ANC includes the buffering capacity due to organic anions as well as that due to bicarbonate. In clear waters, the difference between buffering capacity indicated by alkalinity and ANC is very little, but in brown water, with high humus content, ANC can be significantly higher than alkalinity.

ANC is usually defined as:

$$\text{ANC} = \text{BC-AN} \qquad (13\text{-}1)$$

where :

BC is the concentration of basic cations

AN is the concentration of strong anions (ie anions with a low pK-value). Thus, according to SEPA (4920):

$$\text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}) - (\text{SO}_4^{2-} + \text{Cl}^{-} + \text{NO}_3^{-}) \qquad (13\text{-}2)$$

In most studies of water chemistry ANC has been defined as:

$$\text{ANC} = \text{HCO}_3^{-} + \text{CO}_3^{2-} + \text{OH}^{-} + \text{A}^{-} \qquad (13\text{-}3)$$

Where A^- is the total concentration of organic anions that can take up protons.

A^- can be calculated from the TOC concentration in water and its pH value.

In the background report to SEPAs water quality criteria (report 4920), a suggestion to water quality classification based on the ANC was also given, although this was not adopted in the final criteria. The water quality classes based on ANC are shown in Table 13-7.

Table 13-7 Classification of freshwater based on ANC (SEPA, 4920).

Class	Description	ANC (meq/l)
1	Very good buffer capacity	>0.2
2	Good buffer capacity	0.1 – 0.2
3	Weakly buffering	0.05 – 0.1
4	Very weakly buffering	0.02 – 0.05
5	Insignificant or no buffer capacity	<0.02

In terms of biological effects, ANC has been evaluated with respect to effects on fish populations and effects on bottom fauna (see SEPA, 4920). A summary of these evaluations is given in Table 13-8.

Table 13-8 A summary of evaluations of biological effects at different values of ANC.

ANC meq/l	Effect
	Fish
≥ 0.050	No or only slight reduction in populations.
≥ 0.010	Populations of several fish species are reduced by 25%
-0.015 – 0.00	All fish species in lakes reduced by 50%
≤ -0.015	50% of fish populations disappear.
	Benthic fauna - diversity
≥ 0.030	No effect observed (Raddum-index) on diversity
≤ 0.010	Less diverse fauna
	Benthic fauna - injury
≥ 0.050	No damage to invertebrates
≤ 0.00	Significant injury to benthic invertebrates (and fish)

In Norway, a guideline value for ANC with respect to biological effects was set at 0.02 meq/l. It is also interesting to note that liming of freshwaters in Sweden is not carried out in waters with ANC above 0.05 meq/l.

ANC and alkalinity/acidity has been tabulated for reference lakes and for some running waters in north and south Sweden. These data compilations can be used to compare with background conditions.

pH-value

The water quality classes based on pH-value given by SEPA (4913) are given in Table 13-9.

Table 13-9 Water quality classes based on pH (SEPA, 4913).

Class	Description	pH-value
1	Almost neutral	>6.8
2	Weakly acidic	6.5-6.8
3	Fairly acidic	6.2-6.5
4	Acidic	5.6-6.2
5	Very acidic	<5.6

These classes include a certain margin to cover the fact that lakes and running waters can become significantly more acid than usual under shorter periods during spring when water flow is high. This effect can be extreme in small streams with fast turnover, and the increase in acidity at this time can have significant biological consequences even if the alkalinity is at other times good. Therefore classification of acidification requires investigations of biological parameters as well as of the water chemistry.

Use of measurements of buffer capacity and pH

SEPAs classification of freshwater with respect to acidification is based on alkalinity and pH, because these are the parameters which are most frequently measured. Discussion of classification based on ANC is limited to the background report for environmental quality criteria.

Water within the same ANC-class will have lower alkalinity at high organic matter (humus) concentrations. A better assessment of the buffer capacity and acidification of freshwater should therefore take this into account. The background report to SEPAs water quality criteria therefore suggests alternative classifications based on alkalinity and pH for three different water colour classes. It is assumed that water colour is directly correlated with the organic material content of the water. This classification is shown in table 13-10.

Table 13-10 Classification of freshwater with respect to acidification, based on alkalinity and pH for different water colour classes (mg/l Pt) (SEPA, 4913).

ANC-class	<50 (mg/l Pt)	50-100 (mg/l Pt)	>100 (mg/l Pt)
	Alkalinity (meq/l) at different water colour classes		
1	<0.150	>0.150	>0.1
2	0.100-0.150	0.050 – 0.150	0.020 – 0.100
3	0.050-0.100	0.00 – 0.050	0.00 - 0.020
4	0.00 – 0.050	-0.050 – 0.00	-0.100 – 0.00
5	<0.00	<-0.05	<-0.100
	pH-value at different water colour classes		
1	>7.0	>6.5	<6.2
2	6.5 – 7.0	5.6 – 6.5	5.0 – 6.2
3	6.2 – 6.5	5.0 – 5.6	4.5 – 5.0
4	5.6 – 6.2	4.5 – 5.0	4.0 – 4.5
5	≤5.6	≤4.5	≤4.0

Water hardness

Water hardness is expressed as $CaCO_3$ equivalents in mg/l. The most important impact of hardness on aquatic life appears to be the effect the hardness has on the other more toxic metals such as lead, cadmium, chromium and zinc. Generally, the harder the water, the lower the toxicity of other metals to aquatic life. In hard water some of the metal ions form insoluble precipitates and are removed from solution and are not available for uptake by the organism.

Some water quality criteria for aquatic life (CCME) give water quality criteria for some metals as a function of water hardness. The water quality guidelines given by CCME vary between 1 and 7 µg/l for lead, and between 2 and 4 µg/l for copper, depending on hardness. For cadmium, the guidelines are expressed as a function of hardness.

Sulphate

In Sweden, no water quality criteria for sulphate have been established. In British Columbia, guidelines to protect aquatic life have been established from the available aquatic toxicological data. A water quality guideline of 100 mg/l for dissolved sulphate was established. This guideline is a maximum concentration that should not be exceeded at any time. However, it is suggested that water bodies where concentrations exceed 50 mg/l should be monitored closely, partly because there is conflicting evidence about the sensitivity of aquatic mosses, and partly because at concentrations over 50 mg/l, large sulphur bacteria growths have been observed on river beds, resulting in significant changes to the macroinvertebrate community.

Biological indicators

A number of biological indicators have been suggested for freshwater by SEPA. Some of these indicators are suitable for lakes (planktonic algae, macrophytes). Others, e.g. surface growth of algae, benthic macroinvertebrates and fish can also be used in running water.

Biological indicators usually take the form of indices, which take into account the diversity of the fauna/flora encountered, the abundance of particular taxa (e.g. species, family, group) of organisms, the value of the taxa as indicators, and their sensitivity to the type of contaminant being considered. The use of these biological indicators usually involves a comparison of the index value with that for rivers/lakes which are not affected by point sources of pollution, or which have been characterised with respect to environmental conditions such as acidification, pollution or eutrophication.

One problem with biological indicators is that they are general indicators of the conditions in an ecosystem. When there has been disturbance to an ecosystem which is indicated by biological parameters, it is often not possible to say what the cause of that disturbance has been. Combinations of stressors such as acidity, low oxygen content, turbidity, nutrient shortage/excess and the presence of metals and organic pollutants often make it very difficult to interpret the cause of changes in biological parameters.

Algal growth

Two indices exist for diatoms in surface algal growths, though experience with this type of index is lacking in Sweden and there are few data for background conditions for the use of these indices.

Benthic macrofauna

Four indices have been included in SEPA’s indices for benthic macroinverteberates. These are:

- Shannon’s diversity index (indicates general ecological quality)
- ASPT index (indicates general ecological quality)
- Danish fauna index (indicates organic pollution)
- Acidity index

In addition, other parameters can be used to investigate the effect of metals:

- Occurrence of indicator species
- Total number of taxa
- Median number of taxa/sample
- Density of individuals
- EPT-index (indicates general ecological quality, based on the number of taxa of mayflies (Ephemeroptera), stoneflies (Plecoptera) and caddisflies (Trichoptera),
- Deformation of mouthparts in chironimid larvae (can be used as an indicator for metal pollution).

The distribution of index values in rivers in different ecoregions in Sweden have been tabulated (SEPAs report, 4921). Taxa have been indexed according to their tolerance for low pH on a scale of 0-5, as shown in Table 13-11.

Table 13-11 Index for tolerance of species to low pH (Degerman et al, 1994)

FSI	Lowest pH where survival of the taxa has been observed
0	Not known
1	<4.5
2	4.5-4.9
3	5.0-5.4
4	5.5-5.9
5	>6.0

Sampling points can then be classified according to the most sensitive taxa observed in the samples.

In order to compensate for individual animals which have recently arrived at a sampling point, but which will not survive any period of time, sampling stations are classified as the index where at least three individuals survive. This is called the FSI_3 index.

Fish

SEPA (report 4913) suggest a basis for environmental quality criteria based on investigations of fish populations. Again, classes are given for both environmental conditions and for the extent to which a river or lake differs from background conditions. The classes are based on biologically relevant parameters which are weighed together to give a total index. Classes are given both for lakes and for rivers.

The parameters used for running water are:

- Number of endemic fish species
- Biomass of endemic fish species
- Number of individuals of endemic fish species
- Fraction of salmon-species, based on number of individuals
- Reproduction of endemic fish species
- Occurrence of acidification-sensitive species and life-stages
- Number of exotic species, based on number.

The first five parameters are used for classing of environmental conditions; the last two parameters are used for classing of change from background conditions.

13.2 Environmental quality of Vormbäcken

The study area

At Kristineberg, effluent water from mining area is discharged to the Vormbäcken river. The studied area is part of the Skellefte mining district (complex sulphidic ores). Due to the presence of mineralisations in the upper stretches of the Vormbäcken River, there have been mining activities at a number of locations; e.g. Rävliden, Hornträsk, Kimheden and Kristineberg. All of these mines except Kristineberg have been remediated. Kristineberg is still active, and remediation activities in the tailings ponds area are run in parallel to the mining activities.

At the moment, the mine water is treated in a high density sludge water treatment plant. From the treatment plant, the clear-water phase is discharged into the tailings ponds. The resulting mixture of treated mine water, runoff from the industrial area and drainage water from the tailings ponds at Kristineberg is limed before it is finally released into the Vormbäcken River. In addition, a small watercourse draining the area around the Kimheden mine towards the south has also been diverted into the tailings ponds at Kristineberg.

Plans for the future remediation of the area include the diversion of the Vormbäcken River into the combined tailings and settling pond which will keep the tailings flooded and/or saturated with water. The pond will then be integrated into the natural system, as has been done at other mines (eg Stekenjokk, Gustafsson et al, 1999). If this succeeds in reducing weathering rates sufficiently, liming of the drainage water will no longer be carried out.

Vormbäcken

The Vormbäcken River drains Lake Sörsjön- Hornträsket-Norrsjön and then flows mainly through conifereous forests and mires for approximately 40 km before joining the Vindelälven River at Vormsele. The discharge from Kristineberg flows into the Vormbäcken in the upper reaches of river, approximately 3 km below the discharge from the lake Sörsjön- Hornträsket-Norrsjön.

The total catchment area of the river is approximately 370 km^2.

The river flows through the lake Vormträsket before joining the river Vindelälven. Vormträsket is approximately 25 km downstream of the discharge point from the mine. The main tributaries to the river upstream of Vormträsket are the drainage from the lake Holmtjärn, and the rivers Kimbäcken, Svältamyrbäcken, Svartbäcken and Rökån. Above the lake Vormträsket, the river bifurcates, allowing part of the river to join the Rökån river and flow through the lake Lidträsket, before rejoining the main river course.

Historic data on discharges from Kristineberg

Before the 1960s, the discharge from Kristineberg was characterised by low pH, and high concentrations of iron, sulphate, zinc and copper.

Already at the beginning of the 1960s, the process used for concentration changed to alkaline flotation, which changed the pH of the discharge from Kristineberg. The concentrator plant was closed in 1991.

In more recent years, the discharge from Kristineberg has been alkaline in nature, with high calcium concentrations.

The average concentrations of total Cu, Fe and Zn in the effluent water was lower in 1999 and 2000 than in the 1970s. This reflects the liming, also shown by fact that the effluent water sampled in 1999 and 2000 had a higher average pH.

The drainage at Kristineberg is treated with $Ca(OH)_2$. Liming reduces the metal concentrations of the drainage water significantly, and also gives rise to drainage water which has elevated Ca concentrations.

The Ca present in the treated drainage water may influence the metal speciation in Vormbäcken by either

- competing with other metals for binding sites on particles and dissolved organic matter (DOM), increasing the dissolved and bioavailable forms of other metals and possibly the distance they are transported

or

- causing flocculation of DOM and its associated metals, as well as coagulation of smaller particles and associated metals, thereby decreasing the distance the metals are transported.

In Vormbäcken, the second of these alternatives is thought to be the case (see Sjöblom, 2003).

Ca may also reduce the toxicity of metals in the water by competing for uptake routes into the biota.

Background conditions in Vormbäcken

The concentrations of a number of metals are elevated already in the stretch of Vormbäcken upstream of the discharge from Kristineberg. The major source of Cd, Cu, Pb and Zn is in fact situated upstream from the discharge from Kristineberg mine. The high metal concentrations at the background (upstream) station may be the result of weathering processes occurring in a highly mineralised area, or may reflect the natural background situation. Alternatively, the source of the metals may be previous mining activities in the area around the Sörsjön-Holmträsket-Norrsjön.

The catchment area is the main source of As and Fe. Below the discharge from Kristineberg, a major source of As to the river appears to be situated in the area between sampling stations 9 and Rökå. Parts of this particular area have been hydrothermally altered. Natural elevated concentrations of As have been found elsewhere in the Skellefte mining district.

The main source of sulphate and calcium to the system is the effluent water from the mine area. However, the main effect of sulphate in Vormbäcken is likely to be its contribution to the acidification of the freshwater rather than a direct toxic effect. The sulphate concentration is included in the calculation of the ANC.

A study of old monitoring data from Boliden AB (Sjöblom, 2003) showed that from the point where the discharge from Kristineberg is mixed completely with the river water in Vormbäcken (Aspliden), the average values of sulphate, conductivity, pH, turbidity, Cu, Fe and Zn decrease with distance downstream. The pH decrease which occurred downstream of the discharge from Kristinieberg before liming began was attributed to the continued oxidation of iron and sulphur compounds which were released to Vormbäcken. Since liming has been carried out, the pH decrease downstream reflects the dilution of the alkaline discharge in Vormbäcken. Average colour increases as the river flows past two wetland areas, which act as sources of organic carbon. The lowest turbidity values are found downstream of lakes, which act as settling basins.

The concentrations of Cu, Zn and also sulphate, conductivity and pH decrease stepwise, probably because of dilution by water in the tributaries to Vormbäcken. Iron decreases linearly, more slowly than for Cu and Zn. This is probably because the diluting water in the tributaries also contains high concentrations of iron.

Recipient conditions at present

Tributaries to Vormbäcken

Sampling in 2000 (Sjöblom, 2003) showed that the concentration of Cd, Cu and Zn in all of the tributaries investigated was much lower than those encountered in Vormbäcken. The natural tributaries accounted for between 4 and 12% of the loadings of Zn, Cu and Cd to the system. For lead, they accounted for between 11 and 17%. Lead appears to be mobilised from the catchment area during periods of high flow.

The contribution of Fe, Al, and Mn in the river at Aspliden (that is, background upstream of the discharge from Kristineberg together with the discharge) is about half the total loading (October, 2000).

For arsenic, the natural tributaries account for at least twice the loadings measured at Aspliden (where discharge is completely mixed with river water). The contribution of groundwater to the total load in Vormbäcken is also thought to be high.

Concentrations in surface water

Concentrations in surface water in Vormbäcken and its tributaries from recent MiMi studies (Sjöblom, 2003, sampling in June and October 2000) are shown in table 13-12 below. The concentrations have been compared with SEPAs classification of water quality status, based on the risk for biological effects (SEPA 4913).

The table illustrates that concentration of zinc and copper, and to some extent cadmium, is already very high (class 5, very high concentrations) upstream of the discharge from Kristineberg. The discharge from Kristineberg (Utskov) in comparison has low concentrations of copper and zinc.

Table 13-12 Concentrations of some trace elements, calcium and sulphate in Vormbäcken and tributaries in 2000 (Data from Sjöblom, 2003).

	Site	June 2000						October 2000					
		Zn µg/l	Cu µg/l	Cd µg/l	Ca mg/l	As µg/l	sulphate mg/l	Zn µg/l	Cu µg/l	Cd µg/l	Ca mg/l	As µg/l	sulphate mg/l
Upstream	Storkalven	505	116	1.4	4	0.8	12	704	145	1.8	4	0.7	13
	1	497	112	1.4	4	0.8	12	663	142	1.7	4	0.7	13
	2							588	121	1.5	4	0.8	13
Discharges	Utskov	33	8	0.09	355	0.7	839	69	16	0.1	363	0.8	1040
	3							483	121	1.2	73	1.2	179
	4							15150	527	29	413	18	1359
Downstream	Aspliden	383	84	1.1	66	1	166	619	97	1.5	90	1.1	271
	5	389	77	1.1	59	1.3	143	520	96	1.3	60	2.9	183
	Timmervägen	221	46	0.6	27	1.6	70	312	46	0.8	43	1.9	133
	9	211	41	0.6	32	1.5	76						
	Rökå	196	36	0.5	28	2.2	66	272	39	0.7	38	3.3	123
	Mickeldammet	125	21	0.4	17	2.4	38	168	20	0.4	29	3.4	68
	Brännfors	116	19	0.3	15	2.3	33	147	18	0.3	27	3.5	63
	17	83	11	0.2	11	1.3	26						
	Vormsele	67	9	0.1	11	1.1	24	76	11	0.1	10	1.5	22
Tributaries	6	8	1	nd	2	1.5	1	11	0.8	nd	2	1.7	2
	7	2	0.5	nd	3	0.8	1						
	8	3	1	nd	2	0.9	1						
	10	5	0.9	nd	2	0.6	1						
	11	2	2	nd	2	nd	3	3	0.8	nd	2	0.4	4
	13	27	5	0.04	3	0.7	5	35	6	0.05	3	1	5
	14	2	0.4	nd	2	1.2	1				.		
	15	6	0.7	nd	2	4.4	1	7	0.5	nd	2	5.4	1
	16	10	1	0.02	2	1.5	2	10	1	0.02	2	1.7	1
SEPA 1999:	**Environmental quality criteria for lakes and rivers (Report no 4913)**												
Classification of environmental status													
		Zn	Cu	Cd		As	sulphate	Zn	Cu	Cd		As	sulphate
Class1	very low concentrations	5	0.5	0.01		0.4		5	0.5	0.01		0.4	
Class2	low concentrations	20	3	0.1		5		20	3	0.1		5	
Class3	moderate concentrations	60	9	0.3		15		60	9	0.3		15	
Class4	high concentrations	300	45	1.5		75		300	45	1.5		75	
Class5	very high concentrations	>300	>45.0	>1.5		>75		>300	>45.0	>1.5		>75	
BC AWQG							50						50
BC AWQG							100						100

The concentrations of zinc, copper and cadmium can be seen to decrease generally downstream of the discharge point in Vormbäcken. At Vormsele (where Vormbäcken flows into Vindelälven) the concentrations of zinc and copper have reached the boundary between class 3 and class 4 (moderate to high concentrations) and the concentrations of cadmium have declined to class 2 (low concentrations). Arsenic concentrations in water are generally low. Sulphate concentrations are high and exceed British Columbia's ambient water quality criteria in the discharge water and immediately downstream of the discharge. Again, these concentrations decrease downstream. Calcium shows a similar pattern.

In contrast, the natural tributaries to Vormbäcken have much lower concentrations of zinc and copper. Zinc concentrations are classed very low to low (class 1-2) and copper concentrations mainly as low (class 2). Cadmium and arsenic concentrations are also generally low, with all cadmium concentrations in class 2 (low) and most arsenic concentrations in class 2 (low). However, one tributary, sampling station 15, has the highest arsenic concentrations recorded. This tributary flows into Vormbäcken between Rökå and Mickeldammet. The arsenic concentrations at these two points and at Brännfors, the next sampling point downstream, also have elevated arsenic concentrations compared with upstream.

Sediment

Sediment concentrations have been reported for surface sediment in Vormträsk and Lidträsk on a number of occasions. The sediment concentrations from a number of studies have been summarised in table 13-13 and compared with SEPA's classification of sediment quality status, based on the risk for biological effects (NV report 4913). Concentrations in a reference lake, Aggträsk, were also reported in 1975.

The results show that earlier (1974/75), the concentrations of zinc, copper and lead were higher in Vormträsk and Lidträsk than in the reference lake. Concentrations of arsenic, though very high in sediment in Vormträsk and Lidträsk, were not higher than in the reference lake. Concentrations of copper and lead were generally higher in Vormträsk than in Lidträsk, though for zinc, very high concentrations are found in both lakes. Lower concentrations are to be expected in Lidträsk than in Vormträsk, as the larger part of the flow in Vormbäcken goes via Vormträsk, but not via the bifurcation leading to Lidträsk.

