Active sulphide mine tailings impoundments as sources of contaminated drainage:

controlling factors, methods of characterisation and geochemical constraints for mitigation

Päivi M. Heikkinen

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ACTIVE SULPHIDE MINE TAILINGS IMPOUNDMENTS AS SOURCES OF CONTAMINATED DRAINAGE:

CONTROLLING FACTORS, METHODS OF CHARACTERISATION AND GEOCHEMICAL CONSTRAINTS FOR MITIGATION

by

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Cover: Tailings disposal at the Zinkgruvan mine site, Sweden. (Photo: Päivi M. Heikkinen)

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ABSTRACT

Low quality mine drainage from tailings facilities persists as one of the most significant global environmental concerns related to sulphide mining. Due to the large variation in geological and environmental conditions at mine sites, universal approaches to the management of mine drainage are not always applicable. Instead, site-specific knowledge of the geochemical behaviour of waste materials is required for the design and closure of the facilities.

In this thesis, tailings-derived water contamination and factors causing the pollution were investigated in two coeval active sulphide mine sites in Finland: the Hitura Ni mine and the Luikonlahti Cu-Zn-Co-Ni mine and talc processing plant. A hydrogeochemical study was performed to characterise the tailings-derived water pollution at Hitura. Geochemical changes in the Hitura tailings were evaluated with a detailed mineralogical and geochemical investigation (solid-phase speciation, acid mine drainage potential, pore water chemistry) and using a spatial assessment to identify the mechanisms of water contamination. A similar spatial investigation, applying selective extractions, was carried out in the Luikonlahti tailings area for comparative purposes (Hitura low-sulphide tailings vs. Luikonlahti sulphide-rich tailings). At both sites, hydrogeochemistry of tailings seepage waters was further characterised to examine the net results of the processes observed within the impoundments and to identify constraints for water treatment. At Luikonlahti, annual and seasonal variation in effluent quality was evaluated based on a four-year monitoring period. Observations pertinent to future assessment and mine drainage prevention from existing and future tailings facilities were presented based on the results.

A combination of hydrogeochemical approaches provided a means to delineate the tailings-derived neutral mine drainage at Hitura. Tailings effluents with elevated Ni, SO_4^{2-} and Fe content had dispersed to the surrounding aquifer through a levelled-out esker and underneath the seepage collection ditches. In future mines, this could be avoided with additional basal liners in tailings impoundments where the permeability of the underlying Quaternary deposits is inadequate, and with sufficiently deep ditches.

Based on the studies, extensive sulphide oxidation with subsequent metal release may already initiate during active tailings disposal. The intensity and onset of oxidation depended on e.g. the Fe sulphide content of the tailings, water saturation level, and time of exposure of fresh sulphide grains. Continuous disposal decreased sulphide weathering in the surface of low-sulphide tailings, but oxidation initiated if they were left uncovered after disposal ceased. In the sulphide-rich tailings, delayed burial of the unsaturated tailings had resulted in thick oxidized layers, despite the continuous operation. Sulphide weathering and contaminant release occurred also in the border zones. Based on the results, the prevention of sulphide oxidation should already be considered in the planning of tailings disposal, taking into account the border zones. Moreover, even low-sulphide tailings should be covered without delay after active disposal ceases.

The quality of tailings effluents showed wide variation within a single impoundment and between the two different types of tailings facilities assessed. The affecting factors included source materials, the intensity of weathering of tailings and embankment materials along the seepage flow path, inputs from the process waters, the water retention time in tailings, and climatic seasonality. In addition, modifications to the tailings impoundment may markedly change the effluent quality. The wide variation in the tailings effluent quality poses challenges for treatment design. The final decision on water management requires quantification of the spatial and seasonal fluctuation at the site, taking into account changes resulting from the eventual closure of the impoundment.

Overall, comprehensive hydrogeochemical mapping was deemed essential in the identification of critical contaminants and their sources at mine sites. Mineralogical analysis, selective extractions, and pore water analysis were a good combination of methods for studying the weathering of tailings and in evaluating metal mobility from the facilities. Selective extractions with visual observations and pH measurements of tailings solids were, nevertheless, adequate in describing the spatial distribution of sulphide oxidation in tailings impoundments. Seepage water chemistry provided additional data on geochemical processes in tailings and was necessary for defining constraints for water treatment.

Keywords (GeoRef Thesaurus, AGI): environmental geology, mines, nickel ores, copper ores, tailings, mine drainage, water pollution, surface water, ground water, seepage water, hydrochemistry, trace metals, chemical fractionation, mineralogy, sulfides, weathering, oxidation, selective extraction, Hitura, Luikonlahti, Finland

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I Heikkinen, P.M., Korkka-Niemi, K., Lahti, M. & Salonen, V.-P. 2002. Groundwater and surface water contamination in the area of the Hitura nickel mine, Western Finland. *Environmental Geology* 42, 313–329.

II Heikkinen, P.M. & Räisänen, M.L. 2008. Mineralogical and geochemical alteration of Hitura sulphide mine tailings with emphasis on nickel mobility and retention. *Journal of Geochemical Exploration* 97, 1–20.

III Heikkinen, P.M. & Räisänen, M.L. 2009. Trace metal and As solid-phase speciation in sulphide mine tailings – Indicators of spatial distribution of sulphide oxidation in active tailings impoundments. *Applied Geochemistry* 24, 1224–1237.

IV Heikkinen, P.M., Räisänen, M.L. & Johnson, R.H. 2009. Geochemical Characterisation of Seepage and Drainage Water Quality from Two Sulphide Mine Tailings Impoundments: Acid Mine Drainage versus Neutral Mine Drainage. *Mine Water and the Environment* 28, 30–49.

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P.M. Heikkinen contributed to the studies presented in the original papers as follows:

P.M. Heikkinen was responsible for planning, organizing and conducting most of the data collection, field and laboratory measurements (both chemical and mineralogical analyses; the selective extraction procedure was designed together with M.L. Räisänen) and data processing for Papers I and II. The geophysical measurements for Paper I were carried out and interpreted by M. Lahti, and the ICP-AES/MS and ion chromatography measurements for Papers I and II were performed by the Geolaboratory of the Geological Survey of Finland. Paper I was written by P.M. Heikkinen with guidance from V.P. Salonen and K. Korkka-Niemi, while Paper II was written by P.M. Heikkinen with contributions from M.L. Räisänen.

P.M. Heikkinen was responsible for producing all the Hitura data for papers III and IV. M.L. Räisänen planned and organized the collection and laboratory measurements of the Luikonlahti data used for papers III and IV. P.M. Heikkinen was responsible for processing the data from both study sites and writing the papers III and IV with support from M.L Räisänen. R.H. Johnson provided guidance in geochemical modelling for Paper IV and contributed to the writing of the paper.

1 INTRODUCTION

Low quality mine drainage is a world-wide environmental concern related to the surficial storage of sulphide-containing mine wastes: tailings and waste rocks. It causes degradation of downstream surface and groundwater quality by increased loads of SO_4^{2-}, Fe and contaminative metals (e.g. Ni, Cu, Zn, Pb) and metalloids (e.g. As), resulting in long-term restrictions in the use of water supply, detrimental impacts on aquatic and terrestrial biota and a decrease in the recreational value of the affected water bodies (e.g. Azcue et al. 1995, Nordstrom and Alpers 1999).

The mine drainage issue was first addressed in the 16th century in the mining districts of Central Europe (Agricola 1556), but was more broadly recognized in the early 20th century in the U.S. coal mining sites (Nordstrom and Alpers 1999) and in the 1970s and early 1980s in Canadian metal mines (MEND 2001). To date, the problem of low quality mine waters has been documented all over the world (Allard et al. 1987, Fernandes et al. 1995, Younger 1995, Geldenhuis and Bell 1998, Lottermoser et al. 1999, Kim and Chon 2001, Wolkersdorfer and Bowell 2004 and 2005, Søndergaard et al. 2007). Consequently, substantial research efforts have been focused on issues related to mine drainage, covering aspects of mine drainage generation (Kleinmann et al. 1981, Sullivan et al. 1988, Blowes and Jambor 1990), hydrogeochemistry (Nordstrom and Ball 1986, Younger 1995, Cravotta 2008), contaminant migration from waste deposits to surrounding water bodies (Morin et al. 1982, Allard et al. 1987, Johnson and Thornton 1987, Morin et al. 1988, Herbert 1994, Bain et al. 2000) and impacts on downstream water quality and aquatic biota (Roch et al. 1985, Short et al. 1990, Fuge et al. 1991, Soucek et al. 2000). In addition, methods and techniques have been developed for mine drainage prediction (Sobek et al. 1978, MEND 1989a, Price et al. 1997, White et al. 1999, Banwart and Malmström 2001, Lapakko 2003), prevention (MEND 1989b, MEND 1994, Peppas et al. 2000, Vigneault et al. 2001, Höglund et al. 2004) and treatment (Hedin et al. 1994, Gazea et al. 1996, Benner et al. 1997, Ziemkiewicz et al. 2003), and the performance of different mitigation measures has been investigated (Holmström and Öhlander 1999, Holmström et al. 2001, Carlsson et al. 2002, Carlsson et al. 2003). Despite these efforts, low quality mine drainage persists as one of the main environmental problems associated with mining, particularly base metal and coal mining. A major reason for this is that once mine drainage generation has initiated, it may continue for decades or centuries, and may be difficult and costly to discontinue and mitigate (Price 2003).

In the following, a brief introduction to the key chemical reactions of mine drainage generation and assessment methods is presented and the relevance of the problem to the disposal of sulphide mine tailings in Finland is outlined.

1.1 Overview of processes generating mine drainage in mine wastes

Low quality mine drainage primarily results from the oxidation of iron sulphide minerals (e.g. pyrite FeS_2, pyrrhotite $Fe_{1-x}S$) in sulphide-containing mine waste, once exposed to atmospheric oxygen and water (Table 1). Oxidation of sulphides releases acidity (H^+), Fe^{2+}, SO_4^{2-}, and metals into the pore water of the waste material. The increased acidity further promotes the dissolution of other sulphides and minerals in the wastes, resulting in enhanced liberation of potential contaminants into the pore water. In general, sulphide oxidation primarily depends on the availability of oxygen and/or ferric iron [Fe(III)] (Singer and Stumm 1970, Alpers et al. 1994). Oxygen is a particularly important oxidizing agent in circumneutral conditions, where Fe(III) tends to precipitate as Fe oxyhydroxides (e.g. goethite [α-FeO(OH)] and ferrihydrite

Table 1. Examples of key chemical reactions related to sulphide weathering in mine wastes (compiled from Kleinmann et al. 1981, Nordstrom 1982, Blowes and Ptacek 1994, Nordstrom and Alpers 1999, Plumlee 1999, White et al. 1999, Bigham and Nordstrom 2000).

Reaction	**Reaction formula**
Sulphide oxidation	*Pyrite:* $FeS_{2(s)} + 7/2O_{2(g)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$ $FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(aq)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^+_{(aq)}$ (pH < 4.5) *Overall reactions of pyrite oxidation:* $FeS_{2(s)} + 15/4O_{2(g)} + 7/2H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2H_2SO_{4(aq)}$ *Pyrrhotite ($Fe_{1-x}S$, $x = 0.1$):* $Fe_{0.9}S_{(s)} + 1.95O_{2(g)} + 0.1H_2O_{(l)} \rightarrow 0.9Fe^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 0.2H^+_{(aq)}$
Oxidation of Fe(II)	$Fe^{2+}_{(aq)} + 1/4O_{2(g)} + H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1/2H_2O_{(l)}$
Hydrolysis of Al and Fe; precipitation of secondary Fe minerals	$Al^{3+}_{(aq)} + H_2O_{(l)} \leftrightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)}$ *Amorphous Fe hydroxide*: $Fe^{3+}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Fe(OH)_{3(s)} + 3H^+_{(aq)}$ *Goethite*: $Fe^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow FeOOH_{(s)} + 3H^+_{(aq)}$ *Jarosite*: $3Fe^{3+}_{(aq)} + K^+_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 6H_2O_{(l)} \rightarrow KFe_3(SO_4)_2(OH)_{6(s)} + 6H^+_{(aq)}$ *Schwertmannite*: $8Fe^{3+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 14H_2O_{(l)} \rightarrow Fe_8O_8(OH)_6(SO_4)_{(s)} + 22H^+_{(aq)}$
Carbonate dissolution	*Calcite*: $CaCO_{3\,(s)} + H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + HCO_3^-{}_{(aq)}$ *Dolomite*: $CaMg(CO_3)_{2(s)} + 2H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + Mg^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$
Silicate dissolution	*Olivine*: $Mg_2SiO_{4(s)} + 4H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_4SiO_{4(aq)}$ *Anorthite*: $CaAl_2Si_2O_{8(s)} + 2H^+_{(aq)} + H_2O \rightarrow Ca^{2+}_{(aq)} + Al_2Si_2O_5(OH)_{4(s)}$ *K-feldspar:* $KAlSi_3O_{8(s)} + 4H^+_{(aq)} + 4H_2O_{(l)} \leftrightarrow Al^{3+}_{(aq)} + 3Si(OH)_{4(aq)} + K^+_{(aq)}$

($Fe_5OH_8 \cdot 4H_2O$), Table 1), and is no longer available for sulphide oxidation (e.g. Bigham 1994, Alpers and Nordstrom 1999, Bigham and Nordstrom 2000). In contrast, Fe(III) becomes the dominant oxidant in low pH conditions and the oxidation rate increases (Nordstrom 1982, Alpers et al. 1994). The bacterially catalyzed oxidation of Fe(II) to Fe(III) can further accelerate the oxidation rate (Singer and Stumm 1970, Nordstrom 1982). These overall chemical reactions are a simplification of the complicated oxidation of Fe sulphides, comprising a series of physical, chemical and microbiological processes (Nordstrom 1982, Nordstrom and Alpers 1999).

