Department of Civil and Environmental Engineering

Evolution of sulfide oxidation and attenuation mechanisms controlling acid mine drainage in decommissioned low-sulfide tailings

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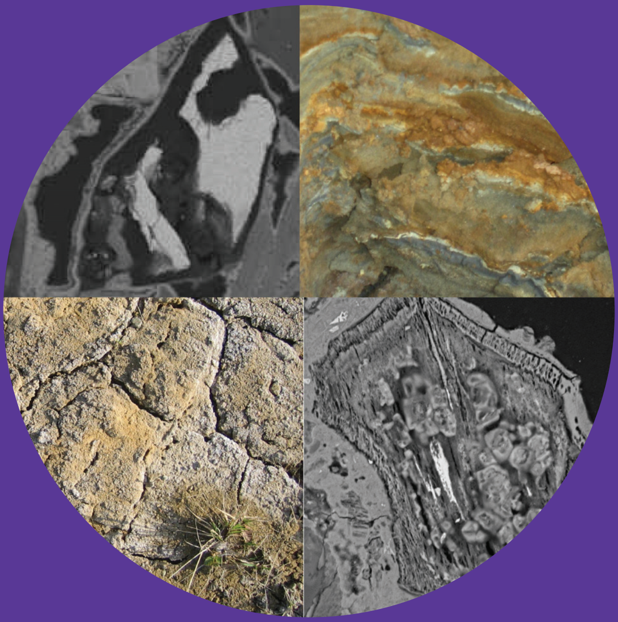
Annika Parviainen



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Evolution of sulfide oxidation and attenuation mechanisms controlling acid mine drainage in decommissioned low-sulfide tailings

Annika Parviainen

Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the School of Engineering for public examination and debate in Lecture hall 1 (V1) at the Aalto University School of Engineering (Espoo, Finland) on the 31st of August 2012 at noon.

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Abstract

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Abstract

Environmental hazards derived from mining have been a major concern worldwide in the past years. Understanding of the consequences of malpractice in waste management and the lack of aftercare is crucial to the sustainability of the future mining industry. Mineralogical and geochemical studies are key to predicting the generation of acid mine drainage (AMD) and to evaluating the stability of a tailings system at an advanced stage of weathering. Site-specific data also assist in selecting the remediation scheme for decommissioned tailings.

This thesis examines the evolution of sulfide weathering and the natural attenuation mechanisms controlling AMD at the Haveri Au–Cu and Ylöjärvi Cu–W–As mine tailings (SW Finland). Environmental investigations of this scale at decommissioned tailings have not been performed in Finland before. A combination of traditional mineralogical methods (optical microscopy, electron microscopy, X-ray diffraction), advanced synchrotron-based techniques, as well as geophysical and geochemical studies assessing elemental dispersion in the tailings (electric resistivity tomography, sequential extraction of solid tailings and water chemistry) provided a comprehensive data set and proved essential for evaluating the retention capacity and stability of secondary Fe(III) minerals in vadose tailings. Further, a study on the geochemistry of lake sediment records from the catchment receiving mine effluents allowed assessment of the long-term impact of AMD.

Half a century after mine closure, the shallow tailings at Haveri and Ylöjärvi had undergone extensive sulfide weathering, mobilizing potentially toxic elements, e.g. As, Co, Cu, Ni, and Zn. Lake sediment data showed that elemental transport had decreased from the contamination peaks to values slightly above the background level. However, at Ylöjärvi high As contents were recorded in pore and groundwater samples. Fe(III) minerals played an important role as a sink for As and divalent cations through adsorption (minor component) and co-precipitation, and cemented layers with accumulations of these phases, detected at both sites, contributed to the natural attenuation processes. Jarosite and goethite trapped As, Cu and SO_4 at the low pH (2.5–3.5) in the Haveri tailings, whereas arsenical ferrihydrite, hydrous ferric arsenate, scorodite, and kaňkite retained As, Co, and Cu at the near neutral pH (4.9–8.9) at Ylöjärvi. The Fe(III) minerals proved important for As retention in altered samples, where the As content in the secondary minerals' fractions approached 90–100% of the total in sequential extractions.

The results indicated that mine waters at the sites deteriorate the water quality at present despite the attenuating processes and also give indication of adequate remediation techniques.

Keywords mine tailings, sulfide oxidation, acid mine drainage, arsenic, trace elements, secondary Fe(III) minerals, natural attenuation, Haveri, Ylöjärvi

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Tiivistelmä

Tekijä
Annika Parviainen

Väitöskirjan nimi
Sulfidien hapettuminen ja pidättymismekanismit happamien kaivosvesien kontrolloijana suljetuilla rikastushiekka-alueilla

Julkaisija Insinööritieteiden korkeakoulu

Yksikkö Yhdyskunta- ja ympäristötekniikan laitos

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Tiivistelmä

Kaivosalueiden ympäristöongelmat ovat herättäneet paljon huomiota viime vuosina. Kaivannaisteollisuuden kestävän kehityksen turvaamiseksi ja aikaisempien virheiden välttämiseksi on selvitettävä, millaisia seurauksia on huonosta kaivosjätteiden huollosta ja jälkihuollon laiminlyönnistä. Mineralogiset ja geokemialliset tutkimusmenetelmät ovat avainasemeassa happamien kaivosvesien ennakoimisessa, rapautuneen rikastushiekkasysteemin stabiiliuden arvioimisessa, sekä ympäristöriskinarvioinnissa ja kunnostusmenetelmien valinnassa suljetuilla kaivosalueilla.