The concentrations of zinc, copper, lead, cadmium and arsenic in Vormträsk's and Lidträsk's surface sediments remained about the same until sampling in 1991. In 1991, enrichment at Kristineberg stopped. The zinc, copper and lead concentrations in surface sediment measured in 1995 showed a decrease in both lakes, presumably because of the reduction in discharge. Arsenic concentrations have increased in both lakes.

In 1995, concentrations of copper and zinc in Vormträsk were classed as high (class 4, though generally in the lower part of the interval) and in Lidträsk were classed as moderate (class 3). Lead and cadmium concentrations were generally classed as low (class 2). Arsenic concentrations in Vormträsk were classed as very high (class 5).

In Lidträsk, the arsenic concentrations were lower, classed as high (class 4). It should be noted that the sediment in the reference lake also had very high arsenic concentrations.

Table 13-13 Concentrations of some trace elements in surface sediments in Vormträsk and Lidträsk (Data from Brånin et al. (1976), Lindeström and Medin(1992), Råberg (2000).

Date	Sample	Reference	Depth cm	LOI %	Fe mg/kg dw	Mn mg/kg dw	Zn mg/kg dw	Cu mg/kg dw	Pb mg/kg dw	Cd mg/kg dw	As mg/kg dw	Co mg/kg dw	Ag mg/kg dw	Hg mg/kg dw
Vormträsk														
1974	Vo7	Brånin 1976	0-2	19.7			813	228	154	4.6		9		
1974	Vo8	Brånin 1976	0-2	31.6			2437	404	228	10		25		
1974	Vo9	Brånin 1976	0-2	26.7			1867	598	186	13.3		76		
1975	Vo7	Brånin 1976	0-1	20.2	128947	282	1037	234	84	3.5	179		3.7	1
1975	Vo8	Brånin 1976	0-1	24.2	330476	1694	3274	565	179	10.8	140		3.2	0.57
1975	Vo9	Brånin 1976		28.4	131469	50724	774	514	131	2.7	429		5.7	0.76
1991	Vo1	Lindeström		29			2190	590	290	9	200			2.48
1991	Vo2	Lindeström		31			2290	610	210	10	290			1.21
1995	Vo1	Råberg		17			1002	178	73	9	223			0.33
1995	Vo2	Råberg		33			1228	337	88	11	444			0.58
Lidträsk														
1974	Li2	Brånin 1976		34.5			2183	255	85	8.5		19		
1974	Li3	Brånin 1976		27.9			1315	194	92	9.2		28		
1974	Li6	Brånin 1976		31.6			2991	548	116	9.3		44		
1975	Li2	Brånin 1976		30.8	104598	1016	758	131	59	2.9	184			0.69
1975	Li3	Brånin 1976		32.3	72222	882	928	176	57	3.5	122			0.56
1991	Li1	Lindeström	yt	32			1210	170	70	6	51			0.35
1991	Li2	Lindeström	yt	31			1790	320	70	6	59			0.25
1995	Li1	Råberg	yt	21			464	95	52	1	132			0.32
1995	Li2	Råberg	yt	32			368	82	37	1	110			0.2
Aggträsk														
1975	Ag 1	Brånin 1976		35.2	258929	508929	364	16	46		679			0.18
1975	Ag 2	Brånin 1976		31	185246	235557	395	95	38		466			0.33
SEPA 1999: Environmental quality criteria for lakes and rivers (Report no 4913)														
Classification of environmental status							**Zn**	**Cu**	**Pb**	**Cd**	**As**	**Co**		**Hg**
Class1	very low concentrations						150	15	50	0.8	5			0.15
Class2	low concentrations						300	25	150	2	10			0.3
Class3	moderate concentrations						1000	100	400	7	30			1
Class4	high concentrations						5000	500	2000	35	150			5
Class5	very high concentrations						5000	>500	2000	>35	>150			5
RIVM, MPA												12		

Biological conditions

Investigations of biological conditions have been carried out on a number of occasions, eg. Brånin et al (1976), Grahn and Hultberg (1979), Ekström (1990), Lindeström and Medin (1992) and Råberg, (2000). Whilst investigations of fish have been carried out (Nilsson, 1991), most of the recent investigations have been concerned with benthic fauna. This section will therefore concentrate on benthic fauna.

In the investigation carried out in 1995 (Råberg, 2000), sampling points in Vormbäcken were upstream of the discharge from the mine, at two points downstream of the discharge before Vormträsk, and at one point below Vormträsk. One sampling point in Rökan, near Lidträsk was also included, as well as two reference sampling points in tributaries to Vormbäcken.

Råberg summarises the results (sampling in 1995) as shown in the table 13-14:

Table 13-14 The results of bottom fauna investigations in Vormbäcken and tributaries (from Råberg, 2000)

Sampling point	Upstream	Below dishcarge	Above Vormträsk	Below Vormträsk	Reference	Reference	Rökån, near Lidträsk
	Vo1	Vo4	Vo5	Vo11	Re2	Re3	Li1
Mayflies, taxa	2	0	3	4	8	8	4
Mayflies, individuals	2	0	103	94	314	481	37
Stoneflies, taxa	6	6	7	6	10	9	5
Stoneflies, individuals	40	26	50	25	275	89	20
Total, taxa	18	14	21	19	33	27	19
FSI_3	1	1	3	3	4	3	3
pH equivalent	<4.5	<4.5	5.0-5.49	5.0-5.49	5.5-5.99	5.0-5.49	5.0-5.49
$FSI_3$1991		1	4	3			
FSI_3 earlier		0	1	1			

In this latest investigation the general pattern shown was of least disturbance in the reference locations, and highest degree of disturbance at the point immediately downstream of the discharge. A high degree of disturbance was also noted at the sampling point upstream of the discharge from the mine, probably because of the high contaminant loadings upstream in Vormbäcken.

At the reference locations, the number of individuals and the total number of taxa was significantly higher than at other locations, as was the number of individuals and taxa of Ephemeroptera (mayflies) and Plecoptera (stoneflies). The acidity index was 3-4.

At the sampling points immediately upstream and downstream of the discharge, fewer individuals were observed. The acidity index was the lowest in Vormbäcken, 1.

The sampling point in Lidbäcken also had few individuals. This however is probably because of sampling difficulties. The acidity index at this point was 3.

Further downstream in Vormbäcken, the disturbance to fauna is not so great, indicating better ecological conditions. The locations upstream and downstream of Vormträsk have a better acidity index (3) and the number of taxa and number of individuals of Ephemeroptera (mayflies) is higher.

In comparison with the investigation done in 1991 (Lindeström and Medin, 1992), it appears that the ecological conditions upstream of the discharge from the mine have deteriorated. At the sampling point immediately downstream of the discharge, no change in ecological conditions is indicated. Further downstream in Vormbäcken above Vormträsk, there does not appear to have been any significant change in ecological conditions. Below Vormträsk and in Lidbäcken, a slight improvement in ecological conditions is indicated.

The use of acidity indices for Vormbäcken is already established as a useful technique (see Råberg, 2000). Lingdells acidity index (FSI) (see Degerman et al, 1994) has been used. Comparison with investigations carried out earlier (Brånin, 1976, Brånin, 1979, Grahn and Hultberg 1979; all summarised in Råberg 2000) can be made for the sampling stations immediately downstream of the discharge from Kristineberg, and two sampling stations further downstream in Vormbäcken, one above Vormträsk and one below. At the sampling point near the discharge, the conditions have improved somewhat from a total absence of individuals before 1991 to some occurrence of the individuals of some taxa in 1991 and 1995. Further downstream, at both the sampling stations above and below Vormträsk, the number of individuals of the taxa observed before 1991 has increased, and one new taxa has been observed. At these two stations, the acidity index has increased from 1 to 3 between 1975 and 1995.

14 Scenario analysis

14.1 Introduction

Assessments of long-term performance of disposed tailings deposits must be based on a firm scientific comprehension of the governing processes. To be able to address the long-term evolution of processes where the time spans are far beyond what is possible to observe in experiments, we must rely on predictive modelling. The models should aim at assessment of the performance of the engineered barriers and the natural environment for very long time scales. To evaluate the performance of the tailings deposits, assumptions must be made on the future evolution of engineered barriers and natural conditions. Formulation of scenarios is a way to describe possible sequences of processes and events influencing the release of the contaminants from the deposits. This is a new approach introduced by the MiMi programme for assessment of mine tailings deposits. The generic methodology, however, has been adapted from significant research and development efforts on both national and international level presently going on within the field of radioactive waste management. The methodology has the purpose to provide systematic ways to develop, document different assumptions and to evaluate consequences of possible future scenarios.

This Chapter gives an overview of the steps involved in such a scenario development procedure. The general description is largely based on reports from the OECD/NEA Working Group on the Identification and Selection of Scenarios for Performance Assessment of Radioactive Waste Disposal (OECD, 1992*)* and from the Swedish Nuclear Fuel and Waste Management Co, SKB (Pers et al, 1999). A systematic scenario method is presented, using interaction matrices to graphically present and structure the studied mine tailings deposits.

Within the MiMi programme, the interaction matrices were used primarily as a tool to stimulate structured discussions among the different researchers. During workshops, different processes and their interaction over time were discussed and screened by specialists and expert from different scientific disciplines. The purposes of these workshops were: to establish a common platform for discussion, to promote interdisciplinary collaboration, to increase the understanding of process interactions, to train the participating researchers in structured interdisciplinary discussion within the performance assessment framework, to demonstrate the role of the different MiMi research activities in the context of long-term performance assessment of tailings deposits, and to document the outcome of the screening of different processes for the overall performance of the deposits. The methodology proved to be an effective way to establish a deeper understanding among the different researchers of the complexity of different process interactions within the deposits and of the need for a multidisciplinary approach and common effort to be able address the central issues. However, the methodology also proved to be very demanding and was therefore not used to its full potential to develop scenarios. The scenario development was instead limited to a more traditional 'What-if'-approach addressing identified disturbances of a more general nature.

14.2 Description of methodology

Scenarios should be regarded as stylised representative futures which, when summed, span the variety of possible futures. It is therefore important that the range of scenarios adopted is sufficiently broad. It is important to note that the individual scenarios do no imply the most probable future developments, but rather aim to quantify the ultimate consequences of different alternative developments over time.

Figure 14-1 shows a schematic of the elements in the scenario development process. The first step in the scenario development is to identify a comprehensive list of factors commonly known as Features, Events and Processes (FEPs). The FEPs are then classified and screened against some pre-defined screening criteria. The FEPs remaining after screening are combined into scenarios that are screened to create a final set of scenarios to be assessed in the performance assessment.

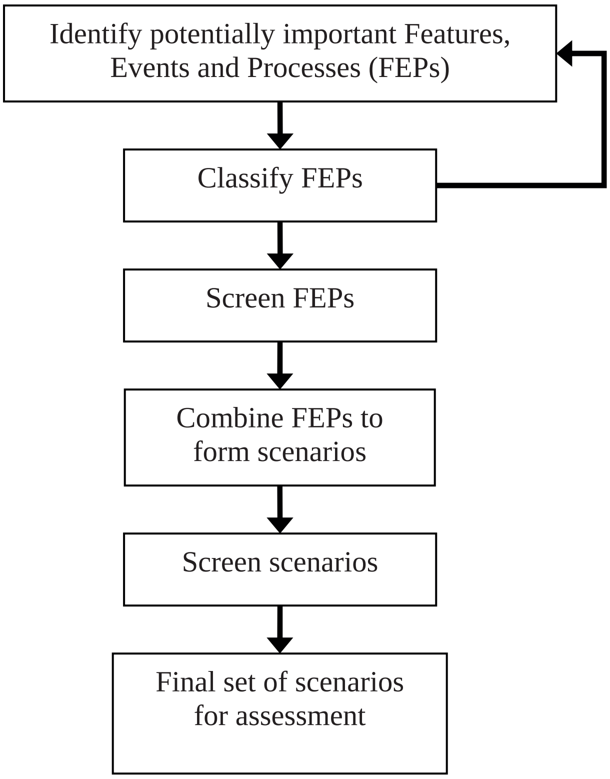


Figure 14-1 Schematic figure of the scenario development process (modified from OECD, 1992).

FEP identification

The list of FEPs created must be comprehensive, traceable and well documented. The identification of FEPs thus needs to include all phenomena that could affect the tailings deposit performance, in order that no interactions are overlooked. Precautions should be made to avoid inadvertent screening of FEPs at the identification stage. In order to ensure that a full spectrum of perspectives is obtained in the identification, specialists from many different disciplines should take part in the FEP identification. One way of using such a group of experts could be to arrange an expert panel creating an initial list of FEPs that is then reviewed by other external experts. It is important to avoid unconscious screening or bias in the identification process. This can be done by ensuring that the group of experts covers a wide range of expertise and interests and by formal elicitation procedures. In the MiMi work, the steering committee developed preliminary lists of FEPs which were then discussed and scrutinized by the entire research group during workshops.

Extensive lists of phenomena have been developed for radioactive waste management in several countries and studies. Examples of such FEPs lists, mainly applicable to deep disposal of radioactive waste in hard rock can be found in Pers et al (1999). An extensive data base of different FEPs has been assembled by the Nuclear Energy Agency (NEA, 1997). To some extent, such compilations comprise FEPs that may be of relevance also for assessment of mine tailings deposits.

Classification of FEPs

Demonstrating that the FEP list is sufficiently comprehensive is a critical aspect of scenario development. In order to make it easier to overview the completeness of the FEP list, classification is an efficient tool. The primary objective of classifying the FEPs is to reveal missing FEPs. Therefore, it is useful to use several different classification systems that examine the system from different viewpoints. Examples of such classification schemes are:

- Natural processes - human activities - waste and deposit induced effects
- Time scales
- Source term - near field - far field
- Probability and consequence
- Scientific discipline
- Release - transport - exposure

Classifying the FEPs according to their cause (natural - human - waste and deposit induced) has been used by for example IAEA.

Classification of FEPs according to the time scale during which the different phenomena take place can be useful as a preparation for screening of FEPs with regard to their relevance in the performance assessment or for judging the level of detail needed in the modelling of the phenomena. Also, classification with respect to time scale allows identification of processes that occur simultaneously so that their probabilities and consequences can be coupled or superimposed when appropriate.

A useful way of classification of FEPs in conjunction with groundwater migration is by the location in which they might occur. A standard division of a waste disposal system is the source term - near field - far field scheme. Different models may be used to simulate phenomena in these different locations. Therefore, obtaining a list of FEPs affecting mainly, for example, the near field will be an important input to the selection and design of the near-field model. It should be noted that some processes relate to the interfaces between source term – near field and near field - far field. These interfaces should therefore be included in the classification schemes.

Classification with respect to probability and consequence provides a basis for the continued treatment of the FEPs in the assessment. For example, FEPs with large consequences occurring with a high probability should be avoided by introducing additional safety measures in the tailings deposit design. Similarly, the treatment of FEPs with small consequences and a low probability could be limited to a qualitative discussion.

Classification according to scientific discipline provides a means to plan the involvement of different experts in the continued treatment and to judge the relative importance of different types of models. The most commonly considered medium for contaminant transport is groundwater. This can be subdivided into transfer of dissolved species, colloidal transfer, etc. In some situations particle transport or erosion may need to be considered as transfer medium. In the far field, the action of animals and plants can in itself be a transfer mechanism.

Screening FEPs

The result of the identification and classification steps is a sorted list of a large number of FEPs that may affect the safety of the tailings disposal system. In order to reduce the amount of detailed analysis required later, the list of FEPs is screened using well-defined and documented screening criteria. Phenomena that are judged to be irrelevant for the performance assessment are screened out. It is very important that the screening process is performed in a transparent way, i.e. that the arguments used and the decisions taken are well documented. In particular, it is important to document the basis for rejecting a particular FEP.

Detailed consequence analysis should be avoided at this stage of the assessment. However, simple bounding calculations may be necessary to provide a good basis for screening decisions. If such calculations are performed, the calculations and underlying assumptions and data used should be clearly documented.

The criteria used for the screening are normally physical reasonableness, regulatory criteria, probability of occurrence and effects on the tailings deposit and site. The screened list of FEPs should consist of phenomena that are judged to be of relevance to the performance of the tailings deposit.

Combining FEPs to form scenarios

Methods used for scenario construction can be grouped into the following main categories:

- Judgmental methods
- Fault tree or event tree analysis
- Systematic methods

In the judgmental methods the assessment team or invited experts select the FEPs they believe to be most important, and define release situations, without a systematic attempt to identify and examine all phenomena and conditions. The judgmental method has by far been the most commonly used method for performance assessment studies. Only limited attention is usually put on the scenario construction. Hence, the FEPs included in the assessments may differ significantly between different assessments. In particular, the reasons for screening FEPs or scenarios out are usually poorly documented, leading to difficulties to scrutinise the work at later stages. This may also hamper the possibility of feedback of knowledge between different assessments.

Fault tree or event tree analyses are two ways of describing logical connections between events. These methods have been extensively used in safety analyses of e. g. chemical plants and nuclear reactors. They are less commonly reported to have been used in conjunction with assessments of waste deposits. However, the methods have sometimes been used within the assessment team to support what has been reported to be judgmental assessments (Höglund et al, 1994a and b). The trend has been to abandon these methods in the context of assessment of radioactive waste disposal for several reasons. Firstly, the processes relevant to waste disposal are generally slow and difficult to define as abrupt events. Secondly, the tree methods are not suitable to handle interaction and feedback between events. Thirdly, the tree techniques are designed to break the system down into smaller components that can be quantified separately. This creates artificial barriers between the FEPs when the objective should rather be to analyse the overall system behaviour. Fourthly, in order to describe the system in sufficient detail, the number of combinations created in an event tree very rapidly becomes intractable.

Several methodologies to systemise and visualise FEPs that influence the performance of waste disposal systems are under development. The aim with the systematic methods is to fulfil the following requirements:

- Systematic identification and review of all FEPs and interactions and combinations of FEPs that can influence the performance of the tailings disposal concept.
- Documentation of decisions made in the development of scenarios as well as in the subsequent assessments in order to ensure traceability of decisions.
- The results should be comprehensive and facilitate the identification of areas requiring further investigations and research.

In the MiMi work, FEPs have been identified, screened and documented for a number of subsystems relevant for a tailings deposit using a systematic method. Extensive as it might be, this work does not pretend to cover the whole system in full detail. The scenario constructions have been made using the judgmental method.

Process system

The process system is defined as the organised assembly of all phenomena (FEP) required for description of the performance of the studied tailings deposit, and that can be predicted with at least some degree of determinism for a given set of external conditions (Andersson et al., 1989).

The Interaction Matrix methodology, which is based on the Rock Engineering Systems (RES) approach, is used as a tool for identification and structuring FEPs in the process system. The RES methodology was originally developed for approaching rock engineering problems (Hudson, 1992) but was tested by SKB as a potential method for structuring of FEPs relevant for the disposal of radioactive waste (Stephansson and Hudson, 1993; Stephansson and Hudson, 1994).

Comparisons between alternative methods (Eng et al., 1994; Skagius et al., 1995), have shown that the matrix structure is suitable for structuring and visualising the process system and makes it easier to present.

Construction of the interaction matrix and assigning priorities to the interactions

The basic principle of the interaction matrix is to list the main features or properties of the system along the leading diagonal elements of a square matrix. The interactions between these main features or properties are defined in the diagonal elements occur in the off-diagonal elements. Before starting the construction of the matrix, the objective of the assessment and the system to be covered by the process system must be defined, since these definitions have implications on the selection of diagonal elements in the matrix. The system definition includes a specification of the physical components of the repository system to be included in the process system, the spatial extension of the process system and the initial and boundary conditions of the system. Once this is done, the diagonal elements are selected and the features introduced in each diagonal element are defined and documented. To be able to describe relations between the process system and the system outside the process system, the boundaries of the process system can be part of the leading diagonal elements of the matrix. A procedure for defining the system is outlined in Figure 14-2.