The acidity of the mine drainage largely depends on the balance between acid producing and neutralising minerals in mine waste, but also on other neutralising reactions such as the protonation of mineral surfaces, mineral alteration or ion-exchange reactions (Blowes and Ptacek 1994, Höglund et al. 2004). The primary neutralising minerals are Ca and Mg carbonates (calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$]), which react relatively rapidly compared to the rate of acid production by sulphide weathering. Dissolution of carbonates maintains the pore water pH close to neutral and releases metal cations into the pore water (Table 1). After the exhaustion of carbonates, a stepwise series of dissolution reactions of available buffering minerals (i.e. siderite, simple Al and Fe hydroxides and aluminosilicates) will follow until the Fe sulphides are depleted and acid production ceases (Morin and Cherry 1986, Ptacek and Blowes 1992, Blowes and Ptacek 1994). In the course of acid buffering reactions, the pH of the drainage ultimately decreases and the amount of dissolved cations in the pore water increases (Table 1; Blowes and Jambor 1990, Blowes and Ptacek 1994, Johnson et al. 2000, Blowes et al. 2003). Based on the drainage water pH, two main types of mining influenced waters ('MIW', Schmiermund and Drozd 1997) have been recognized: low pH acid mine drainage ('AMD') and non-acidic neutral mine drainage ('NMD') (Younger 1995, Pettit et al. 1999, Cravotta et al. 1999). Overall, AMD, with detrimental impacts on aquatic biota and the usability of water bodies, has been more thoroughly studied than NMD, even though the latter may also contain high Fe and harmful concentrations of trace metals (Younger 1995, Pettit et al. 1999, Kirby and Cravotta 2005, Cravotta 2008).

In situ retention of metals released in sulphide weathering is an important process in controlling the quality of mine drainage from waste deposits. In particular, secondary Fe precipitates (e.g. ferrihydrite, goethite, jarosite [$KFe_3(OH)_6(SO_4)_2$], schwertmannite [$Fe_8O_8(OH)_6SO_4$]; Table 1) have been identified as important solid-phase controlling agents for trace metals and metalloids in mine wastes (Alpers et al. 1994, Lin 1997b, McGregor et al. 1998b, Holmström et al. 1999). Retention by these precipitates mainly occurs through adsorption, coprecipitation or by substitution of Fe in the oxyhydroxide structure (Alpers et al. 1994, Cornell and Schwertmann 2003). Adsorption is strongly pH dependent due to the variation in the net surface charge of Fe precipitates (Dzombak and Morel 1990, Alpers et al. 1994) and the differences in adsorption affinities of trace metals (Stumm and Morgan 1996). In general, near-neutral conditions favour the retention of cationic metals, while a decrease in pH increases the adsorption of anions (Dzombak and Morel 1990, Stumm and Morgan 1996). Other secondary minerals (sulphates, sulphides) may also be significant in retaining contaminants in mine wastes (Alpers et al. 1994, Lin 1997a, Nordstrom and Alpers 1999). For example, the formation of covellite (CuS) is known to limit Cu mobility in tailings (Blowes and Jambor 1990, Holmström et al. 1999, Johnson et al. 2000). Overall, the permanence of *in situ* retention is a function of pH-Eh in mine waste and the stability of the retaining mineral phases (Nordstrom and Alpers 1999, Öhlander et al. 2001).

1.2 Assessment and prediction of mine drainage generation from waste facilities

Even though the overall mechanism of mine drainage generation is well understood, the prevention and treatment of low quality effluents requires site-specific studies of waste deposits and the geochemistry of waste materials. This is because each mine site has unique geological and environmental conditions, resulting in complexity in the processes responsible for mine drainage generation. Furthermore, processing of the ore is also case-specific. For these reasons, universal approaches to the management of mine drainage are not always applicable (e.g. Price 2003). The recent European union extractive waste directive (Directive 2006/21/EC) also requires site-specific characterisation of mine waste to prevent or reduce any adverse effects of management of extractive waste on the environment and landscape, and any resultant risks to human health (European Parliament and Council 2006; cf. also Finland's Parliament Decree on extractive wastes 379/2008). The potential of the waste to produce acidity and release contaminants to the surrounding aquatic environment are the major issues in the evaluation of the long-term chemical stability of wastes. This requires mineralogical and geochemical characterisation of the waste materials (Jambor 1994, Price 1997, EC 2004, Lottermoser 2007).

Both laboratory tests and site-specific research methods on mine waste facilities have been developed to predict and evaluate the long-term behaviour of wastes. The laboratory tests include static and kinetic tests that aim at establishing whether the waste material will produce acidity when exposed to surficial conditions (Sobek et al. 1978, Price et al. 1997, White et al. 1999) and to determine mineral weathering and element release rates in waste, in order to evaluate the onset time of AMD and downstream loading from the waste (Price 1997, White et al. 1999). The major advantage of static tests is that they provide a quick, easy to perform, inexpensive tool for mine waste classification (White et al. 1999), whereas kinetic tests are more time consuming but produce data on effluent quality (Hornberger and Brady 1998). The shortcomings of these tests have, however, been discussed rather widely (Sherlock et al. 1995, Hornberger and Brady 1998, White et al. 1999, Jambor 2003, Sapsford et al. 2009). The overall conclusion is that predictions of mine drainage quality should not be based on the tests alone. Instead, they need to be supplemented with other data, such as water quality data from mine sites with similar types of geological deposits (Hornberger and Brady 1998, Lapakko 2003).

Site-specific studies on existing waste facilities comprise investigations on geochemistry, migration and the geochemical evolution of contaminant plumes from tailings impoundments (Morin et al. 1982, Johnson and Thornton 1987, Morin et al. 1988, Herbert 1994) and processes in tailings leading to contamination (Dubrovsky et al. 1985, Blowes and Jambor 1990, Ribet et al. 1995, McGregor et al. 1998a and 1998b, Holmström et al. 1999, Johnson et al. 2000, Ljungberg and Öhlander 2001, Dold and Fontboté 2002, Moncur et al. 2005, Dold et al. 2009). In process studies, mineralogical analyses are combined with geochemical investigations to identify contaminant sources and processes that control element mobility in tailings and affect drainage quality. Selective extractions (e.g. Ribet et al. 1995, Dold and Fonboté 2001 and 2002) or pore water chemical analyses coupled with geochemical modelling (Blowes and Jambor 1990, Johnson et al. 2000, Moncur et al. 2005) are applied to assess element mobility, solid-phase species distribution, and the influence of secondary phases on metal retention. In addition, numerical models have been compiled to simulate sulphide oxidation-related processes in tailings to predict effluent quality from waste deposits (Wunderly et al. 1996, Bain et al. 2000, Banwart and Malmström 2001, Salmon and Malmström 2004). The majority of the site-specific research has focused on closed or abandoned tailings facilities, but some recent papers have also examined the early stages of AMD generation in active impoundments (Smuda et al. 2006, Dold et al. 2009).

Site-specific geochemical studies can be of practical value for tailings management. For instance, they allow description of the onset and spatial extent of sulphide oxidation in tailings. In addition, the fate and speciation of contaminants can be identified, and the susceptibility for mobilisation of contaminants with respect to pH-Eh changes can be assessed. This type of data is required to identify the geochemical constraints for remediation of the facilities in order to select appropriate mitigation procedures and to prevent future loadings from the impoundments (DeVos et al. 1999, Lindvall et al. 1999). Moreover, documentation of drainage water quality allows the identification of objectives and constraints for water treatment.

A further advantage of site-specific studies is that they facilitate timescale evaluation and better understanding of the complex weathering processes and metal retention mechanisms taking place in waste facilities over various time periods. Therefore, they provide analogies of the long-term behaviour of waste materials for future mines with similar ore types and ore processing techniques, providing guidance for the design of new tailings facilities. Direct measurements of drainage water chemistry from existing mine sites further allow the constraining of pH and metal concentration ranges for the future effluent chemistry of equivalent ore types (Plumlee et al. 1999). These analogue approaches nevertheless require data not only from mine sites of different ore deposit types but also from diverse climatic conditions. Climate (precipitation, temperature) can have a strong influence on mineral weathering rates and mineral precipitation (Berner 1995, White and Blum 1995, Dold and Fontboté 2001), and thus also on drainage water composition.

1.3 Tailings-derived mine drainage issue in Finland

In Finland, metal production has been significant since the 16th century with ca. 190 metal mines extracting base metals (Cu, Pb, Zn, Ni) and gold from sulphide ore deposits (Puustinen 2003). At present, there are 8 operating metal sulphide mines (Au, Ni, Cu, Zn, Ag), which annually extract some 4 Mt of ores (GTK 2008). An estimated 139 Mt of sulphide containing tailings have been disposed of on mine sites during the past centuries (GTK's unpublished database of sulphide mine sites). This number is expected to notably increase in the future with the current increased global interest in base metal mining in Finland. For example, Talvivaara mine, with one of the largest known sulphide Ni resources in Europe, started operation in Eastern Finland at the end of 2008. Bioheapleaching of the 340 Mt of measured and indicated Ni-Zn-Cu-Co ore resources is estimated to leave behind approximately 30 Mt of processed ore that will cover an area of ca. 500 ha (Northern Finland Environmental Permit Authority 2007).

Despite the notable volume and long history of sulphide mining and ore processing in Finland, research on the environmental impacts of sulphide tailings disposal and their mitigation has been sparse. The published papers include investigations on the influence of tailings-derived waters on surface water systems by means of aquatic sediment studies (Salminen and Sipilä 1996, Kauppila 2006, Kauppila et al. 2006, Salonen et al. 2006, Kihlman and Kauppila 2009), characterisation of tailings-derived waters (Korkka-Niemi et al. 1999, Räisänen et al. 2005), the formation of Fe precipitates and their significance in the retention of metals from tailings effluents (Kumpulainen and Carlson 2001, Carlson et al. 2002, Kumpulainen et al. 2007), the applicability of geophysical methods in the characterisation of tailings areas and their environmental impacts (Chevrel et al. 2003, Vanhala et al. 2005), the application of groundwater modelling in preventing contamination from a tailings area (Artimo et al. 2004), and the migration of arsenic from a gold mine tailings impoundment (Parviainen and Eklund 2007, Ruskeeniemi et al. 2007). In addition, there are some publications discussing after-care management of tailings facilities (Räisänen and Juntunen 2004, Räisänen 2005, Heikkinen et al. 2008). Altogether, these papers highlight that the mine drainage problem also exists in Finland and there is a need for site-specific studies in Finnish climatic conditions to meet the challenges of remediation of old mine sites and to prevent the generation of low quality mine drainage at future mines.

1.4 Aims and scope of the study

In this work, geochemical and mineralogical methods were used to characterise tailings-derived water contamination around active sulphide tailings impoundments in Finland and to examine the processes and factors that affect contaminant migration from tailings areas.

An extensive surface and groundwater quality assessment was carried out at the Hitura sulphide mine site to investigate the spatial extent and nature of the tailings-derived contamination (Paper I). Sulphide oxidation and subsequent contaminant mobility, as potential causes for the observed water contamination, were then studied in detail in the Hitura tailings using mineralogical and geochemical methods (Paper II). Sulphide oxidation intensity and the factors controlling it were further examined in different parts of the Hitura tailings area (border zone vs. mid-impoundment area; active vs. old impoundment) based on solid-phase speciation of elements (Paper III).

To obtain a more comprehensive insight into weathering in active sulphide tailings areas, analogous spatial investigations to Hitura were carried out at the Luikonlahti tailings impoundment. At Luikonlahti, the operation period was similar to Hitura, but the tailings contained a higher proportion of Fe sulphides than at Hitura, allowing comparison of two sulphide tailings with diverse reactivity (Paper III). In the final phase of the work, the seepage water quality, i.e. the outflow at the toe of the tailings dam, was recorded from these two sites to study the net result of the processes observed within the impoundments. Data on seepage water chemistry was used to identify constraints for water treatment (Paper IV). In addition, annual and seasonal variation in seepage quality was evaluated at Luikonlahti based on a four-year monitoring period (Paper IV).

This synopsis discusses the applicability of the above approaches in describing tailings-derived contamination and its generation in tailings impoundments. The study provides information on the properties of tailings materials and tailings facilities that affect the environmental impacts of active sulphide tailings disposal and should be taken into account in the design, after-care planning and monitoring of the impoundments.

2 STUDY AREAS

Two different types of active sulphide mine tailings areas were selected for the study. The Hitura Ni mine tailings impoundment was chosen because of the known but unresolved water contamination at the site (cf. Korkka-Niemi et al. 1999). The tailings facility of the Luikonlahti Cu mine and talc processing plant was selected as a complementary study area, because it had a similar operational period to Hitura and is within the same climatic zone (Table 2), but represents a different type of ore deposit, sulphide tailings material and impoundment structure from Hitura.

2.1 Hitura Ni mine

The Hitura Ni mine is located in Nivala, western Finland (63°50´N, 25°02´E; Fig. 1). The mine extracts Ni, Cu and PGMs from an ultramafic sulphide complex that is composed of serpentinites with minor amphibole rocks and migmatized mica gneisses (Papunen 1970). Exploitation of the ore body started in 1970. Current annual production is approximately 3 000 tons of Ni in concentrate with a Ni recovery rate of ca. 67% (Kojonen et al. 2003). The main sulphide minerals in the ore include pyrrhotite ($Fe_{1-x}S$), Co–bearing pentlandite [$(Fe,Ni)_9S_8$)] and chalcopyrite ($CuFeS_2$) with accessory mackinawite [$(Fe,Ni,Co)_{1+x}S$], valleriite [$(Fe,Cu)S\cdot3(Mg,Al)(OH)_2$], cubanite ($CuFe_2S_3$) and sphalerite [$(Zn,Fe)S$] (Papunen 1970). The gangue is composed of antigorite, chlorite, calcite and magnetite with additional talc, amphiboles and micas (Papunen 1970, Isohanni et al. 1985).

The ore is nowadays extracted as underground mining and processed by onsite milling with crushing, grinding and flotation. Tailings are spigotted into a nearby tailings impoundment constructed with earthen dams on a formerly glaciated terrain mainly composed of till (Fig. 2). The tailings area contains approximately 12 Mt of tailings covering 110 ha, highest parts rising nearly 30 m above ground level. The tailings are classified as 'non-acid producing' and

Table 2. Summaries of the annual meteorological conditions (temperature, air pressure, relative humidity, precipitation and duration of snow cover) in the locality of the study areas during 1971-2000 (Drebs et al. 2002).

Study area	Observation station	Temperature (°C)	Air pressure (hPa)	Relative humidity (%)	Precipitation (mm)	Snow cover (days)*
Hitura	Nivala	2.4	1011	80	561	151
Luikonlahti	Joensuu airport	2.6	1012	79	643	167

* Value for the winter 1998-1999 (Finnish Meteorological Institute 2000).