Väitöskirjatutkimuksessa selvitetään mineralogian ja geokemian menetelmin sulfidien rapautumisen ja haitta-aineiden luontaisten pidättymismekanismien vaikutusta happamien kaivosvesien laatuun Haverin Au–Cu ja Ylöjärven Cu–W–As kaivosten rikastushiekka-alueilla Lounais-Suomessa. Tutkimus on laajin tähän mennessä Suomessa tehty kaivosympäristöselvitys. Tutkimuksessa käytettiin useita eri menetelmiä: mineralogiset (optinen mikroskopia, mikroanalytiikka ja röntgendifraktio), synkrotroniin perustuvat menetelmät, sekä geofyskaaliset ja geokemialliset menetelmät tuottivat monipuolisen tutkimusaineiston. Tutkimuksessa arvioidaan sekundääristen Fe(III)-mineraalien pidättämiskapasiteettia ja stabiilisuutta rikastushiekassa pohjaveden pinnan yläpuolella. Lisäksi valuma-alueiden järvisedimenttien geokemia mahdollisti kaivosvesien pitkäaikaisten vaikutusten tutkimisen.

Haverin ja Ylöjärven rikastushiekka-alueiden pintakerrosten rapautuminen viiden vuosikymmenen aikana kaivostoiminnan loputtua on aiheuttanut haitta-aineiden (esim. As, Co, Cu, Ni, Zn) liukenemista. Järvisedimenttitulokset osoittivat, että kuormitus on jo laskenut korkeimmista arvoista vähän taustapitoisuuksia korkeampiin lukemiin. Fe(III)-mineraalit pidättivät adsorboimalla ja kerasaostamalla huomattavia määriä As ja metalleja. Sementoituneet kerrokset edistävät haitta-aineiden luonnollisten pidättymismekanismien tehoa. Jarosiitti ja götiitti pidättävät haitta-aineita kuten As, Cu, ja SO_4 happamissa oloissa (pH 2.5-3.5) Haverissa, ja As-pitoinen ferrihydriitti, skorodiitti ja kankiitti pidättivät mm. As, Cu ja Co lähellä neutraalia pH:ta (4.9-8.9). Erityisesti arseenin pidättyminen rapautuneissa näytteissä osoittautui tärkeäksi, missä As-pitoisuus sekundääristen mineraalien perättäisuuttofraktiossa oli jopa 90-100% As kokonaismäärästä.

Tulokset osoittivat, että tutkimusaluieilla kaivosvedet heikentävät veden laatua edelleen, vaikka luontaiset pidätysmekanismit lieventävät ympäristövaikutuksia. Tulokset antavat myös viitteitä soveltuvista kohdekohtaisista kunnostusmenetelmistä.

Avainsanat rikastushiekka, sulfidien hapettuminen, hapan kaivosvesi, arseeni, hivenaine, sekundääriset Fe(III) mineraalit, luontainen metallien pidättyminen, Haveri, Ylöjärvi

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List of original publications

This doctoral thesis is based on the following five original articles numbered with roman numbers.

I:	Parviainen, A., 2009. Tailings mineralogy and geochemistry at the abandoned Haveri Au-Cu mine, SW Finland. **Mine Water and Environment** 28 (4), 291-304.
II:	Placencia-Gómez, E., Parviainen, A., Hokkanen, T., Loukola-Ruskeeniemi, K., 2010. Integrated geophysical and geochemical study on AMD generation at the Haveri Au-Cu mine tailings, SW Finland. **Environmental Earth Science** 61 (7), 1435-1447.
III:	Parviainen, A., Isosaari, P., Loukola-Ruskeeniemi, K., Nieto, J.M., Gervilla, F., 2012a. Occurrence and mobility of As in the Ylöjärvi Cu-W-As mine tailings, **Journal of Geochemical Exploration** 114, 36-45.
IV:	Parviainen, A., Lindsay, M.B.J., Pérez-López, R., Gibson, B.D., Ptacek, C.J., Blowes, D.W., Loukola-Ruskeeniemi, K., 2012b. Arsenic attenuation in tailings at a former Cu-W-As mine, SW Finland. **Applied Geochemistry**, manuscript accepted for publication, Doi:10.1016/j.apgeochem.2012.07.022.
V:	Parviainen, A., Kauppila, T., Loukola-Ruskeeniemi, K., 2012c. Long-term lake sediment records and factors affecting the evolution of metal(loid) drainage from two mine sites (SW Finland), **Journal of Geochemical Exploration** 114, 46-56.

Contribution by the author

A. Parviainen was the principal investigator in all the studies reported in the above-mentioned articles. Her main responsibilities were fieldwork, geochemical and mineralogical investigations, data processing and interpretation, as well as the final conclusions of the studies. She was the leading author for all the articles and prepared them under the guidance of the co-authors.

In Article II, her responsibility was the sampling of and mineralogical and geochemical studies on the Haveri tailings, and their characterization. She compared and interpreted the mineralogical and geochemical data with the geophysical results obtained by electric resistivity tomography (ERT), as well as wrote the manuscript, together with Ph.D. Candidate E. Placencia-Gómez. In Article III, her responsibility was the sampling of tailings solids, tailings pore water and groundwater at Ylöjärvi, laboratory work (sample treatment and preparation, optical microscopy, scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) imaging and analysis, and sequential extractions), and the processing and interpretation of the field observations as well as the mineralogical and geochemical data. She also wrote the article under the guidance of the co-authors. In Article IV, she performed the tailings sampling at Ylöjärvi and part of the mineralogical work (including optical microscopy, SEM-EDS imaging, and electron microprobe analysis (EMPA)), the laboratory work for the sequential extraction method, and wrote the majority of the manuscript. Dr. Mathew Lindsay carried out the synchrotron-based work. In Article V, A. Parviainen's share covered the compilation of the background information by literature search and databases, analyses of the tailings samples and part of the water sample analyses. Dr. T. Kauppila performed the fieldwork and analysis of the lake sediment cores. A. Parviainen had a leading role in writing the manuscript, with contributions from the co-authors.