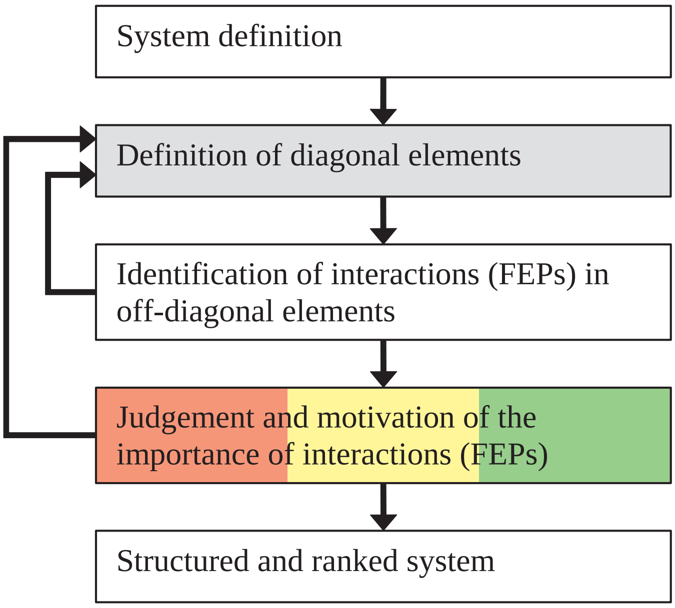
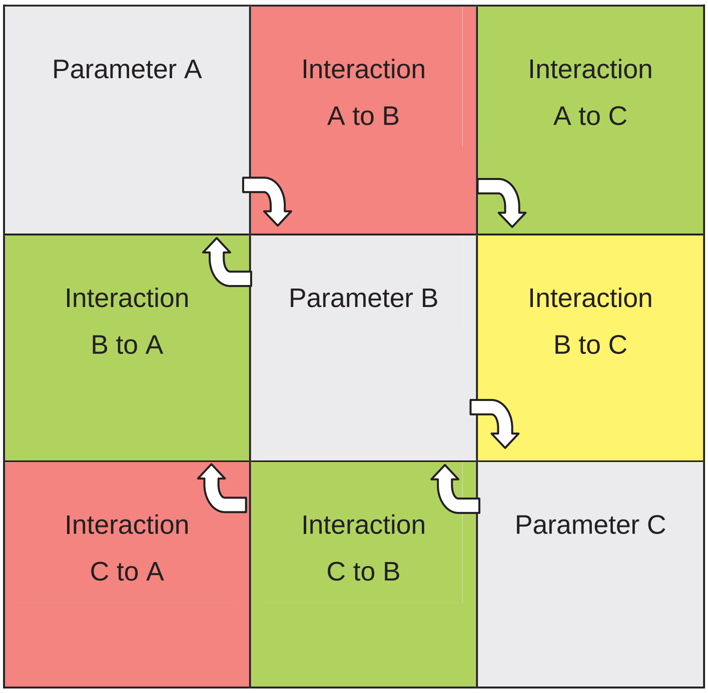


Figure 14-2 Procedure for defining an interaction matrix. Modified from Pers et al (1999).

If the system to be studied and the corresponding matrix are large it may be practical to divide the matrix into sub-matrices. In such cases the overlap between the sub-matrices as well as the way the sub-matrices communicate with each other should be clearly defined. In the MiMi studies, one large matrix has been set up for soil covered tailings that comprise the boundary conditions, the waste and different features of the deposit, and processes affecting the mobilisation and transport of contaminants. Another matrix has been set up for the function of tailings dams which is particularly important for water covered tailings deposits. The two matrices have been treated as separate entities and have not been linked together.

When the leading diagonal elements in the matrix are specified and documented, the interactions between these main features are identified and described by introducing FEPs into the appropriate off-diagonal elements (interaction boxes) in the matrix. All interactions should be binary i.e. they should be direct interactions between features in two diagonal elements and not a path via a feature in a third diagonal element. Each interaction is documented by defining the process or event involved in the interaction as well as the features or properties in the two interacting diagonal elements that are influencing and affected by the process or event. Every off-diagonal element in the matrix should be checked for interactions, and the reason for not having identified any interactions in empty off-diagonal elements should be documented.

The next step is to set priorities to all identified interactions in the matrix by the use of “expert judgement”. The importance of the interactions is judged for the previously defined initial and boundary conditions, using a well-defined and documented priority scale. In order to facilitate later review and re-evaluations, a motivation to the assigned priority should be given and documented together with the competence of the person or group of persons making the judgement. A colour coding can be used to display the priorities in the interaction matrix, see schematic illustration in Figure 14-3.



Parameter A	Interaction A to B	Interaction A to C
Interaction B to A	Parameter B	Interaction B to C
Interaction C to A	Interaction C to B	Parameter C

Priority	Definition
3 red	Important interaction – should be included in the performance assessment (PA)
2 yellow	Interaction identified – should probably be considered in the PA – may require further research
1 green	Interaction identified – need not be considered in the PA
0 white	No identified interaction
grey	Diagonal element with its parameters

Figure 14-3 Principle of the interaction matrix, indicating a colour scheme for ranking the importance of the different interactions (FEPs). Modified from Pers et al (1999).

Both the identification of interactions and the setting of priorities may reveal requirements on modifications of the definitions of the diagonal elements in the matrix. Building the interaction matrix is therefore an iterative process.

The structuring of the process system and the ranking of interactions require input from various information sources covering a broad range of disciplines. Therefore, these actions are preferable done by a group of people with both a general overview of the system and expertise in specific areas.

Documentation system

To facilitate the work with the interaction matrix methodology a documentation system was developed in a database format (Skagius et al, 1995). The database program FileMaker PRO was used for this purpose, and the full documentation system contains two types of databases, one for FEP descriptions and one for matrix specific information. In the MiMi work the FEPs database has been omitted.

The *interaction matrix database* contains the matrix with names of the diagonal elements, representative for the features or properties of the diagonal elements, and colour-coded off-diagonal elements showing the highest priority of an interaction in an element. The database also contains all the different documents defining the:

- Objective of the assessment
- Studied system
- Different leading diagonal elements in the matrix
- Interactions between diagonal elements and assigned priorities with motivations.

The matrix and the different types of documents listed above are accessible via a menu system. In addition, the data records containing the description of the diagonal elements and the interactions between diagonal elements are linked to the matrix. This means that these records can be reached directly from the matrix, which facilitates the search of specific information. It is, of course, also possible to search for specific information directly in the document records without going via the matrix. In the MiMi work, an interaction matrix database has been set up and is briefly described in the following. The full databases have also been made available as runtime versions, which means that the users do not need to have a license to the database program FileMaker PRO. The runtime version allows the user to run and add changes to the database on any PC. The databases are available for download through the website.

14.3 Formulation of scenarios and cases for quantitative assessment

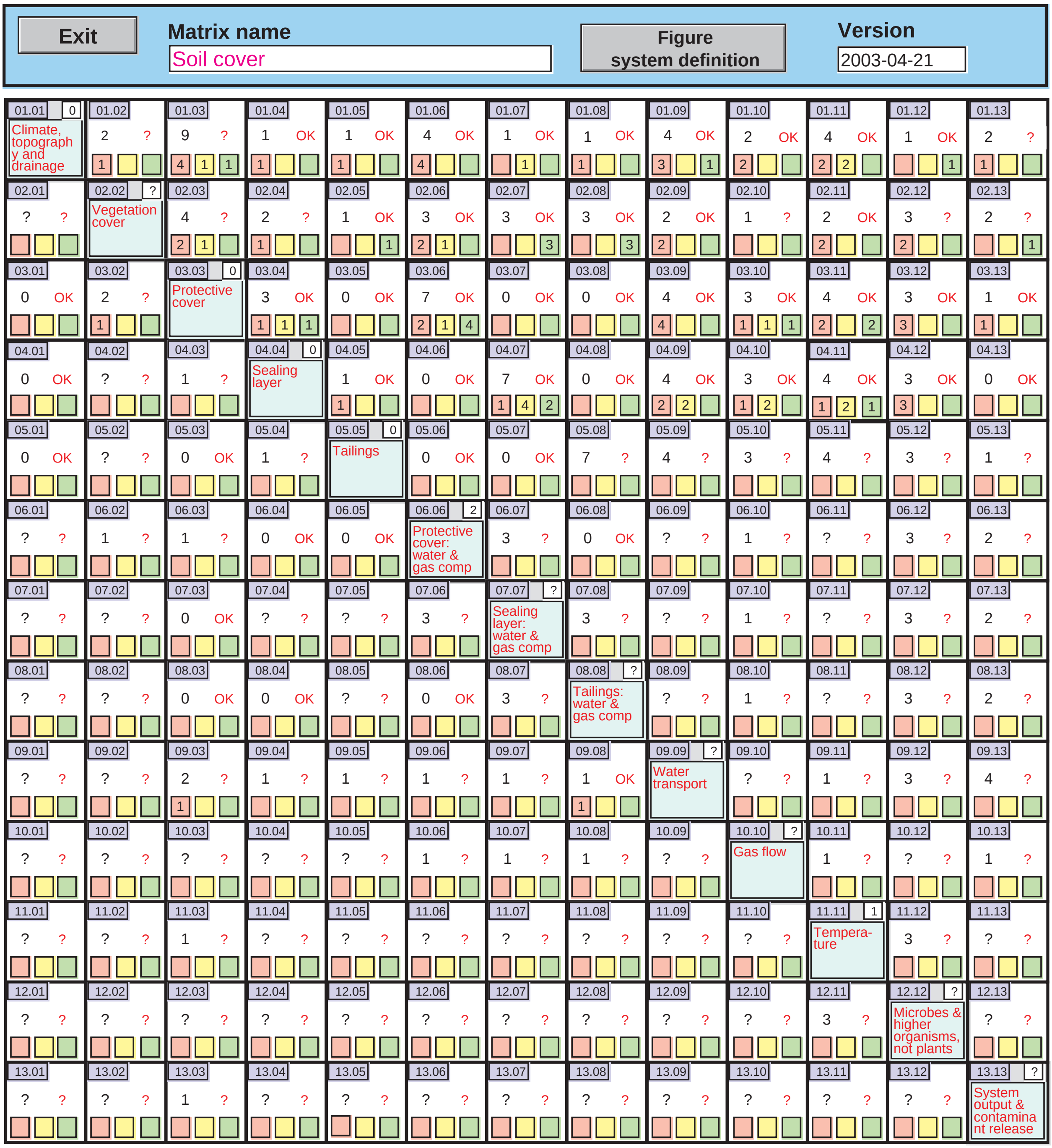
The interaction matrix with its linked documentation can be used to formulate scenarios and to define different cases to be assessed quantitatively. Its main function in this context is to serve as a checklist to ensure that all aspects judged as important are addressed in the analysis of a scenario. The interaction matrix database can also be used to store information on how the identified interactions have been handled in the quantitative assessments.

New scenarios are can be formed as a result of e.g. changes in parameters defining the boundary conditions for the studied system. It is important that the analysis of the consequences of a new scenario is made in a transparent and traceable way and that a new evaluation is made for the interactions affected by the changed conditions. The interaction matrix method can be used for this purpose and provides possibilities for documentation of the new judgements.

The interaction matrix should be regarded as a tool for structured guidance of quantitative analyses of a complex system. However, it must be stressed that the described methodology is a complement, not a replacement for more free and creative thinkning and exploration of the possible long term evolution of the studied system.

14.4 *Interaction matrix for Soil cover*

The interaction matrix set up for soil covered tailings is shown in Figure 14-4. The figure shows the defined diagonal elements. In the database application the user may access the definitions by clicking the link in diagonal box. The following pages give examples of the documentation system included in the interaction matrix methodology. The interested reader is encouraged to test the runtime version available at the MiMi web site (www.mimi.kiruna.se or www.mistra.org/mimi) or on CD-rom (included with the reports in pdf-format).



Matrix name: Soil cover

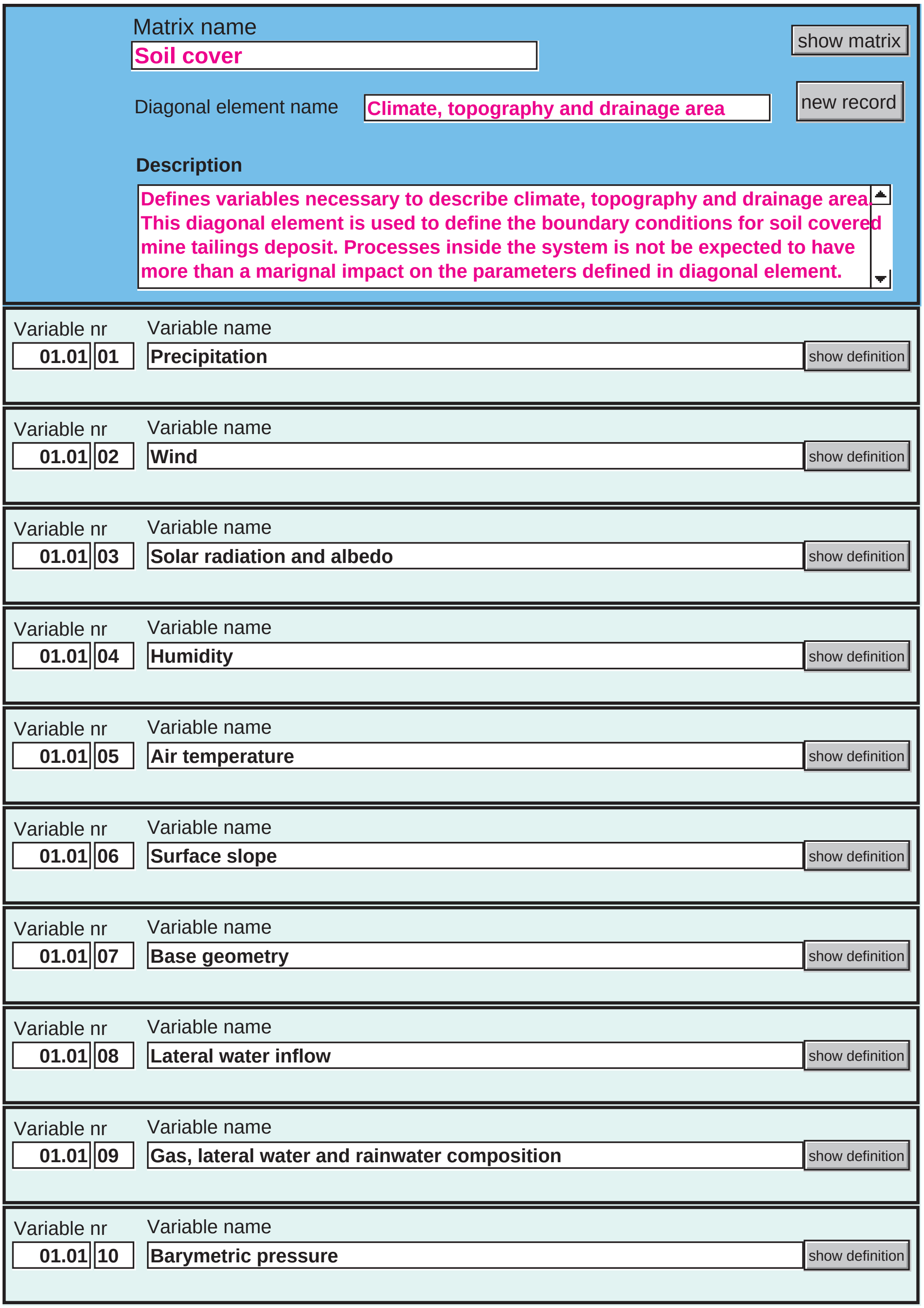
Version: 2003-04-21

01.01 [0] Climate, topography and drainage	01.02 2 ? [1][ ][ ]	01.03 9 ? [4][1][1]	01.04 1 OK [1][ ][ ]	01.05 1 OK [1][ ][ ]	01.06 4 OK [4][ ][ ]	01.07 1 OK [ ][1][ ]	01.08 1 OK [1][ ][ ]	01.09 4 OK [3][ ][1]	01.10 2 OK [2][ ][ ]	01.11 4 OK [2][2][ ]	01.12 1 OK [ ][ ][1]	01.13 2 ? [1][ ][ ]
02.01 ? ? [ ][ ][ ]	02.02 [?] Vegetation cover	02.03 4 ? [2][1][ ]	02.04 2 ? [1][ ][ ]	02.05 1 OK [ ][ ][1]	02.06 3 OK [2][1][ ]	02.07 3 OK [ ][ ][3]	02.08 3 OK [ ][ ][3]	02.09 2 OK [2][ ][ ]	02.10 1 ? [ ][ ][ ]	02.11 2 OK [2][ ][ ]	02.12 3 ? [2][ ][ ]	02.13 2 ? [ ][ ][1]
03.01 0 OK [ ][ ][ ]	03.02 2 ? [1][ ][ ]	03.03 [0] Protective cover	03.04 3 OK [1][1][1]	03.05 0 OK [ ][ ][ ]	03.06 7 OK [2][1][4]	03.07 0 OK [ ][ ][ ]	03.08 0 OK [ ][ ][ ]	03.09 4 OK [4][ ][ ]	03.10 3 OK [1][1][1]	03.11 4 OK [2][ ][2]	03.12 3 OK [3][ ][ ]	03.13 1 OK [1][ ][ ]
04.01 0 OK [ ][ ][ ]	04.02 ? ? [ ][ ][ ]	04.03 1 ? [ ][ ][ ]	04.04 [0] Sealing layer	04.05 1 OK [1][ ][ ]	04.06 0 OK [ ][ ][ ]	04.07 7 OK [1][4][2]	04.08 0 OK [ ][ ][ ]	04.09 4 OK [2][2][ ]	04.10 3 OK [1][2][ ]	04.11 4 OK [1][2][1]	04.12 3 OK [3][ ][ ]	04.13 0 OK [ ][ ][ ]
05.01 0 OK [ ][ ][ ]	05.02 ? ? [ ][ ][ ]	05.03 0 OK [ ][ ][ ]	05.04 1 ? [ ][ ][ ]	05.05 [0] Tailings	05.06 0 OK [ ][ ][ ]	05.07 0 OK [ ][ ][ ]	05.08 7 ? [ ][ ][ ]	05.09 4 ? [ ][ ][ ]	05.10 3 ? [ ][ ][ ]	05.11 4 ? [ ][ ][ ]	05.12 3 ? [ ][ ][ ]	05.13 1 ? [ ][ ][ ]
06.01 ? ? [ ][ ][ ]	06.02 1 ? [ ][ ][ ]	06.03 1 ? [ ][ ][ ]	06.04 0 OK [ ][ ][ ]	06.05 0 OK [ ][ ][ ]	06.06 [2] Protective cover: water & gas comp	06.07 3 ? [ ][ ][ ]	06.08 0 OK [ ][ ][ ]	06.09 ? ? [ ][ ][ ]	06.10 1 ? [ ][ ][ ]	06.11 ? ? [ ][ ][ ]	06.12 3 ? [ ][ ][ ]	06.13 2 ? [ ][ ][ ]
07.01 ? ? [ ][ ][ ]	07.02 ? ? [ ][ ][ ]	07.03 0 OK [ ][ ][ ]	07.04 ? ? [ ][ ][ ]	07.05 ? ? [ ][ ][ ]	07.06 3 ? [ ][ ][ ]	07.07 [?] Sealing layer: water & gas comp	07.08 3 ? [ ][ ][ ]	07.09 ? ? [ ][ ][ ]	07.10 1 ? [ ][ ][ ]	07.11 ? ? [ ][ ][ ]	07.12 3 ? [ ][ ][ ]	07.13 2 ? [ ][ ][ ]
08.01 ? ? [ ][ ][ ]	08.02 ? ? [ ][ ][ ]	08.03 0 OK [ ][ ][ ]	08.04 0 OK [ ][ ][ ]	08.05 ? ? [ ][ ][ ]	08.06 0 OK [ ][ ][ ]	08.07 3 ? [ ][ ][ ]	08.08 [?] Tailings: water & gas comp	08.09 ? ? [ ][ ][ ]	08.10 1 ? [ ][ ][ ]	08.11 ? ? [ ][ ][ ]	08.12 3 ? [ ][ ][ ]	08.13 2 ? [ ][ ][ ]
09.01 ? ? [ ][ ][ ]	09.02 ? ? [ ][ ][ ]	09.03 2 ? [1][ ][ ]	09.04 1 ? [ ][ ][ ]	09.05 1 ? [ ][ ][ ]	09.06 1 ? [ ][ ][ ]	09.07 1 ? [ ][ ][ ]	09.08 1 OK [1][ ][ ]	09.09 [?] Water transport	09.10 ? ? [ ][ ][ ]	09.11 1 ? [ ][ ][ ]	09.12 3 ? [ ][ ][ ]	09.13 4 ? [ ][ ][ ]
10.01 ? ? [ ][ ][ ]	10.02 ? ? [ ][ ][ ]	10.03 ? ? [ ][ ][ ]	10.04 ? ? [ ][ ][ ]	10.05 ? ? [ ][ ][ ]	10.06 1 ? [ ][ ][ ]	10.07 1 ? [ ][ ][ ]	10.08 1 ? [ ][ ][ ]	10.09 ? ? [ ][ ][ ]	10.10 [?] Gas flow	10.11 1 ? [ ][ ][ ]	10.12 ? ? [ ][ ][ ]	10.13 1 ? [ ][ ][ ]
11.01 ? ? [ ][ ][ ]	11.02 ? ? [ ][ ][ ]	11.03 1 ? [ ][ ][ ]	11.04 ? ? [ ][ ][ ]	11.05 ? ? [ ][ ][ ]	11.06 ? ? [ ][ ][ ]	11.07 ? ? [ ][ ][ ]	11.08 ? ? [ ][ ][ ]	11.09 ? ? [ ][ ][ ]	11.10 ? ? [ ][ ][ ]	11.11 [1] Temperature	11.12 3 ? [ ][ ][ ]	11.13 ? ? [ ][ ][ ]
12.01 ? ? [ ][ ][ ]	12.02 ? ? [ ][ ][ ]	12.03 ? ? [ ][ ][ ]	12.04 ? ? [ ][ ][ ]	12.05 ? ? [ ][ ][ ]	12.06 ? ? [ ][ ][ ]	12.07 ? ? [ ][ ][ ]	12.08 ? ? [ ][ ][ ]	12.09 ? ? [ ][ ][ ]	12.10 ? ? [ ][ ][ ]	12.11 3 ? [ ][ ][ ]	12.12 [?] Microbes & higher organisms, not plants	12.13 ? ? [ ][ ][ ]
13.01 ? ? [ ][ ][ ]	13.02 ? ? [ ][ ][ ]	13.03 1 ? [ ][ ][ ]	13.04 ? ? [ ][ ][ ]	13.05 ? ? [ ][ ][ ]	13.06 ? ? [ ][ ][ ]	13.07 ? ? [ ][ ][ ]	13.08 ? ? [ ][ ][ ]	13.09 ? ? [ ][ ][ ]	13.10 ? ? [ ][ ][ ]	13.11 ? ? [ ][ ][ ]	13.12 ? ? [ ][ ][ ]	13.13 [?] System output & contaminant release

🟪 Shows description of interactions between variables defined in the diagonal elements

🟦 Shows description of variables defined in the diagonal element

Figure 14-4 Example of interaction matrix constructed for soil covered tailings.



