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Examensarbete 20 p  
Februari 2004



# Long term heavy metal contamination from leakage water sediments

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## Abstract

### Long term heavy metal contamination from leakage water sediments

*Patrik Brodd*

In this study the chemical stability of leakage water sediments and sludge waste originating from uranium extraction was investigated. Two types of leakage water sediments were sampled, i.e. from a collection pond for untreated leakage water and from a sedimentation pond for chemically treated water. Their properties, including leaching ability, were studied using chemical analyses. The gathered information about the sampled materials was used in order to estimate the contamination potential of firstly the sampled sediments and secondly older extraction sludge, which was not sampled due to practical considerations.

Results showed that both sampled sediments contained large amounts of Ni (54 and 95 mg/kg DM respectively), Cr (42 and 31 mg/kg DM) and U (19 and 86 mg/kg DM). The leaching ability proved to be highly pH dependent for Ni, Zn, U and Cu (70-100% available at pH 3) whereas Fe and As proved to be stable at all pH levels. The acid buffer capacity proved to be high in the collection pond and very high in the sedimentation pond, explained by the high content of lime (65%) and silica oxides (8%).

The sediments in the collection pond proved to be very stable in the tested conditions but uncertainties prevail considering the representativity of the sampling and the reliability of the leaching test conditions for this material.

The contamination contribution from the sedimentation pond was assessed to be small in all treated scenarios, owing to its high content of lime and subsequent high acid buffer capacity. The available metal amounts and corresponding annual loads seemed to be low in comparison to the amounts present in the mill tailings (<6 %).

The large amounts of extraction sludge in the tailings deposit ought to be considered a risk, as the properties of the material are fairly known. In order to reveal more information about the material, sampling and analysis of the sludge pond material is strongly recommended.

**KEYWORDS:** Uranium mining, mill tailings, leakage water, sediments, heavy metals, leaching tests, future risks.

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ISSN: 1401-5765I, UPTEC W04 008  
Sponsor: AB SVAFO

Tryckt av: Geotryckeriet, Uppsala

## Preface

This study was carried out during September 2003 to February 2004 as a thesis for master degree at Uppsala University School of Engineering. It was a part of the on-going work with the reclamation of the Ranstad mine area. The work was done at the SWECO VIAK office in Nyköping. SVAFO AB, the company now responsible for the mine site reclamation, commissioned it.

I would like to thank all the people who have helped me during this study and particularly:

- My supervisors Björn Sundblad and Sara Erjeby at SWECO VIAK in Nyköping, for support, guidance and criticism throughout the study, along with everybody else at the office for making it a very nice working place.
- Professor Ingvar Nilsson for help and criticism.
- Erika Börjesson, SWECO VIAK, for comments on the report and permission to reprint figures.
- Sonja Halmstad for comments on the report.

The financial support from AB SVAFO is greatly acknowledged.



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## 1. INTRODUCTION

In Ranstad, in western Sweden, uranium was mined in the 1960's in order to supply the nuclear programme with fuel. 1500 kg of uranium was extracted, during the limited active time of the mine, but 1.5 million tons of waste products were left behind. From the mine waste (mill tailings and sludge) acid and heavy metal containing leakage water is produced. As a consequence the leakage water needs to be treated in order to prevent environmental contamination.

The environmental effects in the mine waste area have been remedied during the last ten years, aiming at a sustainable solution to the contamination problem. The tailings have been covered, to minimise leakage water formation, the leakage water is collected and treated in a precipitation plant and the water quality in the area is monitored. In the leakage water collection pond and in the treatment plant sedimentation pond, large amounts of sediments have formed during the years. In addition, sludge from the extraction process and older leakage water treatment processes has been disposed in the tailings area.

As a step towards a sustainable final solution to the reclamation work, it is necessary to investigate the long-term chemical stability of sludge and sediments that have formed during the years. This Master thesis aims at investigating the properties and the long-term chemical stability of the sediments formed in the collection pond and the sedimentation pond. Furthermore, this information is to be used to estimate the possible contamination potential of the older sludge deposited in the tailings area.

The first step was a thorough literature survey concerning mining, reclamation work and the specific case of Ranstad. Field sampling of the materials in the collection pond and in the sedimentation pond, along with laboratory analyses of heavy metal content and leaching potential were used to obtain new information on the materials' properties, which was put in relation to the prior studies. Finally the hydrological conditions were compiled in order to permit a meaningful interpretation of the results.

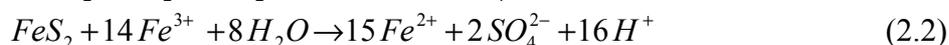


## 2. BACKGROUND AND OBJECTIVES

### 2.1. MINING AND THE WASTE PROBLEM

Metal mining is one of the largest contributors to the waste accumulation worldwide. It has produced and is still producing enormous amounts of waste products, some posing a large threat to the environment. Metals are an essential input in today's society, and their importance is not likely to decrease. A safe disposal of the mine wastes is therefore one of the most urgent environmental issues today.

There are basically two kinds of ores, which are of interest for metal mining. One is the iron-containing magnetite from which iron is extracted. The second type is the sulphidic ores, which is a term for minerals containing sulphur and metals like copper and zinc. The residual mill tailings resulting from magnetite processing form an oxidized and chemically stable product, not easily weathered. On the other hand the mill tailings from sulphidic ore processing contain a large fraction of easily weathered minerals, such as pyrite ( $\text{FeS}_2$ ), together with a substantial content of heavy metals (Alakangas, 2003). Weathering, i.e. oxidation of pyrite implies the production of sulphuric acid, which can occur having either oxygen or ferric ions as oxidant (Equation 2.1 and 2.2; note the difference in produced acid quantity). The produced acid further increases the weathering rate and the result is a continuous mobilization of heavy metals. The term Acid Mine Drainage (AMD) is used to define this acid and metal containing drainage water (Naturvårdsverket, 1998).



Carl Linneaus identified the environmental impacts of AMD on lake and river recipients in the Swedish mining districts already in the 18<sup>th</sup> century, but it was not until the 1970's that the mining waste problem was characterized and quantified nationally (Naturvårdsverket, 1993). In Sweden there are about 1000 mine sites, which together contain approximately 300 million metric tonnes of waste products (*ibid.*). Some of these sites contain large deposits of waste material and produce large amounts of AMD. As a consequence they may need treatment in order to minimize the contamination.

## 2.2. RECLAMATION

Mine site reclamation is a restoration of the contaminated site to a certain environmental quality level, often aiming at fulfilling the environmental goals set by local authorities. The reclamation normally consists of measures to minimize (1) the weathering of the mine tailings and (2) the flux of metals from the deposit, both in order to prevent further heavy metal contamination of down stream water bodies and groundwater. The weathering and transport are normally prevented by reducing the supply of oxygen and infiltrating water (Naturvårdsverket, 1993).

Oxygen can be supplied through four main transport mechanisms (Brady and Weil, 1999):

1. Diffusion: Transport in gaseous phase controlled by the concentration gradient.
2. Convection: Transport in gaseous phase controlled by the temperature gradient.
3. Advection: Transport in gaseous phase controlled by the atmospheric pressure gradient.
4. Dissolved oxygen in the infiltrating water.

Application of a sealing layer can minimize the impact of these four oxygen transport mechanisms. The two most common methods are deposition below an open water surface or deposition using an impermeable cover, which are called wet and dry deposition respectively (Naturvårdsverket, 1998).

The wet deposition is a very effective measure, in terms of preventing weathering since the oxygen diffusion rate in water is much lower than in air (10000 times) according to Naturvårdsverket (1993). However, the waste needs to be constantly covered by a calm water surface and the elevated pressure head on the dams demands rigorous safety measures and continuous control. The dam failures in Los Frailes, Spain and Aitik, Sweden are two cases that seem to indicate drawbacks connected with wet deposition. The two dams mentioned contained mill tailings under daily surveillance and were recently constructed; yet the failures could not be foreseen (Benckert and Göransson, 2001; Lindvall *et al.* 2003a).

However, questions about long-term sustainability also arise when discussing the dry deposition method. In this method the deposit is covered with a layer that minimizes the diffusion of oxygen and the infiltration of water. The layer could consist of a tight clay layer beneath a protective till layer. An elevated ground water table in the till layer further increases the diffusion protection, by forming a water-sealing layer. The till is used for protecting the cover against freezing and erosion damages, and should be complemented with a vegetation cover (Naturvårdsverket, 2002a).

The appropriateness of wet deposition contra dry deposition, in a long time perspective, is currently a matter of discussion. The Swedish Environmental Protection Agency (EPA) tends to recommend dry deposition whereas the mining industry, e.g. the Boliden Company, prefers to use the wet deposition method in many cases (Naturvårdsverket, 2002a; Lindvall *et al.*, 2003b).

## 2.3. CONCEPTS OF METAL CONTAMINATION

The primary mobilization of metals depends on the weathering of minerals in the earth's crust. Weathering is a natural process, which together with erosion transport processes levels the land surface. Weathering takes place at the surface of mineral particles, where chemical reactions proceed towards thermodynamically more favourable states. The quantity of available surface, estimated by the material's texture, is therefore the single most important factor determining the weathering rate (Brady and Weil, 1999).

### 2.3.1. Mobility of metals

Contaminants such as heavy metals are transported more slowly through a soil or sediment than the transporting water because they tend to "get stuck" on their way, a process called retention. This has a chemical explanation and is due to the specific processes adsorption and precipitation (Gustafsson *et al.*, 2002). The precipitation of secondary minerals is an equilibrium reaction, dependent on the ion concentration and the surrounding environment. Adsorption processes depend on the affinity of the ion to adhere to a solid phase, i.e. a soil or sediment particle. As such soils and sediments have a certain capacity to retain heavy metals, determined by characteristics such as organic matter and clay mineral content and composition as well as the content of Fe- and Mn-oxides and carbonates (Salomons, 1995). The characteristics determining retention, due to both precipitation and adsorption, can be named *Capacity controlling parameters* (CCP) or master variables, as done by Salomons (1995) (Table 1).

**Table 1.** Pollutant retention capacity controlling parameters (CCP) of soils or sediments.

CCP	Origin
pH	Geochemical characteristics
Eh (redox potential)	Geochemical characteristics, biological activity
CEC (cat ion exchange capacity)	Mineral content, soil texture
Soil Organic Matter	Organic ligands
Soil structure and texture	Amount of available surfaces
Salinity (complexing capacity)	Iron and manganese (hydro)oxides

Modified from Salomons (1995).

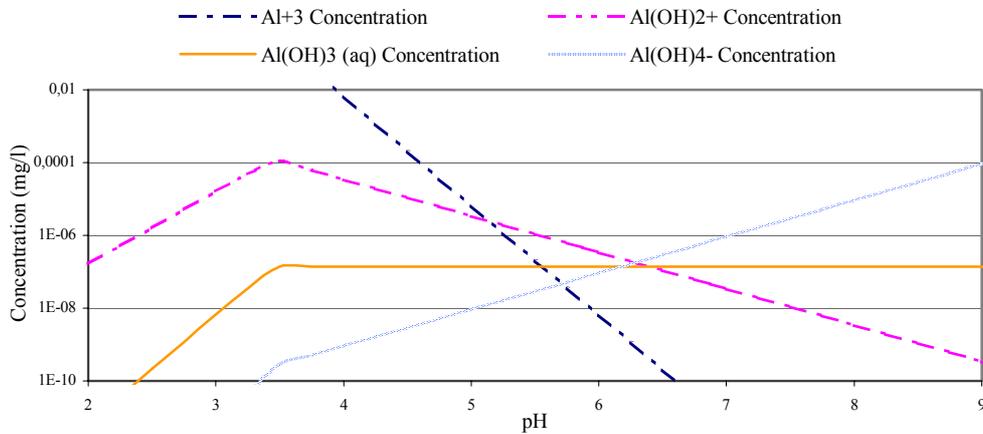
The retention capacity can accordingly change because of changes in the surrounding environment, and of particular interest is the fact that small changes can imply a dramatically reduced retention capacity. Hence there are possibilities for non-linear responses of the pollutant leaching (Wierenga and Brusseau, 1995). Salomons (1995) further described the risk of non-linear responses and the concept of the *chemical time bomb*, which is based on for example the fact that pH is a very important CCP affecting both the adsorption and the solubility. Consequently when the acid buffering capacity of the soil is exhausted a sudden drop in pH may occur after which an extensive metal leaching is to be expected. These non-linear responses may hence provide unwanted "surprises" in the reclamation of contaminated sites.

In a short- time perspective it is sufficient to control the master variables. In a long-term perspective it is also necessary to control what determines the master variables. The long-term approach is necessary due to long term changes in the mobility of the heavy metals and in the soil's storage capacity (Salomons, 1995).

## Precipitation

After the initial mobilization, metals can be immobilized by precipitation as secondary minerals. The solubility of metal containing minerals is highly dependent on the pH of the pore water (Gustafsson *et al.*, 2002). Due to the charge properties, the solubility of a typical metal oxide is lowest at around neutral pH levels, increasing logarithmically with increasing or decreasing pH (Figure 1). Acid conditions therefore imply a strongly increased mobility of heavy metals, since less precipitation occurs.

The likelihood for a pore water solution to get over saturated, followed by precipitation of secondary minerals, can be investigated using geochemical simulation programmes. A static example of such a program is MINTEQA2, and for a dynamic, i.e. time dependent, simulation PHREEQC can be used (Langmuir, 1997). An example of a Minteq simulation result for the solubility of Al can be seen in Figure 1.



**Figure 1.** Solubility of Aluminium hydroxides as a function of pH, calculated with the chemical simulation program Visual-MINTEQ.

## Adsorption-Desorption

Three geochemical mechanisms rest behind the adsorption concept; ion exchange, surface complexation and hydrophobic adsorption (Gustafsson *et al.*, 2002). Common for all mechanisms is that the adsorbing ion needs a ligand, i.e. a particle with a suitable surface to attach to. For that reason only particles with a large specific surface area are actually involved in adsorption, i.e. act as ligands, such as clay minerals, oxides and organic matter.

Ion exchange is due to electrostatic attraction, between a charged ion and a charged particle surface. Most soil particles have negatively charged surfaces, why mostly cations are sorbed by ion exchange (Gustafsson *et al.*, 2002). A special form of ion exchange is the ion pair bonding, also called outersphere complex (Langmuir, 1997). Through this mechanism the metal ion is sorbed closer to the particle than with electrostatic attraction, in the diffuse layer around the soil particle, but not as close as with innersphere complexes.

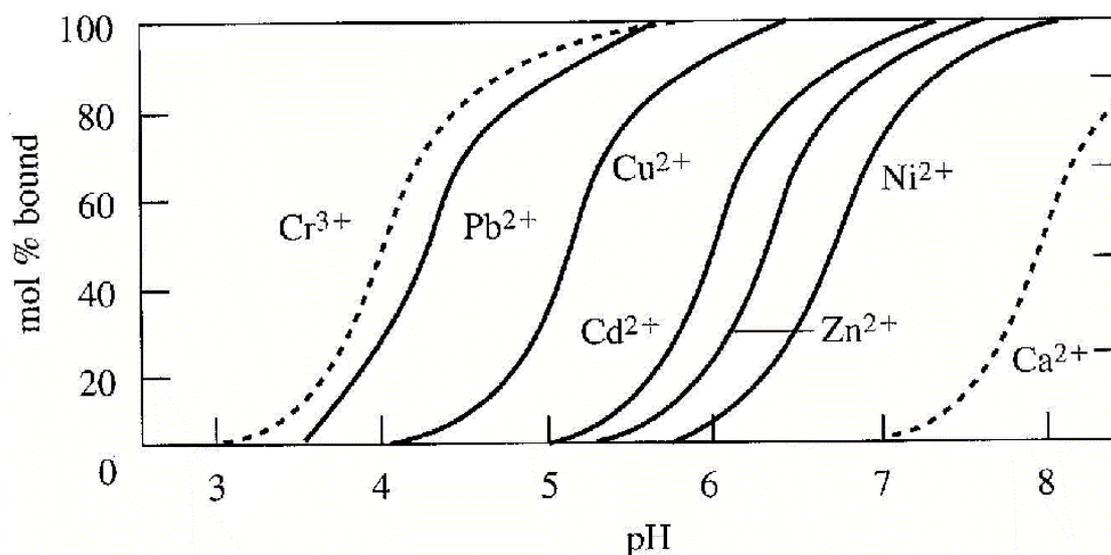
The innersphere complexes involve a covalent bonding between the ion and the ligand, and are generally stronger than electrostatic bonding through ion exchange (Langmuir,

1997). Cat ions have a high affinity to form surface complexes with hydroxyl groups on particle surfaces and with organic acids. Anions, such as sulphate, tend to form surface complexes with oxides, e.g. iron and aluminium oxides (Gustafsson *et al.*, 2002).

The pH value is the single most important variable determining the adsorption rate. The increased activities of negatively charged OH-ions or positively charged H-ions lead to an increased competition for the adsorption surfaces (Lövgren and Sjöberg, 1996). Cations are more strongly adsorbed at higher pH values, and conversely anions are more strongly adsorbed at lower pH values (Gustafsson *et al.*, 2002; Langmuir, 1997).

Lövgren and Sjöberg (1997) closely investigated the adsorption of heavy metals to organic and inorganic ligands, with a particular focus on the mine waste problem. Their results showed that metal ions can be strongly adsorbed to iron(hydr)oxides at high pH. At low pH sulphate ions were strongly complexed leaving the metal cations in solution. It was further concluded that the presence of organic acids had a limited effect on the adsorption of most metals, except for Pb whose adsorption at low pH was strongly enhanced by the presence of organic acids. Furthermore As and Cr were concluded to have very different adsorption behaviour compared to Cu, Pb, Cd and Zn (Lövgren and Sjöberg, 1997), as the former prevail as anions.