Table of Contents

Abbreviations

AEC	Adsorbed-exchangeable-carbonate
AMD	Acid mine drainage
Ag	Silver
As	Arsenic
Aspy	Arsenopyrite
Au	Gold
CH_4	Methane
CO_2	Carbon dioxide
Co	Cobalt
Cd	Cadmium
Cpy	Chalcopyrite
Cr	Chromium
Cu	Copper
$CuSO_4$	Copper sulfate
^{137}Cs	Radioactive isotope of cesium
DO	Dissolved oxygen
EC	Electric conductivity
E_h	Redox potential
EMPA	Electron microprobe analysis
ERT	Electric resistivity tomography
Fe(III)/Fe^{3+}	Ferric iron
Fe(II)/Fe^{2+}	Ferrous iron
FeAs	Fe(III) arsenates
FeOx	Fe(III) hydroxides
Fer	Ferrihydrite
Go	Goethite
Gy	Gypsum
HCl	Hydrochloric acid
HFA	Hydrous ferric arsenate
Hg	Mercury
Hem	Hematite
HNO_3	Nitric acid
H_2S	Hydrogen sulfide
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
Jt	Jarosite
KCl	Potassium chloride
keV	Kilo electronvolt

Mg	Magnesium
Mgt	Magnetite
mV	Millivolt
Mn	Manganese
MNA	Monitored natural attenuation
μ-EXAFS	Extended micro-X-ray absorption fine structure
μ-XANES	Micro-X-ray absorption near edge structure
μ-XAS	Micro-X-ray adsorption spectroscopy
μ-XRD	Micro-X-ray diffraction
μ-XRF	Micro-X-ray fluorescence
nA	Nano ampere
Nb	Niobium
NH_4	Ammonium
Ni	Nickel
O_2	Oxygen
Pb	Lead
pH_{pzc}	Point of zero charge
Po	Pyrrhotite
PRB	Permeable reactive barriers
Py	Pyrite
Schw	Schwertmannite
SEM-EDS	Scanning electron microscopy equipped with energy dispersive spectrometry
SHE	Standard hydrogen electrode
SI	Saturation index
SO_4	Sulfate
S	Sulfur
TSB	Tampere Schist Belt
U	Uranium
W	Tungsten
XRD	X-ray diffraction
Zn	Zink

Preface

In the process of writing this doctoral thesis, I have received considerable help and support from various people who I would like to thank here. First of all, my thesis instructors, Prof. Kirsti Loukola-Ruskeeniemi from the Geological Survey of Finland (GTK) and Prof. José Miguel Nieto from the University of Huelva, are acknowledged for their instructions and guidance. I would also like to thank all the colleges at the Aalto University School of Engineering who helped me with the research and gave moral advice and support: Prof. Kirsti Loukola-Ruskeeniemi (1.1.2005-31.3.2008), Prof. Markku Peltoniemi (1.4.2008-31.7.2009) and Prof. Jussi Leveinen (starting from 1.8.2009) for the supervision of my thesis at Aalto University School of Engineering; M.Sc. (Tech.) Jalle Tammenmaa, Ph.D. candidate Edmundo Placencia Gómez, and Licentiate in Technology Tero Hokkanen for field work assistance and collaboration in an article; Dr Pirjo Isosaari for scientific guidance and showing interest in my studies; Mrs Seija Latvala for providing mineralogical sample preparation; Dr Riitta Juvonen and M.Sc. (Tech.) Matti Viikari for helping out in the laboratory; Ph.D. candidate Mira Markovaara-Koivisto for all our talks and your support; Prof. Erkki Heikinheimo for providing access to the SEM-EDS at Aalto University; and finally Laboratory Technician Jarmo Vihervuori and Laboratory Manager Matti Lojander for generous co-operation in designing and building field and laboratory equipment.

I would like to thank Prof. José Miguel Nieto and his research group, Dr Aguasanta Sarmiento and Dr Manuel Caraballo, as well as chemist Dr Daniel Sánchez Rodas at the University of Huelva, Spain, for their kind advice and for letting me participate in the interesting studies on Aguas Agrias Creek at Tharsis Mine in Huelva. Also, Dr Rafael Pérez López is acknowledged for his enthusiastic participation in a co-authored article and for constructive remarks on this manuscript. I am also grateful to Prof. Fernando Gervilla Linares from the University of Granada, Spain, for his endorsement and generous help, and the Department of Mineralogy and Petrology at the University of Granada is acknowledged for hosting me for the last years of my doctoral studies.

Prof. Carlos Ayora from the Department of Geosciences, Institute of Environmental Assessment and Water Research, Spain, is acknowledged for his guidance and generous help with the geochemical model PHREEQC.

I am very grateful for the scientific collaboration and guidance I received from the Groundwater Geochemistry & Remediation research group from the University of Waterloo, Canada. I would like to express my gratitude to Prof. Carol Ptacek, Prof. David Blowes, Dr Mathew Lindsay, Dr Blaire Gibson and Ph.D. candidate Mike Moncur for experienced instruction and for the opportunity to cooperate.