Fig. 1. Location of the study areas.

‘not potentially AMD generating’ based on a static test (Saari 1996). The impoundment consists of four disposal areas and two settling ponds for water (Fig. 2). Disposal in area “A” stopped ca. 15 years ago (‘old impoundment’), but the facility was left uncovered, and thus exposed to sulphide oxidation. Disposal areas “B” and “C” are currently in use (‘active impoundments’) (Fig. 3a). Area “D” contains jarosite residue from a nearby smelter, and was recently reclaimed with a till cover.

Tailings effluents are collected into drainage ditches surrounding the tailings area (Fig. 3b). Despite the non-AMD character of the tailings materials and the seepage water collection, groundwater contamination with elevated SO_4^{2-} and Ni concentrations was first detected at the beginning of 1980s in private wells around the tailings impoundment. In addition, a nearby water intake plant was later closed due to elevated SO_4^{2-} concentrations (Korkka-Niemi et al. 1999, Heikkinen et al. 2001).

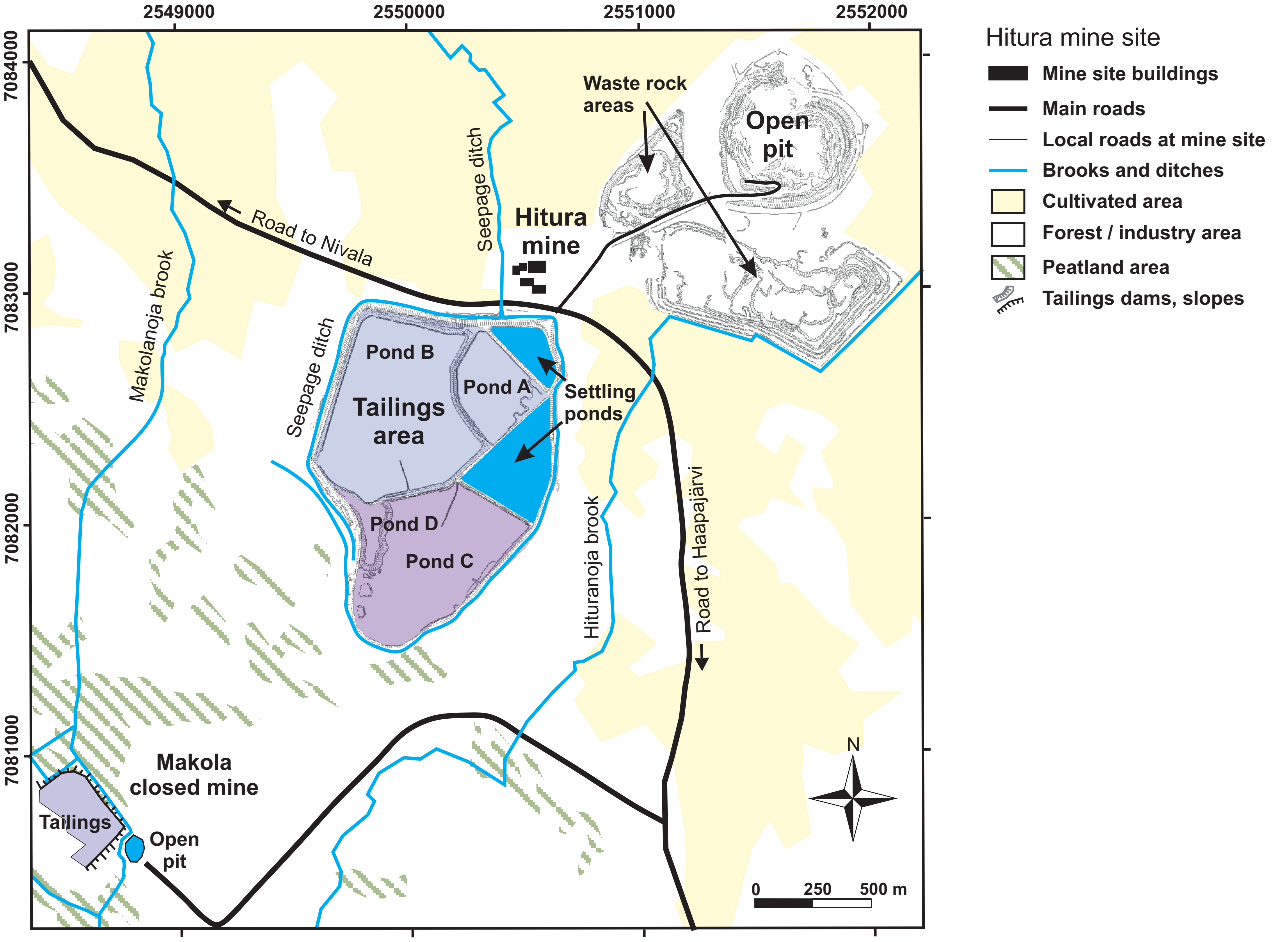

Fig. 2. Overall setting of the Hitura Ni mine and the tailings area. (Base map drawn based on topographic map data © National Land Survey of Finland, permit No. 13/MML/09).

Fig. 3. a) Overview of the Hitura tailings area seen from south in 2004. Disposal area "C" in the front (Photo: Paola Frattini). b) Seepage collection ditch surrounding the Hitura tailings area (Photo: Päivi M. Heikkinen).

2.2 Luikonlahti Cu mine and talc processing plant

The Luikonlahti Cu mine and processing plant operated during 1968–1983 in Kaavi, in eastern Finland (62°56´N, 28°42´E; Fig. 1). They produced Cu, Zn, Co, Ni, and S concentrates by flotation from an Outokumpu-type ore deposit hosted by metamorphosed quartz rocks associated with skarns, carbonate rocks, serpentines and black schists (Peltola 1978, Eskelinen et al. 1983, Peltonen et al. 2008). The main ore minerals in the deposit were chalcopyrite, sphalerite, cobalt-pentlandite (Co_9S_8), pyrrhotite, and cobalt-rich pyrite (FeS_2), and the gangue was composed of quartz (SiO_2) with talc, chlorite, graphite, calcite ($CaCO_3$), tremolite [$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$], and diopside ($CaMgSi_2O_6$) (Eskelinen et al. 1983).

During the last years of metal mine operation and after its cessation, talc production was carried out at Luikonlahti until 2006. The talc ore was extracted from Outokumpu-type soapstone deposits at Luikonlahti and Polvijärvi, and processed by flotation (Eskelinen et al. 1983). These ore deposits are primarily composed of talc (50–70%), magnesite ($MgCO_3$), dolomite [$CaMg(CO_3)_2$], and chlorite with minor magnetite, chromite and sulphide minerals (pyrrhotite, pentlandite) as well as fracture-filling nickel arsenides (niccolite (NiAs), gersdorffite [NiAsS]) (Wiik 1953, Vesasalo 1965, Huopaniemi 1986, Kuronen and Tuokko 1997). Nickel was concentrated from the talc ore (from pentlandite and niccolite) when feasible (Eskelinen et al. 1983).

The Luikonlahti tailings impoundment has been dammed into the drained Lake Petkellampi. It covers ca. 27 ha in formerly glaciated terrain with silt and till, and consists of one disposal area with one settling pond for water (Fig. 4). The 10 to 20 m high tailings dams were constructed of till, waste rock and sulphide-bearing tailings material. The impoundment contains 6 Mt of sulphide tailings overlain by 2.5 Mt of magnesite-rich tailings (Räisänen and Juntunen 2004; Fig. 5). Sulphide tailings are mainly composed of quartz and Fe sulphides with variable amounts of talc, chlorite, calcite, diopside, graphite and base-metal sulphides (sphalerite, chalcopyrite, and pentlandite), whereas tailings from talc processing primarily contain magnesite and talc with minor dolomite, chlorite, micas, and sulphide minerals (Räisänen and Juntunen 2004).

Water from the tailings area is discharged through a settling pond into the local water system (Fig. 4). The elevated As and Ni levels in the discharge, resulting from the magnesite disposal, are treated by adding ferric sulphate to the tailings slurry and lime to the settling pond water (Räisänen and Juntunen 2004). Discharge from the mine site has impacted the surrounding surface water systems (Räisänen and Juntunen 2004, Kauppila et al. 2006, Kihlman and Kauppila 2009).

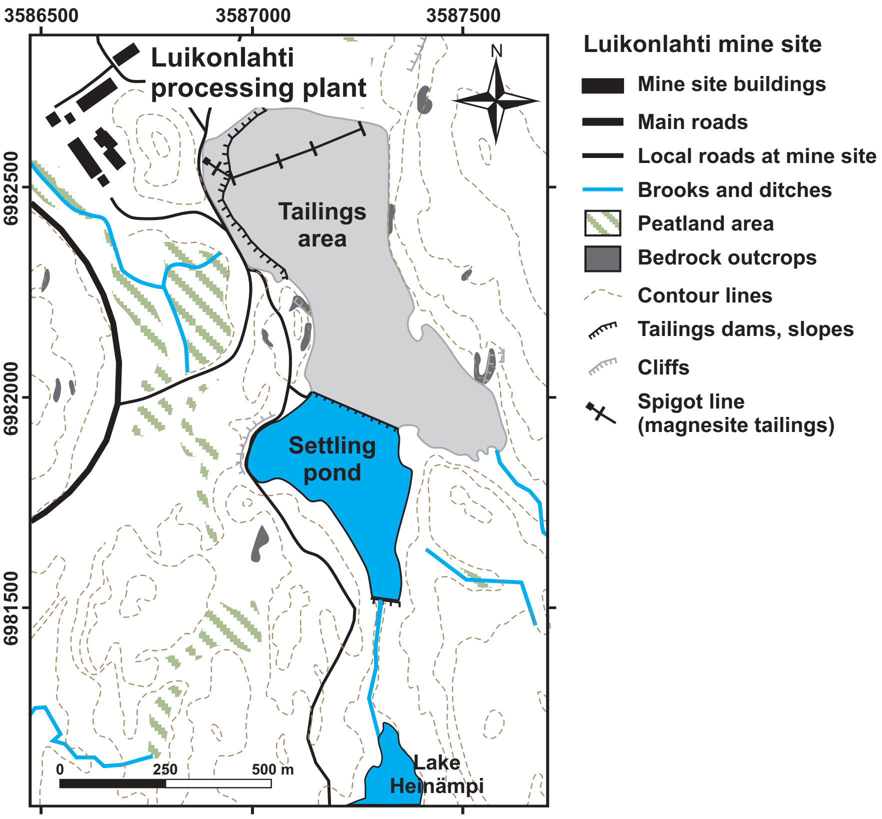

Fig. 4. Overall setting of the Luikonlahti tailings area. (Base map drawn based on topographic map data © National Land Survey of Finland, permit No. 13/MML/09).

Fig. 5. The Luikonlahti tailings area with magnesite tailings covering sulphide tailings in spring 2005. The upper section of the constructed dam is seen on left (Photo: Marja L. Räisänen).

3 MATERIAL AND METHODS

In the following, a summary of the sampling and primary analytical methods will be given to provide an overview of the methodology applied in the present study. Details of the materials and methods are presented in each separate paper, referred to here with their Roman numerals.

3.1 Sampling and sample materials

3.1.1 Water samples

A total of 167 groundwater and surface water samples were collected from the surroundings of the Hitura Ni mine tailings impoundment and from the tailings area to assess the impact of the sulphide mine tailings on water quality (Paper I). Groundwater samples were collected from existing and newly installed monitoring wells and private wells with submersible pumps or tube bailers, and surface water samples were taken with bottle samplers from surface water ponds, streams, tailings settling ponds and from drainage channels around the tailings area. Water volumes in the wells were replaced by pumping prior to sampling. Hydraulic head measurements were made from the wells in conjunction with the sampling to define the groundwater flow pattern in the area.

Geochemical processes in the unsaturated, shallow tailings were studied by analysing pore water quality together with tailings solids from the old impoundment of the Hitura site (Paper II). Pore water samples were collected at eight depths (15–75 cm) from the walls of a pit, dug in the impoundment's surface, using a squeezing technique.

To further characterise the tailings effluents and to determine the constraints for water treatment, additional sampling was carried out at Hitura and also at the Luikonlahti mine site (Paper IV). This sampling comprised samples from seepage waters that surface through the tailings dams and from the drainage channels downstream (and upstream) of the seepage points (Fig. 6). Periods of heavy surface runoff were avoided in sampling. At Luikonlahti, seepage water samples were collected two to three times per year (after snowmelt flush period, in mid-summer and in the autumn) during a four-year period to also evaluate the annual and seasonal variation in the seepage quality.

The collected water samples included unfiltered or filtered (1.2 µm) 500 ml samples for major anion measurements (excluding Luikonlahti) and filtered (0.45 µm), HNO_3-acidified 100 ml samples for dissolved major cation and trace metal analyses. All water samples were kept cold prior to analysis.

3.1.2 Tailings solids

Samples from tailings solids were collected to study mineral weathering and contaminant mobility

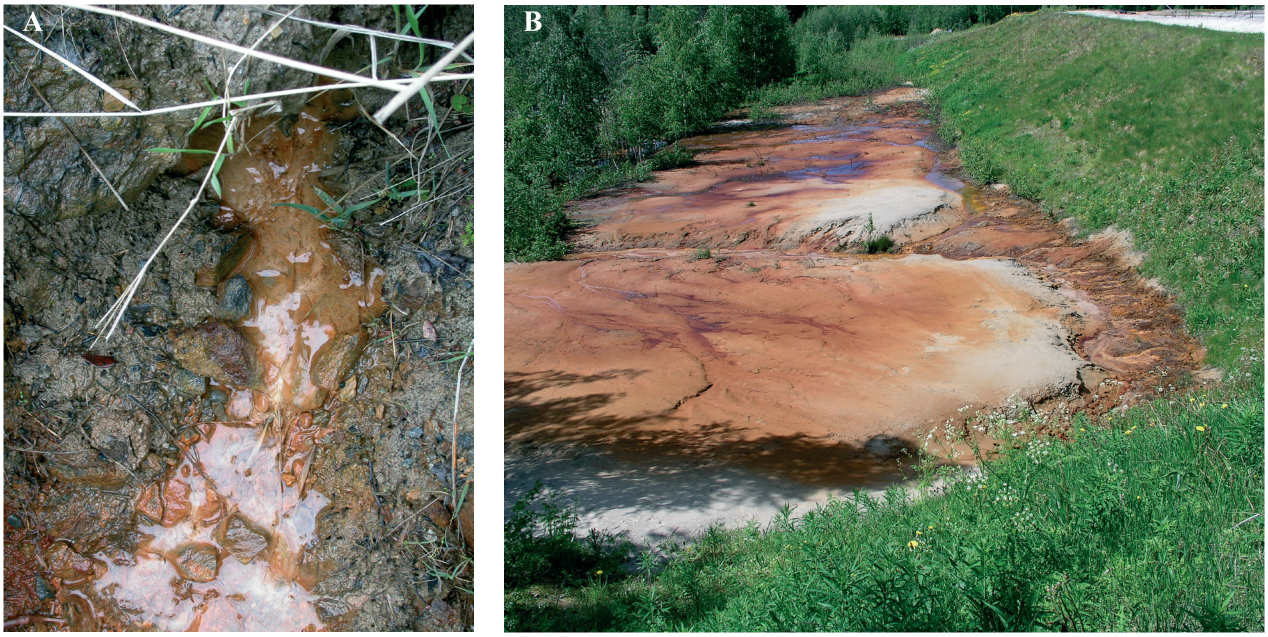

Fig. 6. Examples of seepage water sampling points at a) the Hitura site (Photo: Päivi M. Heikkinen) and b) the Luikonlahti site showing the upper seepage area at the toe of the upper section of the dam (Photo: Tiina Myllymäki).

in the tailings in detail (Paper II), and to define the spatial variation in sulphide oxidation intensity in the impoundments (Paper III).