A typical distribution of the adsorption of metals as function of pH is shown in Figure 2.



**Figure 2.** Adsorption of various heavy metal cations to iron hydroxides as a function of pH (from Langmuir, 1997).

#### *Factors determining pH*

The pH buffering capacity and hence the acid or base neutralising capacity (ANC) of a soil, sediment or water body, is the primary factor determining the effect on the pH value of a change in chemical conditions. Carbonates, reacting rapidly and almost completely, are the primary buffering minerals in a shorter perspective (Langmuir, 1997). The following mechanisms, occurring along a mineralogical titration curve, are ion exchange, Al(OH)<sub>3</sub> dissolution and finally Fe(OH)<sub>3</sub> dissolution (Förstner, 1995). In addition to the shorter perspective, weathering of silicates constitutes a very important long-term buffering reservoir. Research on waste rock in the Aitik mine showed that the eas-

ily weathered carbonates buffered the system well during the initial years (Eriksson and Strömberg, 1996). When the carbonate had been consumed pH decreased once more, but was assumed to slowly rise again owing to silicate mineral weathering.

To be able to conclude if the scenario of a chemical time bomb is plausible, the homogeneity of the pH conditions needs to be investigated, i.e. it has to be determined if the total mass of material reacts simultaneously. Another scenario could be that pH starts to decrease in the peripheral part of the material, or adjacent to the preferential flow paths, hence producing a continuous metal flux from the material.

*The impact of reduction-oxidation reactions – Redox (Eh)*

The second capacity controlling parameter of the retention capacity of sediments identified in Table 1 is the redox state (Eh). The oxidation state of an element can determine its mobility as well as its toxicity (Langmuir, 1997). The major redox elements, i.e. elements with more than one oxidation state, include H, O, C, S, N, Fe and Mn along with redox sensitive trace elements including U, Cr, As, Cu and Mo (*ibid.*). The redox state in sediments is mostly controlled by the microbial degradation of organic matter, which is a reduction-oxidation reaction that takes place in almost all environments (Widerlund, 1999). The organic matter is used as an electron donor and energy source by a variety of microorganisms (Doelman, 1995). The electron acceptors, the oxidants, change as the oxic conditions change thus determining the redox potential. The result is a sequence of reduction/oxidation processes starting with aerobic decomposition and reduction of oxygen and ending with methane formation. The reactions that can take place with increasing depths in a sediment or soil mass are defined in Table 2:

**Table 2.** Reactions taking place in sediments. CH<sub>2</sub>O is a proxy for organic matter.

Process	Formula	No.
Aerobic decomposition:	$CH_2O + O_2 \leftrightarrow CO_2 + H_2O$	(2.3)
Denitrification:	$5 CH_2O + 4 NO_3^- + 4 H^+ \leftrightarrow 2 N_2 + 5 CO_2 + 7 H_2O$	(2.4)
Manganese reduction:	$CH_2O + 2 MnO_2 + 4 H^+ \leftrightarrow 2 Mn^{2+} + CO_2 + 3 H_2O$	(2.5)
Iron reduction:	$CH_2O + 4 Fe(OH)_3 + 8 H^+ \leftrightarrow 4 Fe^{2+} + CO_2 + 11 H_2O$	(2.6)
Sulphate reduction:	$2 CH_2O + SO_4^{2-} + 2 H^+ \leftrightarrow H_2S + 2 CO_2 + 2 H_2O$	(2.7)
Methanogenesis:	$2 CH_2O + \dots + CO_2 \leftrightarrow 2 CH_4 + \dots$	(2.8)

(Modified from Förstner, 1995).

The interplay between pH, Eh and bacterial activity is one of the most important processes to understand when discussing heavy metal contamination and mobility (Werner and Destouni, 1998). Since microorganisms have been proven to strongly affect both the mobilisation and immobilisation processes of heavy metals (Ledin, 1998), the role of microbial activity will consequently be investigated in the following section.

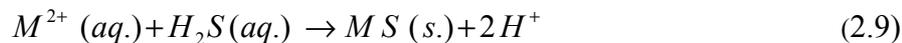
### 2.3.2. Role of microorganisms

The ambient environmental conditions, with respect to pH, Eh, O<sub>2</sub> partial pressure and humidity, determine which microorganisms that may be present. Even in strongly polluted environments specifically adapted microorganisms will be found (Ledin and Pedersen, 1995). Microorganisms need a few basic criteria to be fulfilled; the presence of a carbon source, an electron source, water and an energy source. Organisms which are able to synthesize organic carbon compounds from carbon dioxide are called autotrophs, i.e. they are self-sufficient. Organisms needing organic carbon are called heterotrophs. Since the organic matter content is usually low in mine waste, autotrophic bacteria are generally favoured (Ledin and Pedersen, 2003).

Concerning reclamation activities, it is important to realise that for example covering, might change the microbial activity in the tailings. One must therefore investigate how the activity is changed in order to avoid unwanted side effects (Mills, 2003). Sulphate reduction and precipitation of stable metal sulphides is a wanted effect whereas iron reduction and dissolution of iron hydroxides is an unwanted effect, as these hydroxides are very important for metal retention.

The acidophilic sulphur reducing bacteria *Thiobacillus ferrooxidans*, *T. thiooxidans* and *Sulfolobus acidocaldarius* are often found in sulphidic mine wastes. These bacteria are able to reduce ferric iron to ferrous iron under anoxic conditions (Ledin and Pedersen, 1995). Hence a remobilisation of iron and other co-precipitated heavy metals is possible in anaerobic mine environments. Biological transformation of heavy metals can accelerate the rate of chemical oxidation by as much as 10000 times (*ibid.*). The activity of iron and sulphate reducing bacteria such as *Thiobacillus ferrooxidans* has been shown to increase substantially with a decreasing pH.

When readily degradable organic matter is present together with sulphates, sulphate reduction can be catalysed by bacteria such as *Desulfovibrio* (Ledin, 1998). Bacteria living in bio-films might produce anaerobic micro zones, in an aerobic environment, why it is hard to predict when sulphate reduction may occur (*ibid.*). The biological mineralization of carbon by sulphate reduction (Eq. 2.9) can be followed by metal immobilization (Sjöblom, 2003):



where M is a divalent metal ion. Most metals, except manganese, form insoluble precipitates with sulphide (Sjöblom, 2003). Hence, sulphate reduction is a powerful metal immobilization mechanism.

Nitrate reduction (denitrification) occurs next to O<sub>2</sub> in the reduction sequence, and is therefore likely to occur in wetlands (Sjöblom, 2003). According to Broberg (pers. com.) nitrate-reducing bacteria might form a bio-film that prevents particles from sedimentation and could therefore have unwanted effects on the treatment of AMD. Other reports on this phenomenon have however not yet been found.

In an aerobic environment, iron and sulphur oxidation can take place. The opposite consequences are to be expected as compared to iron and sulphur reduction, i.e. iron oxida-

tion leads to an immobilization of heavy metals whereas sulphur oxidation leads to a mobilization when the stable sulphides are dissolved (Ledin and Pedersen, 1996).

Geochemical engineering is a means to influence the CCP in such a way that metal leaching is inhibited (Salomons, 1995). One way to do this would be to add pH-increasing chemicals. However, costs, uncertain long-term effects, including the effects on the microbiology are regarded as drawbacks. One example of this is the covering of a waste deposit, a measure that on one hand might inhibit chemical weathering of pyrite, but on the other hand enhances the microbial iron reduction due to changed redox conditions (Ledin and Pedersen, 1996).

### **2.3.3. Transport phase**

A transport medium is a prerequisite for AMD formation and metal fluxes. This medium is normally provided by infiltrating water. The time it takes for the infiltrating water to leave the deposit, the residence time, is very important for the composition of the AMD (Werner and Destouni, 1998). For calculations and deterministic modelling, a spatially homogenous water transport is often assumed but research has shown that this is not a defensible simplification since the water flow is very heterogeneous with as little as 20-30% of the particle surfaces actually making substantial contact with the water (Werner and Destouni, 1998). This is the theory of preferential flow which states that water takes shortcuts through macropores or other preferential flow paths on its way through a soil profile (Wierenga and Brusseau, 1995). In other words metals from the particles in contact with rapidly moving water will leach at a fast rate while a much longer time is needed for metals to leach from particles in contact with slowly moving water (Werner and Destouni, 1998). Wierenga and Brusseau (1995) further state that preferential flow has been shown to have large implications for the transportation of contaminants, especially in the saturated zone since the macropores will not contribute significantly to flow at lower water saturation levels.

Preferential flow could have large implications for the risk assessment of the sludge ponds since the structure and the actual flow patterns within the sludge ponds are largely unknown. A further discussion of this in relation to the hydrological conditions in the tailings is made in Section 6.2.

## **2.4. AIM AND OBJECTIVES**

The general aim of this master thesis is to evaluate the potential future risks posed by the sludge and sediments of the Ranstad mine waste site. Of particular interest is to investigate the contamination potential of the sediments collected in the sedimentation and collection pond as well as in the old sludge ponds in order to conclude whether these latter sediments are the source of the observed continuous flux of metals to the leakage water collection pond. The specific objectives are:

1. To clarify the content and biogeochemical properties of the different sludge and sediment types present in Ranstad and to investigate if some of these could have similar long-term responses and environmental impacts.
2. Investigate the stability and heavy metal leaching potential of the sediments in the sedimentation and collection ponds using leaching tests, with the aim to simulate plausible scenarios.
3. To deduce the long-term threat originating from these waste materials within each proposed scenario, in order to provide the basis for a suitable action plan for the safe handling of the materials.

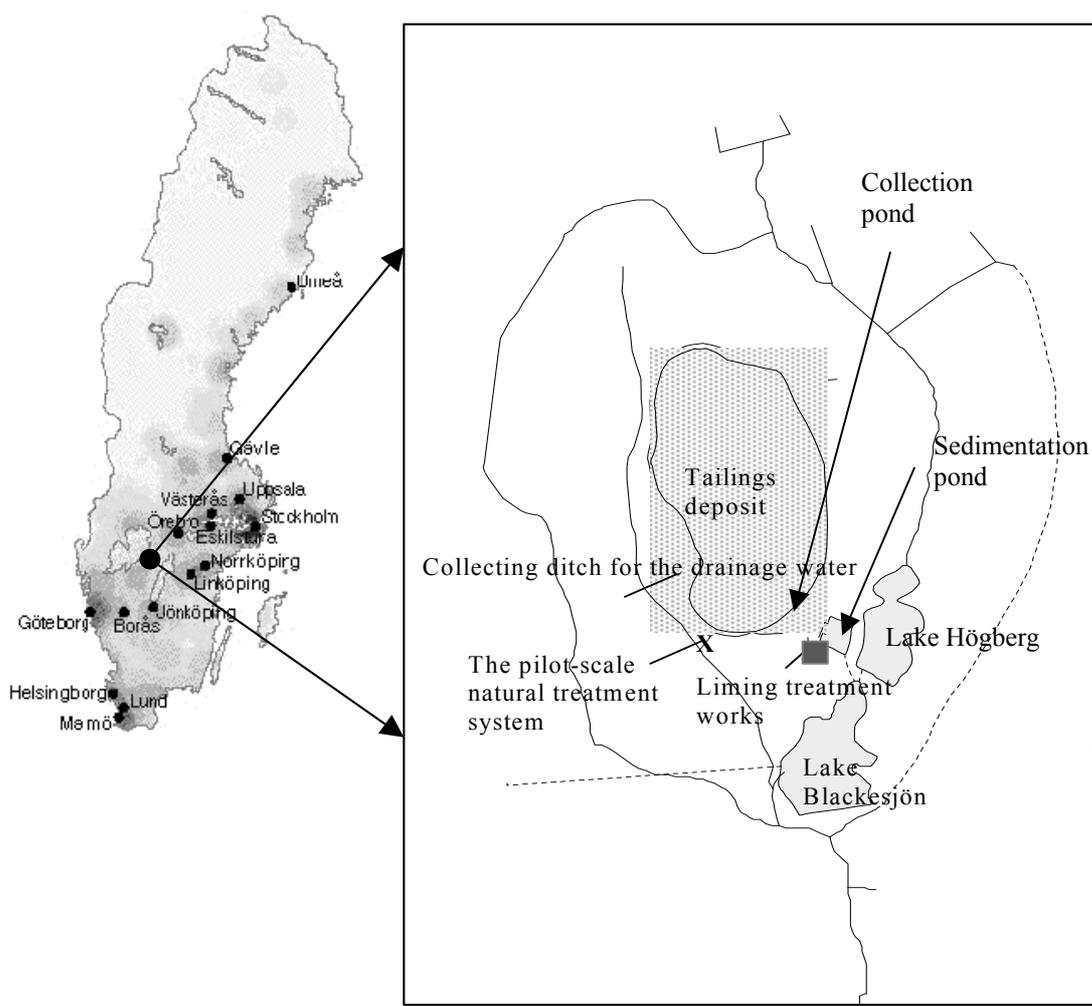


### 3. STUDY SITE: RANSTAD TAILINGS AREA

#### 3.1. SITE LOCATION

The Ranstad tailings deposit area is located on a plain in western Sweden (58°18 N, 13°41 E) (Börjesson, 2002), in the Lidan river basin, which is a sub-basin within the Göta älv river basin (Bergström, 1993). The deposit area is drained by a small tributary to the river Pösan called Marbäcken. The river Pösan flows into the river Hornborgaån, which passes the famous bird spotting lake Hornborgasjön before reaching the river Lidan and finally the lake Vänern (Figure 3).

Close to the plateau mountain Billingen, in the province of Västergötland, sedimentary alum shale is the main bedrock material. The shale has a high content of organic material, sulphur and metals with a high energy content in terms of fossil fuel and uranium. It is estimated to be one of the largest uranium resources in Europe, since a low uranium concentration is compensated by the large amount of accessible ore (Strandell, 1998).



**Figure 3.** Map of the Ranstad area (reprinted from Börjesson, 2002).

The environmental goal set by the county administration is the metal contamination level in the lake Blacke sjön (see section 3.3.5), downstream the tailings area (Erjebj *et al.*, 2003). Water quality monitoring is performed at a number of sampling points surrounding the tailings, in surface waters and groundwater. In this study the focus is on the amount of metals reaching the western ditch and the collection pond. The further transport and retention will not be considered.

For the groundwater aquifers the definition of a boundary is more complicated. No environmental goals considering the ground water quality have been formulated by the county administration, but a substantial groundwater quality monitoring is nevertheless performed in different strata. In order to define a boundary for this study, a vertical plane was assumed just downstream the collection pond where groundwater monitoring was performed.

The tailings area along with the collection ditches and ponds is shown in Figure 4. Groundwater wells can also be seen.

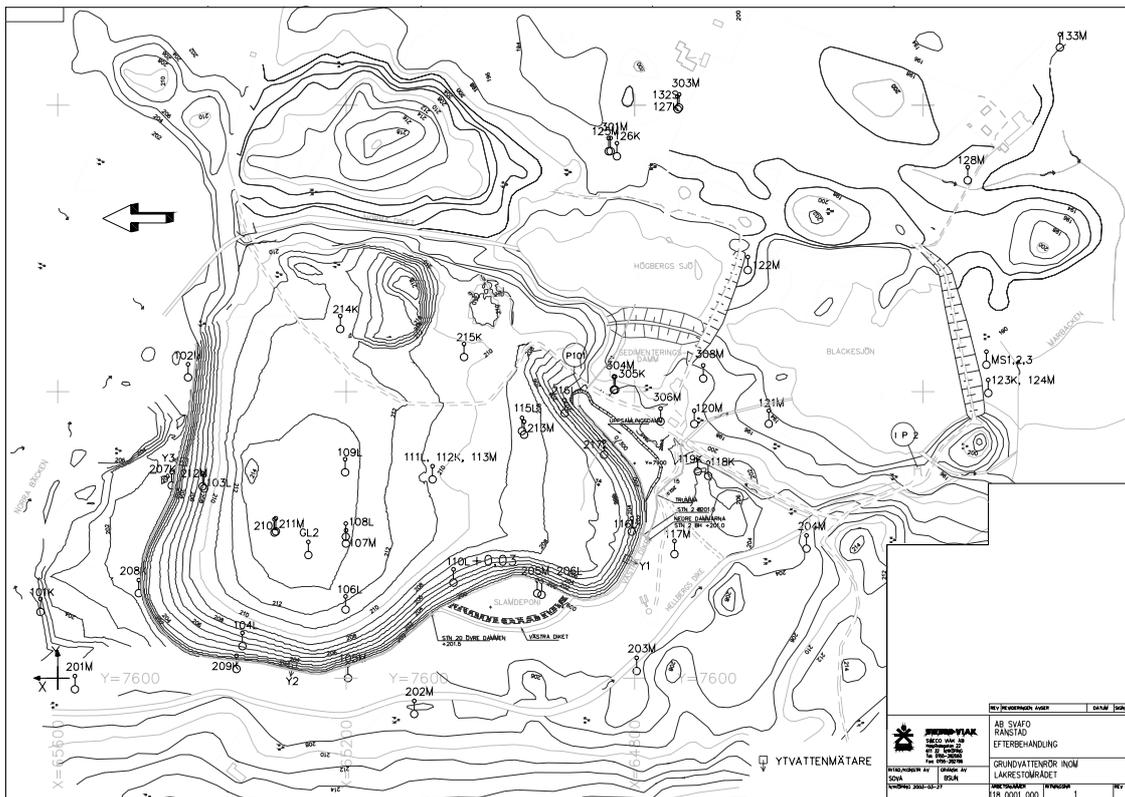


Figure 4. Blueprint of the tailings area.