I appreciate being part of the European Union Life Environment project RAMAS (http://projects.gtk.fi/ramas/index.html), as it was the starting point for my thesis. I am grateful to the whole RAMAS team and especially to Dr Timo Ruskeeniemi, Dr Birgitta Backman and Dr Tommi Kauppila from GTK, and Dr Kirsti Loukola-Ruskeeniemi from Helsinki University of Technology (Aalto University at present). Besides the RAMAS team, many skillful researchers from GTK have participated in my work along the years. Hence, I would like to thank Field Technician M.Sc. Mikael Eklund for assisting in the field; Dr Marja Lehtonen, Ms Sari Summanen, M.Sc. Bo Johanson and M.Sc. Lassi Pakkanen for assisting with the microanalytical work with SEM-EDS and EMPA at GTK. A large amount of the geochemical analytical work was carried out at the chemical laboratory at GTK and later on at Labtium Oy, and I would like to give thanks to Dr Eeva Kallio and Dr Hanna Kahelin for their kind and helpful service. Dr Mati Raudsepp from the University of British Columbia, Canada, is also acknowledged for his hospitable service supplying bulk X-ray diffraction data. Many people were involved and made the fieldwork at Ylöjärvi mine site possible; Mr Erkki Kovero and Mr Kari Lahdenperä from the Finnish Defence Forces and Mr Fredrik Winqvist and Mr Matti Savolainen from Ramboll Oy are acknowledged. I have always been able to rely on Mrs Kathleen Ahonen's Mr Roy Siddal's expertise and enthusiasm in the English correction of my manuscripts.

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Prof. Heather Jamieson from Queen's University, Canada, and Prof. Benedetto De Vivo from the University of Napoli Federico II, Italy, are acknowledged for their pre-examination and constructive comments on this work.

Last but not least, I would like to thank my spouse Manolo and my son Adrián, who was born in December 2009, for their love, and especially Manolo for putting up with me and giving support when I've been stressed out. Also, my family and grandparents have been very supportive, even though they haven't always understood what my work was all about.

Annika Parviainen
6.8.2012

1. Introduction

The extraction industry is volumetrically a major producer of solid and liquid wastes, and its environmental impact is well established worldwide. The mining industry produces waste material in the form of tailings, sludge and waste rock. The profitable ore grade can be as low as, for example, <0.5% for Cu and only a few g/ton for Au, which translates into >99% of waste out of all extracted ore. Hence, the tailings usually cover large areas of several hectares and even up to square kilometers with varying thickness. Especially old mining areas are complex, as in the past there was no rigorous legislation concerning the environmental impacts of mining. The tailings and sludge, produced in the enrichment process of the ore, were commonly deposited with no proper segregation from the natural subsoil directly at the bottom of an adjacent lake or in a topographical depression, and attention was not paid on the aftercare or remediation of the site.

Finland has a versatile mining history with 1032 metal, industrial mineral and carbonate mines that operated between 1530 and 2001, out of which 418 were metal mines producing 698 Mt of extracted ore (Puustinen, 2003). At the beginning of 21st century the mining industry experienced a boom, and 10 metal mines are currently under production, making Finland one of the biggest producers of Au and Ni, and the only producer of chromite in Europe (www.gtk.fi). Each mining area is unique, with its own characteristics and site-specific problems depending on the type of ore deposit, primary ore and gangue mineralogy, implemented extraction and enrichment methods, waste management, the structure and insulation of the tailings dam or lack thereof, remediation procedures, climate, the pH-E_h conditions of the tailings facilities and other factors. Ultimately, the geochemical and mineralogical characteristics of solid mine wastes determine the nature and quantity of contaminants in the drainage. Due to growing environmental awareness, understanding of the implications of adverse mine waste management practices for the environment is valuable for the modern mining industry to avoid the negligence often seen in past operations.

Contamination in mining areas originates from the oxidation of sulfide minerals still present in the tailings or waste rock piles. The small grain size (generally silt to fine sand) of the finely ground tailings enhances the oxidation process when sulfides are exposed to air, rainwater, and bacterial activity. As a result, Fe^{2+}, SO_4^{2-}, trace elements and acidity are released, and this phenomenon is termed acid mine drainage (AMD). In some cases, mine drainage can be pH neutral in character. In particular, potentially toxic elements such as, As, Cd, Hg, and Pb are the focal point in many environmental studies. Even tailings of low-sulfide ores can locally be an important source of AMD, although in some cases an erroneously low S content can be taken as a low contamination risk. Here, tailings containing on average 3 wt.% of S or less are referred to as low-sulfide tailings. The AMD can persist for decades and even hundreds of years after mine closure, causing a long-term impact on the environment. The low quality waters can affect surface water and groundwater bodies, and consequently soils, vegetation, and human exposure. Additionally, tailings solids can have an environmental impact through air by dusting (Corriveau et al., 2011a).

The abandoned Haveri Au–Cu mine was chosen as study case because no prior environmental studies had been conducted at this site and because it is located in the proximity of Lake Kirkkojärvi and the village of Viljakkala. Conversely, at the other target, the Ylöjärvi Cu–W–As mine, previous environmental investigations had revealed As and trace metal contamination in the surrounding surface and groundwater bodies (Carlson et al., 2002; Parviainen et al., 2006; Bilaletdin et al., 2007a; Sorvari et al., 2007). However, no specific studies had been conducted to investigate the contamination source, namely the tailings impoundment.

1.1 Research scope, objectives, and hypothesis

The scope of the doctoral thesis was to understand the origin and extent of the low-quality drainage derived from sulfide oxidation and the consequent elemental mobilization and precipitation of secondary Fe(III) phases in two abandoned low-sulfide mine sites in Finland. The occurrence and mobility of As and trace metals in the tailings impoundments of Haveri and Ylöjärvi mines were investigated by means of mineralogy and geochemistry.