The old impoundment of the Hitura tailings area, exposed to atmosphere for 10–15 years, was selected for detailed characterisation of mineral weathering and metal release (Paper II). A 14-m core of the tailings solids, extending to the underlying Quaternary sediments, was drilled from the middle of this impoundment with a GM100 drilling rig. The core was sampled for mineralogical and chemical analyses in the laboratory. More detailed sampling was carried out from the unsaturated zone of the impoundment by digging a 90 cm deep pit in the shallow tailings and by collecting samples from the walls of the pit for corresponding analyses to those from the tailings core.

Two additional cores were drilled from the Hitura impoundment and four from Luikonlahti to assess the spatial differences in weathering and metal fractionation in the tailings (Paper III). Cores were extracted from different parts of the impoundments (border zone vs. middle part; active pond vs. old disposal area at Hitura) and extended to the bottom of the tailings pile where possible. All samples were kept frozen prior to analysis to prevent further oxidation of sulphide minerals.

3.2 Analytical methods

3.2.1 Characterisation of the waters at the mine sites

3.2.1.1 Water quality measurements

Water quality was measured from groundwaters (Paper I), surface waters (Paper I and IV), pore waters (Paper II) and seepage waters (Paper IV). Electrical conductivity (EC), pH and temperature (T) were analysed in the field with multi-parameter field meters, in conjunction with the sampling. The redox potential (Eh) and dissolved O_2 were measured with portable recording devices when possible (Papers II and IV). At Hitura, alkalinity was further determined in the field with a Hach digital titrator with 0.1600 N or 1.600 N H_2SO_4 to an end point of 4.5 (Papers I, II and IV).

Dissolved concentrations of major cations and trace metals were determined from the filtered (0.45 µm), HNO_3-acidified water samples using AAS and/or ICP-AES/MS (Papers I, II and IV). Major anions were determined from the unfiltered or filtered (1.2 µm) samples of the Hitura site with a spectrophotometer or with ion chromatography (Papers I, II and IV). SO_4^{2-} concentrations for the Luikonlahti seepage and drainage water samples were calculated based on S concentrations measured with ICP-AES/MS, and HCO_3^- values were computed based on charge balance ('missing ion method') for modelling purposes (Paper IV). The missing ion method was applied because alkalinity measurements were not available for Luikonlahti. This approach may, however, result in some error in the HCO_3^- values. This is because charge imbalance may also partly be related to other analytical inaccuracies aside alkalinity measurements, even though the latter typically is the major source of error in charge-balance (e.g. Fritz 1994).

Net alkalinity and net acidity values were further calculated for the seepage water and drainage water samples to evaluate the constraints for water treatment (Paper IV). Calculations were made following the equations presented by Kirby and Cravotta (2005), where

$$\text{Net Alkalinity (mg/L CaCO}_3) = \text{Alkalinity}_{\text{measured}} - \text{Acidity}_{\text{calculated}}, \text{ and}$$
$$\text{Net Acidity (mg/L CaCO}_3) = -\text{ Net Alkalinity.}$$

$\text{Acidity}_{\text{calculated}}$ was computed based on Hedin et al. (1994):

$$\text{Acidity}_{\text{calculated}} = 50[1000(10^{-\text{pH}}) + 2\text{Fe}^{2+}/55.85 + 3\text{Fe}^{3+}/55.85 + 2\text{Mn}/54.9 + 3\text{Al}/27.0]$$

AAS and spectrophotometer measurements were carried out in the laboratories of the Department of Geology at the University of Turku, or of the Hitura mine. ICP-AES/MS and ion chromatography analyses were performed in the Geolaboratory at the Geological Survey of Finland. Replicate samples were collected and analysed in parallel with the primary samples as a quality-control measure. In addition, charge balance calculations were made for samples with sufficient data to determine the accuracy of the analyses.

3.2.1.2 Cluster analysis

Cluster analysis was applied to the Hitura groundwater and surface water data to identify and group hydrochemically different water types (Paper I). The analysis was performed with 12 variables having the largest number of cases without missing values (119 groundwater and surface water samples). Prior to analysis, variables were $\log_{10}$ transformed and standardized to reduce the influence of the non-normal distributions and the scale differences of the variables. Cluster analysis was carried out with Statistica 5.1

software using Euclidian distances and Ward's method as the linkage rule.

3.2.1.3 Geochemical modelling

Geochemical modelling was used to support the interpretation of the pore water (Paper II) and seepage water data (Paper IV), and to simulate the reactions occurring once the seepage waters equilibrate with atmospheric conditions (Paper IV). In the modelling, the geochemical equilibrium model PHREEQC (v.2.13.2.) (Parkhurst and Appelo 1999), supplied with the WATEQ4F database (Ball and Nordstrom 1991), was used to calculate species distributions and saturation indexes (SI) of the water samples. The database was modified to include thermodynamic data from the MINTEQ database and from the literature (Majzlan et al. 2004) for relevant secondary Fe precipitates (ferrihydrite, lepidocrocite, $Fe(OH)_2$, schwertmannite).

3.2.2 Characterisation of the tailings solids

3.2.2.1 Tailings mineralogy

Mineralogy of the Hitura tailings was analysed for the detailed characterisation of the tailings solids (Paper II). The primary mineralogy of the solids was studied using light microscopy and x-ray diffraction (XRD) analysis, while alterations of sulphide minerals, the presence and type of secondary precipitates, and potential sources of Ni were examined with a high-vacuum scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS). All the microscopy was performed on polished thin sections that were prepared from undisturbed, dehydrated samples, impregnated with polyester resin and a methyl ethyl ketone peroxide catalyst (cf. Murphy 1986, Moran et al. 1989). XRD specimens were prepared from fine-ground bulk samples, and were scanned continuously with the diffractometer from 3 to 80°2θ with 0.020° step size and 1 s count time per step. XRD analyses were performed at the Department of Geology at the University of Turku and SEM-EDS measurements were carried out at the Geological Survey of Finland.

Mineral quantities (wt.%, 'normative mineralogical composition') were calculated with the ModAn program (Paktunc 1998 and 2001) using the mineralogical data, XRF bulk compositions and total S concentrations measured with Leco.

3.2.2.2 Tailings geochemistry

Tailings geochemistry was analysed to identify potential contaminants in the tailings and to investigate the degree of chemical alteration of the tailings, by evaluating the solid-phase species redistribution (i.e. 'fractionation') of the key elements related to sulphide oxidation and the associated chemical reactions (Papers II and III).

Identification of potential contaminants was based on total concentration analyses that were performed with XRF or using $HF\text{-}HClO_4\text{-}HNO_3\text{-}H_2O_2$ dissolution together with ICP-AES/MS measurements. Total concentrations of S and C were measured using a Leco induction furnace. The mobility and solid-phase speciation of trace metals (Ni, Cu, Co, Zn, Cr), As, and other sulphide oxidation-related metals (S, Fe, Ca, Mg, Al, Mn) were analysed with a five-step non-sequential (parallel) selective extraction procedure modified after Dold (2001 and 2003). In the extraction procedure the following operational fractions were separated with extractants of increasing aggressiveness: 1) soluble phases (0.01 M NH_4Cl, 1:50/ 0.01 M $BaCl_2$, 1:10), 2) phases bound to carbonates and the exchangeable fraction, including chemically adsorbed phases and surface complexes (1 M NH_4 –acetate, pH 4.5, 1:60; 'acetate fraction'), 3) phases in poorly crystalline Fe oxyhydroxides (0.2 M NH_4 –oxalate, pH 3.0, 1:100; 'oxalate fraction'), 4) the sulphide fraction ($KClO_3$-12 M HCl + 4 M HNO_3, 1:50 / *aqua regia*, 1:100), and 5) the residual fraction containing phases bound to silicate minerals and to poorly soluble oxides ($HF\text{-}HClO_4\text{-}HNO_3\text{-}H_2O_2$ / XRF) (Table 1 in Paper II, Table 2 in Paper III). After the extractions, each supernatant was centrifuged and filtered through 0.45 µm filters, and element concentrations were measured from the solutions with ICP-AES. Chemical analyses were performed on freeze-dried samples that were further ground for total concentration measurements.

Tailings pH was measured to evaluate the balance between the weathering of the acid producing minerals (sulphides) and acid neutralising minerals (primarily carbonates), and to understand element mobility in the tailings. Tailings pH was measured in the field with a pH electrode for the Hitura tailings, and in the laboratory from a 0.01 M $BaCl_2$ solution for the Luikonlahti tailings solids (Paper III).

Chemical analyses were carried out in the Geolaboratory at the Geological Survey of Finland, excluding the extractions in Paper II that were performed at the Department of Geology in the University of Turku.

3.2.2.3 Acid mine drainage potential of the tailings solids

The potential of tailings to produce AMD was evaluated based on neutralisation potential ratios ('NPR') during the detailed characterisation of the tailings solids (Paper II). NPR was calculated based on the following equation:

NPR = NP/AP,

where NP = neutralisation potential ($kgCaCO_3$ equivalent/t material),

and

AP = acid production potential ($kgCaCO_3$ equivalent/t material) (White et al. 1999).

For comparative purposes, the NP/AP ratio was calculated with two methods. In the first, the neutralisation potential ('NP_{min}') of the tailings solids was calculated as a sum of the weighted neutralisation potentials of each component mineral in the tailings sample (cf. Lawrence and Scheske 1997), determined based on the normative mineralogical composition (cf. Paktunc 1999a and 1999b). In the second method, the neutralisation potential ('NP_{carb}') was computed according to the carbonate mineral content of the samples. The acid production potential (AP) was determined using total sulphur concentrations (Leco-S) in both calculations ($AP_{(kgCaCO3/t)} = S(wt\%) \times 31.25$; e.g. White et al. 1999). Interpretation of the results was based on the AMD potentiality classification presented by Price et al. (1997).

Whereas the first approach, using the normative mineralogical composition, takes into account the potential role of non-carbonate minerals as acid neutralising components in mine tailings (Lawrence and Scheske 1997), the carbonate content-based calculation relies solely on the acid buffering capacity of carbonate minerals. In general, carbonates are the most effective neutralising minerals in mine wastes due to their high reactivity and acid buffering capacity in near-neutral pH. Certain silicate minerals (e.g. olivine, serpentine, wollastonite, Ca-plagioclase) may nevertheless also contribute to acid attenuation, particularly over the long-term (Jambor et al. 2002, Jambor et al. 2007).

4 OVERVIEW OF THE INDIVIDUAL STUDIES

In the following chapters, summaries of each individual study of the thesis are presented. The section is arranged according to the original papers.

4.1 Characterisation of tailings-derived groundwater and surface water contamination at the Hitura Ni mine (Paper I)

Elevated SO_4^{2-} and Ni levels in household wells in the vicinity of the Hitura Ni mine since the 1980s suggested that tailings disposal had resulted in groundwater contamination in the area (Korkka-Niemi et al. 1999). A comprehensive study of the groundwater and surface water quality was carried out to assess the nature and extent of the observed contamination (Paper I). In the study, physical and chemical water quality parameters (pH, EC, alkalinity, dissolved cations and trace metals, major anions) were examined from monitoring wells, private wells and surface water channels near the tailings area, and the groundwater flow pattern was defined based on the hydraulic head measurements. The contaminated area was delineated according to the spatial distribution of individual key parameters (defined based on the overall characterisation), the major-ion composition of the waters, and cluster analysis of the hydrogeochemical data.

The results of the overall water quality assessment showed that tailings-derived waters had contaminated the aquifer and surface water bodies close to the Hitura tailings impoundment. The tailings effluents were mainly near-neutral in character, but contained elevated concentrations of SO_4^{2-}, Ni, Fe and Cl^-. The water chemistry thus suggested that sulphide oxidation occurs in the Hitura tailings, introducing Fe, SO_4^{2-} and trace metals into the drainage, but that the tailings (still) contain sufficient amounts of acid-neutralising carbonate minerals to buffer the acidity produced in sulphide weathering, maintaining a circumneutral pH in the drainage (cf. Nesbitt and Jambor 1998, Pettit et al. 1999). Process waters were proposed as an additional source for the high SO_4^{2-} (and Ni) in the tailings-derived waters, since sulphuric acid is used in ore processing at the Hitura mine. Unlike Fe, SO_4^{2-} and Ni, chloride in the tailings effluents is usually not related to sulphide weathering. At Hitura, Cl^- apparently originates from fluid inclusions of the serpentinite ore (cf. Aulanko 1970, Papunen 1970) and, as a conservative ion, concentrates during the recycling of the process water. Overall, Cl^- was a very distinctive element for the drainage waters of the Hitura tailings and could be identified as a one of the tracer elements for the contaminant plume from the tailings.