Matrix name
Soil cover

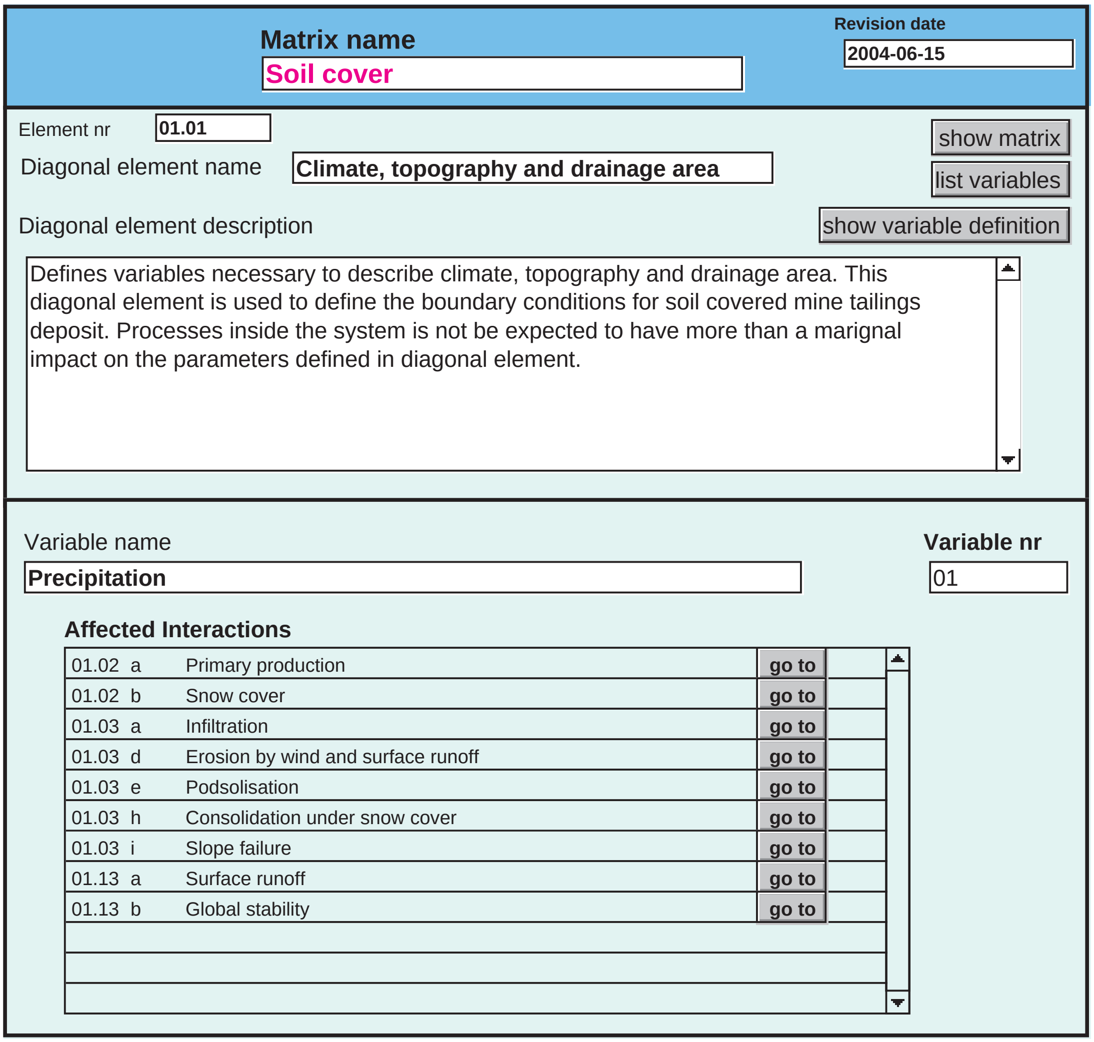
Diagonal element name **Climate, topography and drainage area**

Description

Defines variables necessary to describe climate, topography and drainage area. This diagonal element is used to define the boundary conditions for soil covered mine tailings deposit. Processes inside the system is not be expected to have more than a marignal impact on the parameters defined in diagonal element.

Variable nr		Variable name
01.01	**01**	**Precipitation**
01.01	**02**	**Wind**
01.01	**03**	**Solar radiation and albedo**
01.01	**04**	**Humidity**
01.01	**05**	**Air temperature**
01.01	**06**	**Surface slope**
01.01	**07**	**Base geometry**
01.01	**08**	**Lateral water inflow**
01.01	**09**	**Gas, lateral water and rainwater composition**
01.01	**10**	**Barymetric pressure**

Figure 14-5 Exemple of variable defined for the diagonal element *Climate, topography and drainage area*. In the interactive database application, clicking the button *show definition* leads the user to next level of definitions.



Matrix name
Soil cover

Revision date
2004-06-15

Element nr: **01.01**

Diagonal element name: **Climate, topography and drainage area**

Diagonal element description

Defines variables necessary to describe climate, topography and drainage area. This diagonal element is used to define the boundary conditions for soil covered mine tailings deposit. Processes inside the system is not be expected to have more than a marignal impact on the parameters defined in diagonal element.

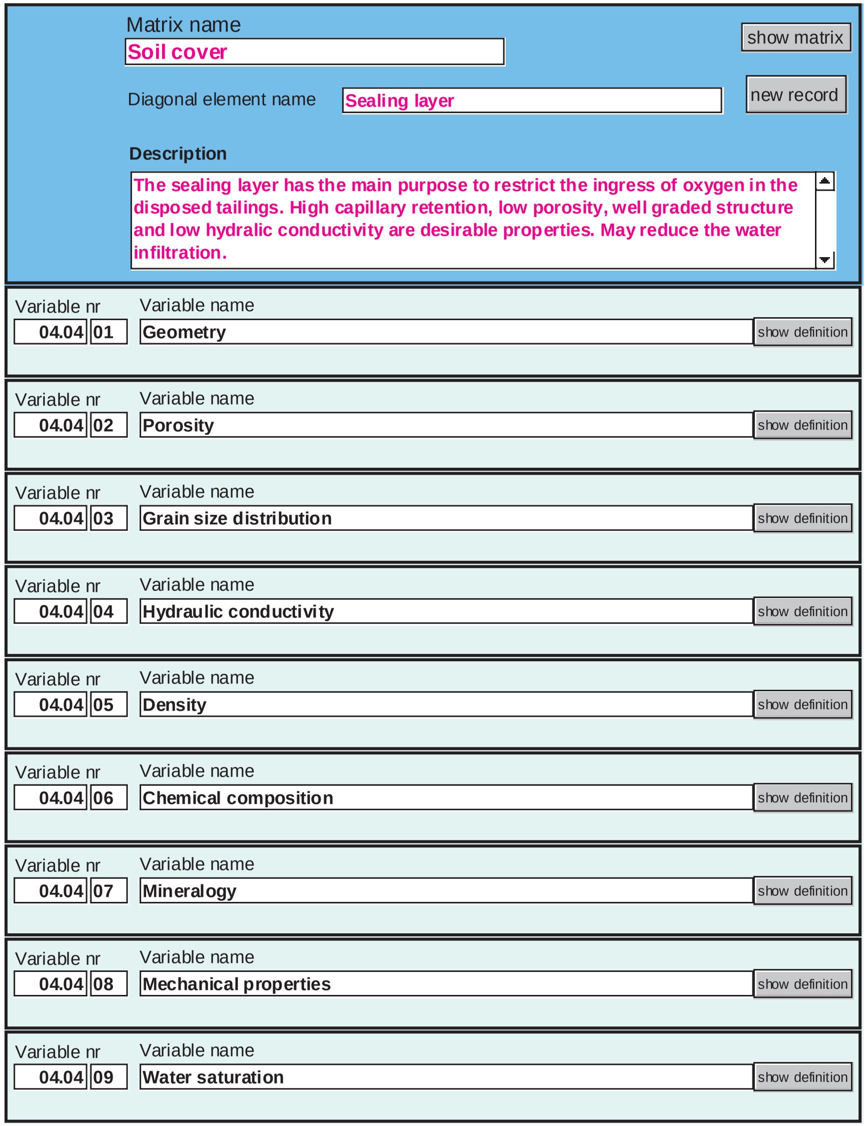
Variable name: **Precipitation**

Variable nr: 01

Affected Interactions

01.02	a	Primary production	go to
01.02	b	Snow cover	go to
01.03	a	Infiltration	go to
01.03	d	Erosion by wind and surface runoff	go to
01.03	e	Podsolisation	go to
01.03	h	Consolidation under snow cover	go to
01.03	i	Slope failure	go to
01.13	a	Surface runoff	go to
01.13	b	Global stability	go to

Figure 14-6 Example of the interaction identified to be affected by the variable *Lateral water inflow* which is a variable in the diagonal element *Climate, topography and drainage area*. The user of the interactive database can move directly to the affected interactions, or may also go back to the variable list or the large matrix.

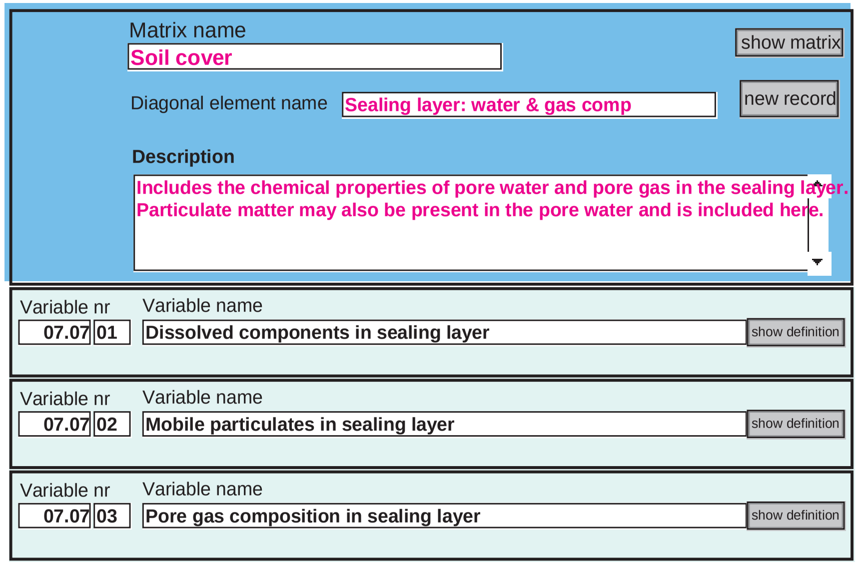


Matrix name
Soil cover

Diagonal element name: Sealing layer

Description
The sealing layer has the main purpose to restrict the ingress of oxygen in the disposed tailings. High capillary retention, low porosity, well graded structure and low hydralic conductivity are desirable properties. May reduce the water infiltration.

Variable nr		Variable name
04.04	01	Geometry
04.04	02	Porosity
04.04	03	Grain size distribution
04.04	04	Hydraulic conductivity
04.04	05	Density
04.04	06	Chemical composition
04.04	07	Mineralogy
04.04	08	Mechanical properties
04.04	09	Water saturation



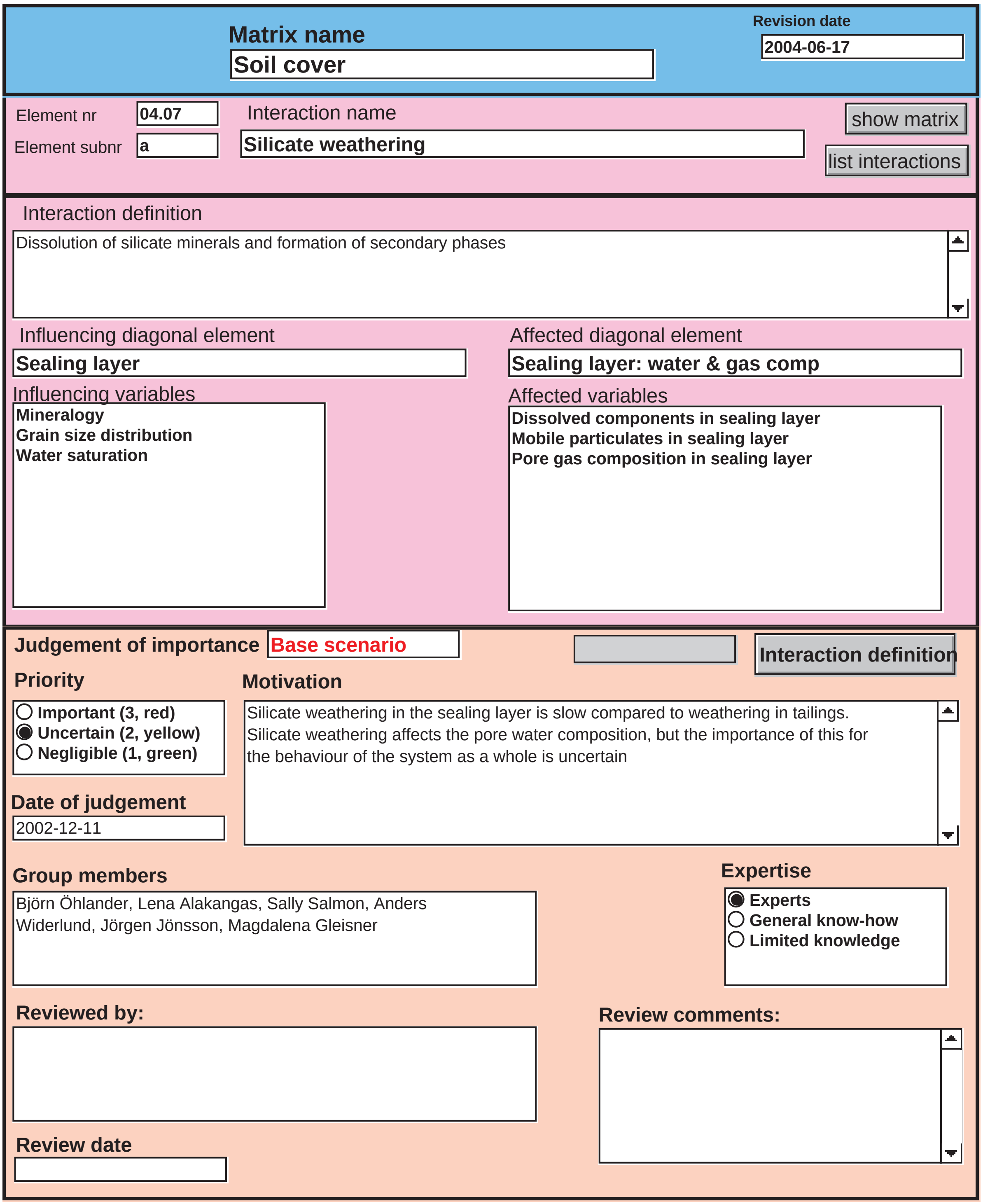
Matrix name
Soil cover

Diagonal element name: Sealing layer: water & gas comp

Description
Includes the chemical properties of pore water and pore gas in the sealing layer. Particulate matter may also be present in the pore water and is included here.

Variable nr		Variable name
07.07	01	Dissolved components in sealing layer
07.07	02	Mobile particulates in sealing layer
07.07	03	Pore gas composition in sealing layer

Figure 14-7 Two more examples of diagonal elements and identified variables defining the *Sealing layer* and the *Water and gas composition* of the sealing layer.



Matrix name: Soil cover

Revision date: 2004-06-17

Element nr: 04.07

Element subnr: a

Interaction name: Silicate weathering

Interaction definition: Dissolution of silicate minerals and formation of secondary phases

Influencing diagonal element: Sealing layer

Affected diagonal element: Sealing layer: water & gas comp

Influencing variables:
Mineralogy
Grain size distribution
Water saturation

Affected variables:
Dissolved components in sealing layer
Mobile particulates in sealing layer
Pore gas composition in sealing layer

Judgement of importance: Base scenario

Priority
○ Important (3, red)
● Uncertain (2, yellow)
○ Negligible (1, green)

Motivation: Silicate weathering in the sealing layer is slow compared to weathering in tailings. Silicate weathering affects the pore water composition, but the importance of this for the behaviour of the system as a whole is uncertain

Date of judgement: 2002-12-11

Group members: Björn Öhlander, Lena Alakangas, Sally Salmon, Anders Widerlund, Jörgen Jönsson, Magdalena Gleisner

Expertise
● Experts
○ General know-how
○ Limited knowledge

Reviewed by:

Review comments:

Review date

Figure 14-8 An example of a defined interaction between minerals and the pore water in the sealing layer. The figure also illustrates the documentation system for judgement, motivation and who made the judgement. Review and revision can also be made and documented.

15 Conclusions and recommendations

The results of seven years of research within the MiMi programme have provided insights and many opportunities to investigate both well-tested and new approaches to mine drainage mitigation, as well as to study specific processes that affect the environmental impact of mining activities. The research efforts have confirmed our previous understanding of dominating processes in and outside of tailings deposits, but have also led to a re-evaluation and re-interpretation of processes that were not as well understood.

The MiMi programme has assessed the performance of soil covers and water covers for the prevention and control of sulphide oxidation in mine tailings. The need for a holistic approach to this assessment has led to a refocus from detailed basic research to the more encompassing and integrated Performance Assessment methodology. This is a new development in the investigation of mine waste deposits, and requires a detailed analysis of the function of various barriers to oxygen diffusion and water infiltration, and to trace element mobilisation within and discharge from these deposits.

The results from MiMi's performance assessment confirm the necessity that the design criteria for the construction of barriers to oxygen and water intrusion into tailings deposits must be based on local conditions, including the acid neutralisation capacity of recipients. For a given construction the produced acidity and its impact on the recipient can be predicted. The primary acidity formed due to sulphide weathering may be neutralised by buffering reactions in the tailings, whereas the released latent acidity can only be accommodated by dilution and acid neutralisation due to mixing with the surface runoff. The composition of the mine tailings will obviously affect the effluent quality, and possibilities for minimizing the amount of waste and the sulphide content should be explored in all cases.

15.1 General

The performance assessment work has identified and provided quantitative estimates of the most important processes governing the performance of sulphidic mine tailings deposits over time. The performance of covered tailings deposits with respect to the release of contaminants is the result of a multitude of physical, chemical and biological processes. A full assessment of the immensely complex interactions of different processes in covered tailings is not conceivable. As a result of ongoing weathering processes in the deposits the conditions will change over time. This calls for an elaborate conceptualisation of the studied systems to allow for long term predictions. In this work, a structured way to finding appropriate simplifications is necessary. Some conclusions and insights of general interest are presented in the following.

Within the performance assessment work a systematic approach has been used to identify the most relevant features and processes. The assessments have used a quantitative approach, with particular emphasis on the long-term function of the studied remediation methods. The outcome of the studies is the result of a major effort undertaken by a multi-disciplinary group of scientists and engineering specialists.

15.2 Governing processes in disposed sulphidic tailings

Sulphide Oxidation and Acid Neutralisation

Mining activities usually give rise to significant quantities of mine tailings that need to be disposed. When the tailings contain sulphides they often need to be protected from contact with oxygen. Any oxygen that enters tailings will react with the sulphides present, mainly the iron sulphides pyrite and pyrrhotite, to form sulphate, acidity and dissolved metal ions. When tailings are covered, the oxygen intrusion rate is restricted and a reaction front will form where the oxygen is consumed. The oxidation of pyrite and pyrrhotite will produce acidity, which may be neutralised by buffering minerals in the deposit, such as aluminium silicates and calcite. The chemical conditions in the tailings will change in response to the acid generation and acid neutralisation, in particular the pH, which may in turn alter the conditions for different retention processes, such as adsorption. The basic processes of sulphide oxidation and acid neutralisation are illustrated in Figure 15-1. Initially, different receding reaction fronts will develop in the tailings, a sulphide oxidation front and acid neutralisation fronts that move with different velocities depending on the relative amounts of pyrite, calcite and reactive aluminium silicates.