The first aim was to describe the primary ore mineralogy as the source of contamination (As and trace elements), and the secondary mineralogy, which influences the retention capacity and the stability of the Fe(III) phases. This study focused on the natural attenuation mechanisms that mitigate the impact of low-quality drainage. The second aim was to investigate the mobilization and transport of elements to the environment, which can be assessed via the geochemistry of the surface water, groundwater and tailings pore water. Additionally, lake sediment records were studied, as they act as a sink for contaminants derived from mining areas and reflect the character of elemental transport during different periods of past contamination. The third aim was to produce comprehensive research data on the mineralogical and geochemical processes at abandoned mine sites in order to raise public and authoritative awareness of the environmental impact of mining, and to improve knowledge of relevant processes when selecting an appropriate and site-specific remediation technique at decommissioned mine sites and when planning aftercare in active mines.

The following research hypotheses were formulated to guide the investigations:

1. Mine tailings of limited extension characterized by a low sulfide content and low neutralization capacity produce AMD, and they have significant and long-term environmental impacts locally.
2. At decommissioned tailings sites, natural attenuation processes govern the quality of the modern drainage water.
3. Comprehensive mineralogical and geochemical research is crucial to understanding the stability of Fe(III) minerals carrying potentially toxic elements and their impact on the potential for attenuation at abandoned mine tailings.
4. Multidisciplinary and site-specific research is required before selecting appropriate remediation techniques at abandoned mine sites. Mineralogical and geochemical data are mandatory in decision making.
5. Decommissioned tailings can be a resource for the future exploitation of valuable elements.

1.2 Articles in this thesis and how they interlink

This research tackled the problem of AMD by examining the mineralogy of tailings, the geochemical distribution of elements in the tailings material, pore water, surrounding water bodies and lake sediments, as well as the geoelectrical characteristics of the tailings at the Haveri Au–Cu mine and Ylöjärvi Cu–W–As mine. The results are presented in the following five peer-reviewed articles.

Article I, “Tailings mineralogy and geochemistry at the abandoned Haveri Au–Cu mine, SW Finland” (Parviainen, 2009), aims to clarify the characteristics of the Haveri tailings solids and the mechanism of metal transport to the surrounding surface waters. The geochemical characteristics of the vadose zone of the tailings and the elemental distribution in different mineral fractions were studied using a five-step sequential extraction method, and the results were compared with mineralogical observations. The findings provide information on the contamination processes, on the transportation of the elements into the surface waters, and also on the neutralization and attenuation potential of the primary and secondary mineralogy of the tailings, respectively.

Article II, “Integrated geophysical and geochemical study on AMD generation at the Haveri Au-Cu mine tailings, SW Finland” (Placencia-Gómez et al., 2010), evaluated the usefulness of electric resistivity tomography (ERT) as a method to geoelectrically image the internal structure of the tailings and the structural features of the subsoil and the bedrock at the Haveri tailings impoundment. The ERT data were compared with the mineralogy as well as the physical and geochemical conditions governing the AMD generation, and areas affected by AMD were delineated. Articles I and II depict the extent of sulfide oxidation and the consequent AMD in the Haveri tailings area, which was successfully imaged by the ERT method.

Both Article III, “Occurrence and mobility of As in the Ylöjärvi Cu–W–As mine tailings” (Parviainen et al., 2012a), and Article IV, “Arsenic attenuation in tailings at a former Cu–W–As mine, SW Finland”, shed light on the behavior of As in the Ylöjärvi tailings. Article III describes the governing geochemical conditions within the superficial tailings and the variation in pore water chemistry, combining these data with mineralogical observations and sequential extraction results. On the basis of the obtained results, suggestions are made for the rehabilitation procedure in order to mitigate As transport to the surrounding surface and groundwater bodies.

Article IV, “Arsenic attenuation in tailings at a former Cu–W–As mine, SW Finland” (Parviainen et al., 2012b), focuses on describing the secondary mineralogical setting of the Ylöjärvi tailings using synchrotron-based methods such as micro X-ray fluorescence (μ-XRF), micro X-ray adsorption spectroscopy (μ-XAS), and micro X-ray diffraction (μ-XRD), together with traditional mineralogical investigation by scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) and by electron microprobe analysis (EMPA). The ferric arsenates (scorodite, $FeAsO_4 \cdot 2H_20$, and kaňkite, [$FeAsO_4 \cdot 3.5H_20$] type) and arsenical ferric (oxy)hydroxides (ferrihydrite [$Fe_2O_3(OH)_9$] type) detected in the vadose tailings imply that natural attenuation is occurring, retaining arsenate from solution. However, the low stability of these phases is discussed and redissolution is suggested.

Article V, “Long-term lake sediment records and factors affecting the evolution of metal(loid) drainage from two mine sites (SW Finland)” (Parviainen et al., 2012c), draws together the mining impact of the studied mine sites at Haveri and Ylöjärvi from the lake sediment records that extend the information before, during, and after the active mining period. According to this article, the sediment records revealed that mine water loading changes in composition and intensity during and after mining, and that before mining activities other land uses (*e.g.* agriculture) in metal-enriched regions can mobilize mining-associated metals.

As a whole, these five articles comprise a comprehensive presentation of the current mineralogical and geochemical state of the vadose zones of the Haveri and Ylöjärvi mine tailings and the implications of the past and current environmental impact in the surroundings. These data provide a good basis for environmental risk assessment, and this investigation strives to provide the necessary information for local environmental officers and decision-makers in order to draw conclusions on the need for remediation and to select the optimal method.