The spatial distributions of individual parameters (EC, pH, SO_4^{2-}, Ni, Fe, Cl^-) showed variable success in delineating the extent of the contamination. The distributions of EC and SO_4^{2-} content were the best single variables to map the extent of the pollution. The distribution of pH showed no clear pattern, while those of Ni and Fe were apparently more susceptible to changing pH-Eh conditions (secondary precipitation, adsorption) than the distribution of the conservative SO_4^{2-} ion (cf. Gray 1996), thus leading to lowered transportation of these metals from the tailings area. The number of Cl^- measurements was so low that delineation of contamination could not be carried out based on the Cl^- distribution.

The overall water chemistry of the tailings effluents showed that the disposal of the serpentinite tailings was not the only pollution source at the locality. The other contaminant sources included the jarosite residue deposited in the tailings impoundment (pond D in Fig. 2) and drainage from the abandoned Makola sulphide mine tailings area (Fig. 2). Similar to the Hitura effluents, these two discharges also contained high EC, SO_4^{2-} and Ni, making the identification of the different contaminant sources more difficult. However, both of these secondary drainages had low Cl^- concentrations and represented typical AMD with a low pH. In addition, the jarosite effluents contained a hundred times higher metal concentrations (Ni, Co, Zn) than the drainage from the serpentinite tailings.

The mixing of the tailings-derived waters with uncontaminated groundwaters was observed as a change in the major ion composition. Waters in the tailings area represented a Mg-SO_4 dominated water type, whereas the natural waters in the area were of the Ca-HCO_3 type, which is the typical water type for Finnish aquifers (cf. Lahermo et al. 1990). Thus the migration of the tailings-derived contaminant plume could be identified as a gradual change from Ca-HCO_3 type water towards the Mg-SO_4 type.

The spatial extent of groundwater contamination was best described using cluster analysis, performed on a combination of 12 variables. With this numerical analysis, it was also possible to differentiate the major contaminant sources. The analysis divided the samples into two main groups: uncontaminated waters (Ca-HCO_3 type waters with SO_4^{2-} and Ni content below national drinking water limits) and waters influenced by the tailings area (Mg-SO_4 waters with high SO_4^{2-}, Ni and Fe). These results indicated that groundwater contamination due to the disposal of the serpentinite tailings was largely limited to the west and north of the tailings impoundment, and the waters south of the impoundment were uncontaminated. This was consistent with the overall groundwater flow pattern in the area, indicating that the main flow direction was from the south-west to the north-east. Thus, the uncontaminated waters located mainly upgradient of the tailings area. Further partitioning of the two major groups into a total of 7 subgroups by the cluster analysis showed that the discharge from the jarosite residue (subgroup 7) had caused part of the contamination observed beside the western part the impoundment. In addition, some incipient pollution was identified in the aquifer south-east of the tailings dam (subgroup 3), where Fe, Mn and SO_4^{2-} concentrations were somewhat higher than in the uncontaminated waters (subgroups 1 and 2). These higher concentrations may, however, also relate to naturally occurring anomalous background values.

The major contamination in the surroundings of the Hitura tailings impoundment was found to be related to the interlobate esker system, running across the tailings area. Based on the results, the high SO_4^{2-} contaminant plume had spread through the esker, underneath the seepage collection ditches, all the way to the Makolanoja brook, located ca. 600 m from the tailings area (Fig. 2). A groundwater flow model, constructed for the site by Artimo et al. (2004), has subsequently confirmed the presence of this flow path. The rest of the observed contamination was most likely due to seepage underneath the seepage collection system through the till units.

4.2 Mineral weathering and contaminant mobility within the Hitura low-sulphide tailings (Paper II)

With groundwater and surface water contamination characterised and spatially delineated around the Hitura tailings area (Paper I), a detailed mineralogical and geochemical study of tailings weathering and subsequent contaminant release was conducted in the oldest, inactive tailings impoundment to assess the influence of sulphide oxidation at the exposed tailings surface on contamination (Paper II). The study was performed on samples collected in the middle of the impoundment, where brownish-red colouring from Fe precipitates was distinctively developed. Mineralogy of the tailings solids was analysed to examine mineral weathering and to assess the AMD potential of the tailings. The release and resorption of possible contaminants was evaluated on the basis of pore water geochemical data and a 5-step selective extraction procedure.

Based on the mineralogical and chemical analyses, the Hitura tailings were low-sulphide tailings (~1% S; < 5% of sulphides) mainly composed of serpentine, micas, talc and amphiboles with only minor carbonates (< 5%). The primary sulphide minerals included pyrrhotite, pentlandite, mackinawite and chalcopyrite.

The 10–15 years exposure of the tailings solids to atmospheric conditions, in a temperate climate, had resulted in the weathering of the sulphide minerals down to 2 m depth. The weathering was most intense in the unsaturated 'oxidation zone' (0–66 cm), where Fe oxyhydroxides occurred as rims around the edges of the sulphide mineral grains and as interstitial precipitates (Fig. 7). The low total S concentrations (< 0.6%; Fig. 7) and abundant Fe (46%) in the oxalate fraction indicated depletion of sulphides and subsequent formation of Fe precipitates. Underneath, the oxyhydroxide rims were absent and less Fe occurred in the oxalate fraction (34%). However, minor sulphide oxidation was indicated by the alteration of pyrrhotite to marcasite along the grain edges ('transitional zone', 66–200 cm; Fig. 7). Deeper in the profile (200–1400 cm), tailings were water saturated and unaltered. Here, Fe and S were mainly in the sulphide fraction (52% and 45%, respectively), and sulphide minerals were intact, showing fresh grain boundaries and internal fractures ('the unaltered zone'; Fig. 7). Overall, pyrrhotite was the most oxidized sulphide mineral in the tailings, being almost completely replaced by Fe oxyhydroxides in the oxidized zone.

Despite the small amount of sulphide minerals, their oxidation had decreased pore water pH (down to 6.6) and alkalinity in the oxidized zone. Judging from the mineralogy and the selective extractions, this was because the buffering capacity of the carbonate minerals was completely exhausted in the surface (Fig. 7). Nevertheless, unweathered sulphide mineral grains still existed in these layers, suggesting that a further decrease in pH is likely in the future. These results were in accordance with the carbonate content-based NP/AP ratio, indicating an excess of sulphides over carbonates and suggesting that the tailings were 'likely AMD generating' (average $NP_{carb}/AP = 0.3$ in unaltered tailings). However, the NP/AP ratio computed from the total mineralogy proposed additional buffering capacity by the silicates, in particular serpentine (average $NP_{min}/AP = 2.7$ in unaltered tailings). In fact, previous studies have shown that fine-ground serpentine may reduce the proton acidity through ion exchange reactions, in which Mg^{2+} is exchanged with H^+ (Luce et al. 1972, Berner 1981). High Mg concentrations in the tailings pore water, which cannot be solely due to weathering of Mg-bearing carbonates, supported the presence of a serpentine buffer. Overall, carbonate mineral buffering maintained a neutral or even basic pore water pH deeper in the tailings (from ~30 cm downwards; Fig. 7), despite the incipient sulphide oxidation.

Based on the results, the sulphide oxidation had released SO_4^{2-}, Fe, Ni and Zn from sulphide minerals into the tailings pore water. A major source of SO_4^{2-}, Fe and Ni was the weathering of pyrrhotite, while Zn was presumably mobilized in the oxidation of sphalerite. Based on the SEM-EDS study, other potential sources for Ni included pentlandite, mackinawite, vallerite and chalcopyrite. These sulphide minerals were, however, only slightly oxidized in the grain edges, whereas pyrrhotite showed only pseudomorphs after the original grains in the most oxidized tailings. The mineralogical data and observations from the selective extractions thus indicated that oxidation of sulphide minerals followed the relative weathering series of sulphides presented, for example, by Jambor (1994) and Plumlee (1999), in which pyrrhotite is the most easily weathering sulphide and chalcopyrite is one of the most resistant sulphides.

In accordance with previous studies (Lin 1997b, McGregor et al. 1998a, Holmström et al. 1999), the mobility of the released Ni, Zn and Fe was controlled by secondary Fe precipitates lower in the oxidation zone, where pore water pH was neutral. This was seen as an increase in Ni and Zn concentrations in the acetate and oxalate fractions (i.e. in the chemically adsorbed form and in the phases in Fe oxyhydroxides; Fig. 7) and as a decrease in the pore water Ni (from 8 mg/L down to 0.2 mg/L) and Zn (from 0.3 mg/L down to 0.1 mg/L) contents. The geochemical modelling suggested that the Fe precipitates in the near-neutral conditions included ferrihydrite, goethite and lepidocrocite. This result agrees with previous studies showing that these phases are prone to precipitate in circumneutral environments (Bigham 1994, Bigham and Nordstrom 2000). Unlike trace metals, pore water SO_4^{2-} concentrations increased below the oxidized zone, indicating transport of SO_4^{2-} down to the water table. This was expected, because mineralogical studies and geochemical modelling indicated only a minor formation of SO_4^{2-} precipitates (mainly gypsum) in the oxidized zone. In addition, the adsorption of SO_4^{2-} to Fe oxyhydroxides is of minor importance at a circumneutral or basic pH (Dzombak and Morel 1990).

Overall, the results indicated that even in low-sulphide tailings sulphide oxidation and subsequent metal and SO_4^{2-} release occur if the tailings are left

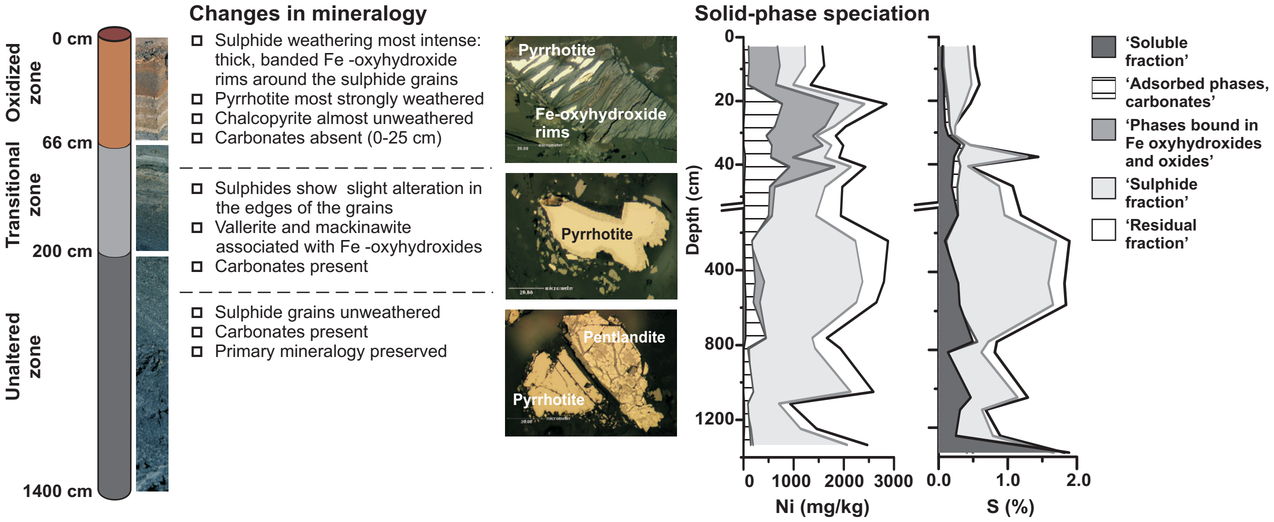

Fig. 7. Mineralogical changes and solid-phase speciation of Ni and S in the Hitura tailings core H1, drilled from the old impoundment (Photos: Päivi M. Heikkinen).

uncovered and exposed to atmospheric conditions after disposal ceases. However, sulphide weathering at the exposed surface of the old impoundment is not the primary reason for the observed trace metal contamination in the waters around the tailings area, since the majority of the released Ni and Zn was immobilized by the secondary Fe precipitates in the oxidized zone. Nevertheless, it is probably a source of SO_4^{2-}, since no major solid-phase controls for SO_4^{2-} were found.

4.3 Spatial variation in element solid-phase speciation and sulphide oxidation intensity in the Hitura and Luikonlahti active sulphide tailings impoundments (Paper III)

As on-going sulphide weathering at the exposed surface of the old Hitura tailings had only a minor effect on the tailings-derived water contamination (Paper II), the degree of chemical alteration of tailings was studied from drill cores in different parts of the impoundment (border zone vs. mid-impoundment; active vs. old impoundment) using geochemical extractions, lithological observations and pH measurements (Paper III). A similar investigation was carried out in the Luikonlahti tailings facility to obtain a more comprehensive view of the influence of tailings mineralogy and physical properties of active disposal areas on the early stages of sulphide weathering and element mobility. These two mine sites have comparable operation periods, but differ in several key characteristics. The Hitura tailings represent low-sulphide tailings (ca. 1.2% S) with a moderate neutralising capacity, dammed above the ground level, while the Luikonlahti tailings are sulphide-rich tailings (~ 7.6% S) with a low carbonate content deposited into a topographic low. Thus, these sites enable the comparison of tailings impoundments with dissimilar flow patterns and materials of diverse reactivity.

Selective extractions and visual observations of the tailings cores indicated that sulphide oxidation with subsequent metal release and the formation of Fe precipitates had occurred at both tailings impoundments. The oxidized layers were marked by brownish-red colouring from Fe precipitates and by increased concentrations of S, Fe and trace metals in the easily extractable phases (soluble fraction, exchangeable fraction, phases bound to poorly crystalline Fe oxyhydroxides and oxides) instead of the sulphide fraction, which was otherwise the primary host for these elements. In addition, absence of Ca in the acetate extractable fraction, i.e. the carbonate-bound phase, suggested dissolution of carbonates. The pH measurements further indicated sulphide oxidation, particularly at Luikonlahti, where the low pH conditions (pH 3.5–4.4) coincided with the layers defined as oxidized based on the extractions and visual observations. In the most acidic layers of Luikonlahti, a presence of Cr and Al in the oxalate fraction instead of the silicate fraction (i.e. residual fraction) suggested dissolution of silicates (presumably chlorite).