## **3.2. HISTORICAL BACKGROUND**

### **3.2.1 The uranium mine**

A former process engineer at Ranstad, Mr. Erik Strandell (1998) provided a detailed description of the uranium mine and its underlying incentives in a recently published book. All information in this section is gathered from his book unless other references are referred to.

The uranium ore was prospected for use in the Swedish nuclear programme just after the Second World War, at a time when there were large political incentives for a domestic uranium supply despite of anticipated high extraction costs.

During the 1950's it was decided to build a large-scale mine and uranium extraction mill at Ranstad. However, already during the construction time the uranium market was relieved from prior trading restrictions. As a consequence the competition from foreign enterprises with ore deposits with up to 1000 times higher uranium concentrations made the Swedish uranium production unprofitable. Still, due to domestic policy considerations, the mining in Ranstad started in 1965 and proceeded at a reduced pace until 1969.

During the operation time 215 metric tonnes of uranium were extracted, and 1.5 million metric tonnes of mill tailings and waste rock were produced. In addition a large amount of sludge was produced, neutralising the process waters and collected leachates. The Swedish government continued to provide funds for plans of future mining and development of the processes during another 20 years, which was done at a laboratory scale. The concession ended in 1984 and the Ranstad extraction plant and mine were closed down.

### **3.2.2. Former processes and waste handling at the Ranstad plant**

Strandell (1998) described in detail the extraction processes used in the Ranstad mill. In short, the procedure was as follows. The ore was extracted in an open pit mine and transported to the mill through an underground tunnel. At the mill the shale was first crushed to a particle size less than 350 mm, and material less than 6 mm was discarded as waste. In order to remove "unclean" shale containing calcite, the material was sorted in a dressing plant where the shale floated and the waste sedimented in a magnetite solution. After dressing, the shale was crushed once more to particles less than 3 mm, the ideal fraction for leaching found in earlier experiments. The crushing resulted in about 10% dust, which was removed as waste. The finely crushed shale was left outdoors for "ripening" during three weeks in order to start the weathering processes and thus speed up the leaching. The leaching took place in large sumps during three days using 15% by weight sulphuric acid at 60° C. The uranium was extracted using ion-exchange, and then purified by liquid extraction and finally precipitated as sodium uranate ( $\text{Na}_2\text{O} \cdot 2 \text{UO}_3$ ).

After the leaching, the shale was considered as waste (mill tailings), which after a cleansing with water was transported with trucks to a waste disposal site (Strandell, 1998). The weathering of the tailings had already begun during the extraction process and the aeration that resulted from the truck transport further accelerated this process. A large

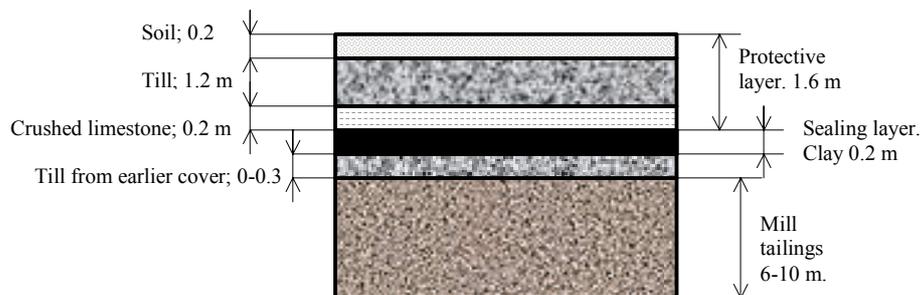
production of strong acid and a release of heavy metals were accordingly to be expected. According to Strandell (1998) amounts and concentrations were underestimated, however, and it was realized that the disposing procedure was inconvenient for future large-scale mining. To address the problem the disposal site was surrounded by ditches, in which the leakage water was collected and further transported to an assembly pond, the Högberg Lake. From this pond the water was pumped back to the mill and treated in a waste purification plant. The treated water was thereafter directed to the lake Blackesjö and pumped across the Billingen mountain to the stream Hornborgaån (Strandell, 1998). In the Högberg lake there was a quite extensive sedimentation of metal precipitates (Sundblad, pers. com.).

All process water from the extraction processes was treated in neutralisation plants, together with the drainage water from the ripening store and the mill tailings deposit (see Section 5.1 for a more detailed description of the process chemistry). The wet sludge thus formed was transported in pipes to the disposal site where it was transferred to ponds in the south-eastern parts of the tailing deposit (Strandell, 1998). Due to problems associated with the treatment of the magnetite suspension from the dressing plant, the suspension was pumped directly to the sludge ponds, without prior purification. In the sludge ponds different kinds of solid waste such as tree stumps and large rocks were also disposed. Eventually the sludge ponds were somewhat dewatered and today form deposits inside the tailings consisting of finer material with a high water retaining capacity.

### **3.2. REMEDIATION AT RANSTAD**

The alum shale has properties similar to a sulphidic ore with large amounts of pyrite present, implying similar waste management problems (Strandell, 1998). The leakage water from the tailings has continuously been collected and treated in a neutralization plant since the active phase of the mine, and the produced sludge was disposed of on top of the tailings in sludge ponds. The tailings were partly covered with a thin till layer in the 1970's (Ranstad Skifferaktiebolag, 1981). Nevertheless when the mining concession ended the need for a sustainable solution of the waste problem was obvious. The reclamation measures started in 1990 after a decision made by the county board in Västergötland (Studsvik AB, 1988).

The disposal site was covered with a three-layer cover, in order to minimize oxygen diffusion and water infiltration as described in (Börjesson *et al.*, 2001). It consisted of an impermeable sealing layer made of clay, a drainage and buffering layer made of coarse grained calcite and on top of this a protective till layer. Finally there was a thin layer of topsoil in order to facilitate vegetation establishment and further increase the protection capacity (see Figure 5).



**Figure 5.** Schematic figure of the mine waste and its cover

As a second measure a new leakage water collection pond and a new leakage water precipitation plant were constructed in 1996 near the disposal site. Further a sedimentation pond was constructed where the treatment plant precipitates were collected. The Högberg Lake was temporarily drained and the contaminated sediments were removed and disposed of on the outskirts of the waste deposit together with a large amount of lime. The stabilization of the sediments hence obtained was estimated to be sufficient to ensure a long-term stable product and permitting a more simple cover, consisting of a single till layer (Sundblad, pers. com.).

An extensive environmental monitoring programme was launched (Erjeby *et al.* 2003). Several sampling sites were established in groundwater aquifers and surface water bodies, which since then have been sampled up to once a week. A monitoring station was established as a reference upstream the tailings area, in the stream *Marbäcken*. Two groundwater reference sites were also established.

The covering of the waste deposit resulted in a significant lowering of the heavy metal concentration in the leakage waters, especially in the northern parts. In the year 2001 the leakage water collected in the upper parts of the western ditch was estimated to be of such a good quality that an increased residence time in the ditch would be sufficient without compromising the environmental goals in the Lake Blackesjön. This was achieved in 2002 by damming the ditch with V-notches at two locations, and thus from the winter 2003 the water from the western ditch no longer passes through the treatment plant (Erjeby *et al.*, 2003).

Still, the groundwater in parts of the tailings remains very acid (pH 3) and shows elevated metal concentrations (section 3.3.4.). Accordingly the leakage water from the southern parts of the tailings is still of such bad quality that treatment measures in the precipitation plant are necessary (Börjesson, 2002).

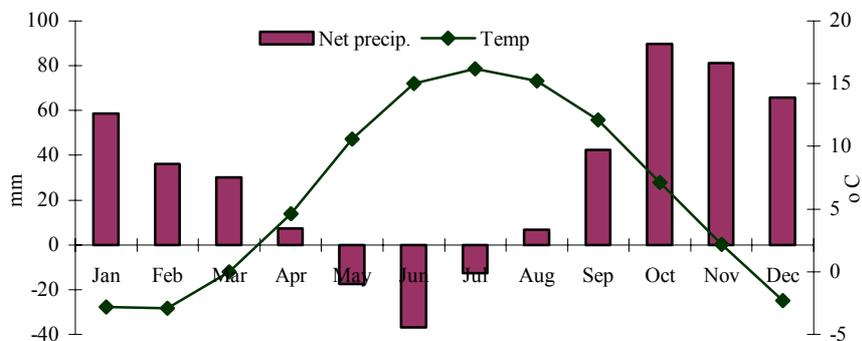
The water from the treatment plant is led to the sedimentation pond where the precipitates are settled, resulting in large quantities of sediments. In the tailings there is a presumably large amount of old sludge, contained in the sludge ponds. One of the remaining questions before the reclamation of Ranstad is completed concerns the long-term stability of these sludge wastes. The acid leakage water might consume the surplus of lime since the earlier stabilization of the sludge ponds did not take this acid input into account. There might be a risk that acid leakage water might also be transported to the collection pond and the sedimentation pond sediments, resulting in an acid input affecting these materials.

In short, it needs to be investigated what is to be expected in the future concerning the leakage water sediment and it is not fully investigated why there is such a difference in leakage water quality between the southern and northern parts of the tailings. This might be due to the sludge ponds.

### 3.3. DESCRIPTION OF PRESENT CONDITIONS

#### 3.3.1. Meteorology

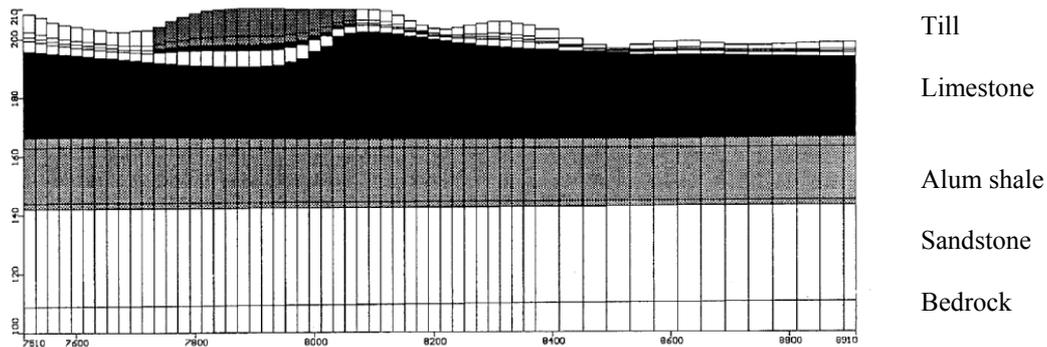
The Swedish Meteorological and Hydrological Institute's (SMHI) weather monitoring station *Skövde* is located close to the Ranstad area and shows a good correlation with earlier site specific measurements of climatic variables (Erjeby *et al.* 2003). Corrected data from SMHI on net precipitation and temperature are presented in Figure 6. The mean annual precipitation is 800 mm. Mean potential evaporation is 450 mm yr<sup>-1</sup> (*ibid.*; Bergström, 1993). The mean monthly temperature peaks at 16.2° C in July and has a minimum in February with -2.9°C.



**Figure 6.** Meteorological conditions at the field site

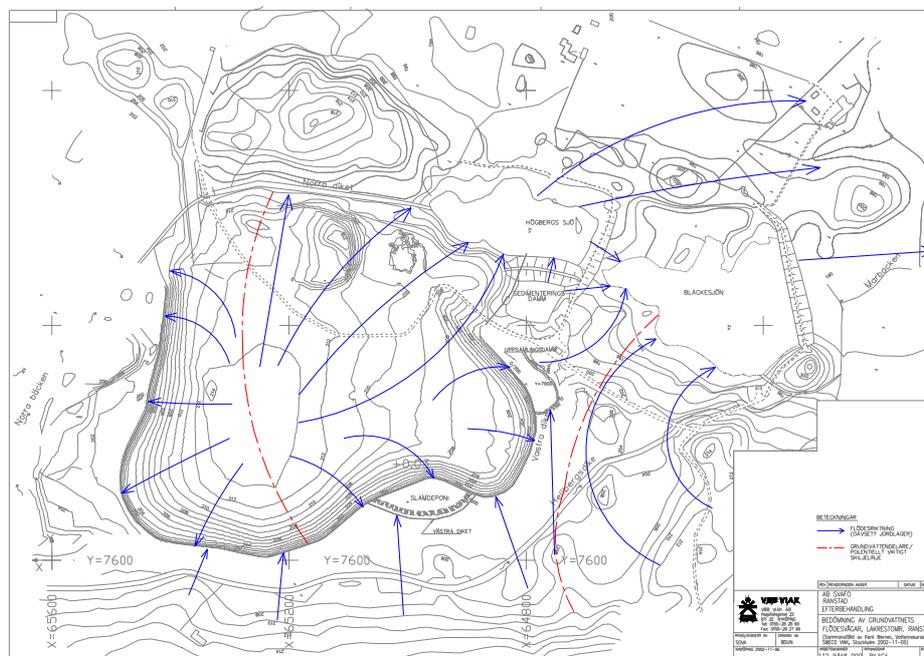
#### 3.3.2. Hydrogeology and groundwater movements

The bedrock in the Ranstad area consists of parallel horizontal layers. The primary bedrock is gneiss followed by sandstone, alum shale and lime stone layers. The soil mainly consists of till (Hägg, 2000). The sand and lime stone layers are aquifers with a high hydraulic conductivity while the alum shale layer constitutes an aquiclude in between them. The tailings deposit is resting on a layer of compacted peat, constituting a low hydraulic conductivity boundary to the till layer. The tailings therefore act as a small aquifer. In all this results in four more or less separated aquifers (Figure 7).



**Figure 7.** Concepts of hydrogeological characteristics.

The groundwater movement in the area was summarized by Werner (2002). Most of the tailings area acts as a discharge area for groundwater, but it is probable that some recharge occurs locally. The main flow direction is a south-easterly directed flow, with a water divide in the northern part of the tailings (Figure 8).



**Figure 8.** General groundwater flow (arrows) and water divides (dotted lines), irrespective of aquifer (Werner, 2002).

In two groundwater modelling studies the groundwater movements and the contamination transport have been further investigated (Magnusson and Liedholm, 1998; Hägg, 1999). The main issues were to clarify the flow and transport patterns and the leakage between the aquifers. Magnusson and Liedholm (1998) concluded that the risk of a contamination impact on the neighbouring freshwater wells was very small. Hägg (1999) on the other hand, showed that a leakage to the sandstone aquifer and a subsequent contamination spreading beyond the monitored area was to be expected, however without presenting a quantitative assessment. Compared to regional water recharge the contaminated addition can be assumed to be small (Erjeby *et al.* 2003).

Werner (2002) discussed the effects of a lowered water level in the sedimentation pond, which is a plausible scenario. The water level of the sedimentation pond ought to largely impact its leakage water collection and a lowering or a dewatering of the pond would most likely have impacts on the water flow in the system. Quantitative conclusions were however difficult to make and further investigations including expanded modelling efforts were recommended. One possible scenario is that the dewatered sedimentation pond would act as an outflow for the leakage water.

### 3.3.3. Hydrological conditions and water balance

In several studies (Erjeby *et al.* 2003; Liedholm and Magnusson, 1998) the water balance in the tailings area has been calculated. A precisely balanced water budget has been difficult to accomplish since measurements of evapotranspiration are missing.

According to Erjeby *et al.* (2003) 53% of the corrected precipitation, which corresponds to 7.0 l/s (900 mm/yr), is estimated to evaporate. The remaining water forms surface runoff (1.7 l/s), infiltrates through the protection layer and is drained by the drainage layer on top of the sealing layer (0.8 l/s) or infiltrates to the tailings to form new leakage water (0.6 l/s). 0.5 l/s is stored in the protection layer aquifer.

A mean value of the balance calculations during the last four years shows a net production of ground/leakage water at a rate of 0.6 l/s (76 mm yr<sup>-1</sup>) in the tailings of which 0.4 l/s percolates to the till aquifer and 0.1 l/s is drained to the western ditch (Erjeby *et al.* 2003). Flow rates were significantly smaller during 2001 and 2002 compared to previous years.

Regional groundwater recharge in the area is estimated to surpass 100 mm per year (Hägg, 1999).

Average flow in the Western ditch 2002 was 5.4 l/s (Erjeby *et al.*, 2003). No quantitative investigation on how this flow will be affected by changes of the water level in the sedimentation pond has yet been performed. Werner (2002) discusses the possibilities for the water divide in the tailings to move due to such changes. A displacement of the water divide would affect the amounts of leakage water in the western ditch and the amount of water reaching the sedimentation pond.

Hence, the collection pond collects most of the leakage water from the tailings southern parts, but the water level in the nearby sedimentation pond probably affects this collection. If the water level of the sedimentation pond were lowered there would probably be an outflow of leakage water also into this pond. The quantity of this inflow can be estimated to be at the most 0.1 l/s according to the water balance studies and comments from Sundblad (2003).

### 3.3.4. Water quality

The county administration has set environmental goals for the water quality in the lake Blackesjön with respect to the annual mean concentration of Fe, As, Pb, Co, Cr, Ni, Zn and U (Erjeby *et al.*, 2003). These goals have been met since 1997, owing to chemical treatment of the water in the collection pond.

The change in water quality before the water reaches the treatment plant is monitored at station 2 (Table 3). In the collection pond (Stn 2) the heavy metal concentrations range from low (Cd) to very high values (As, Fe, Ni, Zn) according to the Swedish EPA's assessment criteria (Erjeby *et al.* 2003). The concentration of uranium corresponds to a high value, the concentrations of the rest of the elements are very low, low or medium (Cr, Ni) in relation to the Swedish EPA criteria.

Groundwater and surface water quality data for the year 2002 are presented in Table 3 and Figure 9. Ground water samples have been filtered through a millipure filter (0.45 µm) prior to analysis.