2. Theoretical framework

2.1 Approaches to studying the tailings environment

In many cases, investigations in old mining areas are initiated when a contamination risk or a direct need for remediation measures is anticipated. Before undertaking remediation actions, it is important to know and understand the current conditions of the tailings impoundment and the origin of the contamination. Determination of the mineral phases in mine wastes is key to understanding the mineral–water interaction, the stability of the minerals and their role in releasing contaminants (Jamieson, 2011). Surface water and groundwater sampling may merely give an indication of the extent of the elemental mobilization from the contamination source. Tailings facilities that have been exposed to atmospheric conditions for extended periods have undergone many processes. For instance, they have experienced substantial sulfide oxidation, mobilization of elements, and retention of dissolved elements by precipitation of secondary Fe(III) phases. Therefore, the remediation techniques used for fresh tailings piles (for instance inhibiting oxygen diffusion for sulfide oxidation in tailings by applying a thick cover and/or raising the groundwater level) do not apply in abandoned mine sites and may only destabilize the current system. Additionally, the uniqueness of each mining environment makes site-specific investigations mandatory, and no generalized model can be applied for all mining areas. Therefore, a series of cost-effective and less time consuming mineralogical and geochemical investigations are recommended to determine the governing processes within the tailings.

Mineralogical studies allow assessment of the extent of oxidation processes, the stability of minerals and the potential for natural attenuation processes. Understanding of mineral–water interaction requires detailed mineralogical investigations, and there is a set of approaches to accomplish this. Traditional methods such as optical microscopy (reflected light), SEM-EDS, EMPA, and bulk X-ray diffraction (XRD) are useful in characterizing textural relationships and identifying mineral phases, but their faultless use can sometimes prove challenging, as the studied Fe(III) phases commonly possess a μ-scale grain size, poor crystallinity, and may contain water. These methods can be supported by novel and more advanced mineralogical techniques, such as synchrotron-based methods including μ-XRF, μ-XRD, and μ-XAS (Table 1). With the help of the molecular-scale techniques, the solid phase speciation and bonding characteristics of the secondary Fe(III) phases can be investigated. This is important in determining the transformation processes in solid tailings through weathering, and in evaluating, for instance, the potential stability and bioavailability of As in mine wastes. Many studies have successfully employed micro X-ray absorption spectroscopy (μ-XAS) (Paktunc et al., 2003, 2004; Beauchemin and Kwong, 2006; Kwong et al., 2007; Slowey et al., 2007; Mitsunobu et al., 2008; Chen et al., 2009), micro X-ray diffraction (μ-XRD) (Flemming et al., 2005; DeSisto et al., 2011), and combinations of these methods (Walker et al., 2005, 2009; Endo et al., 2008; Corriveau et al., 2011). Additionally, micro X-ray fluorescence (μ-XRF) has been employed to examine elemental distribution (Endo et al., 2008; Walker et al., 2009).

Table 1. Conventional and novel synchrotron-based methods used in mineralogical investigations of tailings and their application.

Method	**Abbreviation**	**Application**
Reflected light and transmitted light microscopy		Identification of sulfide minerals and imaging textural relationships
Scanning electron microscopy equipped with energy dispersive spectrometry	SEM-EDS	Back-scattered imagining, qualitative chemical spot analysis, and elemental mapping
Electron microprobe analysis	EMPA	Back-scattered imagining, quantitative chemical spot analysis, and elemental mapping.
Bulk powder X-ray diffraction	XRD	Identification of mineral phases
Synchrotron-based micro-X-ray diffraction	μ-XRD	μ-scale identification of mineral phases
Synchrotron-based micro-X-ray absorption near edge structure	μ-XANES	Study of oxidation states of solid material
Synchrotron-based extended micro-X-ray absorption fine structure	μ-EXAFS	Study of bonding characteristics in mineral structures
Synchrotron-based micro-X-ray fluorescence spectroscopy	μ-XRF	High-resolution 2D-elemental mapping

Equally important to the mineralogical observations is the geochemistry of the tailings material. Analysis of the chemical composition by a pseudo-total digestion that is optimal for contaminated soils (*e.g. aqua regia*) gives quantitative information on the contaminants, but selective and sequential extractions allow the assessment of elemental distribution in different mineral phases attacked in each extraction step. These extraction procedures can therefore mimic the mobilization of elements into solution under various environmental conditions. In a non-sequential selective extraction procedure, separate subsamples are leached with extractive solutions of increasing chemical aggressivity. The stronger extractants are expected to also dissolve the phases leached with the weaker solutions. Therefore, the amount of each fraction is calculated by subtracting the concentration of the weaker extraction from the next step. The sequential extraction procedure, on the other hand, uses the same sample through the entire extraction sequence, but with rinsing between steps. The results of each extraction step directly represent the quantity of elements extracted in the fraction. Both extraction methods are widely used in the analysis of mine tailings (Ribet et al., 1995; Dold and Fontboté, 2001, 2002; Carlsson et al., 2002; McGregor and Blowes, 2002; Dold, 2003; Alakangas and Öhlander, 2006; Heikkinen and Räisänen, 2008; Corriveau et al., 2011b). However, their accuracy and selectivity have been criticized (Hall et al. 1996; McCarty et al. 1998), as they depend on many factors such as the chemicals applied, the procedure conditions (time, temperature, and exposure to light), and the sample-to-volume ratio. Sequential extractions have been questioned because of some undesired reactions (*e.g.* precipitation) caused by the remnants of previous reagents or sample losses during filtration, which may reduce the recovery in later steps of the procedure (*e.g.* Hall and Pelchat, 2005). However, Dold (2003, Table 2) compared the results of a detailed mineralogical study by XRD with the results of selective extractions, and showed that these extraction methods offer a powerful tool for the study of elemental mobilization and retention in mine tailings.