Based on the distribution and extent of the oxidized zones, several factors affected the intensity of sulphide oxidation and related reactions in the Hitura and Luikonlahti tailings facilities. They included tailings disposal history and strategy, the impoundment structure and water table level, and the reactivity of the tailings. At Hitura, the redistribution of trace metals (Ni, Co, Zn, Cu) was only marked in the unsaturated tailings of the old disposal pond. There, sulphide minerals had been exposed to atmospheric conditions, because the tailings were left uncovered after disposal ceased. In contrast, continuous disposal of the tailings slurry had reduced sulphide oxidation in the surface of the currently active Hitura impoundment as a result of the burial of fresh sulphide grains and the increased moisture content of the unsaturated tailings (cf. Nicholson et al. 1989), and only minor redistribution of trace metals was observed. At depth, in the saturated parts of the mid-impoundment, where dissolved oxygen is not available, tailings were unoxidized, showing no fractionation of S or trace metals. In contrast, some redistribution of Ni, Co and Zn was observed in the dry border zone, where oxygen diffusion may occur through the tailings dam. More marked fractionation of metals (in particular Ni; present even in the easily extractable fraction) and the absence of carbonate-bound Ca were, however, detected in the coarse-grained bottom layers of the border zone, suggesting the presence of a paleosurface.

At Luikonlahti, the higher reactivity (i.e. Fe sulphide content) of the sulphide tailings had resulted in thicker oxidized layers than at Hitura, despite the similar operation times, the continuous tailings disposal and the covering of the sulphide tailings with the magnesite-rich tailings. The spatial distribution of the oxidized layers indicated that the intensity of sulphide weathering was largely controlled by the water table level in the impoundment and the disposal strategy of the tailings. The sulphide tailings were currently water saturated in the east, where the bedrock barrier, together with the low permeability base, contributes to a higher water table than beside the earthen dam in the west. Furthermore, the disposal of the magnesite tailings has mainly occurred from the northeast corner of the facility, resulting in the thickest magnesite layers (5.9 m) in the east, which further reduces oxygen diffusion into the sulphide tailings below. As a result, the sulphide tailings in the east were largely unaltered with trace metals and S found in the sulphide fraction and neutralising carbonates present in the tailings solids. In contrast, intensive sulphide oxidation extended down to several metres depth in the sulphide tailings closest to the earthen dam in the west, where the tailings were unsaturated and currently covered with a 1 m thick layer of magnesite tailings. Here, notable amounts of metals and S were found in the easily leachable fractions. Apparently, a delay in the burial of the sulphide tailings has promoted the oxidation of the reactive sulphides in the unsaturated conditions. Sorting of the tailings during disposal may also have enhanced oxidation through increased porosity in the proximity of the dam, since coarser particles generally settle closer to the dam when the tailings slurry is spigotted from the dam (cf. Robertson 1994, Al and Blowes 1999). The magnesite tailings on top of the sulphide tailings showed only minor trace metal redistribution as a result of the short exposure due to continuous disposal of these low-sulphide, less reactive tailings.

Based on the extraction results, the mobility of the trace metals released in sulphide weathering was controlled by secondary sorption by Fe oxyhydroxides and oxides in both tailings impoundments. However, the adsorption was strongly pH dependent and was presumably also influenced by the redox conditions in the tailings. Trace metals were retained by Fe precipitates (trace metals found in the acetate and oxalate fractions) in the two near-neutral tailings types (i.e. Hitura sulphide tailings, pH 7.4–8.9; Luikonlahti magnesite tailings, pH 6.8–7.4), whereas a notable part of the metals was in a soluble form in the acidic, oxidized Luikonlahti sulphide tailings (pH 3.5–4.4), despite the presence of some Fe precipitates. This is in agreement with Dzombak and Morel (1990), stating that the adsorption of cationic metals to Fe oxyhydroxides decreases with decreasing pH as the net surface charge of the Fe precipitates becomes more positive. The mobility of trace metals in the Luikonlahti sulphide tailings may additionally be due to desorption of the retained metals as a result of the dissolution of the previously precipitated secondary Fe phases, since these minerals are prone to dissolve with increasing acidity or with a shift to more reducing conditions (Schwertmann and Murad 1983, Ribet et al. 1995). The latter is possible when water table is raised in the tailings after sulphide oxidation has initiated (cf. Holmström et al. 2001), such as in the mid-impoundment of Luikonlahti. Reductive dissolution of Fe precipitates is also a possible reason for metal mobility from the paleosurface of the bottom layers of the Hitura border zone core, where trace metals were in the easily leachable fraction instead of the acetate or oxalate fractions, despite the circumneutral conditions.

The study showed that extensive sulphide oxidation may occur even in active tailings areas during disposal, particularly if reactive tailings are unsaturated with water after disposal and there is a delay in the burial of the sulphide grains. Furthermore, the study indicated that sulphide oxidation with subsequent mine drainage problems may occur beside the impoundments dams and not only at the tailings surface. Based on the results, metal release from the paleosurface in the border zone of the Hitura impoundment is a potential reason for the observed Ni contamination in the waters around the tailings facility.

4.4 Seepage water chemistry of the Hitura and Luikonlahti tailings impoundments (Paper IV)

Seepage water and drainage water quality (pH, EC, O_2, redox, dissolved cations and trace metals, major anions, total element concentrations) was studied from the surroundings of the Hitura and Luikonlahti tailings impoundments to evaluate the factors controlling the chemistry of waters seeping through the tailings dams and to identify the constraints for water treatment (Paper IV). At Luikonlahti, several samples were collected each year during a four-year monitoring period to evaluate the annual and seasonal variation in the seepage quality. Geochemical modelling was applied to study how the seepage water chemistry changes once the seepages become drainage waters by equilibrating with atmospheric conditions.

On the basis of the overall water chemistry, tailings mineralogy (and thus the deposit geology) was the most distinct factor causing diversity in the seepage quality between the two sites. The Hitura low-sulphide, Mg-rich tailings from Ni processing, containing some acid neutralization capacity (due to Mn-bearing carbonates and abundant serpentine), produced mainly circumneutral (average pH 6.2), net alkaline, Mg-SO_4 dominated seepages with high contents of Ni (average of 0.8 mg/L), Mn (average of 5.7 mg/L) and Fe (average of 42 mg/L). In contrast, the effluents from the sulphide-rich, multi-metal Luikonlahti tailings, with some calcite and Ca silicates in the gangue, were mainly net acidic, acid (average pH 4.6) Ca-SO_4 type waters with a high trace metal (Zn 3.6 mg/L, Ni 0.7 mg/L, Cu 0.4 mg/L, Co 0.3 mg/L; on average) and Fe content (average of 150 mg/L). Based on the results of the tailings weathering (Papers II and III), the neutral character of the Hitura seepages is due to both the limited sulphide oxidation and the moderate acid buffering capacity of the tailings. On the contrary, the acid effluents at Luikonlahti reflect the intensive weathering of the sulphides and the low buffering capacity in the tailings (Paper III). Despite the limited sulphide oxidation, the Hitura seepages contained a higher amount of SO_4^{2-} (average of 5200 mg/L) than the Luikonlahti effluents (average of 1830 mg/L). The Fe:SO_4 ratio (and the Na:SO_4 ratio) of the seepages indicated that the high SO_4^{2-} content in Hitura was partly due to the sulphuric acid used in the ore processing and not only caused by pyrrhotite weathering. In contrast, the source of SO_4^{2-} was more directly the sulphide oxidation in Luikonlahti.

The variation in source materials and the weathering stage of the tailings along the seepage flow paths resulted in differences in pH and metal contents between the seepage points. This was particularly true at Luikonlahti, where the three major seepage points ('upper seepage' at the base of the upper dam section; 'toe seepage' at the base of the impoundment; 'settling pond seepage' by the clarification pool) had distinctive characteristics. The upper seepage had an acid pH (<4.3) and high metal (Cu, Co, Ni, Zn, Fe, Al) content as a result of a flow through the oxidized, unsaturated sulphide tailings and the sulphide-bearing dam. The abundant Cu and Si in this seepage implied that sulphide oxidation has proceeded to chalcopyrite weathering and that aluminosilicate weathering has started in the oxidized tailings. In fact, previous results have shown that Cu was released from sulphide minerals and the carbonate mineral buffer was completely exhausted in these layers (Paper III). In contrast, a less acid pH (average pH 4.6) and abundant Zn was observed for the toe seepage as a result of a flow through the saturated, mainly unoxidized, sulphide tailings and a till-lined waste rock dam. In these deeper tailings layers the carbonate buffer still existed (Paper III). Unlike the upper seepage and toe seepage, the seepage from the settling pond was near-neutral (average pH 6.7) and contained Ni. This seepage reflected the origin from the magnesite tailings and the process waters from talc production, clarified in the settling pond prior to discharge into the local surface water system. Overall, the trace metal distribution in the seepages was a result of the composition and weathering stage of the tailings but also the mobility of each metal due to pH control.

At Hitura, the variation in geochemistry between the various seepage points was less distinctive than at Luikonlahti. However, the seepage point close to the oldest disposal area had a slightly acid pH (5.6) and contained elevated Al, Si and trace metals, suggesting a greater extent of weathering along the flow path to that seepage than to the others. In contrast, the influence of source materials was clearly seen at Hitura, with ten to a hundred times higher Co, Ni and Zn concentrations in the drainage waters than in the seepages as a result of the pumping of the jarosite-derived contaminated groundwater into the drainage channel.

Based on the annual and seasonal variation in pH and metal contents of the Luikonlahti seepages, the hydrological setting of the site and also the structural modifications made to the tailings impoundment further influenced the seepage quality. Metal (Zn, Ni, Co, Cu, Fe, Al) concentrations fluctuated widely during the four-year monitoring period, but the lowest concentrations occurred in the upper seepage in the early summer, *after* the peak in local discharge resulting from the snow-melt and spring rains. The spring flush may remove the weathering products precipitated in the impoundment during the winter and dilute the subsequent effluents (cf. Søndergaard et al. 2007). In general, the fluctuation in element concentrations was wider in the upper seepage than in the lower seepage. This was apparently largely due to the shorter retention time of water in the flow path of the upper seepage than in the toe seepage. Overall, the trend in metal and SO_4^{2-} concentrations was decreasing and that of pH increasing during the monitoring period. Furthermore, the water quality changed temporarily from net acidic to net alkaline in the upper seepage. These changes were most likely due to the thickenings of the magnesite tailings on top of the sulphide tailings that had taken place during the monitoring period.

Geochemical modelling showed that exposure of the seepage waters to atmospheric conditions will notably change the pH and metal content of the seepages, but the direction of these changes will depend on the net alkaline or net acidic character of the seepages. Based on the model, equilibrium with surficial conditions increased pH (> 7) in the net alkaline waters of the study areas (all Hitura seepages and Luikonlahti settling pond seepage and upper seepage in June 2006), despite the proton acidity produced by precipitation of secondary Fe and Al oxyhydroxides and oxides [$Fe(OH)_3$(a), ferrihydrite, $Al(OH)_3$, $Al(OH)SO_4$ and/or gibbsite]. In addition, the model suggested a notable decrease in Al and Fe contents (down to the µg/L level) as a result of the formation of secondary Fe and Al precipitates, and a minor adsorption of Ni, Cu, Zn and Mn to the Fe precipitates. In contrast, a further decrease in pH (down to pH 3.1–3.6) was predicted for the net acidic waters of Luikonlahti (upper seepage, toe seepage), and no adsorption of trace metals was observed in the model due to the low pH conditions. Fe and Al concentrations remained also high, despite the suggested precipitation of amorphous $Fe(OH)_3$, Na-jarosite and/or schwertmannite, which resulted in a minor decline in SO_4^{2-} concentrations. The model-predicted changes in pH and in metal behaviour were in accordance with data presented from coal mines (Kirby and Cravotta 2005, Cravotta 2007, Cravotta 2008).

Constrains for treatment of the tailings effluents were defined based on the seepage water quality assessment. A decrease in the loads of SO_4^{2-}, Fe, Mn and Ni, while maintaining pH close to neutral, should be the objective for the treatment of the net-alkaline seepages of the Hitura site. The geochemical modelling together with previous research (Hedin et al. 1994, Ye et al. 2001, Batty et al. 2008) suggested that a combination of aerobic and anaerobic treatment systems could be useful in this respect. In Luikonlahti, continued monitoring was proposed instead of a treatment strategy since the seepage water quality was observed to still be adjusting to the recent modifications made in the tailings impoundment.

5 DISCUSSION AND RECOMMENDATIONS

The results of the papers I–IV highlight the importance of an integrated study of the tailings areas, using several research methods and materials, to assess the nature, spatial extent and the reasons for tailings-derived water contamination and to examine the geochemical and mineralogical constraints for remediation and prevention of further contamination. In the following discussion, the applicability of the different approaches to characterise the causes and effects of tailings-derived contamination will be considered. In addition, observations pertinent to the future assessment and prevention of mine drainage from existing and future tailings facilities will be discussed.

5.1 Assessment of dispersal of tailings-derived contamination and recommendations for water quality monitoring

The water quality assessment from the Hitura mine site emphasized the importance of a detailed characterisation of water chemistry when investigating tailings-derived contamination to identify the critical contaminants and indicator elements, and to assess the extent of the pollution (Paper I). Obligatory (i.e. environmental permit-based) water quality monitoring of tailings-derived waters at Finnish mine sites rarely calls for these types of studies. Instead, monitoring typically focuses on a limited suite of key parameters, mainly defined according to the commodities of the extracted ore and, in some cases, the major chemicals used in the ore processing. For example, in case of sulphide mine tailings, these parameters usually include pH, EC, SO_4^{2-}, Fe and the extracted base metals, such as Ni for the Hitura mine. The case study from Hitura showed that this set of parameters was adequate in defining the major contaminants (SO_4^{2-}, Ni) related to Hitura serpentine tailings, and the distributions of EC and SO_4^{2-} were also reasonable in assessing the extent of the tailings-derived contamination. Certain limitations in this type of approach were, however, identified.

Based on the Hitura example, a permit-based water quality assessment may ignore critical contaminants and other contaminant sources at the site. At Hitura, where there were other pollution sources at the locality and within the impoundment (beside the serpentine tailings), a limited set of water quality parameters would have neglected the presence of Co and Zn from the jarosite residue. It would also have been insufficient to separate the contamination between the different sources (high EC and SO_4^{2-} drainage also from the abandoned Makola mine site and the jarosite residue) and from anomalous background concentrations (in particular Fe), leading to incorrect interpretation of the spatial extent of the contamination related solely to Hitura mine tailings. Furthermore, the assumption that mine drainage is generally acidic and can thus be traced based on pH values, would have been misleading, since the Hitura effluents appeared to be near-neutral in character, representing the less well documented NMD (e.g. Cravotta et al. 1999, Pettit et al. 1999) with pH values corresponding to the pH of Finnish natural waters (cf. Lahermo et al. 1990, Lahermo et al. 1996).