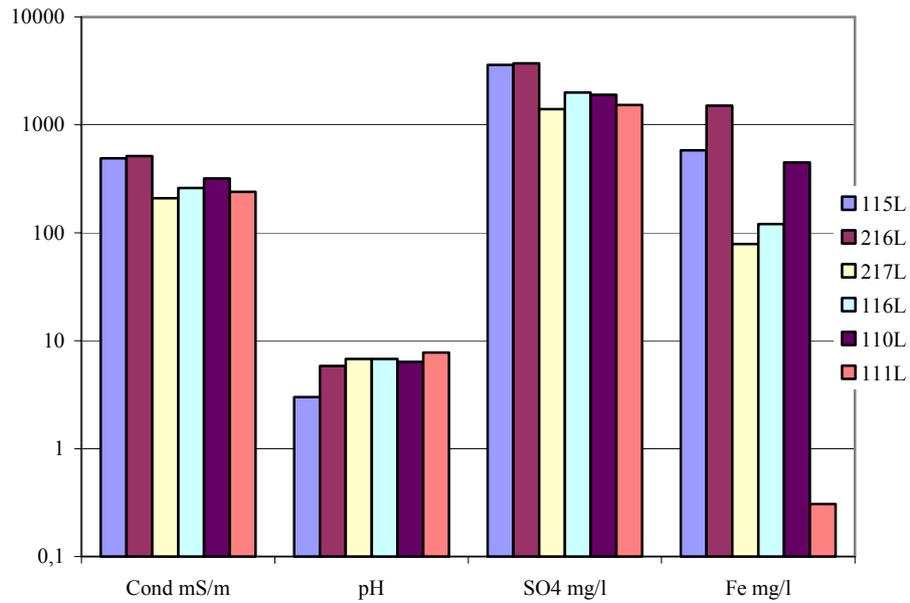
**Table 3.** Measured water quality in the western ditch and in a selection of groundwater well, average values for 2002. L=mill tailings aquifer, M = till aquifer, K = limestone aquifer. Wells are shown in Figure 4.

	Surface water		Ground water					
	2	115L	Lsouth <sup>1</sup>	111L	213M	Msouth <sup>2</sup>	101K <sup>3</sup>	305K
Temp	9.2	96	194	10.8	21	19.7	4.78	170
kond mS/m	185	490	328	240	220	102	44.5	220
PH	7.5	3	6.5	7.8	7.4	8	7.9	7.2
TOC mg/l	4.0	-	-	-	-	-	-	-
DOC mg/l	4.4	-	-	-	-	-	-	-
N-tot mg/l	2.5	-	-	-	-	-	-	-
PO4-P mg/l	0.0	-	-	-	-	-	-	-
SO4 mg/l	973	3600	2380	1529	1270	428	26.5	1350
Alk. HCO3 mg/l	290	1	213	133	355	193	240	290
Ca mg/l	384	415	481	391	365	198	79.3	495
Fe mg/l	21.2	580	568	0.31	0.33	0.05	0.05	32.5
Mg mg/l	54.2	220	71.5	224	115	12.1	5.55	101
Al µg/l	10.5	52500	13922	3.05	8.5	4.05	1.25	2.5
As µg/l	0.5	1035	65.6	0.63	0.75	1.15	0.63	4.8
Co µg/l	5.2	205	25.6	8.63	13.5	1.07	0.12	3.2
Cr µg/l	2.0	105	2.97	0.4	0.5	0.56	1.2	0.81
Cu µg/l	0.9	38.5	0.97	1.43	156	1.16	0.68	0.49
Mn µg/l	3164	5150	13956	5743	13250	348	77.5	2900
Ni µg/l	29.0	1450	135	32	51.5	7.53	12.8	16.5
Zn µg/l	14.6	1550	104	16.5	268	7	12.3	8
U µg/l	25.3	495	159	260	24.5	5.58	0.63	5.35

<sup>1</sup>Lsouth is an average of the sampling wells 216L, 217L and 116L.

<sup>2</sup>Msouth is an average of the sampling wells 304M, 306M and 308M

<sup>3</sup>Upstream reference stations



**Figure 9.** Comparison of groundwater quality between different parts of the tailings with respect to four key variables; electrical conductivity, pH and the concentration of sulphate and iron. The first four are located in the very southern part of the deposit, the last two in the middle of the deposit.

## 4. METHODS

### 4.1. EXPERIMENTAL DESIGN

In order to fulfil the objectives of the thesis a methodology to simulate the prevailing conditions in the tailings area was developed. The aim was to evaluate the controlling parameters in the sludge waste and to investigate what determines the sediments' chemical stability. Laboratory experiments were set up in order to simulate these controlling parameters, using site-specific samples. The obtained information was then transferred to the real site conditions.

A screening of the problem was deemed necessary due to limitations in time and resources. This meant that no sampling of the sludge ponds inside the tailings was done since the exact location of the ponds was not clear. Furthermore the heterogeneity of the material was thought to make a representative sampling difficult, since a large set of samples would probably be needed. Accordingly an unwanted, extensive penetration of the sealing layer would be needed, which might compromise its effect. Instead it was assumed that the old sludge had the same properties as the recently produced sludge, whose properties are now known.

In search of a realistic model describing the behaviour of the sludge materials, when submitted to external inputs, the controlling parameters in the sludge were defined. This was done by using the theoretical background given in Section 2 together with the site description in Section 3. Hence, the two most important factors determining the possible transport of metals from the sludge waste were considered to be pH and redox potential (Eh). In addition the texture was determined to identify the approximate size range of the reactive surfaces.

The first step was to characterize the sediment materials with respect to their content of major elements and heavy metals (Section 4.3.1.). Thus sediment samples were taken in the sedimentation pond and the collection pond and sent for chemical analysis. In order to reveal the conditions in the ponds along with the possible oxygen status in the bottom waters a single characterization of the water bodies was done. Preferably the redox conditions in the sediments should have been investigated, however such measurements were not included in the study because of their huge complexity (Norrström, pers. comm.).

The next step was to investigate the mobility of the heavy metals. This was done in leaching tests. In the leaching test the environment was supposed to correspond to future possible conditions that might occur in the sediments. It should also give indications of the importance of the presumed controlling parameters, i.e. pH and Eh, to allow a discussion of which circumstances should be avoided.

In order to investigate the impacts of the controlling parameters, four different experimental treatments were set up, each one corresponding to a (plausible) level of pH or Eh (see Section 4.3.3.). The leakage of heavy metals at each of these levels was then determined. Since the weathering of the tailings produces sulphuric acid (Section 2.1), and a correspondingly high sulphate level is found in the leakage water, sulphuric acid was chosen to be the acidifying agent in the experiments. The leakage tests were designed

using the guidelines from the Swedish EPA (Naturvårdsverket, 2002b), where the methodology of a pH static test is described.

The acid neutralising capacity of the materials was determined using information on acid consumption in the leakage tests. The amount acid needed to lower the pH value to 5 or 3 in the experimental environment, could be used as an indicator of the neutralising capacity of the material *in situ*. Calculations were done to determine the amount of pH 3 water that the material could tolerate before a decrease in pH would occur. Using the obtained information concerning plausible inflow (Section 3.2.4.) a plausible time dimension could be obtained. The specific methodology of the calculations is described in Section 4.4.1.

The following step was to estimate the total mass of heavy metals potentially available for leaching. This was achieved by using the information on leaching behaviour obtained in the leaching tests followed by an upscaling to the actual amounts of sediment material present in the sedimentation pond.

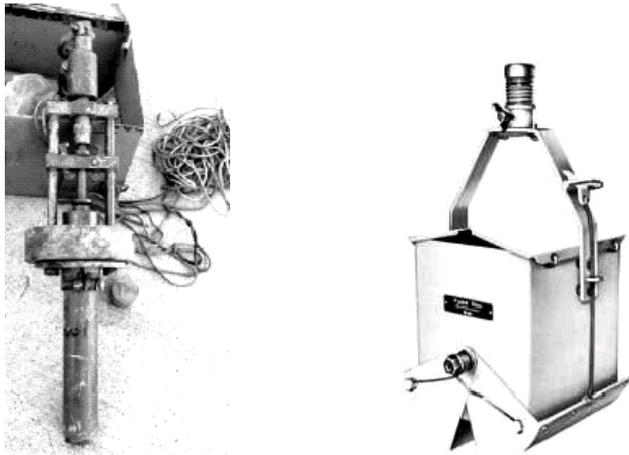
Using the figures provided in section 5.1 together with the new test results, calculations were also done of the total content of heavy metals in the old sludge, i.e. the sludge formed in the neutralisation plants and in the treatment plant during the active phase of the mine until its closure. The properties of the sedimentation pond sediments were assumed to be transferable to the old sludge, in order to allow for some estimations of the contamination potential.

However, no calculation of available mass in the collection pond was done since no estimation on the total amount of present sediments has been done. The calculation procedure is further described in Section 4.4.1.

## **4.2. FIELDWORK**

Sampling of sediments and a basic investigation of the water bodies were conducted in Ranstad on October 8, 2003. Fieldworkers were Magnus Crantz, Alcontrol Laboratories and Patrik Brodd. The weather was cloudy, with a moderate wind and a temperature at around 5° C. Within two hours after the sampling all samples were transported to *Alcontrol Laboratories* in Skara. There each sample was homogenised through careful mixing with a spoon and divided into representative subsamples for the following analyses.

For the sediment sampling the first choice was to use a core sampler, with a 25 cm long plexiglass tube with a diameter of 2.5 cm, in order to take undisturbed samples showing different sediment strata. An *Ekman* collector was planned to be a second alternative if the tube sampler would not give satisfying results due a to hard bottom or uncohesive sediments. The samplers are shown in Figure 10. Two portable field measurement instruments for electric conductivity (*WTW LL196*), dissolved oxygen concentration and temperature (*WTW OXI196*) were used.



**Figure 10.** Used sediment samplers. To the left a core sampler (gravitation) and to the right an Ekman collector.

#### **4.2.1. Sediment sampling in the sedimentation pond**

20 sediment cores were collected with the tube sampler on 20 approximately equally distributed locations in the pond, avoiding areas close to shore and the outlets from the treatment plant. Surplus water was removed from each core. Each core was subsequently emptied into one bulk sample, contained in a clean plastic bag.

#### **4.2.2. Sediment sampling in the collection pond**

The tube sampler was used to collect six sediment cores from six evenly distributed locations in the deeper north-eastern part of the pond. In the southern, more shallow part of the pond, the sediment layer was thin and the bottom hard, why the Ekman collector was used. One sample was taken from four locations, evenly distributed over the south-western part of the pond.

#### **4.2.3. Water body characterization**

In the collection and sedimentation ponds vertical profiles of electrical conductivity, dissolved oxygen concentration and temperature were measured using the field instruments. Readings on one location in the deepest part of each pond were done each 0.5-meter from the bottom to the water surface.

### 4.3. CHEMICAL ANALYSES

*Analytica* made the solid phase analyses, *Mikrokemi* determined total organic carbon, the *Swedish Geotechnical Institute* (SGI) conducted the leaching tests and texture analyses, and *Alcontrol* analysed the leaching fluids (Table 4). The analytical methods are described in the sub-sections below.

**Table 4.** Summary of the laboratory analyses.

	<i>Sedimentation pond</i>	<i>Collection pond</i>
<i>Solid phase analyses</i>		
Metals <sup>1</sup>	X	X
Dry matter (DM) <sup>1</sup>	X	X
Texture/particle size <sup>2</sup>	X	X
Total organic carbon <sup>3</sup>	X	X
Loss on ignition (LOI)	X	X
<i>Leaching tests<sup>2</sup></i>		
pH 3	X	X
pH 5	X	X
Ambient pH	X	X
Reduced redox state	X	X
<i>Analyses of leaching fluids<sup>4</sup></i>		
Metals		All fluids

<sup>1</sup> Analytica, Luleå; [www.analytica.se](http://www.analytica.se)

<sup>2</sup> Swedish Geotechnical Institute, Linköping; [www.swedgeo.se](http://www.swedgeo.se)

<sup>3</sup> Mikrokemi, Uppsala; [www.mikrokemi.se](http://www.mikrokemi.se)

<sup>4</sup> Alcontrol, Linköping; [www.alcontrol.se](http://www.alcontrol.se)

#### 4.3.1. Solid phase analyses

The water content and dry matter were determined by drying the samples at 105°C for four hours. Subsequently the organic matter content was determined by calculating the loss after heating the samples to 550°C and the corresponding Remains After Heating (RAH) is given as a result. This was followed by a loss on ignition analysis (LOI), i.e. measurement of the loss from heating to 1000°C. A final measure of the organic content was the analysis of total organic carbon (TOC), on dried material.

The analyses of metal content were done using two different methods; melting and leaching. The methodologies are further described by the laboratory in question (package MG1-N). First the samples were melted with LiBO<sub>2</sub> and followed by a dissolution in HNO<sub>3</sub>, the resulting melted ash was analysed with Inductively Coupled Plasma Atom Emission Spectroscopy (ICP-AES), which yielded the content of macroelements – SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. Then a second set of samples was leached in concentrated HNO<sub>3</sub> and heated in a closed container in a microwave oven in order to determine the content of trace metals. The leachate was then analysed with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for As, Cd, Co, Cu, Hg, Pb and U along with ICP-AES for Ba, Be, Cr, La, Mo, Nb, Ni, S, Sc, Sn, Sr, V, W, Y, Zn and Zr. The precision ranges from +/-15 to +/- 30 % deviation. ICP-MS has a lower detection level than ICP-AES, and accordingly a lower degree of uncertainty (Harris, 1999).

### **4.3.2. Texture analysis**

The particle size distribution of the samples was measured by SGI. First the samples were sifted through a 2 mm sift, for a first division between fine and coarse material. Secondly sifting through a 0.06 mm sift was done. Then sedimentation analysis was used which gave the all the particle fractions smaller than 0.06 mm. The sedimentation analysis was done through dispersing the sample in sodium-hexa-meta-phosphate where after it was let to rest to allow the particles to settle. The sedimentation time is then measured which gives the soil texture. The dry weight densities of the samples were determined in conjunction to the sedimentation analysis.

No further sifting was done to determine the larger fractions than 2 mm and fractions inbetween 2 and 0.06 mm because of lack of material.

### **4.3.3. Leaching tests**

A leaching test procedure was done based on the methodology suggested by the Swedish EPA (Naturvårdsverket, 2002b) but modified to suit the specific conditions at Ranstad. It was based on the pH-static test “Influence of pH on leaching with continuous pH control” (pp 15-16) with the modification that sulphuric acid was used instead of HNO<sub>3</sub>. Four levels were chosen in order represent a span of possible scenarios; pH 3 (worst case), pH 5, the ambient pH of the sediments and finally the pH obtained at low oxygen conditions. The last alternative aimed at simulating reducing conditions and was achieved by replacing the air in the sample with Ar gas.

During the first four hours acid was added to the sample in a batch with continuous mixing, so as to reach the target pH. During the next 40 hours mixing occurred in order to reach equilibrium conditions, whereafter the pH level was checked again during the following 4 hours with the limitation that only a small amount of acid was allowed to be added. The total testing time was hence 48 hours, after which the leaching fluids from each level was separated from the sediments by filtration (pore size 0.45µm) and were sent for chemical analysis.

### **4.3.4. Analyses of leaching fluids**

The leaching fluids were analysed for the content of trace metals and macroelements. K, Ca, Mg and Na were analysed with ICP-AES and Fe, Mn, Al, Co, Sr, U, As, Ba, Cd, Cr, Cu, Ni, Pb and Zn were analysed with ICP-MS. Uncertainty levels ranged from 15% (Fe) to 30 % (Zn).

## 4.4. CALCULATIONS

### 4.4.1. Calculations on acid neutralising capacity

The laboratory reported the volume of acid needed for each material to reach each pH level. A multiplication with the molarity of the acid used resulted in a corresponding neutralization capacity in proton equivalents for each material, before the pH level would be reached. Hence the result is the amount of  $H^+$  that is tolerable before a pH decrease will occur. The calculations followed Equation 4.1 below.

$$ANC_{pH} = \frac{\sum_{i=1}^k (V_{acid,i} \times M_{acid,i} \times z)}{m_{sample}} \left[ \frac{\text{moles } H^+}{\text{kg DM}} \right] \quad (4.1)$$

Where  $ANC$  = Acid Neutralization Capacity to the stated pH. [mole kg DM<sup>-1</sup>]  
 $V_{acid,i}$  = Volume of added acid at time i. [L]  
 $M_{acid,i}$  = Concentration of the acid added at time i. [mole L<sup>-1</sup>]  
 $z$  = mole of protons per mole of added acid. [-]  
 $m$  = mass of sample used in the experiment. [kg DM]

### 4.4.2. Calculations on metal leaching ability and available amounts

The first step was to calculate the leaching ability of each metal at each leaching test level for the collection pond and sedimentation pond sediments. This was done by dividing the recorded leached concentration of metal with the recorded total concentration of metal. The leaching ability  $\Psi$ , or availability, was hence obtained as a percentage of the total content (Equation 4.2).

$$\Psi_{pH}^{Me} = \frac{C_{leached}^{Me, pH}}{C_{total}^{Me, pH}} \times 100 \quad [\%] \quad (4.2)$$

Where  $\Psi_{pH}^{Me}$  = leaching ability of metal Me at level pH [%]

$Me$  = the metal in question

$C^{Me, pH}$  = recorded concentration of each metal at each pH [mg / kg DM]

Secondly the total mass of each metal ( $m_{total}^{Me}$ ) present in the sedimentation pond and the sludge ponds, was evaluated using the total mass of sediment present and the concentration of each metal obtained in the solid phase analysis (Equation 4.3). Since no measurement of the total amount of sediments was done in this study, it was necessary to rely on previous estimates. For the collection pond no estimates of the total amount of sediments was available and accordingly no calculations were done. In the sludge ponds the concentration of metals were presumed to be identical to the concentrations recorded in the sedimentation pond sediments.

$$m_{total}^{Me} = C_{total}^{Me} \times V_{total} \times \rho \times DM \quad (4.3)$$

where  $\rho$  = the bulk density of the sample material in question

$DM$  = the dry matter fraction

Finally the total mass of each metal, calculated above, was multiplied with its leaching ability. This gave the total amount of available metal at each one of the four experimental levels, thus forming the potential load of contamination at each scenario (Equation 4.4).

$$m_{available}^{Me, pH} = m_{total}^{Me} \times \Psi_{pH}^{Me} \quad (4.4)$$

#### 4.4.3. Calculations on possible load

The rate of metal release at pH 3 was calculated by dividing the amount of available metals with the time of mobilisation. However an estimation of this time was needed, and was obtained by using the information on ANC together with plausible scenarios of the material's reaction to an exposure to acid water. To do this two alternatives were used concerning the nature of the actual neutralization process; (A) a completely linear response or (B) a non-linear response. The first approach presumed that a continuous pH drop would occur starting in the peripheral parts of the exposed material (a control volume of 1 kg). The second presumed that no pH drop would occur until all acid neutralization capacity in the whole mass of material was consumed in which moment the pH would drop. The scenarios are described in Table 5 and 6. Hence in alternative A the output was the annual load of each metal and in alternative B the total load along with the total time until this would be released.