Pore water chemistry and physicochemical conditions help in the assessment of elemental mobility in solution and the stability of the mineral phases. Dissolution of the primary sulfide minerals, the original source of the contamination, is controlled by pH-E_h conditions and by the presence of sulfide-oxidizing bacteria. The biochemical conditions are equally important for the stability of secondary Fe(III) phases, which may play an important role in the sequestration of contaminants such as As. The mobilization of the elements from the impoundment can be examined with the help of surface water and groundwater chemistry. The geochemical equilibrium model PHREEQC (Parkhurst and Appelo, 1999) allows the determination of the aqueous species and saturation indices (SI) of mineral phases that may play a key role in the mobilization/immobilization of trace elements. A geochemical code has importance in predicting what minerals may precipitate in the AMD environment in cases when mineralogical identification of the poorly crystalline or amorphous phases is not possible.

Non-invasive geophysical methods have proven effective tools in detecting contaminated sites and can be used in the detection of AMD generation and its flow paths, for instance in groundwater (Martínez-Pagán et al., 2009; Martín-Crespo et al., 2010).

This thesis research aimed to understand the processes that led to the current conditions and AMD generation, and the possible attenuation mechanisms mitigating the effects of low quality waters at the Haveri and Ylöjärvi mine tailings. These aims were approached by using the above-mentioned techniques, and as a whole they comprised a comprehensive study providing crucial information for selecting a remediation scheme.

Table 2. A summary of the sequential extraction procedures used in Articles I, III and IV. The procedure was the same in all Articles except for step 2A (Articles I and IV) and step 2B (Article III). The third and fourth steps are referred to as secondary Fe(III) minerals' fractions in the text. (AEC = adsorbed-exchangeable-carbonate, schw = schwertmannite, fer = ferrihydrite, jt =jarosite, go = goethite, mgt = magnetite, hem = hematite)

Sequence	Procedure	Preferentially dissolved minerals	References
Step 1 "Water-soluble"	1.000 g of sample into 50 mL deionized H_2O shake for 1 h at RT	Water-soluble fraction, fluorescent sulfates, e.g., gypsum	Dold (2003)
Step 2A "AEC"	Residue 1 + 20 mL of 1.0 M CH_3COONa shake for 6 h at RT	Adsorbed and exchangeable ions, carbonates	Hall et al. (1996)
Step 2B "AEC"	Residue 1 + 1.0 M CH_3COONH_4 pH 4.5 shake for 2 h, at RT	Adsorbed and exchangeable ions, carbonates, vermiculite	Dold (2003)
Step 3 "Fe(oxy) hydroxides"	Residue 2 + 0.2 M $(NH_4)_2C_2O_4$ pH 3 shake for 1 h in the dark, at RT	Amorphous Fe(III) precipitates, e.g., schw, two-line fer, jt, MnO_2	Dold (2003)
Step 4 "Fe oxides"	Residue + 0.2 M $(NH_4)_2C_2O_4$ pH 3 in water bath at 80° for 2 h	Residual Fe(III) precipitates (e.g., higher ordered fer, go, jt) and primary Fe(III) oxides (mgt, hem)	Dold (2003)
Step 5 "Sulfides"	Residue 4 + 750 mg of $KClO_3$ and 5 + 10 mL of 12 M HCl + 10 mL of 4 M HNO_3, water bath at 90° for 20 min	Primary and supergene sulfides and organics	Hall et al. (1996); Dold (2003)

2.2 Alteration processes and AMD generation in the tailings environment

Sulfide minerals of no economic value and in most cases a minor proportion of exploited minerals end up in the tailings, where the finely ground sulfides tend to oxidize when they come into contact with rainwater and air. Under tailings conditions, the relative resistance of sulfide oxidation generally follows the increasing order of pyrrhotite [$Fe_{(1-x)}S$] – sphalerite [ZnS], galena [PbS] – pyrite [FeS_2], arsenopyrite [FeAsS] –

chalcopyrite [$CuFeS_2$], but the susceptibility to alteration varies under different conditions and due to grain size variations and other factors (Jambor, 1994). Table 3 presents the basic chemical reactions (1–11) occurring in the tailings that contribute to the generation of AMD.

Pyrite is oxidized by oxygen according to Reaction 1. The released Fe^{2+} ions are oxidized to Fe^{3+} by Reaction 2 and can hydrolyze to form ferric hydroxide (R3) or act as an oxidant (R4) at low pH (<2). Reaction 1 releases 2 H^+, while the overall hydrolysis reaction (R5) produces 4 H^+. Pyrrhotite is another commonly abundant sulfide mineral in the tailings. The oxidation (R6) kinetics of pyrrhotite is faster than that of pyrite, making it an important contributor to AMD generation. Arsenic (As) is a principal contaminant in many mining areas, and arsenopyrite is one of the most common sources of As contamination (R7). Reaction 7 in itself does not produce acidity, but upon oxidation of As^{3+} (R8) and further hydrolysis of Fe^{3+} (R3) acidity is formed. The whole reaction is described in Reaction 9. The oxidation of chalcopyrite by Reaction 10 does not produce acidity, but the overall Reaction 11, which takes into account the oxidation of Fe^{+2} and hydrolysis, produces 4 moles of H^+.