The acid neutralisation by calcite is of particular interest since it is a very fast process in comparison with other common minerals present in mine tailings. If the tailings contain a substantial amount of calcite the release of acidity and trace elements to the recipient may be small over extended periods of time. However, the acidity produced by the pyrite oxidation will tend to consume the calcite. In addition, infiltrating water from rain and snowmelt, equilibrated with atmospheric carbon dioxide, will add to the consumption of calcite in the tailings. In the zones where calcite has been depleted, acid neutralisation will be provided by aluminium silicates in the tailings. In the same manner as for calcite, the acid neutralising silicate minerals will be consumed to varying degree depending on their abundance in the tailings.

Also, as a result of biological processes in the soil cover the concentration of carbon dioxide in infiltrating water may be significantly increased, at least during the summer. Due to this, increased amounts of carbon dioxide may be transported into the tailings with the infiltrating water. It has been shown in model calculations that an increased content of carbon dioxide would lead to a slightly decreased pH in the tailings porewater but also a more extensive acid neutralisation by different minerals in the tailings. When degassing of the excess carbon dioxide occurs as the leachate is released into the near-recipient, this would result in a slight increase of the pH. Hence, the ratio between oxygen and carbon dioxide that enters the tailings is of importance for the acidification effects in the near-recipients.

Consistent with theoretical estimates, observations from the obtained field data at Kristineberg show that 50-75% of the primary acidity produced in the oxidation of pyrite is neutralised by weathering of chlorite, a magnesium aluminium silicate. Field data suggest that further acid neutralisation may be provided by dissolution of calcite. Field observations show that both aluminium and magnesium are significantly decreased or depleted in the solid phase of the weathered zone of the old tailings, which supports the observations presented above. The acid neutralisation supplied by weathering of aluminium silicates will considerably prolong the persistence of calcite neutralised conditions in the disposed tailings.

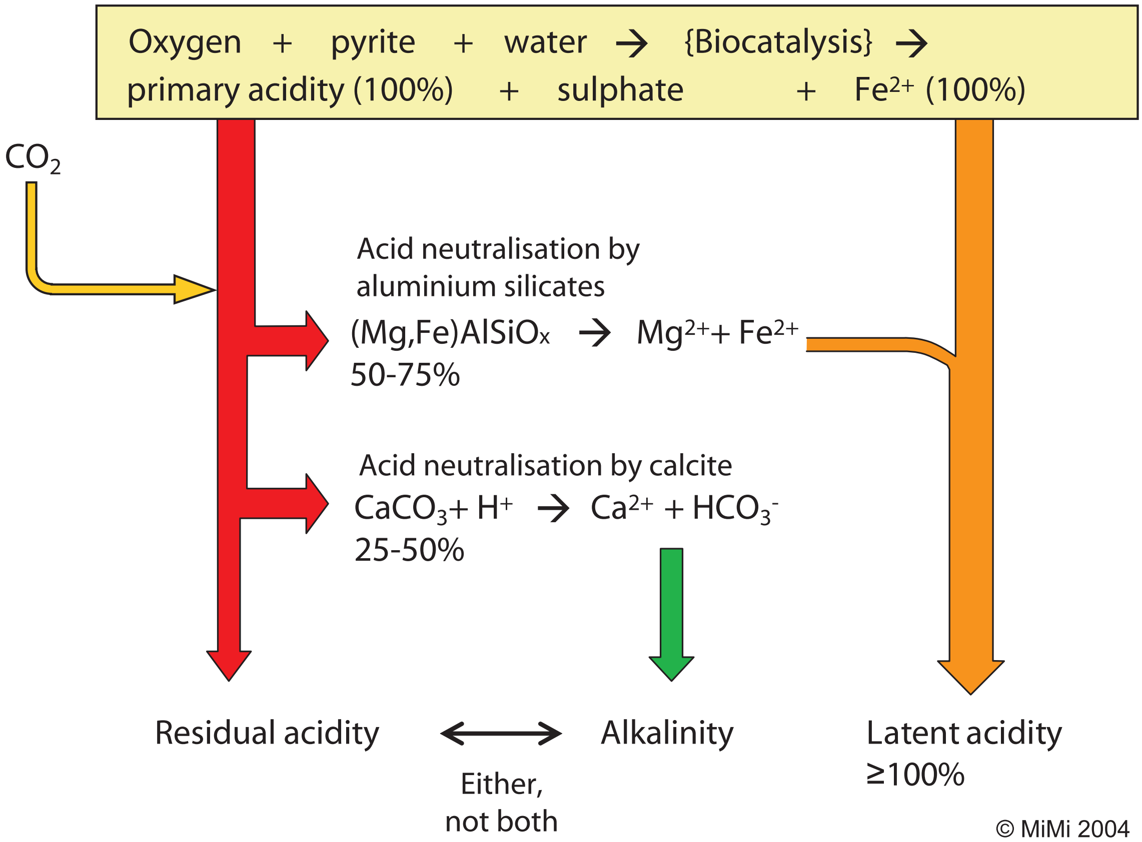


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Figure 15-1 Schematic illustration to the oxidation of pyrite causing primary and latent acidity, and different acid-neutralisation processes in mine tailings. Numbers refer to interpretations of present day situation at Kristineberg.

Latent Acidity

As a result of the primary weathering of pyrite in the tailings certain amounts of ferrous iron will be formed and transported by the leachate water. Due to the different acid neutralisation reactions this leachate water may be slightly acidic, neutral, or slightly alkaline. However, the ferrous iron can be regarded as an additional, latent acidity, in that further oxidation will occur when the leachate is released into ditches or other surface water bodies in contact with the atmosphere. There ferric iron is formed which hydrolyses and precipitates as ferric iron oxyhydroxide. The latent acidity is therefore expressed first when the leachate has been released to the surface water system. This means that the acid neutralisation capacity in the tailings material will not be effective for the latent acidity in the leachate water. Hence, any residual acidity (remaining after acid neutralisation processes in the tailings) and the latent acidity in the leachate water instead need to be neutralised downstream of the tailings impoundment. Such neutralisation may be provided by the buffering of the natural alkalinity of the surface runoff with which the leachate water is mixed. Although the neutralisation of primary acidity due to weathering of e.g. chlorite, or other aluminium silicate minerals that may contain appreciable amounts of ferrous iron (e.g. biotite), may add to the release of ferrous iron from the deposit and hence to the latent acidity, the amount of latent acidity formed is essentially proportional to the oxygen ingress in the disposed tailings. Under acidic conditions, neutralisation by chlorite, or other aluminium silicates, may also release dissolved aluminium, which may add to the latent acidity. At a given location, the amount of residual (primary) acidity and latent acidity that could be acceptable for the local recipient system would thereby set a requirement for the maximum oxygen intrusion into the disposed tailings, see illustration in Figure 15-2. Additional acid neutralisation may also be provided by liming of the downstream water system, though this is an active method and would be feasible during a limited period of time rather than as a long-term commitment.

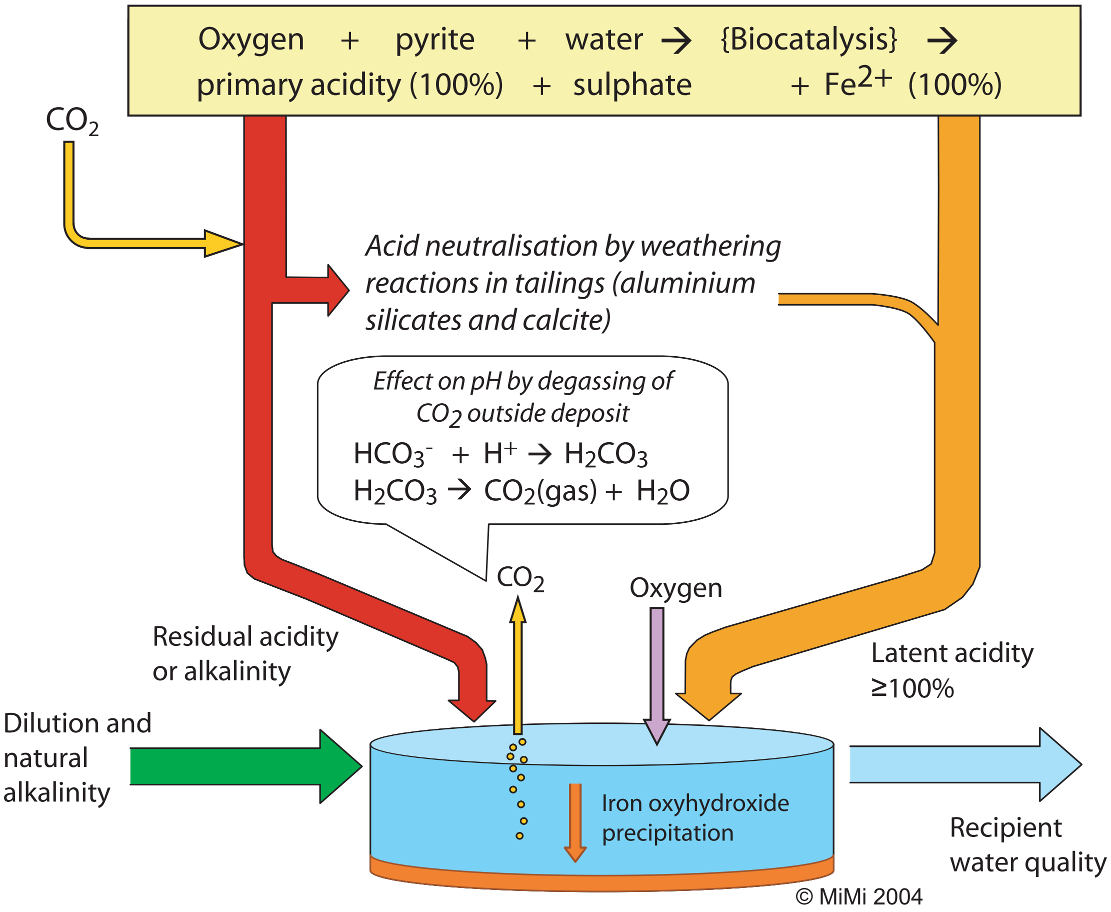

Figure 15-2 Schematic illustration to the overall system of acid generation and acid neutralisation at a sulphidic tailings deposit.

Formation of Siderite

A possible retainment process for the latent acidity could be formation of the mineral siderite, $FeCO_3(s)$. This iron(II)carbonate is abundant in nature and is known to form in freshwater sediments under anaerobic conditions. Thermodynamic studies, within MiMi and elsewhere, show that siderite could form below the oxidation front if carbonate minerals are present. However, it has not been possible to find supporting data from field studies that quantifiable amounts of siderite form as secondary mineral in tailings deposits. Indeed, the MiMi field observations show high concentrations of ferrous iron in the pore waters. This would not be observed if substantial siderite formation had occurred. Further, recent laboratory investigations reported in the literature suggest that the precipitation rate of siderite is about eight orders of magnitude slower than the precipitation rate of calcite. Due to lack of supporting field observations and the reported laboratory data on slow precipitation kinetics we conclude that siderite is not a credible retention mechanism for the latent acidity (i.e. dissolved ferrous iron) with today’s knowledge. In the performance assessment analysis this process has therefore been neglected.

Formation of solid oxides, sulphates, carbonates etc

Precipitation of iron and different trace metals as oxides, sulphates or carbonates may occur in the deposit or in its close vicinity. In limited supply, virtually all O_2 available is consumed by the oxidation of the most easily oxidised component, i.e. sulphide/disulphide is oxidised to sulphate. Hence, the ferrous iron remains unoxidised, and the chemical composition of the pore water in tailings is characterised primarily by its high concentrations of Fe^{2+} and SO_4^{2-}. Once exposed to atmospheric conditions the discharging groundwater Fe(II) is oxidised to Fe(III), which is readily hydrolysed and precipitated as oxyhydroxides or hydroxysulphates. In waters with high sulphate concentrations and low pH iron hydroxysulphates are commonly formed such as jarosite $(H,Na,K)Fe_3(OH)_6(SO_4)_2$ and schwertmannite $(Fe_8O_8(OH)_6SO_4)$. While jarosite is formed under strongly acidic conditions ($pH<\approx2.5$), schwertmannite precipitates in slightly less acidic waters. Experimental studies of schwertmannite have shown that a transformation to goethite may occur, a process accompanied with the release of acidity. It is therefore interesting to note that the formation of such mixed iron hydroxyl sulphates phases could act as a source of acidity when transformation to more stable iron oxyhydroxide takes place.

Under oxygen depleted conditions expected in covered tailings deposits, jarosites and other Fe(III) precipitates are less likely to be formed.

Other processes than sorption and secondary sulphide formation may also be active in regulating the attenuation of some metals within the deposit, and may thus affect the release to surrounding areas and surface waters. For example, lead may form low soluble carbonates and sulphates, and zinc may form low-soluble carbonates. However, the efficiency of carbonates to retain both zinc and lead is dependent on pH, as the solubility of the carbonates are generally higher at acidic pH. The formation and dissolution of carbonates also affects the alkalinity/acidity of the leachate.

Adsorption of trace elements on sulphides and formation of secondary sulphides

Different metal sulphides are dissolved in a congruent way at the oxidation front. This means that elements such as iron, copper, zinc, cadmium, lead and arsenic are released into the pore water. Different sulphide minerals in the tailings downstream the oxidation front will adsorb trace element from the pore water. Trace elements adsorbed to sulphides, in particular pyrrhotite, may also react to form secondary sulphides that are retained in the tailings. The mechanism responsible for this is the formation of secondary sulphides that are less soluble than the pyrrhotite. A generic formula for the process, simplifying the structure of pyrrhotite to FeS(s), would be (reaction 15-1):

$$Me^{2+} + FeS(s) \rightarrow MeS(s) + Fe^{2+} \tag{15-1}$$

In this process, iron is released as the secondary sulphide is precipitated. Strong evidence for the formation of secondary sulphides has been found for copper, probable evidence for cadmium and lead (although not unambiguously distinguishable from possible adsorption processes), and possible evidence for arsenic, in the collected field data from Kristineberg. These observations are also consistent with modelling results. As the weathering continues, more and more pyrrhotite will be consumed. If the pyrrhotite would become exhausted, the attenuation of metal ions due to the reaction above would cease. Formation of secondary sulphides as a result of reactions with pyrite is also conceivable. However, firm and conclusive evidence for such a process is lacking in the literature as well as within MiMi research results.

The mechanism for arsenic immobilisation is not necessarily the same as described above. Recent experimental findings report that arsenic may be adsorbed or incorporated in the mineral structure of pyrite. The structure found has a certain resemblance with arsenopyrite, though this mineral would not be expected to form under low temperature and pressure conditions. In effect, the arsenic seems to be strongly captured by such a process which would be consistent with the field observations from Kristineberg. Lacking reliable data, modelling has not been able to predict this effect.

Zinc does not form sulphides of low enough solubility to replace iron in pyrrhotite to appreciable extent. Hence, zinc can to a larger extent be expected to be released from the deposit. This is also consistent with field observations where the zinc release is greater in comparison with the other trace metals.

Different processes leading to immobilisation of trace elements in the tailings are schematically depicted in Figure 15-3.

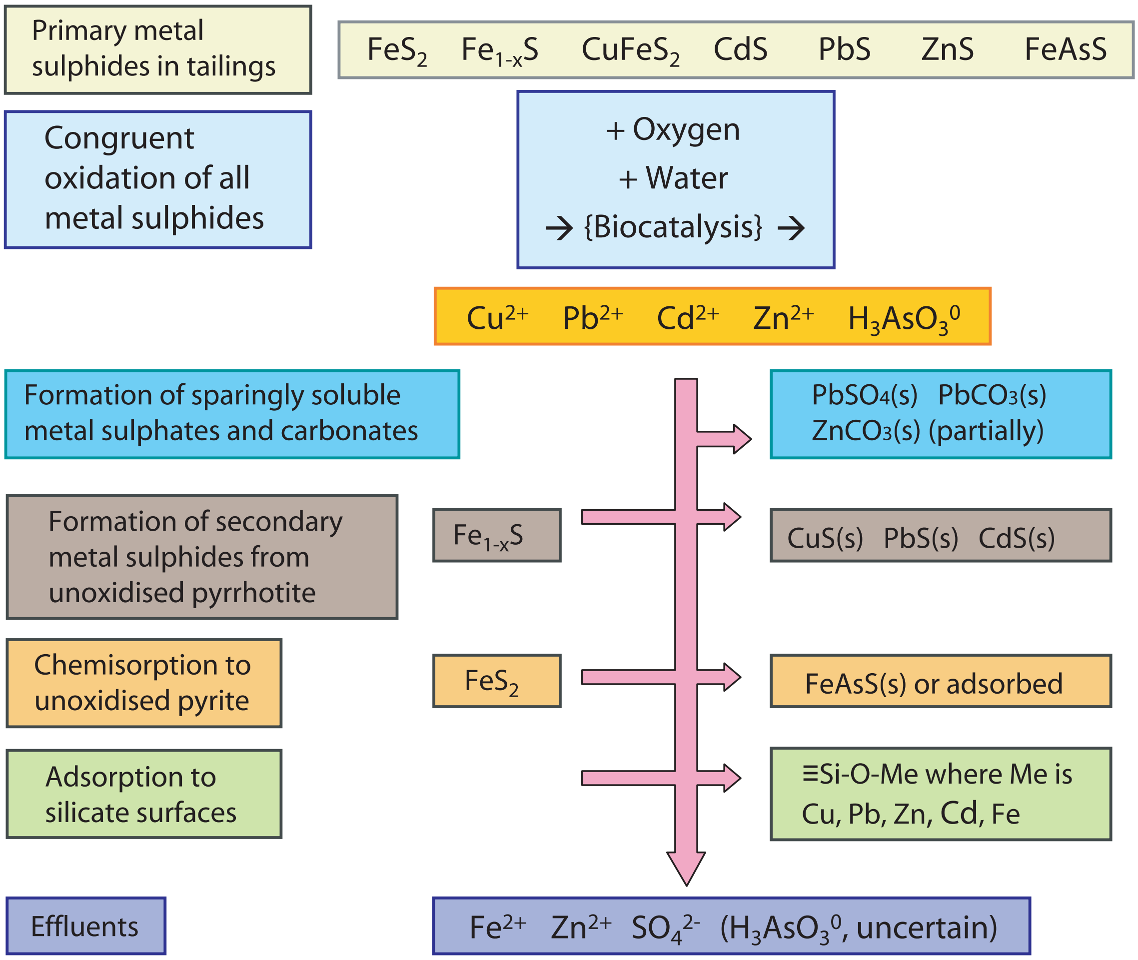

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Figure 15-3 Illustration to different chemical processes in sulphidic mine tailings leading to immobilisation of trace elements within the deposits.

Adsorption of metals to silicate minerals

Different silicate minerals are abundant in mine tailings. Silicates often constitute more than 50% of the tailings mass. The specific surface area is high due to crushing and grinding. The high surface area means that a large number of adsorption sites are exposed to the interstitial porewater. Different trace elements dissolved in the porewater may interact with the sorption sites at the silicate surfaces and form ion exchange and surface complexes that are attached to the solid surface. The affinity of different trace elements to form surface complexes varies with pH and redox state. Different trace elements may also compete for the available surface sites. At a given pH, the fraction of surface sites occupied by different trace elements increases with increasing concentrations of the trace metals. The amount of surface sites depends on the composition of the silicate minerals, but can be estimated in the order of ten to hundred mol/m^3 tailings. The maximum amount of trace metals that can be adsorbed to these sorption sites has been estimated in the order of a few kg/m^3 tailings. However, many of these surface sites may to a significant part be occupied by metals released during processing in the dressing plant. These estimates show that adsorption to the surface of silicate minerals in the tailings can accommodate only a part of the metals that are mobilised by the weathering processes. The adsorption may lead to reduced release rates of trace elements to the near-recipient during a period of some years. Adsorption of trace elements to silicate minerals in the tailings are therefore judged to be of low to intermediate importance for the regulation for the overall release to the recipients.

Effect of transport time on the release to recipients

The above mentioned processes, leading to acid neutralisation and capture of different metals and metalloids as secondary precipitates, are relevant for the upstream and central parts of the tailings deposits where the leachate water has a long transport distance, and corresponding transport time, from the active oxidation front to the exfiltration in the near-recipient, e.g. a ditch. The flow of water and contaminants through the disposed tailings may also be influenced by the occurrence of preferential flow paths, which would reduce the residence time and decrease the contact area between water and reactive mineral surfaces. A long path ensures that sufficient contact with reactive mineral surfaces is offered for the slow acid neutralisation reactions to occur to an appreciable extent. The formation of secondary sulphide precipitates requires that metals released by the primary weathering are brought in contact with more soluble sulphide phases, in particular pyrrhotite, in the unweathered tailings. Since pyrrhotite is often present in small amount (in the order of a percent), it may gradually become depleted and a moving reaction front would develop. The rate, by which such a front moves, is dependent on the rate of oxidation at the weathering front, the amount of metals released which may form secondary low-soluble sulphide precipitates and the amount of pyrrhotite.