**Table 5.** Description of scenarios used for the calculations in the sludge ponds. Both response alternatives were used in all five scenarios.

SCENARIO	Infiltration Q (l/s)	ANC (H <sup>+</sup> <sub>ekv</sub> / kg)	Output alt. A <sup>1</sup> φ	Output alt. B <sup>2</sup> Φ and T <sub>total</sub>
I	0.6	100 % of experimental	Annual load per metal (kg/year)	Time to response (years). Total load per metal (kg).
II	0.6	50 % of experimental		
III	0.6	25 % of experimental		
IV	1.2	100 % of experimental		
V	1.2	25 % of experimental		

<sup>1</sup>Linear response – continuous metal flux.

<sup>2</sup>Non linear response – instantaneous metal load.

In the sedimentation pond a plausible, bad case, scenario was set to 0.1 l/s infiltrating water holding pH 3 and a neutralization capacity of the sediments as the measured (Scenario I). A middle scenario was used where the amount of infiltrating water was set to 0.1 l/s but where the material only contained 50% of the measured ANC (Scenario II). A worst-case scenario was set to the double amount of infiltrating water and a neutralization capacity of 50 % of the one measured under laboratory conditions (Scenario III).

**Table 6.** Description of scenarios used for the calculations in the sedimentation pond. Both response alternatives were used in all three scenarios.

SCENARIO	Infiltration Q (l/s)	ANC (H <sup>+</sup> <sub>ekv</sub> / kg)	Output alt. A <sup>1</sup> φ	Output alt. B <sup>2</sup> Φ and T <sub>total</sub>
I	0.1	100 % of experimental	Annual load per metal (kg/year)	Time to response (years). Total load per metal (kg).
II	0.1	50 % of experimental		
III	0.2	50 % of experimental		

<sup>1</sup>Linear response – continuous metal flux.

<sup>2</sup>Non linear response – instantaneous metal load.

In addition, the calculated annual load from the sediments was put in relation to the average annual load recorded in the collection pond the last year. Each metal load was therefore calculated and presented as the percentage of the load today, in order to show the influence of each sediment mass.

In all, the calculations followed the procedures below.

$$t_{1kg} = \frac{ANC_{pH3}}{Q_{est.} \times [H^+]_Q} \quad (4.5)$$

$$\phi_{Me} = \frac{1}{t_{1kg}} \times C_{leached}^{Me, pH3} \quad (\text{Alternative A}) \quad (4.6)$$

$$\left\{ \begin{array}{l} T_{total} = t_{1kg} \times m_{total} \\ \Phi_{Me} = m_{available}^{Me, pH3} \end{array} \right. \quad (\text{Alternative B}) \quad (4.7)$$

where  $t_{1kg}$  = the time it takes to reach pH 3 in 1 kg material [years]  
 $Q$  = the inflow of acid groundwater affecting the material [ $m^3$ /yr]  
 $[H^+]_Q$  = the acid concentration of the inflowing groundwater [moles/ $m^3$ ]  
 $\phi_{Me}$  = annual load of the relevant metal [kg/yr]  
 $T_{total}$  = time to pH 3 in the whole mass of material  
 $\Phi_{Me}$  = instantaneous load at time T of metal Me

## 5. RESULTS

The first section contains the results from the literature study, describing the chemical processes that produced the sludge waste deposited in Ranstad. In the following sections the results from analyses and calculations done within this thesis are presented.

### 5.1. THEORETICAL CONTENT IN SLUDGE AND SEDIMENTS

The uranium extraction process, i.e. the leaching with sulphuric acid, had a minor influence on the chemical content of the crushed alum shale according to prior analyses found in Strandell (1998). See Table 7. Nevertheless process waters contained high concentrations of heavy metals, which after the uranium extraction had to be immobilized before the process water could be let to the recipient (Table 8). Strandell (1998) provided a detailed description of the process chemistry of the former wastewater treatment in the Ranstad plant. The process waters were during the active time of the mill, depending on their origin, treated in one of the two neutralization plants (NP1 and NP2) whereas the leakage waters from the ripening storage and the tailings area were treated in the wastewater treatment plant (WWP).

**Table 7.** Chemical content in original alum shale and mill tailings.

	Shale (%)	Tailings (%)
<i>SiO<sub>2</sub></i>	44.9	45.5
<i>Al<sub>2</sub>O<sub>3</sub></i>	12.3	12.0
<i>Fe<sub>2</sub>O<sub>3</sub></i>	8.7	7.1
<i>CaO</i>	1.5	1.2
<i>MgO</i>	0.8	0.7
<i>Na<sub>2</sub>O</i>	0.2	0.2
<i>S</i>	6.9	6.4
<i>P</i>	0.08	0.01
<i>As</i>	0.008	0.007
<i>U</i>	0.03	0.008
<i>C<sub>org</sub></i>	15.5	15.5

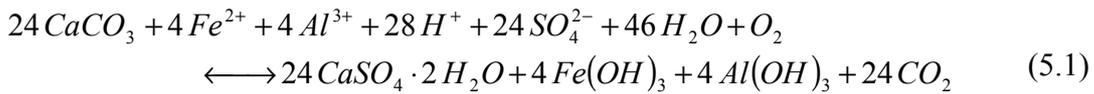
From: Strandell (1998)

**Table 8.** Metals in solution in process fluids and formed sludge.

	Fluids (mg/l)	Sludge (mg/l)
<i>Fe</i>	8900	
<i>Al</i>	8900	
<i>Ca</i>	900	500
<i>K</i>	4100	8400
<i>Mg</i>	2600	5100
<i>Mo</i>	40	
<i>V</i>	160	
<i>SO<sub>4</sub></i>	132000	46000
<i>PO<sub>4</sub></i>	5200	
<i>SiO<sub>4</sub></i>	700	
<i>U</i>	680	<1
<i>Na</i>		5800
<i>NH<sub>4</sub></i>		1200
<i>Mn</i>		200
<i>Ni</i>		30
<i>Zn</i>		0,6
<i>B</i>		3,5
<i>Sn</i>		0,2
<i>Cd</i>		<0,8
<i>Co</i>		0,8
<i>As</i>		<0,08
<i>Cr</i>		<4
<i>Cu</i>		2

From: Strandell (1998)

In NP1 uranium-free percolate from the ion exchange process was treated at a rate of 50 m<sup>3</sup> h<sup>-1</sup> at full operation speed. The percolate was an acid solution (pH 2) containing principally iron, aluminium and sulphate ions. It was neutralised with lime sludge as shown by the following schematic reaction (Strandell, 1998):



The reaction was done using a large surplus of lime (35%) and oxygen (6-7 times). At 40°C a five-hour reaction time was needed in order to completely oxidise the ferrous (II) ions to ferric (III) ions. In the final solution pH barely surpassed 7 (Hellberg, 1975). At full operation speed the total sludge production was 400 000 m<sup>3</sup> yr<sup>-1</sup> all of which was pumped to the ponds in the tailings area.

In NP2 a set of acid solutions were treated, including the cleansing waters from the leakage basins and the extraction processes. The procedure and reaction chemistry was the same as in NP1. The capacity was 100 m<sup>3</sup>h<sup>-1</sup> but the resulting sludge quantity was lower than in NP2. Based on Strandell (1998) the total produced sludge volume can be estimated to 0.57 Mm<sup>3</sup>, with 3/7-operation speed during 4.5 years.

In the WWP 6000 – 11000 m<sup>3</sup> day<sup>-1</sup> leakage water from the tailings area and the ripening storage, principally consisting of ferrous- and ferric sulphate, were treated with hydrated lime yielding a mixture of Fe(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> and FeCO<sub>3</sub>.

In a report considering the waste handling and early remediation (Ranstad Skifferaktiebolag, 1981) it was stated that the main constituents in the sludge waste were remaining lime and gypsum together with iron- and aluminium hydroxides. It was further said that the total amount of solid material in the sludge was estimated to 200 000 metric tons. The sludge was deposited on an area of approximately 5 ha, in ponds confined by tailings in the southern parts of the tailings area. For an approximate location of the sludge ponds see Figure 11.

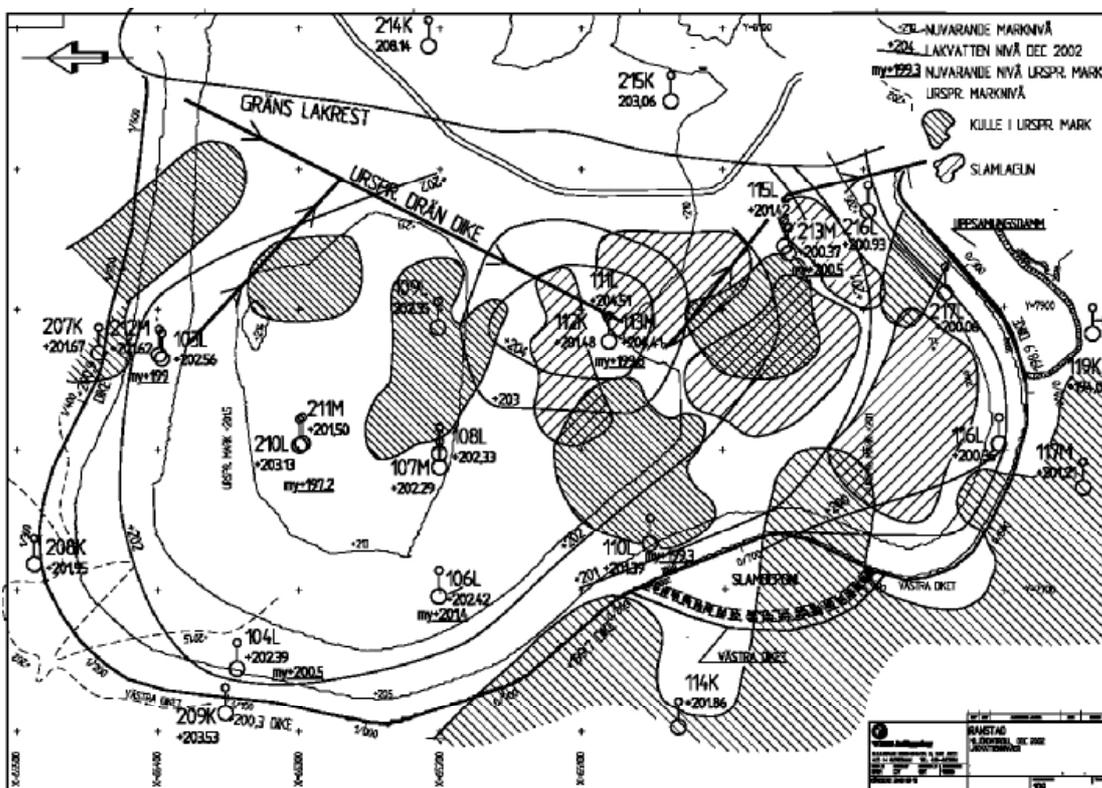


Figure 11. Location of the sludge ponds.

Agnedal (1974) discussed the waste problems experienced in Ranstad. He stated that the treatment process in the neutralization plants was not driven far enough to reach neutral conditions, why a complete iron oxidation was not achieved in the extraction solutions during the operation of the plant. In the sludge ponds the pH level was further reduced and many metals were remobilised and collected in the leakage water. This leakage water was supposed to have been completely neutralized in the treatment plant (WWP) to at least pH 9 whereafter the sludge was re-transported to the sludge ponds. However once again it was affected by the decreasing pH in the sludge ponds and metals were thought to be remobilised. Periodically there was barely a recirculation of the leakage water back to the tailings area, i.e. no achieved treatment (Agnedal, 1974).

Magnesium was deemed to be the most important metal to consider, and rates of this was used as a measure of the impact of the sludge ponds on the leakage water. This is possible since the rate of solute magnesium to solute iron was about 1 to 100 in (experimental) leakage water originating only from pyrite containing mill tailings whereas in the leakage water ditches the ratio could approach 1 to 4 (Agnedal, 1974). The reason for the high Mg content in the sludge was not because an external source of Mg was used in the process but because its high solubility made its concentration magnify throughout the recirculation of the process waters.

No figures concerning the quantity of produced sludge from the WWP have been found in any of the archived documents.

Observations of difficulties from the operation time recited by Strandell (1998) include the use of chlorine gas to further enhance the chemical reduction and sedimentation of iron and manganese during one of the first operation years. This was abandoned when no effect was recognized. Furthermore cleaning water from the dressing plant did not work in either of the treatment plants. Magnetite rich water was therefore disposed directly in the sludge deposit.

## 5.2. RESULTS FROM FIELD WORK AND ANALYSES

### 5.2.1. Visual inspection of sediments

In the sedimentation pond, the thickness of the sediment layer had a large variability, ranging from a few centimetres to more than the entire sampling tube (>25 cm). The thickness may at the thickest parts possibly surpass 3 meters according to Sundblad (2003). Most of the sampled cores were intact and of a viscous and cohesive nature. The colour varied between deeply red, through pale red to white and occasionally some black layers were present. No particular smell, e.g. of H<sub>2</sub>S, was recognised.

In the collection pond the sediment layer was thin, about 4-7 cm, except for in the deepest part in the northeastern part of the pond (near the outlet) where the thickness was estimated to be 20 cm. Gravel and some plants were present at the bottom of the pond. The sediment was of a different nature compared to that in the sedimentation pond; it was more porous and had a higher water content and a lower strength. The colour was mostly reddish, often with black parts further down in the profiles. No specific smell could be identified from the sediments.

### 5.2.2. Sediment content

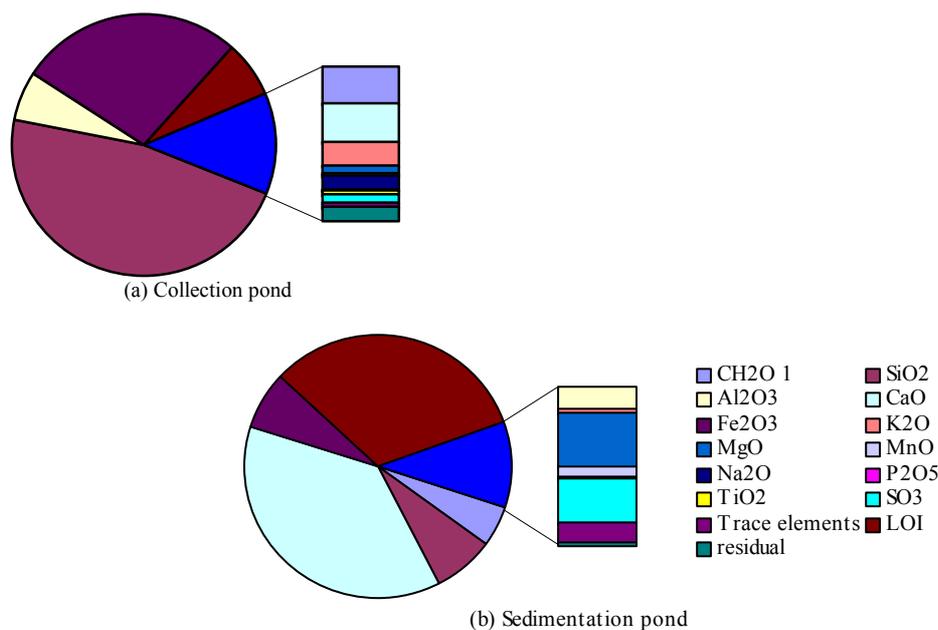
The total contents of macro elements are shown in (Table 9) and the content of trace metals in Table 10. Major constituents were Si (predominant in the sediments from the collection pond), Fe (collection pond) and Ca (predominant in the sedimentation pond), balanced by O (see also Figure 12).

**Table 9.** Content of major constituents in % per dry weight material (% DM)

		Collection pond	Sedimentation pond
DM	%	40.6	17.4
TOC	%DM	1.3	2.1
CH <sub>2</sub> O <sup>1</sup>	%DM	3.25	5.25
RAH	%DM	95.1	93.6
SiO <sub>2</sub>	%DM	48.5	7.58
Al <sub>2</sub> O <sub>3</sub>	%DM	6.28	1.66
CaO	%DM	3.2	39.4
Fe <sub>2</sub> O <sub>3</sub>	%DM	28.3	7.63
K <sub>2</sub> O	%DM	1.98	0.32
MgO	%DM	0.64	3.73
MnO	%DM	0.18	0.66
Na <sub>2</sub> O	%DM	1.16	0.17
P <sub>2</sub> O <sub>5</sub>	%DM	0.09	0.04
TiO <sub>2</sub>	%DM	0.32	0.05
SO <sub>3</sub>	%DM	0.66	3.05
Trace	%DM	0.37	1.3
LOI	%DM	7.3	34.6
Sum <sup>2</sup>	%DM	99.0	100.2

<sup>1</sup>Simplified formula for organic matter, calculated by multiplying the TOC with the scaling factor 2.5 (Mw<sub>CH<sub>2</sub>O</sub>/Mw<sub>C</sub>)

<sup>2</sup>Sum of oxides, trace elements and LOI. The separate measure of organic matter is not included.