In contrast, the presence of other contaminants and pollution sources in Hitura could be identified with detailed hydrogeochemical characterisation of the tailings-derived waters and surrounding water bodies, using different methodological approaches. The spatial extent of the contamination and the inputs from the major contaminant sources were best described using cluster analysis, where a combination of several chemical variables was studied instead of examining single parameters. The changes in the ratios of major cations (Ca, Mg, Na, K) and anions (SO_4^{2-}, Cl^-, HCO_3^-) (i.e. in the water types) also reflected, even in small concentrations, the migration of the tailings-derived contaminant plume to the surroundings. The advantages of the cluster analysis and water type approaches are well documented in hydrochemical investigations and in spatial delineation of the influence of anthropogenic sources on water quality (Ashley and Lloyd 1978, Suk and Lee 1999, Güler et al. 2002, Holland and Witthüser 2008), but these methods are less commonly applied in a similar context in mining environments (e.g. Kimball et al. 2006).

The study further indicated that conservative ions can be useful single natural tracers of tailings-derived contamination. At Hitura, Cl^- was observed to be a good indicator element for the effluents from the serpentine tailings, since Cl^- initiated from the ore and no other significant Cl^- sources existed at the site. Al et al. (2006) also showed the significance of Cl^- as a hydrochemical signature in defining a tailings-derived plume. In their study, Cl^- originated from process chemicals and not from the ore, as at Hitura.

Furthermore, the Hitura water quality assessment demonstrated that a detailed 3D-characterisation of the Quaternary deposits from the planned tailings disposal area is needed (soil type, stratigraphy, hydraulic conductivity and connections) to prevent loading from the facility. This is to determine whether natural deposits at the site have sufficiently low hydraulic conductivity or if additional basal structures are required to prevent seepage from the tailings area into the surrounding aquifers (cf. Hutchison and Ellison 1992, Lottermoser 2007). In the Hitura case, the water quality assessment results, together with the detailed Quaternary deposit mapping and groundwater modelling (Pietilä 2000, Salonen et al. 2001, Artimo et al. 2004), showed that the major water contamination was due to construction of the tailings area partly on top of a low-relief esker complex that had a gravelly core with a high hydraulic conductivity. These deposits are also the primary aquifer at the locality. Inadequate basal structures of tailings facilities are a common cause for tailings-derived groundwater contamination (e.g. Morin et al. 1982, Hutchison and Ellison 1992, Bain et al. 1995, DeVos et al. 1995). At Hitura, additional spreading of the tailings-derived waters had occurred underneath the seepage collections ditches, suggesting an insufficient depth of the ditches. A similar problem has been observed, for example, at the Pyhäsalmi mine site in western Finland (Northern Finland Environmental Authority 2009). If the current hydrogeological knowledge of the Hitura soil deposits would have been available prior to the construction of the impoundment, the present contamination could presumably have been avoided. To date, clay liners have been installed beside the tailings dams to prevent further spreading of tailings-derived waters through the esker (cf. Artimo et al. 2004) and the depth of the seepage ditches has been increased. In theory, these types of issues should not arise with future mines, because current legislative regulations require impermeable basal structures for tailings impoundments if hazardous waste (e.g. high sulphide, AMD generating waste) is to be deposited in the facility.

The Hitura example showed that it will be important to include periodic measurements of the total water chemistry in future routine water monitoring programmes of the tailings areas alongside the key parameters. This is to detect any possible spreading of unexpected pollutants already during the operational phase of the mine and to initiate preventive measures. The need for hydrogeochemical characterisation of the mine site waters will also actualise at the stage of designing the water treatment systems for the contaminated effluents (Hedin et al. 1994, Gazea et al. 1996, Benner et al. 1997).

Overall, the water assessment suggested that water contamination in the surroundings of the Hitura tailings impoundment is a combined result of the initial sulphide oxidation in the tailings, inputs from the process waters and effluents from the jarosite residue. It was, however, realized that a more detailed assessment of the tailings properties would be needed to properly identify the processes leading to contamination and to evaluate the geochemical constraints for the preventive measures (see Papers II–IV).

5.2 Mineralogical and geochemical characterisation of tailings in the assessment of tailings weathering and contaminant mobility

The investigation of tailings weathering as a potential cause for the observed water contamination at the Hitura site demonstrated the value of a combined mineralogical and geochemical study of the tailings (Paper II). While the contaminant sources and the degree and depth of mineral alterations were identified with mineralogical observations, the geochemical analyses (total chemistry and selective extractions of the tailings solids, pore water chemistry) were a tool to assess the distribution and mobility of the contaminants in the tailings. A similar combination of mineralogical analyses with both pore water analyses and selective extractions has previously been used by Gunsinger et al. (2006), while most earlier studies have included either pore water analysis (Blowes and Jambor 1990, Johnson et al. 2000, Moncur et al. 2005) or selective extractions (Ribet et al. 1995, Dold and Fontboté 2001 and 2002) along with mineralogical studies. The interpretation of the results can further be supported by geochemical modelling. In this study, for instance, the modelling was particularly useful in defining the secondary phases that were expected to precipitate. This was significant, since the mineralogical composition of these poorly crystalline phases was not measurable with the mineralogical techniques available for the present study, due to the small quantities of the precipitates in the tailings.

Mineralogical investigations were of particular value in supporting the interpretation of results from the selective extractions and in identification of minerals contributing to acid neutralisation in the Hitura tailings. Since the extractions are more or less operationally defined and never 100% selective in extracting different phases (e.g. Hall et al. 1996, McCarty et al. 1998), the dissolution of unexpected minerals may occur during the extractions. Even though the extraction results from the Hitura tailings were in general agreement with the observations from the mineralogical analysis, some uncertainties emerged. For example, a notable amount of Fe was detected in the oxalate fraction in the unaltered zone, where occurrence of secondary Fe precipitates was unlikely. In addition, some S and base metals also unexpectedly occurred in the silicate fraction instead of the sulphide fraction. Most of these uncertainties were, however, resolved with the support of the mineralogical information. The oxalate Fe was found to originate from the dissolution of magnetite (cf. Chao and Zhou 1983) that was present in the unaltered zone, while the occurrence of sulphide minerals as intergrowths or inclusions in silicates and/or the presence of base metals in the crystal structures of silicate minerals (cf. Papunen 1970) explained the residual S and base metals. Based on this experience, it is apparent that the method presented by Dold (2001), in which the mineralogy is measured before and after the extractions, will provide further accuracy to the interpretations of selective extractions and would be of benefit particularly at new study sites.

The Hitura case study also addressed the importance of mineralogical investigations in evaluating the potential of the tailings to produce acid mine drainage. The AMD potential of the tailings is commonly predicted based on static tests that estimate the neutralisation and acid production potential of tailings based on chemical analyses; for example NP is measured based on acid titrations (cf. White et al. 1999). The major disadvantage of the simple NP tests is that the vigorous acid titration may also dissolve minerals whose weathering is kinetically so slow in nature that they cannot contribute to buffering of the acidity produced by sulphide minerals (cf. Jambor et al. 2002, Jambor et al. 2007). This was also observed at Hitura. Based on a previous static test, the Hitura tailings were classified as 'not potentially AMD generating' (NP/AP = 10.1:1; Saari 1996). The mineralogy-based NP values of the present study revealed that the high neutralisation capacity of the tailings, in fact, largely results from the abundant serpentine (accounting for 66% of the calculated NP_{min} in the unaltered tailings), instead of the carbonate minerals. Indeed, the excess of sulphides over carbonates suggested that the tailings are 'likely AMD generating' ($NP_{carb}/AP = 0.3:1$ in average). Due to its slower weathering rate, serpentine is not as effective an acid neutralising mineral as carbonates (cf. Sverdrup 1990). It is thus clear that the static test underestimated the potential of the Hitura tailings to produce AMD. However, since serpentine presumably does have some buffering capacity through ion exchange processes (cf. Luce et al. 1972, Berner 1981), estimation based solely on the carbonates may also be misleading. In fact, field investigations by Moncur et al. (2005) and Gunsinger et al. (2006) have shown that silicate minerals, such as Ca-plagioclase, biotite and chlorite, can be important acid neutralizing minerals in tailings. In accordance with previous research (Sherlock et al. 1995, Jambor and Blowes 1998), predictive tests of tailings are highly recommended to be supported by mineralogical studies.

Overall, the study emphasized the need to prevent sulphide oxidation, even in low-sulphide tailings, without delay, for example by covering the tailings with a low permeability cap or submerging them under water (cf. MEND 1989b, MEND 1994, Höglund et al. 2004) after continuous disposal ceases. It was seen that when tailings of this type were left uncovered, sulphide oxidation occurred in the shallow tailings releasing Ni, Zn and SO_4^{2-} into the tailings pore water. In the near-neutral conditions the released metals were retained by secondary Fe precipitates and further transport of the metals was inhibited. In contrast, downward migration of SO_4^{2-} occurred, since there were no solid-phase controlling agents to limit its transport. If, however, the conditions become reducing or more acidic in the future, redissolution of the generated Fe precipitates may occur, resulting in the release of the immobilized metals (Schwertmann and Murad 1983, Ribet et al. 1995). In the Hitura case, an increase in acidity is possible in the tailings after all the carbonates are depleted, unless serpentine is able to buffer the acidity. Thus, remobilization of the secondarily retained metals is probable in the future. Covering of these oxidized layers may, nevertheless, also result in redissolution of the Fe precipitates and subsequent liberation of the metals (cf. Carlsson et al. 2003). This could be avoided in the future by an immediate covering of even the low-sulphide tailings after the disposal ceases to prevent the initiation of sulphide oxidation. According to Blowes et al. (1995), the onset of sulphide oxidation may occur within 2–3 years of the ending of tailings deposition.

One important conclusion of the study was that the mid-impoundment reactions at the exposed tailings surface were not solely responsible for the observed metal contamination in the waters around the Hitura tailings area. Instead, at this site, the focus should be on processes occurring in the border zones of the tailings facility to understand the causes of the contamination (Papers III and IV).

5.3 Selective extractions in evaluating the spatial distribution of sulphide weathering in active tailings impoundments: implications for design and closure

The examples from Hitura and Luikonlahti demonstrated that selective extractions, coupled with visual observations and pH measurements, were applicable to the study and spatial conceptualization of the degree of chemical weathering in the tailings area as a whole (Paper III). At both locations, the overall intensity and extent of sulphide oxidation with subsequent metal redistribution, dissolution of acid buffering carbonates and formation of secondary Fe precipitates could be described with selective extractions. Visual observations of the tailings cores assisted in defining the extent of sulphide weathering, while pH measurements provided supplementary data on the weathering intensity and on the balance between the primary acid producing and neutralizing minerals in the tailings. In both cases, the interpretations of the results were complemented by the previous observations and prior knowledge of the tailings mineralogy (Paper II, Räisänen and Juntunen 2004). Previous studies have also applied corresponding solid-phase speciation methods to investigate sulphide tailings (e.g. Fanfani et al. 1997, McGregor et al. 1998a and 1998b, Dold and Fontboté 2001, Carlsson et al. 2002), but not to the same extent in describing the spatial distribution of the onset of sulphide oxidation and the geochemical alteration of tailings in active tailings impoundments.

Similar to the study of the Hitura tailings (Paper II), some uncertainties in the interpretation of the selective extraction procedures were, however, identified. The uncertainties were largely related to lack of detailed mineralogical observations of the analysed samples, but to some extent also to the design of the extraction procedures. For example, $BaCl_2$ solution was not adequate to separate soluble S due to its partial precipitation as $BaSO_4$ (cf. Hendershot and Duquette 1986). This was despite the chosen low molarity of the extractant. Nevertheless, a trend in soluble S concentrations in the tailings cores could be detected, because of an excess of S over Ba. Furthermore, the suitability of the selected extraction series for the solid-phase speciation of As requires further studies. In fact, somewhat different procedures have been proposed for As speciation due to its oxyanionic nature (Wenzel et al. 2001, Ko et al. 2003). In future studies, the applicability of the selective extraction procedure could be increased with combined mineralogical analysis (cf. Dold 2001).

Based on the study, an important aspect for the design and after-care of the tailings facilities is that sulphide oxidation and contaminant release may initiate even within active tailings disposal areas. Despite its significance for tailings management, the early stages of sulphide oxidation in operating impoundments have received little attention in previous studies (Smuda et al. 2006, Dold et al. 2009), while most research has focused on closed or abandoned tailings facilities to improve the knowledge of AMD generation and to develop remedial techniques (e.g. Blowes and Jambor 1990, Ribet et al. 1995, Holmström et al. 1999, Carlsson et al. 2002). The Luikonlahti example nevertheless showed that a thick weathering zone may develop and AMD generation may already start during the disposal phase. Therefore, it is important to also examine the state of chemical alteration of tailings in active impoundments prior to designing the post-closure measures. This is particularly to avoid unexpected metal release from secondary precipitates of previously oxidized layers as a result of change in pH-Eh conditions in tailings after remediation (e.g. Holmström et al. 2001).

The commencement and intensity of the oxidation in active tailings impoundments depended on several factors, including tailings reactivity (Fe sulphide content), the water saturation level and time of exposure. An oxidized zone of several metres in thickness had developed in places at Luikonlahti, where reactive tailings were presumably unsaturated after disposal and burial of fresh sulphide grains was delayed (due to shifts in the discharge point). In contrast, only a 0.7 m thick oxidized zone was detected in the low Fe sulphide Hitura tailings, after some 10–15 years of exposure to surficial conditions. The thickness of the oxidation zone in the old Hitura pond is similar to those in closed, uncovered sulphide tailings facilities from comparable climatic conditions (Blowes et al. 1998, McGregor 1998b, Holmström et al. 2001, Ljungberg and Öhlander 2001), but the oxidized layers were exceptionally thick at Luikonlahti, given the active disposal. In contrast, continuous disposal of tailings decreased sulphide oxidation in the surface of the active impoundment at Hitura, where the tailings were less reactive than at Luikonlahti. While the Hitura tailings had maintained a near-neutral pH despite the sulphide weathering, the higher reactivity and more extensive sulphide oxidation had resulted in acidic conditions at Luikonlahti. Importantly, the acidic conditions at Luikonlahti had caused leaching of trace metals from the oxidized tailings towards the tailings water table, promoting the generation of acidic effluents from the facility. This emphasizes the importance of preventing sulphide oxidation during mining operations and the active disposal of tailings, instead of only after closure. During the disposal phase this means ensuring continuous burial of the tailings materials and maintenance of a high water table throughout the facility (cf. MEND 1989b, Elberling and Damgaard 2001, Höglund et al. 2004), when possible.