The situation close to the edge of the tailings deposit is somewhat different. Leachate formed near the edge of the deposit may have a very short transport distance to the exfiltration area in the near-recipient. Therefore the contact time may be too short to allow for an efficient acid neutralisation. It can be expected that any initial calcite would contribute to the acid neutralisation with reasonable efficiency, whereas, the acid neutralisation due to weathering of aluminium silicates would be expected to be less effective due to slow reaction kinetics. Estimates made within MiMi show that a zone of a few meters may be subjected to a reduced acid neutralisation capacity due to the edge effects. This may be important also for the formation of secondary sulphide precipitates which may occur only as long as pyrrhotite remains in the tailings downstream the weathering zone, hence the process will cease when pyrrhotite becomes depleted, which would occur first near the edge of the deposit.

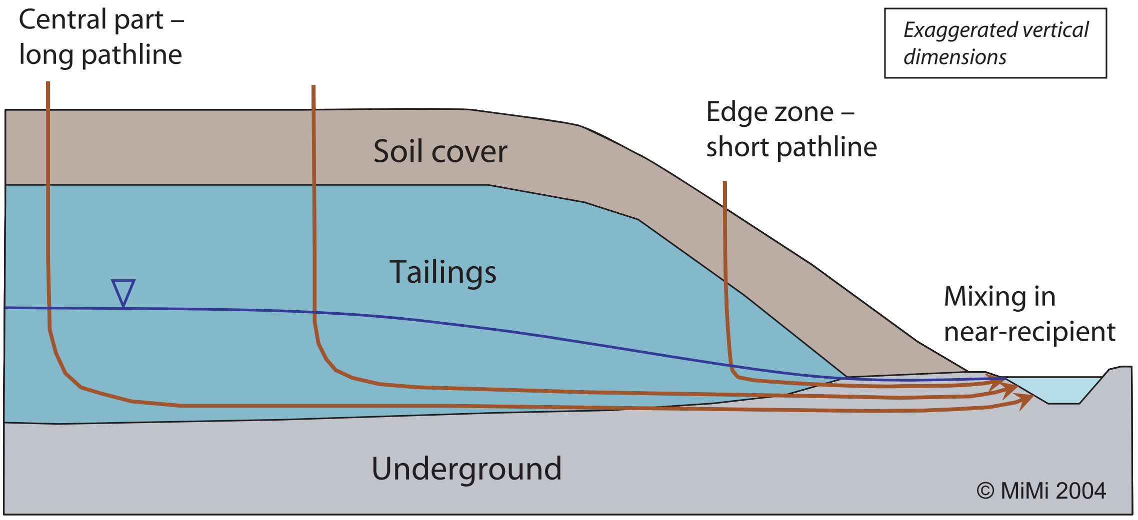

Figure 15-4 Schematic illustration to the contribution of different flowpath lines to the total leachate released into the near-recipient. The long pathline from the inner parts of the deposit represents long contact time between leachate and tailings material.

It should be emphasised that the water quality encountered in the near-recipient is an integral effect of the leachate water expelled from both the central part and the edge zones of the deposit, as illustrated in Figure 15-4. The different leachate waters mix and the water quality may be further influenced by different biogeochemical reactions that occur near the exfiltration point. Hence, even if the water quality would be satisfying in the central parts of a deposit, this is not a guarantee for good water quality in the near-recipient, considering the impact by mixing of leachate from the edge zones and the effects of latent acidity upon oxidation. The additional effect of the edge zone may need special consideration in the remediation plans.

Impact of microorganisms

A number of reactions of interest in disposed tailings (e.g. sulphide and iron oxidation) are influenced by microbial metabolism. By influencing the reactions, the microorganisms have the ability to increase the reaction rates, under the appropriate conditions. However, the overall oxygen consumption rate also depends on the availability of reactants, and the reaction rates may slow down due to accumulation of reaction products.

One important microbially mediated reaction is the oxidation of metal sulphides by oxygen. Under well oxygenated conditions the oxygen consumption rate can be significantly increased by microbial catalysis. However, in tailings covered by soil or water, only small amounts of oxygen are transported into the tailings; therefore, in this case the overall oxygen consumption rate is limited and controlled by the intrusion rate of oxygen, despite microbial catalysis. Different estimates show that, for covered systems, the overall oxygen consumption rates are much lower than would be expected in uncovered systems. Chemical reaction rates alone would be sufficient to explain the oxygen consumption rates. This observation does not indicate that bacteria are not participating in the oxidation reactions, but suggests that their activity is limited since the overall sulphide oxidation rates can be explained without considering the effect of sulphide-oxidizing bacteria.

Field observations at Kristineberg show a significant loss of iron from the oxidised zone. However, minor amounts of iron sulphides may still remain in the tailings when the receding oxidation front has passed, e.g. due to passivation by secondary minerals forming at the surfaces of the sulphide minerals. Further, the dissolved ferrous iron may be incompletely washed away by the percolating water and trapped in pockets of stagnant pore water, or may be transported back to the oxidised zone above the oxidation front as a result of upward molecular diffusion or periodical fluctuations of the groundwater table. Only small amounts of iron are expected to be available in the oxidised zone above the oxidation front due to these processes, as compared to the amount of iron released from the sulphide oxidation process. Nevertheless, the presence of small amounts of ferrous iron above the oxidation front could be sufficient to sustain a population of iron oxidising bacteria. Field investigations at Kristineberg have indeed identified high numbers of iron-oxidizing bacteria in the oxidised zone close to the pyrite oxidation front, whereas iron-oxidizing bacteria were not identified below the oxidation front.

Another example of microbially mediated processes is the oxidation of ferrous iron to ferric iron in the effluent zones, which is the reaction responsible for the acidification caused by the latent acidity. At slightly alkaline or neutral pH the chemical reaction rate is fast and would proceed at a significant rate. However, due to the acidity released by hydrolysis of the ferric iron the pH usually drops. Under acidic conditions, catalysis by iron-oxidizing bacteria is necessary for the reaction to occur at an appreciable rate. Extensive field observations confirm the microbial catalysis of this reaction under acidic conditions in surface water bodies receiving mine drainage waters containing ferrous iron.

A result of the growth of microorganisms (e.g. bacteria) in a tailings impoundment is the accumulation of biomass where these organisms are present. This biomass consists of living cells, dead cells, and organic degradation products. The accumulation of organic material is suggested by the presence of heterotrophic bacteria in these areas – bacteria that use organic matter as carbon source. Although organic carbon can bind metals, this is not considered a significant process in the tailings since concentrations of total organic carbon are very low. Organic carbon in dissolved form has also been measured, but sulphate complexation with dissolved metals will greatly out-compete complexation with organic compounds, because of the much greater concentrations of dissolved sulphate.

Studies within the MiMi programme have shown that iron- and sulphide-oxidizing bacteria are present within and outside the tailings impoundments. Therefore, in MiMi´s Performance Assessment work, microorganisms are assumed to be omnipresent and effective in their catalysis of metal sulphide oxidation and ferrous iron oxidation. However, the overall reaction rate of metal sulphide oxidation in covered deposits will not be controlled by the microbial catalysis, but rather by the supply of oxygen.

Sulphate reducing bacteria are frequently found in a wide range of ecological systems where the requirements of organic substrates and dissolved sulphate are fulfilled. The organisms are found in greatest numbers in anaerobic environments, although the absence of oxygen is no longer considered necessary for sulphate reduction. The use of sulphate reducing bacteria in the treatment of acid mine drainage is favourable in many respects: sulphate reduction can result in increased pH and precipitation of metal sulphides. Continuous supply of a suitable nutrient source is, however, needed to establish and maintain sulphate reduction. The amount of organic carbon is likely to be a limiting factor for the activity of sulphate reducing bacteria in many tailings impoundments. Different constructed systems have been employed using sulphate-reducing bacteria that include: artificial wetlands, fixed-bed anaerobic filters, and sludge reactors.

15.3 Conclusions – Soil covers

The soil cover technique is a passive method which has been found to be fairly robust. Soil cover technique is applicable to many different situations including tailings deposited in drained areas. Soil covers are therefore important components for remediation of complex mining areas where combinations of different methods may be used to develop an optimised concept. Soil covers and water covers have both been regarded as best available techniques according to EU.

The material used for the covers are natural tills that have proven to be persistent over very long time. Natural till deposits are present almost everywhere in the central and northern part of Sweden and may supply ample evidence as natural analogues for the possibility to construct long term stable deposits if designed correctly.

Soil covers have been shown to restrict the oxygen flux into disposed tailings and hence restrict the weathering of metal sulphides. Thereby the soil cover technique fulfils its purpose to mitigate the production of acid mine drainage. A prerequisite for the function is that the water balance in the sealing layer of the soil cover can be maintained over long time. Further, the local availability of suitable soil qualities in sufficient amounts is necessary for soil covering to be a viable remediation option.

The performance assessment analysis has shown that the weathering of sulphides can be expected to be significantly reduced, but does not stop entirely. Since there will be a certain level of acidity production, the availability of acid neutralising material in the tailings deposit is a requirement for the leachate water to be close to neutral when released to the recipient.

Remediation of mine tailings needs to account for site-specific factors including the recipient conditions. The impact on the recipient is to a large degree dependent on the reduction of oxygen intrusion. For soil covered tailings the primary produced acidity may be expected to be significantly counteracted by internal acid neutralisation by the tailings themselves. The latent acidity will be expressed first when the leachate has reached the near-recipient. The latent acidity is of the same magnitude as the primary acidity and acid neutralisation for the latent acidity will have to be provided by the downstream system. Acid neutralisation may be achieved by dilution and natural alkalinity in surface runoff with which the leachate is mixed. During operation, this can also be achieved by active liming or supply of other acid neutralising materials in the near-recipient system, i.e. in ditches or leachate collection ponds. To avoid acidification of the recipients the dilution and natural alkalinity will provide direct criteria for the necessary protection against oxygen intrusion. The reason for this is that the oxygen intrusion is directly transferable to the amount of acidity formed, in particular the latent acidity.

The protection against oxygen intrusion is to a large degree dependent on the possibility to construct a soil cover that can maintain high water saturation in at least part of its structure. In Sweden, the most common technique consists of a sealing layer with low permeability and high capillarity, over which is placed a protective layer of more permeable and less water retaining soil. The capillary characteristics and the hydraulic conductivity of the sealing layer in combination with the climatic and hydrological conditions will determine the effectiveness of the soil cover to restrict the oxygen flux. Modelling studies and field observations show that the soil covers are effective in restricting the oxygen intrusion, but during periods of drought the sealing layer may partly be drained with significantly increased oxygen ingress as a result. This effect could be counteracted by e.g. increased thickness of the sealing layer and the protective cover, however at a significant cost. Installation of a synthetic liner might be effective in the short-term perspective, but due to questionable durability over longer time it must be disregarded as a viable permanent option.

Well graded till materials have favourable properties for construction of soil covers. Well graded means that the particle size distribution is such that the voids between the larger particles are filled out by successively smaller particles to create a material with low porosity and low hydraulic conductivity. This means that a certain content of clay is necessary, but it does not need to be very high in order to achieve a low hydraulic conductivity. Well graded till also has favourable strength and deformation characteristics. In most places in Sweden, till deposits of suitable quality can be found.

The hydraulic conductivity of the sealing layer is strongly dependent on the degree of compaction. It is therefore necessary to compact the soil during construction of the soil cover. As a result of compaction, a less permeable and more water retaining sealing layer can be obtained. However, laboratory studies within MiMi and elsewhere have shown that the hydraulic conductivity of the sealing layer is vulnerable to freeze and thaw. This is particularly a problem for so called over-consolidated soils. Over-consolidation in this application means that the sealing layer has been heavily compacted during construction of the cover to a degree that is in excess of the passive overload of the protective cover, i.e. its weight. After only one, or a few, frost cycles the sealing layer has been restored to the degree of compaction corresponding to the passive overload and a corresponding hydraulic conductivity. For the till studied within MiMi investigations, the hydraulic conductivity increased by a factor in the order of ten when exposed to a few cycles of freezing and thawing. No large displacements of grains were required to obtain this increase of the hydraulic conductivity. Samples of the same till that were compacted to a somewhat lower density (about 2100 kg/m^3 compared to 2190 kg/m^3) likewise showed a factor of ten higher hydraulic conductivity. The strong dependence of compaction result on the hydraulic conductivity underlines the importance of adequate testing of compaction and hydraulic conductivity when designing a cover. The studies of the frost depth at the Kristineberg mine site shows that during the run of the MiMi field studies, i.e. 1998-2002, the frost has at the most reached to the depth of 1.0 m below the ground surface, about 0.5 m above the sealing layer. This is not a proof that frost cannot reach deeper at some time in the future; extreme events are certainly possible, such as a cold winter with very thin snow cover. However, calculations of frost depth, based on analyses of a large amount of observations of frost depth in different soils as a function of cold amount and the impact of snow cover on frost depth as presented by Knutsson (2004), show that the probability for frost depths greater than 1.5 m is small. It should be observed though, that this conclusion is based on the assumption that measured cold amounts from the hitherto series of measurements of temperature in Sweden (comprising a series of about 100 years) is representative also on a longer time scale.

Root intrusion in sealing layers would probably create root channels that in the end can form macropores, and lead to higher permeability and oxygen diffusivity of the layer. However, root intrusion in layers of highly compacted fine-grained till seems to be less probable. Previous research show that roots do not penetrate into fine-grained soils if higher stress than 3-5 MPa are required for penetration, which is deemed to be the case for sealing layers that are adequately compacted and protected from processes that may decrease the over-consolidation state reached by compaction (e.g. frost action).

The protective cover should protect the sealing layer from effects such as drying by evaporation, frost action, root penetration and erosion. However, the protective cover may itself be vulnerable to erosion. If large amounts of water accumulate in the soil cover it is important that lateral runoff can take place in the protective soil. In many cases the tailings deposits cover large areas and have a flat surface. This means that, following a major rain event, large amounts of water need to be expelled from the top of the impoundment. Of major importance for Swedish climate is also the period of snowmelt, commonly accounting for a significant part of the annual runoff, occurring during a period of a few weeks. Diversion of water can occur as a combination of different processes: percolation into the sealing layer and the tailings, lateral runoff in the protective layer, surface runoff, and evapotranspiration to the atmosphere (see

Figure 15-5). For Swedish climate, the evapotranspiration may accommodate only part of this. Provided that the sealing layer has a low hydraulic conductivity, the percolation will also be restricted. Hence, a lateral transport of water must account for the remaining part. If the surface area is large, this means that huge amounts of water need to be transported towards the edges of the deposit. If the runoff is slow this means that the water table will rise in the protective cover, eventually resulting in the formation of ponds within the deposits. Runoff of large amounts of water could mean a risk for overcresting, if the ponds reach the crest of the deposit. Another effect could be the establishment of exfiltration zones in the slopes. When such zones develop there is a risk for inner erosion of the protective soil. Both overcresting and inner erosion may result in local erosion zones in the cover, ultimately resulting in parts of the tailings being exposed. The potentially harmful effects of erosion may be prevented by an appropriate selection of soil material for the protective cover, which should not have too low hydraulic conductivity. Further, the surface of the deposit may be shaped in order to create runoff paths that are protected from erosion by gravel or other means. The design of the protective cover should consider the ability to divert water. Slopes need to be dimensioned to allow for a lateral runoff without risk for inner erosion or sliding due to high pore pressure; generally this means that slopes of low angle need to be used. In order to reduce the risk for high pore pressure, the base of the slope should be well drained and not be in direct contact with water, such as in ditches or ponds.

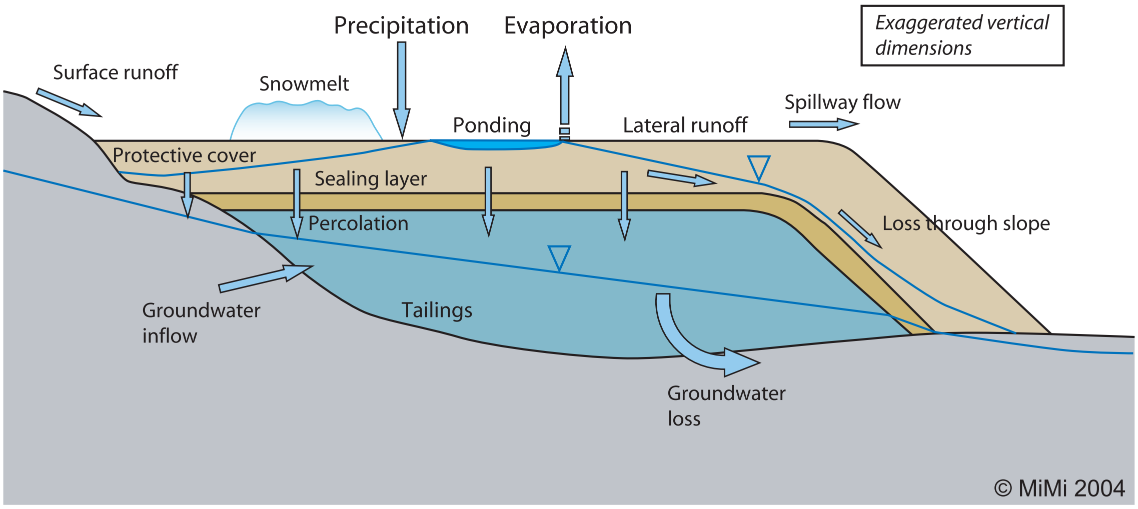

Figure 15-5 Illustration of the water balance in soil covered tailings deposits.

The hydraulic situation in the groundwater zone of the tailings also needs some consideration. The infiltrating water and the laterally inflowing groundwater must be transported away from the deposit in a controlled way. A critical point is again the downstream exfiltration area where excessive pore pressures must be avoided. If accumulation of groundwater occurs, this would result in a raised groundwater table in the tailings. Near the edges of the deposit, a raised groundwater table could mean that the lower parts of the slopes of the soil cover may act to dam up groundwater, eventually creating a situation where inner erosion or sliding of the soil and parts of the tailings may occur. Therefore, the impact of internal and external erosion processes needs to be considered in the design of the slopes.

Consideration of some extreme events for soil covered tailings

In the performance assessment the effects of prolonged and extremely dry periods have been studied for soil covered deposits. It has been found that even very long dry periods will only marginally affect the water content of the sealing layer. Not even for a consecutive five year period of drought summers, with normal winter precipitation, the oxygen intrusion rate would change noticeably.

The performance assessment studies have also shown that even for dramatic failure scenarios, such as a major erosion damage, the consequences will be limited, although not necessarily desirable. This would lead to a drastic increase of the local oxygen exposure, whereas the effect on the overall tailings deposit remains limited since the damage would not, with any reasonable likelihood, cover a major part of the deposit. Further, the maximum oxidation rate would become limited by either the intrusion of oxygen or the reaction kinetics. If deep erosion damages would occur in the soil cover, an evaluation of this scenario has shown that a certain self-healing may even be expected. Similar conclusions can be drawn considering a possible slope failure in a part of the deposit. Although this may lead to exposure of a larger portion of the tailings, it is still deemed to be minor compared to the area of the deposit.

If an extreme event would occur, such as the one described in this section, the processes are fairly slow and active measures would be possible to take.

15.4 Conclusions – Water covers

Water covers can be applied to mine tailings in order to restrict the exposure to oxygen. The transport of oxygen by diffusion in water saturated tailings is slow. When compared to the diffusion of oxygen in air the rate is approximately 10 000 times slower. Hence, if diffusion could be ensured to be the governing transport mechanism this would be a powerful barrier. Further, the solubility of oxygen in water is only about 0.3-0.4 mol/m^3, equivalent to 10-15 mg/l, depending on temperature. To compare, the oxygen content in air is about 9.4 mol/m^3, equivalent to 300 mg O_2/l. The low oxygen solubility in water is therefore a significant barrier to oxygen intrusion in water covered tailings. Soil covers and water covers have both been regarded as best available techniques according to EU.

For diffusion to be the governing transport mechanism, the water must be stagnant and not allowed to be mixed. Within the submerged tailings this criterion is most likely fulfilled and diffusion can be expected to control the oxygen ingress. However, in the water column that protects the tailings from contact with the air the situation is different. As a result of wind, water will be forced to flow in the same direction as the wind near the surface. An equally large stream of water will sweep over the bottom in the opposite direction. This will cause a major current in the water column which will bring down oxygenated water to the top of the tailings.

The wind will also induce waves, which will cause local circulation of water in the water column. This effect of local currents in the water is superimposed on the major current described above. Under conditions when the waves reach a certain height the local mixing will extend to the surface of the submerged tailings and resuspension may occur.