**Figure 12.** Contents of macro elements in %; metal oxides and loss on ignition, in the collection pond (a) and the sedimentation pond (b).

**Table 10.** Contents of micro elements: heavy metals and sulphur as mg/kg dry weight (DM).

		Collection pond	Sedimentation pond
<b>As</b>	mg/kg DM	12.8	8.16
<b>Ba</b>	mg/kg DM	345	80.9
<b>Be</b>	mg/kg DM	1.45	0.66
<b>Cd</b>	mg/kg DM	0.36	0.68
<b>Co</b>	mg/kg DM	11.6	16.2
<b>Cr</b>	mg/kg DM	41.7	30.9
<b>Cu</b>	mg/kg DM	13.5	62.8
<b>Mo</b>	mg/kg DM	11.5	3.0
<b>Ni</b>	mg/kg DM	53.8	94.6
<b>Pb</b>	mg/kg DM	10.0	4.99
<b>S</b>	mg/kg DM	2650	12200
<b>Sr</b>	mg/kg DM	99.4	230
<b>U</b>	mg/kg DM	19.0	85.7
<b>V</b>	mg/kg DM	39.3	32.9
<b>Zn</b>	mg/kg DM	51.6	129

### 5.2.3. Leaching results

The pH levels obtained in the leaching tests were 3.0, 4.1, 7.6 and 7.8 for the collection pond sample (Table 11), and 3.0, 4.9, 8.7 and 8.9 in the sedimentation pond sample (Table 12). Leaching of metals occurred at high rates at the lowest pH level and at lower but yet considerable rates at the middle pH level. At ambient pH, i.e. at near neutral and basic conditions respectively, almost no leaching was recorded. This was also the case at the fourth experimental level, i.e. ambient pH with reduced (red.) conditions. The obtained redox potentials ranged from +460 to +520 mV in the collection pond and from +410 to +750 mV in the sedimentation pond, i.e. no reducing conditions were obtained.

**Table 11.** Results from leaching tests at four different levels on the collection pond sediments. Bold font indicates that proposed threshold values<sup>1</sup> for a classification of non-hazardous waste is exceeded.

pH		Collection pond				REF <sup>1</sup>
		3	5.1	7.6	7.8 (red)	
Conductivity	<i>mS/m</i>	299	232	87,7	86,4	
Redox Eh	<i>MV</i>	542	499	422	460	
Fe	<i>mg/kg DM</i>	1686	2.47	<0.5	<0.5	
Mn	<i>mg/kg DM</i>	446	258	0.31		
Mg	<i>mg/kg DM</i>	377	340	85	78	
Al	<i>mg/kg DM</i>	139	0.09	<0.02	0.03	
U	<i>mg/kg DM</i>	8.93	0.02	0.12	0.09	
Zn	<i>mg/kg DM</i>	8.83	0.41	0.02	<0.02	40
Ni	<i>mg/kg DM</i>	<b>7.24</b>	1.85	<0.005	<0.005	5
Co	<i>mg/kg DM</i>	1.79	0.43	0.01	0.0007	3.5
Cu	<i>mg/kg DM</i>	1.69	0.01	0.01	0.008	20
Ba	<i>mg/kg DM</i>	0.48	0.54	0.36	0.36	
Cr	<i>mg/kg DM</i>	0.038	<0.006	<0.005	<0.005	7
Sr	<i>mg/kg DM</i>	10.9	10.3	2.6	2.9	
Cd	<i>mg/kg DM</i>	0.15	0.018	<0.0005	<0.0005	0.2
Pb	<i>mg/kg DM</i>	0.05	0.008	0.005	<0.005	7
As	<i>mg/kg DM</i>	0.02	<0.006	<0.005	<0.005	2

<sup>1</sup>Acceptable leaching level at L/S 10 permitting a classification of non hazardous waste proposed by the Swedish Association of waste handling agents (RVF REF).

**Table 12.** Results from leaching tests at four different levels on the sedimentation pond sediments. Bold font indicates that proposed threshold values<sup>1</sup> for a classification of non-hazardous waste is exceeded.

pH		Sedimentation pond				REF <sup>1</sup>
		3	4.9	8.7	8.9 (red.)	
Conductivity	<i>mS/m</i>	967	811	142	143	
Redox Eh	<i>mV</i>	753	521	413	407	
Mg	<i>mg/kg DM</i>	23220	22680	1818	1800	
Mn	<i>mg/kg DM</i>	4386	3150	0.60	0.55	
Al	<i>mg/kg DM</i>	3741	391	0.21	0.19	
Fe	<i>mg/kg DM</i>	581	<0.63	<0.5	<0.5	
U	<i>mg/kg DM</i>	92.9	4.41	0.15	0.098	
Zn	<i>mg/kg DM</i>	<b>92.9</b>	11.6	<0.02	<0.02	40
Ni	<i>mg/kg DM</i>	<b>86.4</b>	<b>56.7</b>	0.034	0.046	5
Cu	<i>mg/kg DM</i>	<b>49.0</b>	0.42	0.31	0.22	20
Sr	<i>mg/kg DM</i>	19.4	23.9	2.1	2.6	
Co	<i>mg/kg DM</i>	<b>12.6</b>	<b>4.79</b>	0.007	0.004	3.5
Cr	<i>mg/kg DM</i>	2.19	0.030	0.011	<0.005	7
Ba	<i>mg/kg DM</i>	0.92	0.88	0.035	0.037	
Cd	<i>mg/kg DM</i>	0.59	0.15	<0.0005	0.001	0.2
As	<i>mg/kg DM</i>	0.07	0.013	<0.006	0.004	2
Pb	<i>mg/kg DM</i>	0.04	0.0076	<0.006	<0.005	7

<sup>1</sup>Acceptable leaching level at L/S 10 permitting a classification of non hazardous waste proposed by the Swedish Association of waste handling agents (RVF 2002).

Fe was the most strongly leached metal in the collection pond (1.7 g/kg DM at pH 3). Mg was the most strongly leached in the sedimentation pond (23 g/kg DM at pH 3), followed by manganese in both cases (0.45 g/mg DM resp. 4.4 g/mg DM). Highly leached trace metals were also Al, U, Ni and Zn. The contaminant release from the sedimentation pond was in general approximately ten times higher than the release from the collection pond, with the exception of iron.

#### 5.2.4. Acid consumption and corresponding neutralization capacity

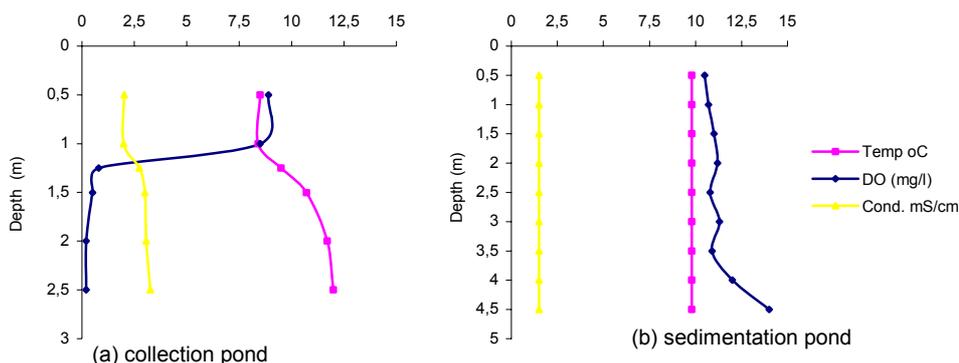
To achieve the target pH level sulphuric acid was added in the quantities shown in Table 13. The sedimentation pond sediments were very stable and demanded a large addition (10 mol/kg) of sulphuric acid in order for the buffer capacity to be consumed and the pH value to decrease. The addition made was larger than the one expected and as a consequence the target liquid to solid ratio (L/S) could not be maintained; it ended at 13 instead of 10 for the sedimentation pond sample. Table 13 also provides information on the neutralization capacity of the two samples, i.e. the amount of protons tolerable before pH 3 and pH 5 are reached. The collection pond sample proved to tolerate approximately 1 mole per kg dry weight material before the buffer capacity was consumed. The sedimentation pond sample needed approximately 10 moles per kg dry weight material before the pH decreased.

**Table 13.** Acid consumption and corresponding neutralisation capacity

	Weight (g)	time (hrs)	pH	Total amount added acid				Final			
				volume (ml)	Conc (M)	volume (ml)	Conc (M)	[H <sup>+</sup> ]eq (moles)	[H <sup>+</sup> ]eq (moles/kg)	volume (ml)	L/S (-)
<b>Collection pond</b>											
pH 3	60.4	0	8.91	-	-	-	-	-	-	-	-
		4	2.81	18.5	1	-	-	0.037	0.61	-	-
		44	3	33.9	1	-	-	0.068	1.12	-	-
		48	3	34.5	1	-	-	0.069	1.14	628	10.4
pH 5	61	0	8.9	-	-	-	-	-	-	-	-
		4	5.14	21.0	1	-	-	0.042	0.69	-	-
		44	5	30.9	1	-	-	0.062	1.01	-	-
		48	5	30.9	1	-	-	0.062	1.01	599	9.8
<b>Sedimentation pond</b>											
pH 3	30.8	0	8.91	-	-	-	-	-	-	-	-
		4	2.81	100	1	8.2	18	0.348	11.3	-	-
		44	3	100	1	8.2	18	0.348	11.3	-	-
		48	3	100	1	8.2	18	0.348	11.3	398	12.9
pH5	30.8	0	8.9	-	-	-	-	-	-	-	-
		4	5.14	88.3	1	7.8	18	0.316	10.27	-	-
		44	5	88.3	1	7.9	18	0.318	10.32	-	-
		48	5	88.3	1	7.9	18	0.318	10.32	386	12.5

### 5.2.5. Characterisation of the studied water bodies

The water bodies of the collection pond and the sedimentation pond proved to be different in terms of oxygen content and electrical conductivity of the water. The profiles obtained from measuring the dissolved oxygen content, electric conductivity and temperature in the water showed that the sedimentation pond was completely mixed at the sampling occasion whilst the collection pond had a clear thermo- and halocline at around 1.25 m. depth (Figure 13.a and b). Anoxic conditions seemed to be present in the bottom water layers of the collection pond opposed to the sedimentation pond where the bottom water was well aerated.



**Figure 13.** Profiles obtained from conductivity, oxygen and temperature measurements in the collection pond (a) and the sedimentation pond (b).

### 5.2.6. Sample texture

Sample texture analysis showed that 100 % of the particles in both samples had a diameter of less than 2 mm. Furthermore 65% of the samples were smaller than 0.06 mm. In the sedimentation pond 4.6% of the particles were smaller than 0.002 mm compared to 25% of the particles in the collection pond.

The bulk density of both samples was determined to 2700 kg / m<sup>3</sup>.

## 5.3. RESULTS FROM CALCULATIONS

### 5.3.1. Leaching ability

The metal leaching ability was calculated as the percentage of leached quantity compared to total content for each metal at each leaching test level. There was generally a greater leaching ability in the sedimentation pond compared to the collection pond (Table 14 and 15). There U, Ni, Mn, Cu, Co, Cd and Mg proved to be particularly mobile in an acid environment (75-100 % leached at pH 3). At pH 5 the leaching ability was substantially lower, yet Mg, Mn and Ni maintained a high leaching ability whereas the leaching ability of uranium diminished completely. Notable is also that arsenic and iron were essentially immobile at all pH levels (at oxidised conditions) in both materials. In the collection pond the leaching ability was lower for all metals compared to the sedimentation pond; uranium, cadmium, zinc and manganese were the most mobile metals. The pH level affected the result substantially particularly for U, Cd and Zn. All results are presented in Table 14 (collection pond) and 15 (sedimentation pond).

**Table 14.** Leaching ability of metal contaminants in the collection pond, calculated as leached quantity divided by total quantity for each metal and pH level. Bold font indicates leaching ability greater than 30% of total content.

pH	Collection pond				
	3.0	5.1	7.6	7.8 (red.)	
Fe	%	0.9	0.0	0.0	0.0
K	%	1.8	1.6	1.3	1.2
Ca	%	25	26	7.9	7.0
Mg	%	9.7	8.8	2.2	2.0
Na	%	0.7	0.7	0.6	0.6
Mn	%	<b>33</b>	19	0.0	0.0
Al	%	0.4	0.0	0.0	0.0
Co	%	15	3.7	0.1	0.0
Sr	%	11	10	2.6	2.9
U	%	<b>47</b>	0.1	0.6	0.5
As	%	0.2	0.0	0.0	0.0
Ba	%	0.1	0.2	0.1	0.1
Cd	%	<b>42</b>	4.9	0.1	0.1
Cr	%	0.1	0.0	0.0	0.0
Cu	%	12	0.1	0.1	0.1
Ni	%	13	3.4	0.0	0.0
Pb	%	0.5	0.1	0.1	0.0
Zn	%	17	0.8	0.0	0.0

**Table 15.** Leaching ability of metal contaminants in the sedimentation pond, calculated as leached quantity divided by total quantity for each metal and pH level. Bold font indicates leaching ability greater than 70% of total content.

pH	Sedimentation pond				
	3.0	4.9	8.7	8.9 (red.)	
Fe	%	1.1	0.0	0.0	0.0
K	%	19	14	6.4	6.7
Ca	%	2.2	2.1	0.3	0.3
Mg	%	<b>100</b>	<b>100</b>	8.1	8.0
Na	%	18	19	9.5	10
Mn	%	<b>86</b>	62	0.0	0.0
Al	%	43	4.5	0.0	0.0
Co	%	<b>78</b>	30	0.0	0.0
Sr	%	8.4	10	0.9	1.1
U	%	<b>100</b>	5.1	0.2	0.1
As	%	0.9	0.2	0.0	0.0
Ba	%	1.1	1.1	0.0	0.0
Cd	%	<b>87</b>	22	0.0	0.1
Cr	%	7.1	0.1	0.0	0.0
Cu	%	<b>78</b>	0.7	0.5	0.4
Ni	%	<b>91</b>	60	0.0	0.0
Pb	%	0.8	0.2	0.1	0.1
Zn	%	<b>72</b>	9.0	0.0	0.0

### 5.3.2. Possible load from old sludge ponds

An estimation of the total amount of sludge present in the tailings was carried out, in order to estimate a possible load from the sludge ponds. An operation speed of the stated 43 % of maximum capacity during 4.5 years meant an actual sludge production from NP1 of 0.77 Mm<sup>3</sup>. Estimating the dry substance quota to 5% and a dry density of

2700 kg/m<sup>3</sup> this corresponds to 10500 tons of dry material now present in the tailings. Using the old laboratory results in table 8 (Section 5.1.), 0.77 Mm<sup>3</sup> of sludge contains approximately 4000 tons of magnesium, 150 tons of manganese, 23 tons of nickel, 1.5 tons of copper and 0.4 tons of uranium *in solution* of which an unknown quantity has been mobilized and left the tailings with the leakage water. The 35% surplus of lime used in the treatment process would present a large buffer of acidity, but how much that has already been consumed is unknown.

As an alternative approach, the figure of solid mass of old sludge, 0.2 million metric tons, found in the statement by Agnedahl (1971, see Section 5.1), was used to calculate the total amount of metals in the sludge ponds. To enable this it was assumed it contained the same rates of metals that were found in sedimentation pond sediments. Then the amount of available metals was calculated, using the figures on availability obtained in the leaching tests. Results of total metal content included 1000 metric tons of Mn, 2000 Metric tons of Al, 20 Metric tons of Ni and 17 Metric tons of U (Table 16). Availability depended largely on pH level, peaking at approximately 800 metric tons of available Mn and Al at pH 3.

The total time until the acid buffer capacity would be exhausted ( $T_{total}$ ) ranged from 15000 years to 120000 years depending on which scenario that was used (Table 17).

**Table 16.** Amounts of heavy metals in sludge pond sediments using stated approximated sludge mass and rates found in analysis of sedimentation pond sediments.