The spatial conceptualization of the Luikonlahti and Hitura tailings areas further highlighted that sulphide oxidation can also occur along the proximal areas of the impoundment, close to the dams, and not only at the exposed surface. At both locations, the metal redistribution in the drill cores close to the dams was more intensive and extended deeper than in the middle parts of the impoundments. Beside the impoundment dams, tailings material is typically coarser than in the mid-impoundment as a result of hydraulic sorting during disposal carried out from the crests of the dams, thus increasing the porosity of tailings and promoting oxygen diffusion (Nicholson et al. 1989, Robertson 1994). In addition, the proximal tailings may contain more sulphide minerals than the distal tailings, because of the preferential settling of dense particles close to the discharge point (Sherriff et al. 2007). The Hitura results further suggested Ni release from the deep paleosurfaces of the border zone tailings. Thus, when planning the impoundment design and post-closure measures, the border zones should also be taken into account as potential sources of mine drainage generation, and not only the exposed surfaces, for example, by considering various alternatives for tailings disposal, such as the central discharge of thickened tailings (Al and Blowes 1999) or underwater disposal (MEND 1989b, Höglund et al. 2004). The latter technique will also prevent the formation of paleosurfaces during the temporary cessation of disposal.

Overall, the results showed that Hitura tailings were still largely unaltered in the active impoundment and thus covering of the tailings would be an appropriate treatment technique after the closure of the facility. The covering should, however, be sufficient to prevent future oxidation of the sulphides and also to reduce the amount of infiltrating water (e.g. Höglund et al. 2004, Lottermoser 2007). Due to the structure of the impoundment, it is not possible to sustain a high water table and a wet cover is not applicable. Instead, a dry cover would be appropriate (cf. Höglund et al. 2004). In addition to covering the tailings surface, an additional liner in the border zones should be considered. At Luikonlahti, the impoundment is to be used by the next owner of the Luikonlahti processing plant, and thus post-closure measures are not yet topical. Nevertheless, the thickness of the magnesite tailings cover has been increased on top of the sulphide tailings (cf. Paper IV) and this is expected to improve the seepage water quality by providing additional pH-buffering capacity (Räisänen 2005). In fact, the monitoring results from Luikonlahti suggested that seepage water quality has already slightly improved (Paper IV). However, the eventual mitigation methods of the tailings impoundment must address the deep oxidized tailings sections close to the dam.

5.4 Seepage water quality assessment: controlling factors and applications for water treatment

Seepage water quality assessments were useful in identifying the constraints for treatment of the tailings water, but also in providing additional information on the chemical alteration of the tailings (Paper IV). Based on the assessments, several factors in the tailings areas affect the seepage quality, in particular their pH value and metal contents. These factors include source materials, the intensity of weathering of tailings and embankment materials along the seepage flow path, input from the process waters, the water retention time in tailings, and climatic seasonality. The variation in seepage properties was significant between the two different types of tailings areas and it was also notable within a single impoundment. This diversity should be quantified to design appropriate water treatment systems. This is because each treatment strategy is targeted for a particular water composition, and the performance of the systems thus depends on the homogeneity of the inflowing waters (Brodie 1993, Hedin et al. 1994, Gazea et al. 1996, Skousen et al. 1998, Ziemkiewics et al. 2003). Similar to the impact assessment of the tailings-derived waters (cf. chapter 5.1, Paper I), characterisation of the seepages should be based on a comprehensive set of water quality measurements (including field measurements of pH, T, redox, dissolved O_2, alkalinity and laboratory measurements of major cations, trace metals and anions) instead of a limited suite of parameters.

The seepage water quality assessment provided an additional insight into the chemical processes in the tailings. It also confirmed some of the findings of previous studies (Papers I–III). For example, the assessment supported the earlier indications (Paper I) of the influence of the process waters on the water chemistry at Hitura with a significant input of SO_4^{2-}. The seepage chemistry also confirmed that chemical reactions in the border zone tailings (i.e. weathering, release from paleosurfaces) contribute to contaminant release from the Hitura impoundment, as was suggested based on the solid-phase speciation of the tailings solids (Paper III). Notably, the outflow from the Hitura tailings area contained significant amounts of Ni and Fe, even though *in situ* retention of the released metals (Ni, Zn) and Fe was observed in the oxidized shallow tailings (Paper II). The Hitura study also showed that the drainage water quality in the seepage collection ditch (Paper I, Paper IV) may sometimes deviate notably from that of the seepages (Paper IV), and may thus give a misleading signal of the tailings effluent quality, unless seepage chemistry is examined. At Hitura, the high metal content in the drainage waters originated from the discharge from the jarosite residue.

At Luikonlahti, the seepage water measurements underlined the influence of source materials and weathering of the tailings along the flow paths on the outflow quality. Seepages with differing pH and metal contents were observed to surface through the Luikonlahti tailings dam depending on the location of the outflow point. Similar to Hitura, the seepage chemistry at Luikonlahti supported the results of the previous study on chemical alteration of the tailings (Paper III). For example, the seep with the lowest pH and elevated Si content was observed below those layers where the selective extractions suggested the most intensive oxidation of sulphides, absence of the carbonate buffer and occurrence of silicate weathering (Paper III). In addition, the high trace metal content of the toe seepage, to which the flow path runs mostly through the unaltered tailings, confirmed the proposed mobilization and downward leaching of metals in the tailings (Paper III). Here, an additional input of metals and acidity may result from the dam materials (i.e. waste rocks).

The example from Luikonlahti further demonstrated that the annual and seasonal changes in seepage water quality must be documented during the assessment, to estimate the annual loading from the site (Paper IV). Even with an infrequent sampling scheme (2–3 samples/year), the hydrological setting of the site was found to exert a major impact on the seepage water pH and metal content. Overall, the lowest concentrations of metals occurred in late June, after the discharge peak due to snow-melt and spring rains. These fluctuations must be taken into account in planning any water monitoring or synoptic sampling campaigns. In addition, the water treatment system could obviously be more accurately dimensioned based on a data from a monitoring programme that takes into account the seasonal variation at the site (e.g. with a sampling frequency of four times per year) than with data from only one-off sampling. In fact, seasonal and annual changes in water quality are listed as one of the essential parameters for passive treatment system design (cf. Watzlaf et al. 2000, Gusek 2002).

The Luikonlahti seepage water monitoring data also indicated that modifications to the tailings impoundment may markedly change the tailings effluent quality, for example from net acidic to net alkaline, and have a major influence on the water treatment design. In addition, it may take several years before the chemical processes in the tailings – and thus the seepage water quality – stabilize after modifications. Therefore, it seems reasonable that the concluding decisions on post-closure water treatment designs would only be made after finalizing the closure of the impoundment, in particular if intensive weathering has taken place in the impoundment, to ensure maximum long-term performance of the treatment system.

Due to the recent changes in the water chemistry at Luikonlahti, prolonged monitoring was proposed instead of a treatment strategy. This was to observe whether the seepages turn permanently net alkaline. This would be critical for the treatment design, since an additional input of alkalinity would no longer be required (Hedin et al. 1994, Younger 2001, Kirby and Cravotta 2005). In contrast, the seepage water quality of the Hitura site was more stable between the different sampling points and sampling campaigns. Consequently, constraints for a treatment strategy to decrease the loads of SO_4^{2-}, Ni, Fe and Mn were identified with the support of geochemical modelling. The geochemical model predicted that the net alkaline Hitura seepages would remain neutral after equilibration with atmospheric conditions, and Fe, (Mn) and Ni contents would decrease through the precipitation of the Fe oxyhydroxides. Based on this, an aerated settling pond may be used with subsequent anaerobic bacterial treatment for SO_4^{2-} (cf. Hedin et al. 1994, Ye et al. 2001). However, testing of the applicability of the proposed treatment procedure with measured flow rates and in the Finnish climate would still be needed to design the treatment system in detail and to evaluate its long-term performance and maintenance (e.g. Gusek 1993, Hedin et al. 1994, Skousen et al. 1998).

The study showed that drainage from a single tailings area may include both net alkaline and net acidic waters, requiring two different approaches in the treatment. These two drainage types were identified at both study locations. At Hitura the jarosite residue produces net acidic waters that differ from the main tailings-derived seepages, while at Luikonlahti the net alkaline seepage of the settling pond deviated from the other effluents. In designing the mitigation strategy, it is important to decide whether these waters are treated separately or are allowed to mix with the main discharge prior to treatment. Geochemical modelling with adequate flow data could be applied to address this question. Overall, support from the geochemical modelling in the data interpretation was found to be particularly useful at Hitura, where the drainage water in the seepage collection ditch differed from the equilibrated seepages.

6 SUMMARY AND CONCLUSIONS

This thesis studied the factors that control the generation of contaminated drainage in active sulphide mine tailings impoundments and methods that can be used to characterise these factors. In addition, geochemical constraints for the prevention and treatment of the drainage were assessed. The results can be utilized in the design of new tailings facilities and in the study, after care planning, and monitoring of existing tailings areas. The following conclusions were made:

1) A comprehensive set of water quality measurements is required to identify potential contaminants and

indicator elements in order to quantify the dispersal of tailings-derived waters to the surroundings of tailings facilities. The use of only a limited suite of permit-based parameters in water monitoring may neglect critical contaminants or lead to an incorrect interpretation of the spatial extent of the contamination.

At Hitura, neutral drainage with elevated SO_4^{2-}, Fe and Ni had deteriorated water quality around the tailings area. A combination of hydrogeochemical approaches (cluster analysis of several water quality parameters, major ion composition, and the identification of single key variables, such as Cl^-) provided a means to establish the extent of the tailings-derived waters and to distinguish them from the other low quality drainages at the site.

A levelled-out esker was identified as a major pathway for the discharge from the Hitura tailings impoundment. This highlights that the hydraulic properties of the Quaternary deposits and basal structures of impoundments are critical in the design of facilities in formerly glaciated areas with a highly diverse geometry of deposits. Similarly, the seepage collection ditches around tailings facilities should be sufficiently deep to avoid seepage underneath the constructed drainage channels.

2) Characterisation of the chemical alteration of tailings provides a means to determine the processes responsible for tailings-derived water contamination and the geochemical constraints for mitigation. A high-resolution study that employs a combination of mineralogical methods, selective extractions and pore water chemistry would provide a detailed insight into the chemical reactions that control the fate of contaminants in the tailings. Conceptualization of the geochemical zonation and the spatial extent of chemical alteration in the tailings is, nevertheless, possible based on selective extractions, pH measurements and visual observations of tailings cores from different parts of the tailings areas. Mineralogical observations are, however, recommended to support interpretations of selective extractions.

Predictive tests for AMD generation should also be supported with mineralogical observations to identify which minerals contribute to acid neutralisation in the test. The mineralogical NP calculations of the Hitura tailings indicated that the high NP values measured in static tests resulted from the abundant serpentine instead of carbonate minerals. In contrast, the carbonate-based NP/AP ratio suggested that the tailings are ‘likely AMD generating’. Thus the static tests seemed to overestimate the readily available acid buffering capacity of the tailings.

3) Prevention of sulphide oxidation in tailings already needs to be addressed in tailings facility design and active tailings disposal during mining operations, especially for highly reactive tailings. Based on the spatial assessment of tailings weathering, a delay in the burial of sulphide tailings may result in extensive sulphide oxidation even during active disposal. This is especially if the high Fe sulphide tailings are unsaturated with water after disposal. As a result, acidic conditions may form and promote the leaching of potentially harmful metals from the tailings during the operation. In contrast, continuous disposal can be sufficient to decrease sulphide oxidation in the surface of low-sulphide tailings.

Even in low-sulphide tailings, measures to prevent sulphide oxidation should, nevertheless, be taken shortly after continuous disposal ceases. Otherwise, sulphide oxidation with subsequent SO_4^{2-}, Fe and trace metal release will commence. In the old Hitura tailings, where neutralizing reactions were sufficient to maintain a neutral pH despite sulphide weathering, the released metals were retained by secondary Fe precipitates in the shallow tailings, but downward migration of SO_4^{2-} occurred.

The design of a tailings facility should also consider the prevention of sulphide oxidation in the border zones of impoundments and during temporary cessations of disposal. In both study areas, oxidized layers were detected along the proximal areas of the facilities, where the tailings were unsaturated with water. In addition, a paleosurface at depth in the border zone was a source of Ni in the Hitura tailings effluents.

4) The seepage waters represent the net result of the materials and the processes operating in the tailings pile. Observations of seepage water properties therefore support other methods employed to study the reactions in the tailings. Drainage waters are less accurate predictors of the processes along the tailings water flow paths, because they have already undergone geochemical changes once equilibrated with surficial conditions.

Seepage waters of varying characteristics may emanate from a single tailings area if the flow paths leading to different seepage locations transect geochemically differing zones. Process water input may also be significant in the effluents. Identification of this input requires sufficient knowledge of the chemicals used in the ore processing and documentation of the process water quality. Seasonal hydrological changes cause additional fluctuations in seepage water properties. The magnitude of these fluctuations depends on the seepage water flow paths. Modifications to the tailings impoundment may also markedly change the effluent quality. The fluctuations and diversity in the tailings discharge must be quantified for the design and dimensioning of the water treatment facilities.

Seepage water quality assessment was essential in identifying constraints for water treatment. In addition, geochemical modelling contributed to the assessment of various treatment options. However, the long-term fluctuations in the seepage pH and metal content at Luikonlahti, after thickening of the magnesite cover, highlighted that concluding decisions on mitigation strategies should only be made after seepage water quality has adjusted to the post-closure conditions in the impoundment.

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This PhD thesis comprises a synopsis and four original papers dealing with effluent quality from active sulphide mine tailings impoundments. Studies include comprehensive hydrogeochemical characterisation of tailings seepages, surrounding aquifers and surface waters. Detailed and spatial mineralogical and geochemical studies were employed to assess the geochemical processes within the tailings responsible for the low quality mine drainage from the impoundments. Based on the results, observations pertinent to future assessment and mine drainage prevention from existing and future mine sites are presented.

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