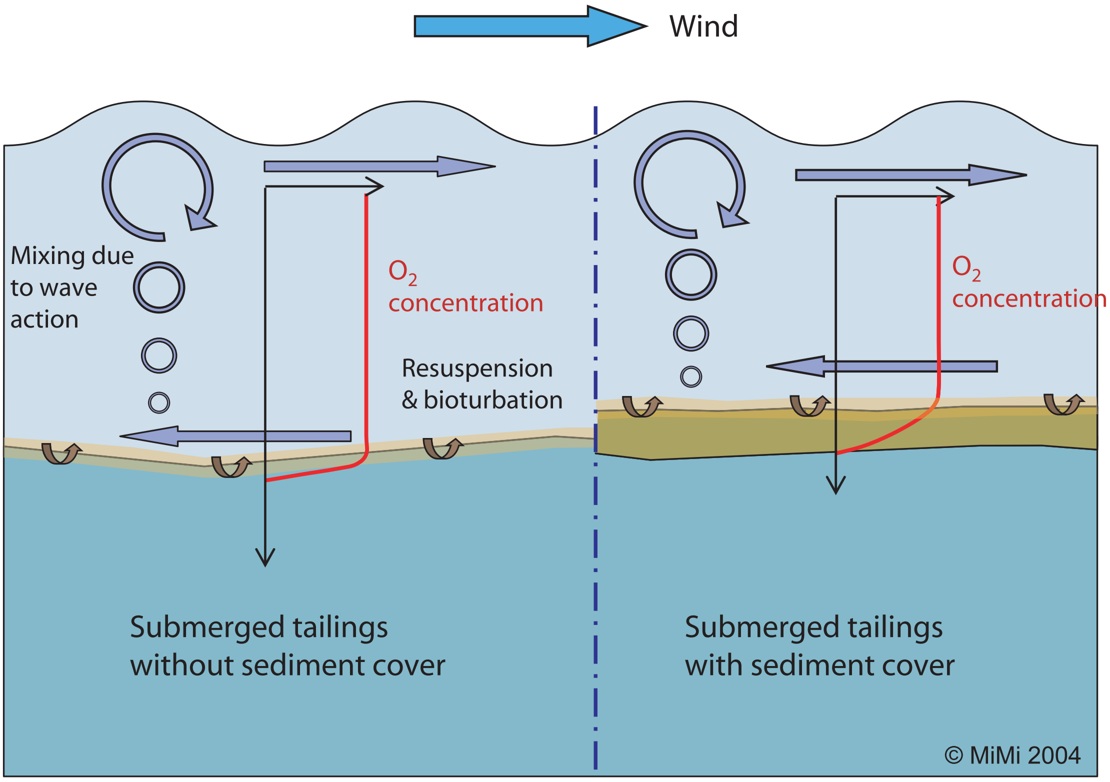

Figure 15-6 Illustration of the transport of oxygen from the water column to the submerged tailings. Influence by wind, wave action, resuspension and bioturbation is indicated. To the right, a thin sediment cover has been applied to improve the performance.

In effect, these mechanical mixing processes will enhance the transport of oxygen from the water surface to the bottom water where it will contribute to the oxygen ingress in the submerged tailings. Field observations show that the entire water column in tailings impoundments remains essentially fully saturated with respect to oxygen. In order to reduce the risk for resuspension, breakwaters can be constructed which will restrict the maximum wave height for a given situation.

Considering the presence of fully oxygenated water in contact with the tailings surface, the estimated ingress of oxygen will initially be large when fresh tailings are in contact with oxygenated water. For these conditions, estimates show that the initial overall iron sulphide oxidation rate is limited by the reaction kinetics. Gradually a sulphide depleted tailings layer will form, through which the oxygen will have to diffuse. The diffusion distance will gradually increase with time and the oxidation rate decrease. Factors such as resuspension and bioturbation will tend to prolong the period before the diffusion rate will be the limiting factor. Natural sedimentation on the tailings surface is a process that would tend to provide a protective cover which further would decrease the intrusion of oxygen. A possibility exists to provide a thin sediment cover as a component of the remediation plan, as illustrated in Figure 15-6, which may significantly improve the protection against oxygen intrusion during the initial phase.

Provided that the constructions are such that no resuspension occurs, the rate of oxidation after some decades will become lower than that in the Soil cover base case. Thereafter it will gradually decrease over time. However, there is a major difference in the release mechanisms of both trace elements and acidity. This is discussed in the following paragraphs.

The oxidation of metal sulphides in the submerged tailings will produce acidity and dissolved metals. Due to the close proximity to the overlying water column, upward diffusion of released components will start immediately. To a certain extent, diffusion will also occur into the deeper parts of the tailings, however, due to the diffusion resistance a build-up of the concentration will occur, which results in gradually decreasing concentration gradients downwards. Due to this, an asymmetric concentration gradient will develop, leading to upward diffusion of the major part of the released reaction products into the water column. Hence, only minor acid neutralisation by calcite or aluminium silicates in the tailings can be accounted for. Therefore, most of the primary acidity formed will have to be neutralised by the surface water system, unless the tailings have a high content of calcite. The latent acidity formed as a result of weathering would also need to be neutralised by the surface water system. This means that, for a comparable oxygen ingress rate, about the double acidity loading to the surface water system is to be expected, as compared to when primary acidity is neutralised in the tailings.

The release of ferrous iron into the oxygenated water column can be expected to result in oxidation to ferric iron, followed by hydrolysis and subsequent formation of ferric iron oxyhydroxide precipitates. Depending on the water residence time and the ability of the surface water body to accommodate the released acidity by means of acid neutralisation, the oxidation process may occur to varying degrees within the impoundment. If the acid neutralisation and pH-buffering is high, the iron is expected to rapidly oxidise and precipitate in the impoundment. However, a fraction of the iron precipitates may also form colloidal phases that do not settle, such that the overall retainment of iron precipitates within the impoundment will be less effective. If the formed precipitates settle, a sediment layer will start to form over the tailings. With increasing time this would result in a gradually decreasing oxygen intrusion into the tailings, due to an increasing length of the diffusion path through this sediment layer. Thus, the formation of iron precipitates has an interesting impact on the performance of the water cover. Additional sediment formation may occur due to the inflow of natural particulate matter from the drainage area. Possible disturbances include the escape of iron from the impoundment to the recipient before oxidation and/or settlement has occurred, recurrent resuspension due to wind and wave action, bioturbation and varying sedimentation depending on location (c.f. erosion bottoms and sedimentation bottoms of natural lakes).

The possible formation of a sediment layer consisting of ferric iron oxyhydroxides, in the following abbreviated as SIPs (secondary iron precipitates), may provide an opportunity for many of the released trace elements to adsorb. In particular, the adsorption of arsenic to SIPs is frequently observed. Whereas arsenic has a fairly strong sorption to SIPs for slightly alkaline, neutral and acidic conditions, the adsorption of metals such as zinc and cadmium requires neutral or alkaline pH to become effective. This underlines the need for sufficient acid neutralisation of the surface water system to maintain a near-neutral pH, in particular during the initial time. This is particularly essential for the SIP layer where adsorption of trace elements is dependent on pH, as exemplified in Figure 15-7. If the conditions would turn acidic, a significantly increased release of trace elements, in particular metals, could occur.

As a consequence of the upward diffusion, the released trace metals from sulphide oxidation will not be brought in contact with unreacted iron sulphides in the tailings. This has the drawback that trace elements cannot be expected to be captured in the tailings by reactions forming secondary sulphide minerals (see above). It is thus expected that the sorption of trace elements to SIPs is the primary immobilisation mechanism in a water covered tailings impoundment.

The impact on the recipient is to a large degree dependent on the reduction of oxygen intrusion. For water covered tailings, acid neutralisation of both the primary produced acidity and the latent acidity, which is of the same amount as the primary acidity, will have to be provided by the surface water system. Acid neutralisation may be achieved by dilution and natural alkalinity in surface runoff with which the leachate is mixed. During operation, this can also be achieved by active liming or supply of other acid neutralising materials in the pond, i.e. in ditches or leachate collection ponds. To avoid acidification of the recipients the dilution and natural alkalinity will provide direct criteria for the necessary protection against oxygen intrusion. The reason for this is that the oxygen intrusion is directly transferable to the amount of acidity formed, including the latent acidity.

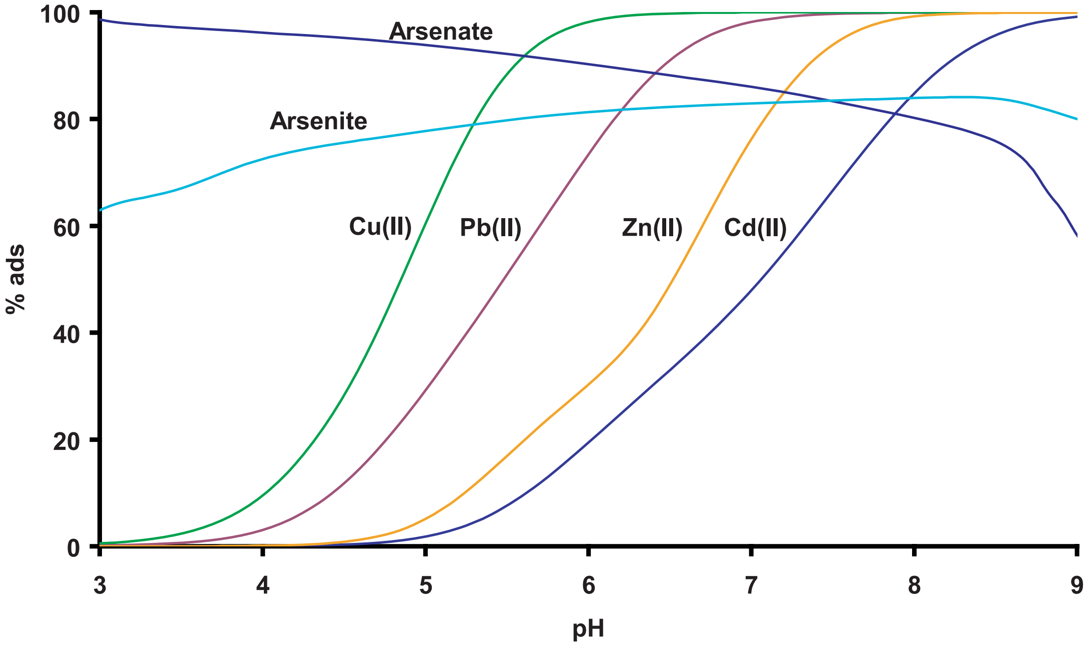

Figure 15-7 Illustration to the pH-dependence of adsorption of some metal ions to Fe oxyhydroxide (goethite). Data for Cu(II), Cd(II), Pb(II) and Zn(II) from Palmqvist et al. (1997) for As(III) from Lützenkirchen and Lövgren (1998) and for As(V) from Lützenkirchen and Lövgren (unpublished results).

A requirement for an effective water cover is that the water balance is maintained at all times. In most cases, the water balance relies on the function of a dam construction. In the MiMi studies, issues related to the construction and the evaluation of the long-term performance of dams have only been briefly assessed and then only with respect to some basic function requirements. Thus, for the MiMi performance assessment evaluations, any dam constructions have been assumed to be in good condition and risk for dam failure has not been addressed. Natural analogues can be found to dam constructions, in terms of natural lakes dammed by quaternary soil structures. Studies of such analogue formations, that have remained intact since the last glaciation, have indicated that hydraulic gradients on the order of 2-5% can be maintained. This may lead to the conclusion that 5 % is the upper limit for what is possible to maintain without maintenance in the long term. However, naturally deposited soils with a morphology that can form a dam wall also show relatively high hydraulic conductivity (eskers and superficial moraines) and this can also be a reason why higher hydraulic gradients are not found in nature. In Swedish practice, an empirical rule of thumb in designing dams for long-term stability that formulate an expression between the friction angle of the soil and the hydraulic gradient, leads to a hydraulic gradient about 0.3-0.4, i.e. 5-10 times the hydraulic gradients observed for natural analogues.

Water covering can be a viable option if the local hydraulic conditions are suitable. In order to maintain the water balance, the tailings are usually disposed in a valley or other low-lying areas in the topography. A local exfiltration area where the water balance is naturally positive is likely to be preferable for this purpose (see also discussion on lake disposal in following sections). The water balance requires that the precipitation and local catchment area can supply sufficient amounts of water to keep the tailings under the necessary depth of water. The demand for water in this respect is given by the area of the deposit, the local precipitation and evapotranspiration, the lateral inflow of runoff from the catchment area, the flow through spillways to recipients and the loss of water through the underground and dam constructions (see Figure 15-8).

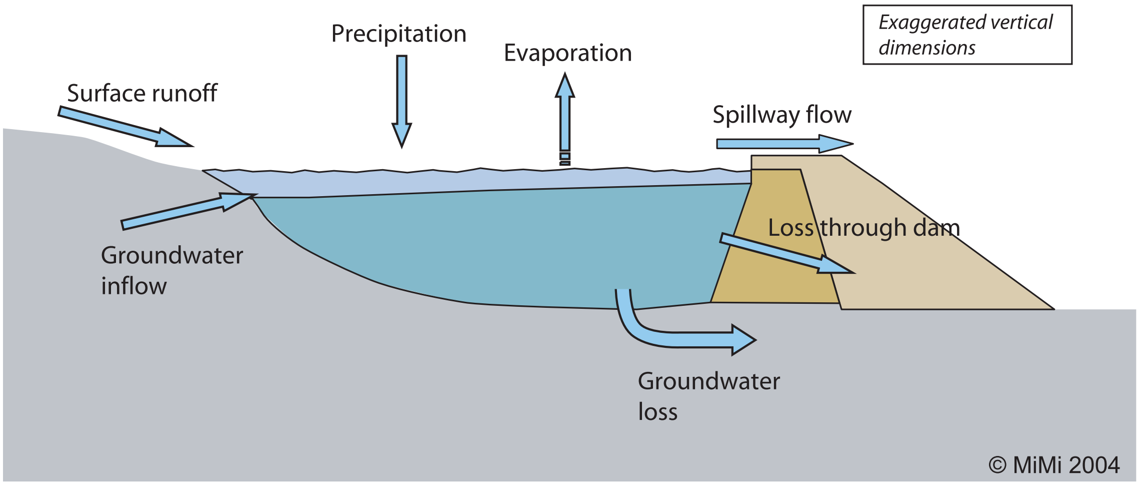

Figure 15-8 Schematic water balance for an impoundment of submerged tailings.

In an eight year follow-up of the function of the water covered tailings deposit at Stekenjokk, it was found that there were no signs of acidification and minor trace element discharge, despite the net acidification potential of the tailings. A mass balance of sulphate indicates oxygen ingress of at most 0.1 mol O_2/m^2/year. Detailed field observations show that a 4 mm sediment layer, rich in organic matter, as well as a layer of precipitated iron oxyhydroxides, had formed in the impoundment. Oxygen profiles show complete oxygen consumption in the uppermost 14-17 mm of the tailings. Comparing these observations with the generic predictions for the MiMi base case, we conclude that a close resemblance is obtained regarding the oxygen ingress when accounting for the effect of the sediment layer. For the high alkalinity of the surface runoff at Stekenjokk - an effect of the carbonate content of the bedrock in the area - the conditions would not be expected to become acidic for the estimated oxygen ingress rate. This finding does not contradict the projections for the MiMi base case considering the difference in local acid neutralisation capacity.

Consideration of some extreme events for water covered tailings

Scenario studies have shown that if the water balance would fail, such as due to a significant loss of water in the impoundment, a significant increase of the rate of oxygen intrusion into the tailings would be expected. Estimates have also shown that, in such a scenario, the presence of a thin sediment cover would not be sufficient to significantly reduce the oxygen exposure. In this sense, the water cover technique would be less robust than the soil cover technique.

15.5 Some quantifications

This section attempts to quantitatively illustrate some of the main processes in deposits for sulphidic mine tailings.

All subsequent processes are driven by the intrusion of oxygen that oxidizes the sulphides in the tailings, generating acidity and releasing trace elements. MiMi has therefore spent much effort on the methods used to reduce the oxygen intrusion rate.

In the soil cover case, the sealing layer is the main barrier to oxygen intrusion. In the base case it is assumed that the design is such that the water table is located in the tailings and the water saturation of the cover is determined by the suction properties of the sealing layer material. For a material similar to that used in Kristineberg the oxygen intrusion rate will be on the order of 1 mol/m^2,year. Sensitivity analyses and expert judgements have been used to test this value. The uncertainties are such deemed to be about a factor of two.

This leads to a production of an effluent that could carry in the order of 50 tonnes per year of iron precipitating somewhere downstream for a deposit of the size of Kristineberg.

The runoff flow needed for neutralization of the effluent acidity in the leachate water seeping through the deposit is in the order of hundred times the leachate flow, depending on the natural alkalinity of the recipient. For the Kristineberg deposit, the required runoff is approximately equal to the flow rate in river Vormbäcken.

The overall oxidation rate is very insensitive to the sulphide concentration in the tailings when the barrier functions as intended because it is the oxygen intrusion rate that governs the overall oxidation rate.

The oxygen intrusion rate can be decreased by using materials with more or better clays that have a higher water retaining capacity. Designing a deposit where the water table is within the sealing layer has the same effect.

The oxygen intrusion rate and therefore the effluent rate of the latent acidity can be reduced at most by factor of about 30.

For the water cover, the initial intrusion of oxygen is in the order of 3 mol/m^2/year, decreasing to 1 mol/m^2/year after some decades. A sediment layer of e.g. 10 cm would reduce the rate further by about a factor of 10.

The water flow and natural alkalinity needed to neutralize the primary and latent acidity is about twice as high for the water cover as for the soil cover for the same oxygen intrusion rate.

Analysis of some extreme scenarios for both soil covered and water covered tailings impoundments show that increased acidification and trace element release rates would be expected if the function of the covers are significantly deteriorated. However, the effects are not necessarily of a very sudden character and corrective measures would therefore be possible.

15.6 Related techniques

Lake disposal

From a technical and scientific point of view, the deposition of the sulphidic tailings in natural lakes of sufficient depth would constitute a very safe disposal alternative. Provided that the tailings are covered with a suitable layer and a sufficient amount of buffering compounds to buffer any initial acid generation, it would be very difficult to construct a scenario that would jeopardize the long-term environmental performance of such a solution. It also needs to be ascertained that there is no risk of contaminating the groundwater via fracture zones, since lakes in Sweden are commonly located along fracture zones. In most cases natural lakes are exfiltration areas and the risk for groundwater contamination would be small.

Pit lakes

An interesting option for the disposal of sulphidic tailings would be to use deep pit-lakes. Pit-lakes have a large relative depth which would counteract the mixing of the water column. MiMi studies have shown that anoxic conditions can be maintained in the bottom waters. The available volume in pit-lakes may, however, be substantially smaller than the volume of tailings. An interesting option would therefore be to use the pit-lakes for the disposal of e.g. pyrite concentrates, possibly obtained from the depyritisation of tailings. The limited cross-section area of the pit-lakes would also make covering of disposed tailings/concentrates less costly.

Constructed wetlands

Constructed wetlands may be considered for tailings impoundment with high groundwater table. In many cases a wetland could be expected to develop over time in water covered impoundments. However, the option also exists to create or stimulate the development of a wetland in the impoundment. A wetland cover could supply a self-sustaining organic cover of the tailings, thereby contribute to restricting the ingress of oxygen in the tailings and would also constitute a protection against erosion and wave action. Some wetland plants have been reported to release oxygen in the root zone, which is not desirable. A thin layer of soil over the tailings surface could serve as a medium for the root zone without affecting the oxygenation of the superficial tailings. At present the experience of constructed wetland systems over long time are limited. Nevertheless, the method is interesting and would provide a means for stimulated natural integration of tailings impoundments if proven efficient.

Downstream wetland systems

Downstream wetland systems may potentially act as scavengers and traps for trace elements released to the recipients. The association of trace elements to particulate phases and sedimentation may be important mechanisms in some recipients. However, in the investigations performed within the MiMi programme, the efficiency of the downstream natural wetland systems as traps for trace elements was low. In particular the following factors were found important in this aspect:

- The water flow through the wetland areas was highly canalised, which meant:
    - A short residence time of the flowing water in the wetlands.
    - Small contact area between the flowing water and the wetland materials.
    - Only partial effect of the wetland as a trap for particulate material suspended in the water phase.
    - Anaerobic processes may occur in the wetland material with sulphate reduction, but the contact and exchange with the flowing water was restricted and no substantial formation of trace metal sulphides could be noted.
- The wetland areas were frozen during the high floods during the snowmelt, which meant:
    - During the period of the highest water flow and highest water levels, the wetland areas were completely inactive – the water just flushes through the wetland areas.

A more ideal wetland would consist of an overflow area, possibly with the ability to accommodate large amounts of water during the snowmelt period. However, such a wetland system may be difficult to find at most locations. A conclusion is therefore that for the climatic conditions prevailing in Sweden, the effectiveness of downstream wetland systems for treatment of mine drainage is significantly hampered.

15.7 Performance Assessment Analysis – A Tool for Research and Tailings Management

The performance assessment methodology has been developed by researchers and engineers within the framework of radioactive waste management. The methodology was developed in response to a need for reliable predictions of the performance of a disposal system for radioactive waste over a long time. In essence, this can be formulated as a question: – *How can we reliably predict the performance of a system over a period of time which cannot be provided by experimental observations?*

The performance assessment methodology has been thoroughly tested and applied to safety studies of for final storage of radioactive waste and the experience has shown that the methodology is flexible and reliable.

It has been realised that a similar need exists for assessments of the complex processes that occur in disposed mine waste deposits. In the present work, a performance assessment methodology has been adapted and applied to the conditions relevant to disposed sulphidic, potentially acid generating, mine tailings. During the second phase of the MiMi programme, the performance assessment methodology has been used as a tool to guide the need for complementary research studies, as well as for structured synthesis of the results. This has allowed necessary focussing of the research activities and has enabled insights and important conclusions to be drawn.