	Total	Available		
		pH 3	pH 5	natural pH
<b>Fe</b> Kg	1,1E+07	1,2E+05	6,0E+01	5,0E+01
<b>Mg</b> Kg	4,5E+06	4,5E+06	4,5E+06	3,6E+05
<b>Mn</b> Kg	<b>1,0E+06</b>	8,8E+05	6,3E+05	1,2E+02
<b>Al</b> Kg	<b>1,8E+06</b>	7,5E+05	7,8E+04	4,2E+01
<b>Co</b> Kg	3,2E+03	2,5E+03	9,6E+02	1,5E+00
<b>Sr</b> Kg	<b>4,6E+04</b>	3,9E+03	4,8E+03	4,2E+02
<b>U</b> Kg	1,7E+04	1,7E+04	8,8E+02	3,0E+01
<b>As</b> Kg	1,6E+03	1,4E+01	2,5E+00	6,0E-01
<b>Ba</b> Kg	1,6E+04	1,8E+02	1,8E+02	7,1E+00
<b>Cd</b> Kg	1,4E+02	1,2E+02	3,0E+01	5,0E-02
<b>Cr</b> Kg	6,2E+03	4,4E+02	6,0E+00	2,2E+00
<b>Cu</b> Kg	<b>1,3E+04</b>	9,8E+03	8,3E+01	6,3E+01
<b>Ni</b> Kg	<b>1,9E+04</b>	1,7E+04	1,1E+04	6,9E+00
<b>Pb</b> Kg	1,0E+03	7,7E+00	1,5E+00	6,0E-01
<b>Zn</b> Kg	<b>2,6E+04</b>	1,9E+04	2,3E+03	2,0E+00

**Table 17.** Time to impact; total time needed to reach pH 3 (depending on scenario).

Scenarios	$T_{total}$ (years)
<b>I</b>	119300
<b>II</b>	59600
<b>III</b>	29800
<b>IV</b>	59600
<b>V</b>	14908

Calculations on the possible continuous annual load originating from sludge pond sediments were done using the estimated solid mass of sludge pond sediments (200 000 metric tons; see section 5.1) and the results from the analysis of the sedimentation pond sediments. Five different scenarios regarding neutralization capacity of the sludge and the percolating water flow velocity were assumed (described in Section 4.4.3), thus the calculations were done for each one of these five scenarios. A comparison to the average annual load to collection pond recorded in station 2 during 2002 was also made for each scenario, and the estimated load from the sludge ponds are given as the percentile of this in Table 18. Results showed a very varying possible influence of the sludge ponds compared to the loads experienced today, from 0 to 77 % depending on which metal and scenario considered. Largest influence was estimated for the load of Al (5-40 kg/yr), U, Cu, Ni and Zn whereas the influence of the sludge ponds on the load of Mg seemed to be very low.

**Table 18.** Annual load of heavy metals originating from sludge ponds using different scenarios with respect to water flow velocity and neutralization capacity. Comparison to the annual load registered in the western ditch / collection pond (Station 2).

Metal	Stn 2. kg/yr	Scenarios I		II		III		IV		V	
		kg/yr	%	kg/yr	%	kg/yr	%	kg/yr	%	Kg/yr	%
Fe	4192	0.97	0.02	1.95	0.05	3.89	0.09	1.95	0.05	7.79	0.19
Mg	6816	37.7	0.55	75.4	1.11	151	2.21	75.4	1.11	302	4.43
Mn	532	7.36	1.38	14.7	2.76	29.4	5.53	14.7	2.76	58.8	11.1
Al	128	6.27	<b>4.91</b>	12.5	<b>9.82</b>	25.1	<b>19.6</b>	12.5	<b>9.82</b>	50.2	<b>39.3</b>
Co	1.4	0.02	1.57	0.04	3.13	0.08	6.27	0.04	3.13	0.17	12.5
Sr	87	0.03	0.04	0.06	0.07	0.13	0.15	0.06	0.07	0.26	0.30
U	5.2	0.14	2.77	0.29	5.54	0.57	11.1	0.29	5.54	1.15	22.2
As	1.3	0.00	0.01	0.00	0.02	0.00	0.04	0.00	0.02	0.00	0.08
Ba	6.2	0.00	0.02	0.00	0.05	0.01	0.10	0.00	0.05	0.01	0.20
Cd	0.0	0.00	2.78	0.00	5.56	0.00	11.1	0.00	5.56	0.01	22.2
Cr	0.2	0.00	1.76	0.01	3.52	0.01	7.05	0.01	3.52	0.03	14.1
Cu	0.9	0.08	<b>9.60</b>	0.16	<b>19.2</b>	0.33	<b>38.4</b>	0.16	<b>19.2</b>	0.66	<b>76.8</b>
Ni	8.8	0.14	1.65	0.29	3.29	0.58	6.59	0.29	3.29	1.16	13.2
Pb	0.3	0.00	0.02	0.00	0.05	0.00	0.09	0.00	0.05	0.00	0.19
Zn	8.2	0.16	1.89	0.31	3.79	0.62	7.57	0.31	3.79	1.25	15.1

- I. 0.6 l/s and 100% of neutralization capacity of sedimentation pond sediments.
- II. 0.6 l/s and 50% of neutralization capacity of sedimentation pond sediments.
- III. 0.6 l/s and 25% of neutralization capacity of sedimentation pond sediments.
- IV. 1.2 l/s and 100% of neutralization capacity of sedimentation pond sediments.
- V. Worst case: 1.2 l/s and 25% of neutralization capacity of sedimentation pond sediments.

### 5.3.3. Possible load from sedimentation pond sediments

Results from the calculations described in Section 4.4.3 of possible load from the sedimentation pond included 200 metric tons of Fe, 33 tons of Al, 320 kg of U and 350 kg of Ni. The total load (Table 19) peaked at pH 3, where 16 metric tons of Mn, 320 kg of U and Ni proved to be available. The total time for a depletion of the acid buffer capacity in the sedimentation pond was calculated to at least 3300 years (Table 20).

The annual continuous load of metals in all three scenarios from the sedimentation pond is found in Table 21 (using the linear acid neutralisation alternative). Results showed a small impact, ranging from 0 to 6 %, of the leached load from the sedimentation pond sediments compared to the average annual load at station 2 (Table 21).

**Table 19.** Amounts of heavy metals (total and available) in sedimentation pond sediments.

		Total	Available		
			pH 3	pH 5	ambient pH
<b>Fe</b>	kg	2,0E+05	2,2E+03	1,1E+00	9,4E-01
<b>Mg</b>	kg	8,4E+04	8,4E+04	8,4E+04	6,8E+03
<b>Mn</b>	kg	1,9E+04	1,6E+04	1,2E+04	2,2E+00
<b>Al</b>	kg	3,3E+04	1,4E+04	1,5E+03	8,0E-01
<b>Co</b>	kg	6,1E+01	4,7E+01	1,8E+01	2,7E-02
<b>Sr</b>	kg	8,6E+02	7,3E+01	9,0E+01	8,0E+00
<b>U</b>	kg	3,2E+02	3,2E+02	1,7E+01	5,7E-01
<b>As</b>	kg	3,1E+01	2,7E-01	4,7E-02	1,1E-02
<b>Ba</b>	kg	3,0E+02	3,4E+00	3,3E+00	1,3E-01
<b>Cd</b>	kg	2,5E+00	2,2E+00	5,7E-01	9,4E-04
<b>Cr</b>	kg	1,2E+02	8,2E+00	1,1E-01	4,2E-02
<b>Cu</b>	kg	2,4E+02	1,8E+02	1,6E+00	1,2E+00
<b>Ni</b>	kg	3,5E+02	3,2E+02	2,1E+02	1,3E-01
<b>Pb</b>	kg	1,9E+01	1,5E-01	2,8E-02	1,1E-02
<b>Zn</b>	kg	4,8E+02	3,5E+02	4,4E+01	3,8E-02
<b>Mo</b>	kg	4,3E+01	0,0E+00	0,0E+00	0,0E+00
<b>V</b>	kg	1,2E+02	0,0E+00	0,0E+00	0,0E+00

**Table 20.** Time to impact; total time needed to reach pH 3 (depending on scenario).

Scenarios	T <sub>total</sub> (years)
<b>I</b>	13400
<b>II</b>	6700
<b>III</b>	3350

**Table 21.** Annual load of heavy metals originating from sedimentation pond sediments using different scenarios with respect to water flow velocity and neutralization capacity. Comparison to the annual load registered in the western ditch / collection pond (Station 2).

Metal	Stn 2. kg/yr	Scenarios I		II		III	
		kg/yr	%	kg/yr	%	kg/yr	%
<b>Fe</b>	4192	0.16	0.00	0.32	0.01	0.65	0.02
<b>Mg</b>	6816	6.29	0.09	12.57	0.18	25.15	0.37
<b>Mn</b>	532	1.23	0.23	2.45	0.46	4.90	0.92
<b>Al</b>	128	1.05	0.82	2.09	1.64	4.18	3.27
<b>Co</b>	1.4	0.00	0.26	0.01	0.52	0.01	1.04
<b>Sr</b>	87	0.01	0.01	0.01	0.01	0.01	0.02
<b>U</b>	5.2	0.02	0.46	0.05	0.92	0.10	1.85
<b>As</b>	1.3	0.00	0.00	0.00	0.00	0.00	0.01
<b>Ba</b>	6.2	0.00	0.00	0.00	0.01	0.00	0.02
<b>Cd</b>	0.0	0.00	0.46	0.00	0.93	0.00	1.85
<b>Cr</b>	0.2	0.00	0.29	0.00	0.59	0.00	1.17
<b>Cu</b>	0.9	0.01	1.60	0.03	3.20	0.05	6.40
<b>Ni</b>	8.8	0.02	0.27	0.05	0.55	0.10	1.10
<b>Pb</b>	0.3	0.00	0.00	0.00	0.01	0.00	0.02
<b>Zn</b>	8.2	0.03	0.32	0.05	0.63	0.10	1.26

- I. 0.1 l/s pH 3 percolating water and 100% of measured neutralization capacity.
- II. 0.1 l/s pH 3 percolating water and 50 % of measured neutralization capacity.
- III. Worst case: 0.2 l/s pH 3 percolating water and 50% of measured neutralization capacity.

## 6. DISCUSSION

### 6.1. DISCUSSION ON RESULTS AND FIELDWORK

#### 6.1.1. Pond characteristics

The characteristics of the collection pond with stratified conditions and anoxic sediments are similar to those of a natural ground water supplied lake. The lack of oxygen is probably due to that the inflowing groundwater has a low oxygen content and contain Fe(II) ions. The following oxidation to ferrous iron consumes oxygen. The black strata in the deeper parts of the sediment samples clearly indicate sulphate reduction and the corresponding formation of sulphides, even though no smell of H<sub>2</sub>S was recorded. On the other hand the conditions in the sedimentation pond are quite unnatural with apparently oxygenised sediments due to the addition of lime and the aeration in the treatment plant. A limited level of oxygen demanding biological activity can be presumed because of the high pH levels. Nevertheless some of the sediment samples contained black layers further down in the profile, which indicates anoxic conditions in the deeper parts of the sedimentation pond sediments. A limited occurrence of metal sulphides can hence be expected also here.

#### 6.1.2. Solid phase analyses

The occurrence of metal sulphides was further indicated by the solid phase analyses. Sulphur rates proved to be high in all analysed materials, particularly in the sedimentation pond. The exact speciation is unknown, but it is likely that sulphides and sulphates, e.g. gypsum (CaSO<sub>4</sub> \* 2 H<sub>2</sub>O) or absorbed sulphate ions predominate.

When considering the different estimates of organic matter, i.e. LOH, TOC and LOI, differences in results were striking. Particularly the loss on ignition (LOI) results greatly exceeds TOC and loss on heating (LOH) results in the sedimentation pond, indicating that something else, apart from organic matter, also is lost at this higher temperature. A possible explanation can be that calcium carbonate can be part of the LOI since it decomposes and melts at 900°C (Aylward and Findlay, 1998). Total content of lime and calcium carbonate could therefore approach 65 % rather than the stated 40% in the sedimentation pond, thus including the part of the LOI not explained by organic matter content.

However, LOI can also reflect a vaporization of structurally bound water, as noted by Lövgren (2001). Furthermore thermal decomposition of iron(III) hydroxosulphates is stated to be possible at around 600°C (*ibid.*). In Lövgren (2001) the sum of all oxides and LOI well surpassed 100 %, which was explained by a double counting of sulphates, which hence was concluded to partly be included in the LOI. In the collection- and sedimentation ponds the sum of all oxides including sulphate (presumed all recorded sulphur is in the form of sulphates) was very close to 100%, indicating that the amount of sulphates lost in the LOI analysis is low. On the other hand, it is uncertain which species of sulphur that actually prevail. However, if sulphides would be dominating, their lower molecular weight implies that the residual term would grow larger. The deficit in the mass budget would confirm that no sulphur is double counted, and that no sulphates are included in the LOI. Finally, it remains possible that some other previously uncon-

sidered in the total analysis compound makes up for the deficit or is included in the LOI, although it seems unlikely since no previous studies have recorded it. Conclusively the LOI analysis ought to have been a measure of carbonates, why the CaO figures in Table 9 are an underestimate of the total lime content.

When compared to acid consumption records, the high rates of carbonates are confirmed by the buffer capacity that was experienced when trying to acidify the sedimentation pond sample. Nevertheless, the amount of consumed acid did not correspond completely to the high lime content. While acidification records (Section 5.2.4) showed a neutralisation capacity of 10 moles of protons per kg sample, a 65% lime content ought to imply a neutralization capacity of approximately 65 moles per kg material. A total reaction between lime and sulphuric acid can therefore not be presumed. The reason for this is probably the short experiment time (48 hrs) during which there was no time for a complete dissolution of the carbonates present.

In the collection pond high content of SiO<sub>2</sub> was found. High rates of chisel oxides are an indication of the slow weathering of silicates, which then have precipitated as secondary silicate minerals. The stated 50 % seems like an overestimate of these quite stable minerals to have been transported with the leakage water. This might instead indicate that the sediments taken in the collection pond partly contained material from the bottom sealing (clay till), instead of merely recent sediment. The sampling experience allows this scenario since difficulties aroused during the sampling and the different materials could have been mixed using the 'Ekman' collector. Even more, the fluffy uppermost recent sediments, which are easily resuspended, might not have been caught in the sampling at all. If this were the case, it could mean that all stated results from the collection pond sediments are underestimates of the actual level, to an uncertain level. However the rate of Fe oxides (30%) was very elevated compared to till (5%) why one might conclude that at least 50% of the sampled material ought to have been recent sediments.

The recorded rates of heavy metals in the sediments in both ponds seem surprisingly low. When compared to the Swedish EPA threshold values for contaminants in soils, only the content of nickel (in both ponds) impedes the classification of the material as a soil suitable for sensitive land use (Table 22).

**Table 22.** Content of selected heavy metals and As with colour coded classifications when applicable (using guidelines and comparison values for lakes and stream sediments from Swedish EPA (Naturvårdsverket, 2003)).

<i>mg/kg TS</i>	As	Cd	Cr	Cu	Ni	Pb	Zn	V	Co
<b>Collection pond</b>	13	0.36	42	13	54	10	52	39	24
<b>Sedimentation pond</b>	8.1	0.68	31	63	95	5.0	130	33	16
<i>Threshold 1*</i>	15	80	120	100	35	80	350	120	30
<i>Threshold 2**</i>	15	300	250	200	150	300	700	200	60
	I. No deviation;	2. Small deviation	3. Significant deviation	4. Large deviation	5. Very large deviation				

\*Threshold value for sensitive land use according to Swedish EPA (Naturvårdsverket,1997)

\*\*Threshold value for less sensitive land use with groundwater protection according to Swedish EPA (*ibid.*)

If relying on the general guideline values from the Swedish EPA the sediments have contamination levels not very different from average Swedish lake sediments. According to this, the materials could even be suitable for construction since the threshold values are not exceeded. However it is insufficient to rely on the guideline values since guideline values are missing for some of the most interesting metals, e.g. uranium. Therefore a set of local reference values of the rate of metals in local stream sediment would have been very useful, but no sampling of suitable reference material has been carried out in the area. The bedrock in the area is easily weathered, implying a natural mobilization of metals, as shown by the heavy metal load in the river Hornborga and the elevated background metal values in the Ranstad area.

In a study of mine leakage water sediments in Northern Sweden, Widerlund (1999) reports concentrations of heavy metals 3-5 higher than those found in the collection pond at Ranstad, except for Ni, which had a slightly higher level in Ranstad. U was not measured.

Is it possible to transfer the properties of the sedimentation pond sediments obtained in the laboratory analyses to the sludge pond material? When comparing the theoretical content of the sludge pond material (Section 5.1) with the recorded content in the sedimentation pond sediments (Section 5.2.2) they coincide well. The sludge now disposed in the sludge ponds was produced by the same basic methodology of lime precipitation, from a leakage water of similar characteristics (high levels of U, Fe(II), Ni). Major constituents were stated to be unconsumed lime, gypsum, iron and aluminium hydroxides in the sludge ponds. Analyses of the sedimentation pond material revealed 65 % lime and calcium carbonates, 8% iron hydroxides and 2% aluminium oxides as the first, second and fourth constituent. The 8% silica oxides were the third largest constituent, and not theoretically accounted for in the sludge ponds. This post might be explained by that leakage water now is older compared to when the sludge ponds were formed; slowly weathered silicates have now started to weather in the tailings and secondary silica minerals have re-precipitated in the sedimentation pond when pH levels were higher. A similar precipitation also seems to occur in the collection pond.

### **6.1.3. Leaching test and calculations results**

The sedimentation pond sample proved to be very stable to pH changes; a large amount of acid was needed in order to obtain the lower pH levels. This was quite expected in view of the large lime additions, which generate buffer capacity. However when a lower pH was reached the leaching was substantial, proving extreme pH dependence for a majority of the immobilised metals.

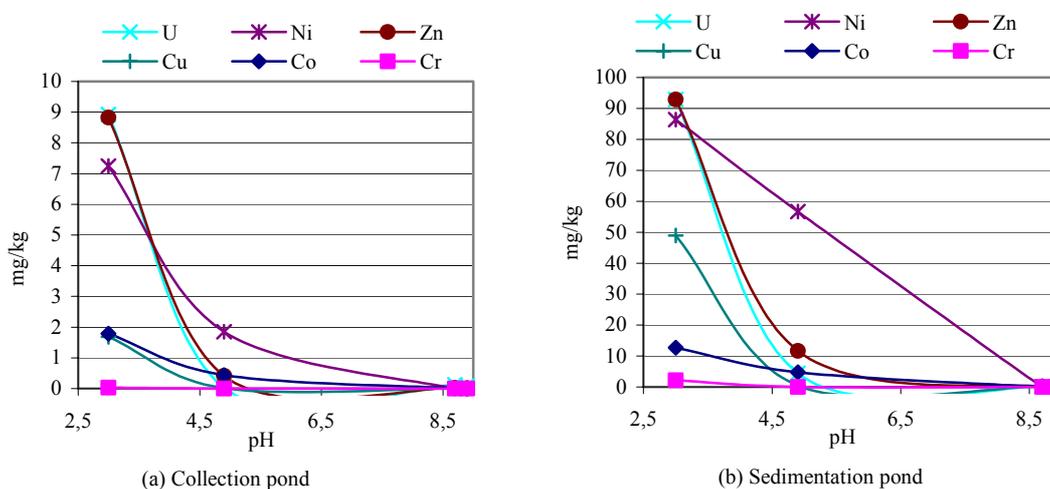
In the collection pond, the sediments showed a smaller buffering capacity (one tenth of the one in the sedimentation pond) but the recorded metal leaching was only one tenth of the one recorded in the sedimentation pond. This may be due to a lower total content of heavy metals, but the calculations of leaching ability showed the same trend. The metals in the collection pond sediments seem as a consequence more stable and unwilling to remobilize even at low pH, than the sedimentation pond sediments. However, the uncertainties considering the sampling might affect this result why general conclusions concerning the chemical stability of the collection pond sediments should be avoided.

The obtained leaching abilities for each metal proved to be well in coordinance with the expected results. The leaching abilities were generally higher in the sedimentation pond sample, where on one hand U, Ni and Mn reached leaching abilities of 90 –100% at pH 3. On the other hand the leaching ability of Fe, As and Pb was almost zero which is further discussed below.

The Swedish Association of Waste Handling Agents (RVF) has proposed threshold values of acceptable leaching for a waste to be classified as non-hazardous, for eight heavy metals (RVF, 2002). These values constitute the right hand column of Table 11 and 12. Results show that the analysed sediments can be disposed of as non-hazardous waste, if the unaltered pH level results are considered. However, the threshold values for nickel are exceeded for both sediments at pH 3 and for the sedimentation pond sediments at pH 5.3 as well. Furthermore the values for Co, Ni, Cu and Zn are exceeded in the sedimentation pond sample at pH 3, and for Co also at pH 4.9.

The treatment supposed to investigate the effect of low O<sub>2</sub> concentration and hence a reduced redox environment does not seem to have worked. The results were almost identical to the treatment with no such effort, and the recorded redox potentials in the leaching fluids were as high. The reason for this could be that the sediments became fully aerated during the sampling occasion and the following homogenisation and preparation. Hence, oxygen minimised conditions during such a limited time as 48 hours could not affect the redox potential. The results from the fourth treatment are as a consequence considered as unreliable, and are left out of the discussion.

When considering the response to a lower pH for each metal, the results in the both tests showed the same trend (Figure 14).



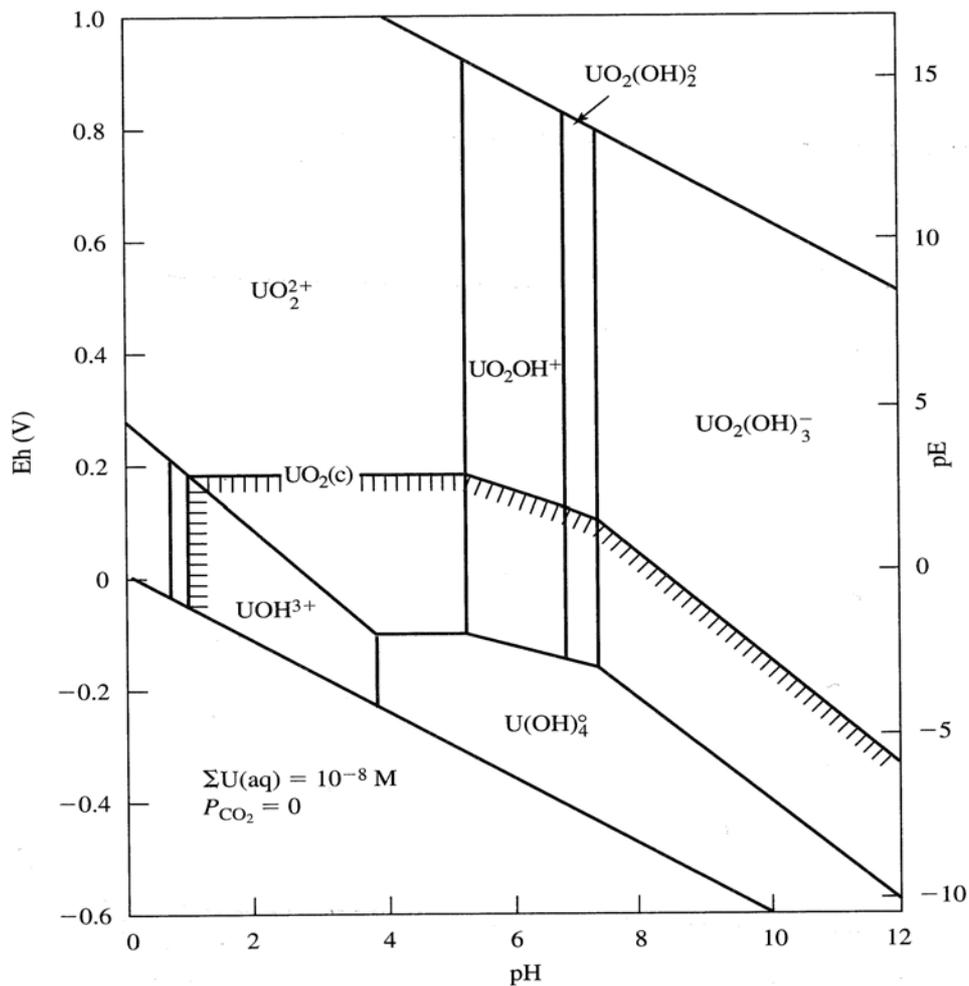
**Figure 14.** Selection of heavy metal leaching responses as function of pH in the collection pond (a) and the sedimentation pond (b).

Uranium, zinc, aluminium, chromium and cobalt had a drastically pH dependent behaviour. Plots of leaching versus pH level indicated a linear decreasing leaching ability at rising pH, with approximately all leaching occurring below pH 4. This behaviour of aluminium is also reported by Eriksson and Strömberg (1996), owing to the solubility of Al(OH)<sub>3</sub> starting at pH 3.8 (Figure 14). A similar stable hydrocomplexation at pH above 4-5 is normally valid for chromium (Gustafsson *et al.*, 2002). Langmuir (1997) reports

that uranium forms stable complexes above pH 5; in the form of U(IV) with carbonates and in the form of U(VI) with water and sulphates ligands. The solubility of amorphous and crystalline uranyl ( $\text{UO}_2$ ) is described to boost at pH 4. However all geochemistry of uranium is highly redox dependent (*ibid.*), why interpretations without such an investigation might be too hasty. Nevertheless, taking the prior results into account the predominant species of uranium in Ranstad seems to be  $\text{UO}_2$ , since pH 4 seems to be the critical pH level.

For zinc the major immobilization process tend to be electrostatic adsorption, with strength ranked to medium (Gustafsson *et al.*, 2002). Cobalt ought to behave similarly as zinc, in view of their similar ionic radii and charge (both have a radius of 0.75 Å and a double positive charge according to Aylward and Findlay (1998)). A linear desorption with pH is therefore to be expected and also found in the results.

The redox dependence of U and Cr (see e.g. Langmuir, 1997 or Section 2.3) was not shown in the experiments, since no difference in result could be seen between in the reduced Eh treatment. Figure 15 gives an indication on how the results ought to have looked like.



**Figure 15.** Eh-pH diagram for aqueous species of U in the U-O<sub>2</sub>-H<sub>2</sub>O system. The stippled line is the solid/solution boundary for  $\text{UO}_2$ . Modified from Langmuir (1997).

The second group of metals with similar leaching behaviour that can be identified are Ni, Mn and Mg. They showed a very clear pH dependence but their critical pH level seems higher (Figure 14). Recorded leaching levels indicated that leaching is substantial already at pH 5, after which the increase at pH 3 is less dramatic. At near neutral or slightly alkaline conditions, the leaching is very limited. For nickel, this behaviour was only observed in sedimentation pond sample, whereas in the collection pond sample Ni behaved as the metals in the first group. Gustafsson *et al.* (2002) state that Ni should behave as Zn, why its classification is unclear. It seems probable that Ni-hydroxides were present in the sedimentation pond and dissolution of these minerals occurred at low pH (Börjesson, pers. com).

Mg is weakly electrostatically sorbed (Gustafsson *et al.*, 2002) why the high observed sensitivity to a small pH decrease seems reasonable. The behaviour of manganese is supposed to be clearly redox dependent (Langmuir, 1997) why the interpretation here is more complex. No reducing redox state was obtained instead results indicate a pH dependent dissolution of manganese (hydr)oxides of which no reference in the literature has been found.

However, one test occasion is not enough to be able to draw conclusions on the behaviour of the solubility and adsorption/desorption mechanisms of each metal in the sediments.

Arsenic and lead showed a very small pH dependence, and low leaching potential at all pH levels. Therefore arsenic and lead can be concluded to be stable at oxic conditions no matter the pH. The attempted reducing test level did not show any different effect, but the recorded redox level was still elevated (+700mV). The sole redox dependence of arsenic is also confirmed in the literature (e.g. Langmuir, 1997), where it is stated that the mobile arsenic species predominates at reducing redox conditions. At oxic conditions the easily adsorbed arsenate species predominates (Gustafsson *et al.*, 2002).

A comparison with leaching abilities obtained in a leaching test on burned alum shale (*Rödöfyr*) done by Envipro (2003) shows similar results, with high leaching abilities for particularly Zn, Ni and Cu and very low leaching abilities for As and Pb. In general lower leaching abilities were recorded but this can be explained by differences in the leaching test procedure, since a higher pH level was used in that study.

To be able to compare the results from these leaching tests with other test results of similar materials (e.g. Envipro, 2003) a strictly standardised method would have been useful. However, the simulation of the actual present conditions would have been less authentic, why it is recommended in future studies to use a standard method as a complement. The proposed method is in that case the availability test (Naturvårdsverket, 2002b), which further expands the theoretical time scale by using a L/S quota of 100.

The amount of organic carbon present in the water in the collection dam (see Section 3.2.5.) is too low to expect a substantial complexation of metals to organic ligands (Nilsson, pers. com.). Similar conclusions were made by Börjesson (2002). Nevertheless, TOC should have been measured in the leachates from the leaching tests in order to investigate the role of adsorption to organic ligands. This is strongly recommended for future studies.

## 6.2. WILL THE SCENARIOS COME TRUE?

The main objective of the leaching tests in this study was to determine if one should expect a future considerable metal load from the sludge wastes in Ranstad. Crucial for such a conclusion is to discuss whether the materials react in the same way in the simplified laboratory experiments as in the reality. The leaching tests were designed to simulate a range of possible future conditions, but the time scale was compressed drastically. This implies that the long-term buffer reactions, and the microbial effects on redox conditions are not at all included. Furthermore a long-term equilibrium is hardly attained, why it is uncertain how the pH would react in a prolonged experiment without further acid addition. It is plausible that the pH level would slowly increase in view of the results of other studies (e.g Eriksson and Strömberg, 1996). Nevertheless the used tests give indications on how the sediments could react in a future exposure to acid water inflow.

In the calculations of possible load from the sludge wastes, two scenarios on how the percolating acid water would react with the sludge were used. These two scenarios, the non-linear and instantaneous versus the linear continuous reaction, were chosen. They both represent completely opposite extreme cases, why neither might be very realistic. More plausible could be a combination of the two, where locally enclosed bodies of sludge reach unstable pH conditions and subsequently leaching metals, as contamination pulses. In a long time perspective, the average annual load could in this case be similar to the linear continuous load.

### *Collection pond*

The sediments in the collection pond appeared to be anoxic with some presence of sulphides. All the same, the leaching tests performed in aerobic conditions did not show any evidence of sulphide oxidation and a following extra acid production. The recorded leaching of heavy metals was quite low, with leaching abilities well below the results in the sedimentation pond. The collection pond sediment seemed fairly stable irrespectively of pH in this study. If an anaerobic formation of the sediments is presumed, the elevation of Eh does not seem to affect the stability to any great extent.

Anoxic conditions in the bottom waters may be favourable for the sediment stability, if large amounts of metal sulphides are present. However the leaching tests in this study did not provide support for this. On the contrary the results indicate stable conditions when aerated.

The amounts of heavy metals present in the collection pond sediments ought to be fairly low, considering the very limited sediment amount and their recorded content. However if the sampling technique was inappropriate, as indicated by the large content of silica oxides, conclusions are hard to draw. Hence, specific calculations of potential load would not have been very useful for the discussion. Rather a renewed sampling of the material using a different, more careful, method would have been more useful.

The collection pond functions similarly to a lake system, disturbed with respect to sulphate and metal content yet natural, which ought to have started to reach equilibrium conditions. As put out by Förstner (1995), a mobilisation of heavy metals occurs because of a movement of the equilibrium that once immobilised the metals. Such a mobilization could occur from a mechanical effect, changed redox conditions or changed

temporal variations, along with changed pH conditions due to an exhausted buffer capacity in the whole tailings area. The assessment of the risk of the latter is however not studied in this thesis. Conclusively, while at status quo the heavy metals in the collection pond sediments may well stay put, whilst caution and consideration might be needed before changing the conditions in the collection pond.

### *Sedimentation pond*

When the probable long-term buffer capacity of the sedimentation pond sediment is added to the recorded large short-term buffer capacity, this material appears very stable. The 13000 years of continuous out flow of acid leakage water (pH 3) needed in order to consume the buffer is probably an underestimate. It seems even quite unlikely that pH 3 conditions could ever be attained naturally from out flowing leakage water. Yet the possibility of a local pH decrease in relation to the preferred flow paths could remain, as well as a smaller pH decrease, which could affect the heavy metal load for particularly Ni and Co. In this case short periods of metal leaching could be experienced.

However, the available amounts of heavy metals present in the sedimentation pond sediments are very small (2%) compared to the estimated amount in the sludge ponds. Calculations on possible load also indicated a very small effect from the sedimentation pond sediments compared to the total load experienced from the tailings area today.

### *Sludge ponds*

When considering the sludge ponds the assessment of future potential leakage becomes difficult. The amount of available metals in this material seems very large, and its buffer capacity is unknown. A discussion on the possible loads from the sludge ponds is similar to the one for the sedimentation pond. The same uncertainties prevail considering the nature of the acid-base reaction and the following leakage flux, but the uncertainties concerning the buffer capacity is much larger. The scenarios chosen ought to embrace the possible situations, yet the choice of scenario heavily affects the result. The impact of sludge ponds range from 10% to 77% for Cu and from 0% to 15% for Ni depending on scenario, using two examples. In general the impact of the sludge ponds is extensive for some (unexpected) metals like Al and Cu, whereas for uranium and nickel the impact is less. Magnesium, which was used as an indicator of weathering by Agnedahl (1974) (see Section 5.1), has an estimated impact of 1 to 4%, i.e. not at all in correlation to the earlier results. The reason for this is yet to be discovered.

The uncertainty of the actual used surplus of lime and the actual pH level in the sludge ponds compromises relevant conclusions. It is possible to assume different scenarios, where the acid neutralization capacity is set at different plausible levels together with possible flows of percolating water but one cannot determine the most realistic.

Even more the uncertainties concerning the buffer capacity in the sludge ponds make it possible that it is already exhausted today, and that the scenarios are fulfilled. The load of heavy metals experienced today from the whole tailings area would consequently be due to the sludge ponds to the extent calculated in this study.

### **6.3. FUTURE NEEDS FOR INVESTIGATION**

In order to be able to make reliable conclusions about the future contamination potential of the sludge ponds, sampling and further characterization of this material is needed. Analyses of acid neutralization potential should be done together with a determination of total heavy metal content and its leakage potential. Similar leakage tests as in this study could be used complemented with a standard availability test (described in Naturvårdsverket, 2002b).

For a more thorough investigation of redox dependency of the collection pond sediments, an additional sediment sampling should be done. The investigation should comprise a differentiation of the sediment layers along with pore water analyses, all done in an oxygen free environment. The proposed methodology is described in Widerlund (1999) and consists of freezing the sediment cylinders where after they are sliced in layers for analysis. Then one determines the metal rates in the solid material and pore water in each slice with particular interest to the top layer. Through this method it is possible to investigate in what directions the metal diffuse, and the relation between the solid material and pore water.



## 7. CONCLUSIONS

- The collection pond sediments seem to be stable at the tested conditions. However the sampling performed in this study might have been inappropriate and unrepresentative. Nonetheless, only small amounts of available heavy metals are probably present compared to the annual load from the tailings.
- The sedimentation pond sediments are very well buffered to pH changes due to the high content of lime, but a long time continuous inflow of acid groundwater might nevertheless affect its chemical stability. Low pH (pH 5 and below) in the pond must therefore be avoided in order to prevent a mobilisation of particularly uranium, nickel and aluminium. The plausible average annual load from the sedimentation pond is however low in comparison to the present annual load from the whole tailings area.
- The sludge ponds may very well contribute to the acid mine drainage from the tailings area. The actual content and acid neutralization capacity of the material remain uncertain but it seems plausible that approximately 17 metric tons of uranium and 20 metric tons of Ni could be available at low pH. Calculations of possible annual load, using different scenarios concerning acid neutralization capacity and quantity of acid inflow, showed an impact ranging from 3-22% for U and from 2 to 13% for Ni compared to the total load today. For Al and Cu the impact was larger, peaking at 75%. However the underlying assumptions are uncertain, why further investigations are needed.
- In total, there seems to be a significant risk that the sludge wastes severely affect the water quality in the Ranstad area and will continue to do so for a long time. The risk seems to be almost exclusively posed by the old sludge ponds, why an additional investigation of these is needed.



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