The performance assessment methodology is a quantitative approach where the importance of different processes is estimated using best available data. To make it possible to perform quantitative calculations addressing the multitude of physical and biogeochemical processes involved, it is often important to discern in each specific case which of the different processes are of importance and which that can be neglected. When data are lacking, estimates can be made and sensitivity analyses performed to determine whether it is a critical parameter. If so, experimental data need to be determined. In this way, the most important parameters are identified, paying attention also to the interaction between different entities. This has also provided a means for guiding and prioritising the ongoing research activities, thus creating a dynamic feed-back between the performance assessment work and the different research groups.

The performance assessment analysis is made for a proposed design or idea for the waste facility. The characteristics of the mine waste should form the basis for the waste management strategy. Information from Acid Base Accounting (ABA) tests and Humidity Cell tests give information on the weathering characteristics of the waste. These tests can be regarded as established standard tests and constitutes valuable references that enable comparison between different sites. However, the MiMi studies have shown that additional information may improve the basis for long term predictions. The approach recommended by MiMi is to complement the above information with analyses of the total element content of the waste material, mineral analyses (Thin section microscopy, XRD etc) in combination with competent model predictions of the weathering processes, using best available thermodynamic and kinetic data for relevant minerals. This approach has been very successful and has been able to explain observations in field and laboratory. In depth studies have been able to narrow the gap between theoretical estimates, laboratory data and large scale field observations.

The experience from MiMi's performance assessment work shows that the application of a structured and holistic methodology as a platform for interpretation and synthesis has been fruitful and would be strongly recommended for assessments of complicated and scientifically challenging tasks. Ideally, such an approach should be applied already during the planning phase of a major research, mining or remediation project.

15.8 General recommendations for management of sulphidic tailings

A general strategy for the management of sulphidic mine tailings is illustrated by Figure 15-9. In a generic case, less waste with reactive properties would mean fewer problems. This statement certainly needs to be qualified, such that the characteristics of a particular waste stream and the options available at a particular waste storage facility are usually more important than the actual amount of waste. When moving up the stairs, fewer options will remain as redundant possibilities. The lower part of the stair represents a so called front-end strategy, i.e. avoid the occurrence of a problem, whereas the upper part represents a back-end strategy, i.e. handling of a problem that has already occurred. Whereas the front-end strategy is preferable from a philosophical point of view, both strategies are commonly used and necessary in a real situation.

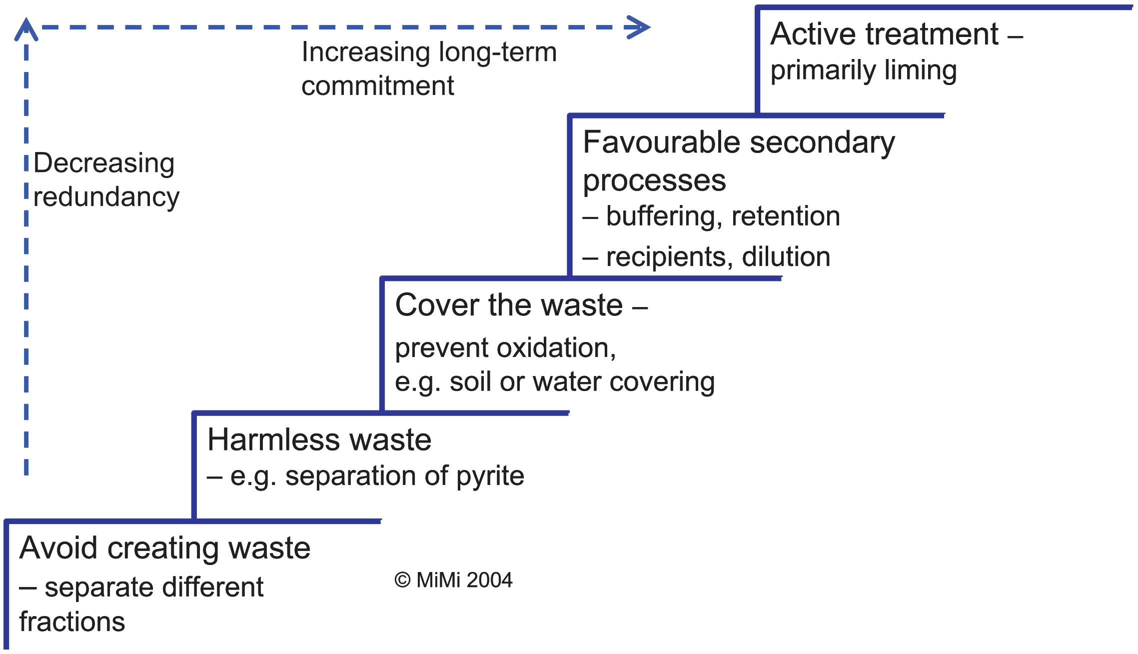

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Figure 15-9 Illustration of a general strategy to achieve safe handling of sulphidic mine tailings in the long-term.

Waste minimisation

The ultimate and visionary goal of any waste management plan would be to avoid the production of waste. In most situations this would not be a realistic goal. For the mining industry the amount of waste materials produced is considerable; therefore, a complete elimination of the waste is not within reach. The mining industry is looking for possibilities to reduce the amounts of waste, which could potentially save considerable costs. However, the exploitation of low-grade ores tends to increase the amount of waste for an equivalent amount of produced metal. Also separation and separate handling of extracted rock materials which are essentially free of sulphides has become important.

Less harmful waste

The next strategy would be to produce waste which is harmless from an environmental point of view. The MiMi research has focussed on sulphidic tailings, generally considered to be the most reactive waste, though waste rock may give rise to similar leachates. It is readily concluded that the presence of sulphides, especially iron sulphides, in the waste is the primary cause of a complex series of biogeochemical reactions regulating the environmental loading. Therefore, if the amount of sulphides could be reduced to very low levels, then the environmental issues would be of less concern. Different factors are important in this sense, for example:

- The efficiency of the used ore extraction method – methods with high specificity and precision may extract only the desired ore minerals (although not necessarily reduce the sulphide content of tailings).

- High degree of separation of sulphidic minerals may provide options for returning the undesired fractions of sulphide minerals into the mine voids – on the condition that the geochemical conditions are suitable and that this does not compromise the mechanical integrity of the mine.

- Pretreatment of tailings, e.g. enhanced heap-leaching, may deplete the sulphide content prior to disposal in the impoundment (although buffering capacity of the tailings will also be consumed in the leaching process).

In the ideal case of complete exhaustion of all metal sulphides in the tailings, the need for qualified handling involving protection from contact with oxygen will be minimised. However, it has been shown that even small remnants of metal sulphides in the tailings may induce an undesired oxidation process. The relative amounts of metal sulphides and calcite in the tailings determine whether or not an acid drainage will occur at some time in the future. For the water covered tailings case with very low content of metal sulphides, a sulphide depleted zone will establish more rapidly, having the benefit of a decreasing rate of oxygen diffusion from the free water body.

Cover the waste

Having considered the options mentioned above, the deposited waste must be handled appropriately in the impoundments. A complication in the practical handling is that the waste is produced as a result of ore extraction over an extended period of time. During this time the waste must be isolated from contact with air to avoid oxidation. The most commonly used method for this is to keep the tailings flooded in impoundments. The water acts as a barrier to oxygen and keeps the bulk of the tailings essentially unoxidized during the operational phase of the mine. Different aspects of soil covers and water covers are discussed earlier in this chapter and are not further treated here.

Favourable secondary processes

Different processes act to dilute, neutralise, delay and capture potentially hazardous components in the leachate water released by the weathering processes in the disposed tailings. Over a long time, the ability of the tailings themselves to neutralise acidity produced by the oxidation processes may be very efficient in mitigating the load of acidity to the recipients. Different trace elements may also be captured and immobilised due to formation of secondary sulphide phases in the tailings, whereas other elements may be retained by sorption processes. Estimates have shown that trace elements may be captured in the tailings over hundreds or even thousands of years. It is therefore recommended that a thorough characterisation of the tailings material is made to determine reliable data for these mechanisms and to perform quantitative predictions of the long term efficiency, taking into consideration the site specific conditions.

The leachate water expelled from the disposed tailings will mix with the runoff water in the local catchment area which will result in dilution and further neutralisation by the natural alkalinity. In the recipient, the association of trace metals to particles in the water phase may lead to sedimentation and immobilisation in sediments. Wetlands may be effective sinks for trace elements and particles.

Active treatment

Most waste management plans include a period of active treatment of mine waters, process waters from the dressing plant and leachate collected during operation of the tailings impoundment. Active treatment would not generally be considered a long-term solution. However, in Canada, waste management schemes involving active liming over extended periods of time have been reported. In view of an urge to find passive solutions, active treatment should be restricted to the operational phase and a limited period of time following this.

Different semi-passive treatment systems may be defined either as active treatment or passive treatment during a limited period of time. Examples of such methods may include reactive barriers, limestone drains, oxic/anoxic ponds and constructed wetlands. The experiences of such systems over long time are limited at present.

15.9 Designing for closure

A prerequisite for the establishment of a safe and environmentally responsible mining operation should be that the whole life-cycle of the mine and the produced waste are considered, see illustration in Figure 15-10. This should include thorough consideration of the potentially long-term environmental risks from the waste in the disposal phase. To achieve an environmentally responsible mining it is important that:

- A holistic approach is taken of the management and associated risks and costs over the entire mine life-cycle.
- The mining operation and its associated waste management plans are designed for closure from the very start of a new mine.
- Adequate attention is given to quantification of the long-term environmental function and consequences of the disposed mine waste.

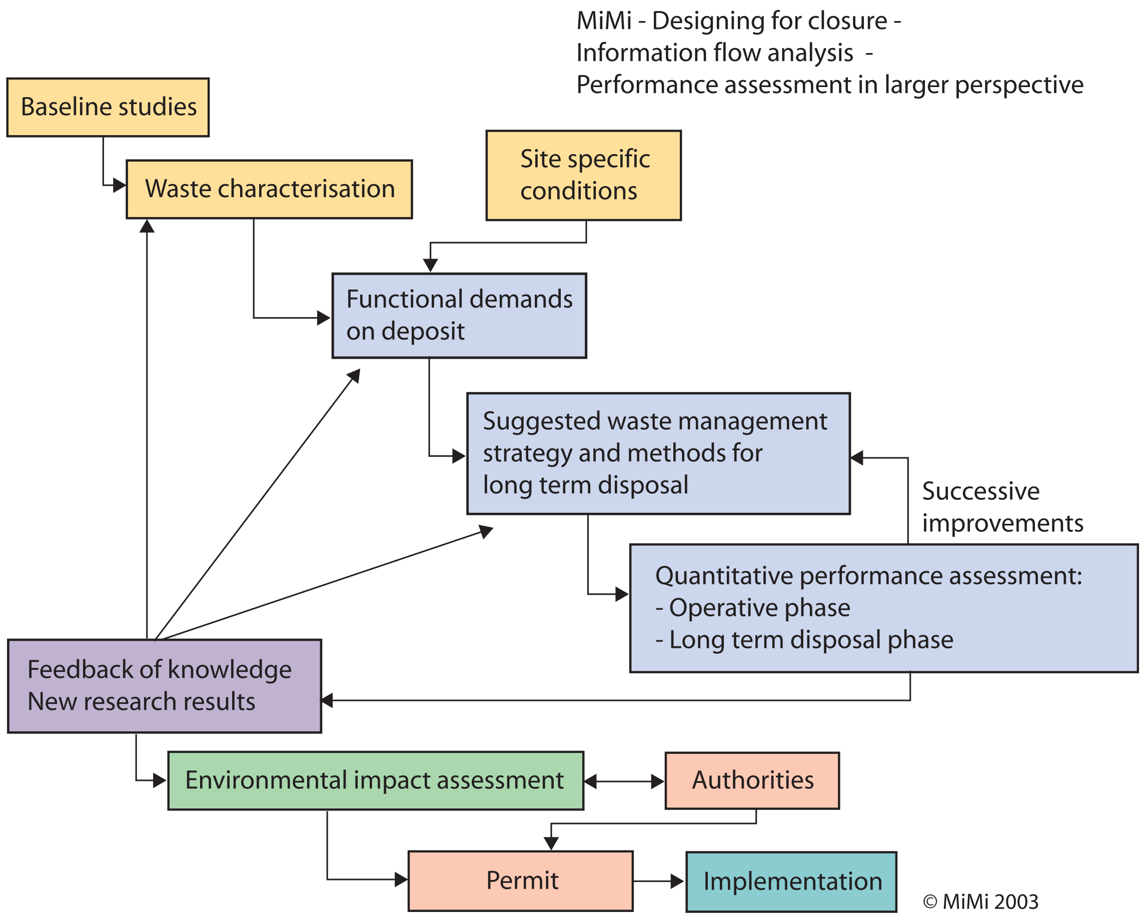

Figure 15-10 Illustration of the information flow in a Design for closure-approach and the role of the performance assessment analysis in this scheme.

Generic construction premises

During operation, the different strategies applied for material handling may include both active and passive methods. Active methods include effluent water cleaning, continuous liming etc. However, for the long-term storage phase, only passive methods can be applied. The functional life-time of the long-term disposal structures are on the order of thousands of years, which stretches far behind any possible demands for monitoring, maintenance and supervision.

Some fundamental construction premises for responsible long-term management have been determined (Höglund, 2002) which include:

- Options for final closure should be addressed already in application for a permit for a new mine
- Local conditions must be accounted for
- Adequate characterisation of the waste material is necessary
- Predictions of the weathering characteristics should be made
- Design should be tailored to find a suitable and robust site specific solution
- A structured performance assessment should be carried out - focussing on the long-term function

- Ecological integration must be assumed; therefore a search for solutions that work coherently with nature is necessary, because counter-acting nature over time is not possible.
- Synthesis from the performance assessment analysis should be used as a feed-back to improved design - an iterative process should be applied.

Generic demands on different remediation methods

From this, some fundamental demands on feasible closure options have been developed (Höglund, 2002):

- Very long functional life-time is required
- Passive methods must be applied
- All constructions must be robust and stable
- We need to demonstrate the longevity beforehand in a robust scientific way
- Simple, transparent and reliable model tools are necessary
- The relevant time-scales are hundreds - thousands of years
- We must learn from nature - ecological integration is necessary

A long functional life-time is required. For the Swedish conditions, an anticipated life-time of a waste deposit would reach over a period of several thousand years. In many instances the amount of sulphides in the waste would be large enough to sustain a weathering over extended periods of time. As a result of striving for long-term efficient remediation methods, the acid generation would be much slower, but on the other hand, be stretched out over a longer time. Hence it would be reasonable to project the life-time of a tailings deposit until the onset of the next glaciation period, expected to occur within the next 5000 to 60000 years. The action of the inland ice will be dramatic on any structure placed on the ground surface, which would provide an ultimate limit for the life-time of any waste deposit.

It is quite clear that over time spans of several hundreds or even thousands of years we cannot rely on remediation options requiring active maintenance or active treatment. Hence, passive treatment options need to be searched for. By passive methods we infer methods that are not in the need for active maintenance, replenishment of material, repair or other corrective measures. However, the used methods should as far as possible allow for active measures in the future if this would be considered favourable.

In this respect the development of remediation strategies including e.g. constructed wetlands, as outlined in Figure 15-11, may become an important long-term principle for the future (Stoltz and Greger, 2002a-b; Stoltz et al, 2001; Stoltz and Greger, 2003).

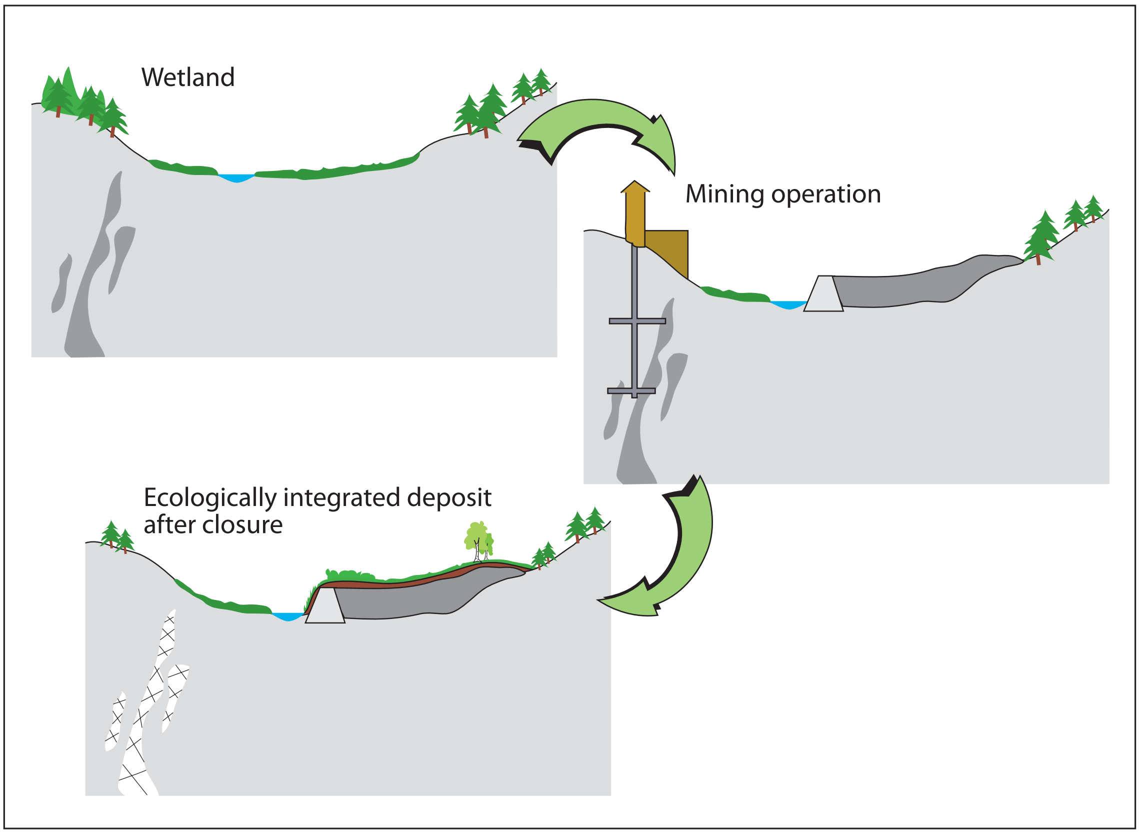

Figure 15-11 Schematic illustration of a possible mine life-cycle, including the back-end stage of the mine waste disposal using a constructed wetland concept.

15.10 Open scientific and technical issues

Important future research issues

The following items have been identified as the most important research needs for the future:

- Finding design criteria for inherently long-term stable tailings dams without the need for maintenance.
- Finding quantitative evidence and firm documentation of the necessary environmental conditions and longevity for secondary minerals forming as a result of weathering in sulphidic mine tailings. In particular this would be of importance for the formation of secondary sulphide phases as a capture process for copper, lead, cadmium, arsenic and possibly zinc.
- Finding further proof for the long-term efficiency of silicate weathering reactions in covered tailings deposits and natural soils as a means to neutralise the acidity released due to sulphide oxidation.
- Developing novel technologies for source term reduction by means of selective material handling and separation, as well as pre-treatment of sulphidic tailings.
- Finding appropriate design criteria for economically and environmentally efficient disposal of waste rock and historic mine waste sites.
- Alternative disposal methods, e.g. combined disposal of different types of waste products to enhance the overall performance.
- Quantification of AMD transport and attenuation in catchments – modelling and field studies necessary for assessment accordingly to the new EU water directive.
- Quantification of geochemical attenuation processes in tailings deposits – laboratory and field investigations of MiMi-proposed mechanisms: focus on possibly scale-dependent extent and rate as well as risk for/effect of remobilisation and coupling to physical transport.
- Assessment of scale dependent rates of weathering (sulphides and aluminosilicates) – particular focus on mineralogical heterogeneity, aging and particle size effects.
- Finding further evidence for the impact of physical processes such as freeze and thaw for the function of soil cover materials over long time.
- Developing improved and scientifically firmly based waste characterisation methods to support future assessments of the performance of tailings deposits over time.
- Systematically improving the understanding of the processes of importance for the long-term integration of tailings deposits with the surrounding biosphere.

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MISTRA
Foundation for Strategic Environmental Research
Gamla Brogatan 36–38, 111 20 Stockholm,
Sweden
Tel: +46-8-791 10 20
Fax: +46-8-791 10 29
E-mail: mail@mistra.org
Internet: www.mistra.org

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MiMi is a multidisciplinary research programme with the aim of developing and improving methods for the mitigation of the environmental impact of mining waste. The annual production of mining waste in Sweden is about 55 million tonnes. Finding economically and environmentally efficient methods to manage the waste is therefore a strategic issue for the Swedish mining industry and the environmental authorities.

MiMi has been funded by the Swedish Foundation for Strategic Environmental Research, Mistra. The programme has been a collaborative effort involving seven Swedish universities, a number of engineering companies and experts from the mining industry. Mistra has invested 78 million SEK in the programme during the period 1997–2004. During the final phase of the programme significant emphasis has been put on issues related to the long-term performance of different remediation methods, using a so called Performance Assessment methodology.

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