Some sulfides not containing iron, such as galena, do not produce acidity upon oxidation, but nevertheless contribute to the contamination in the tailings environment. However, impurities of Fe in the mineral structure, for example in the case of sphalerite, cause these minerals to produce acidity as well. Other impurities, such as As in pyrite or Cd in sphalerite structure, may cause high concentrations of potentially toxic elements in the aquatic environment.

Secondary Fe(III) precipitates (such as hydroxides, oxyhydroxides and oxyhydroxysulfates), as well as aluminum and magnesium phases adsorb and co-precipitate trace elements mitigating the trace element release and transport from the tailings. In the low pH range, As and other oxyanions are less mobile and readily adsorbed, whereas cations tend to be adsorbed with rising pH. Lead has the lowest adsorption edge (*i.e.* pH region), followed by Cu, Zn, Cd and Ni (Dzombak and Morel, 1990; Smith, 1999). The surface charge of the adsorbent minerals is also pH-dependent. The mineral surface is positively charged when the solution pH is below its point of zero charge (pH_{pzc}), which means that common Fe oxides and hydroxides (*e.g.* hematite [Fe_2O_3], $Fe(OH)_3$, goethite [α-FeOOH] have 8.5–9.3 pH_{pzc}) are positively charged in the range of natural soil pH and also in the acidic tailings environment, adsorbing oxyanions. In the same pH range, clay minerals (*e.g.* montmorillonite 2.5 pH_{pzc}) are negatively charged and consequently preferentially adsorb cations (Cheng et al., 2009).

The precipitation of secondary Fe(III) phases is dependent on the pH of the solution (Fig. 1). Goethite has a wide pH range, precipitating at acidic to neutral conditions, ferrihydrite [$Fe_2O_3(OH)_9$] at pH >5, schwertmannite [$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$] at pH 2.8–4.5, and SO_4 concentrations of 1000–3000 mg/L, and jarosite [$KFe_3(SO_4)_2(OH)_6$], hydronium jarosite [$(H_3O)Fe(SO_4)_2(OH)_6$], and natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] at pH <3 and SO_4 >3000 mg/L (Bigham et al., 1992, 1996; McGregor and Blowes, 2002; Jambor, 2003). Ferric arsenates are a common sink of As in the tailings environment, but the stability of the ferric arsenates of varying Fe/As molar ratios is controversial.

Cemented layers or hardpans can form where the accumulation of these minerals and, for instance, ferric arsenates and efflorescent salts (*e.g.* gypsum [$CaSO_4 \cdot 2H_2O$]) is abundant, contributing to the natural attenuation processes within tailings impoundments, since the secondary iron precipitates can adsorb and co-precipitate trace elements such as arsenic (Blowes et al., 1991; Moncur et al., 2005; Graupner et al., 2007). Tailings that contain pyrrhotite are more likely to form cemented layers than pyrite-rich tailings because of the greater reactivity of pyrrhotite (Alakangas and Öhlander, 2006, and two references therein: Ahmed, 1995; Agnew and Taylor, 2000). However, these accumulations may be transitory due to changes in pH-E_h conditions, leading to the subsequent release of potentially toxic elements.

Acid neutralization may occur when acidic waters come into contact with country-rock minerals with a neutralizing capacity. If very abundant, the buffering minerals may be responsible for neutral drainage waters. Carbonates, especially calcite [$CaCO_3$], are the most important minerals readily contributing to the buffering process when the pH starts to decrease. Calcite buffers (R12 in Table 1) the pH of the pore water in the range from 6.5 to 7.5 (Blowes and Ptacek, 1994). Reaction 12 consumes one mole of H^+, which means that four moles of calcite are needed to neutralize one mole of pyrite in Reaction 5. Bodénan et al. (2004) and Johnson et al. (2000) reported that even when present in small amounts, calcite reacts readily and can maintain a near-neutral pH. However, over time, the neutralizing potential of calcite is expected decrease as it is consumed.

Aluminum and Fe(III) (oxy)hydroxides can also contribute to the acid-neutralization processes when carbonates have dissolved (Blowes and Ptacek, 1994; Jurjovec et al., 2002; Gunsinger et al., 2006). The dissolution of Al hydroxides buffers the pH at 4.0–4.3, whereas Fe (oxy)hydroxide dissolution occurs at a pH below 3.5 (Blowes and Ptacek, 1994). Silicate minerals in the tailings become important in the acid-neutralization processes only at a very low pH <1.3 (Blowes and Ptacek, 1994; Jurjovec et al., 2002). However, biotite is known to weather in less extreme conditions, at pH <3.1 (Taylor et al., 2000), and can be a source of potassium in secondary jarosite (Jambor, 2003).

Table 3. Principal alteration reactions in tailings environment.

$$FeS_2(s) + 7/2\ O_2(g) + H_2O \rightarrow Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 2H^+(aq) \tag{1}$$

$$Fe^{2+}(aq) + \tfrac{1}{4}O_2(g) + H^+(aq) \rightarrow Fe^{3+}(aq) + \tfrac{1}{2}H_2O \tag{2}$$

$$Fe^{3+}(aq) + 3H_2O(aq) \rightarrow Fe(OH)_3(s) + 3H^+(aq) \tag{3}$$

$$FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O(aq) \rightarrow 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq) \tag{4}$$

$$FeS_2(s) + 15/4\ O_2(g) + 7/2\ H_2O(aq) \rightarrow Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \tag{5}$$

$$Fe_{(1-x)}S(s) + (2-x/2)O_2(g) + xH_2O(aq) \rightarrow (1-x)Fe^{2+}(aq) + SO_4^{2-}(aq) + 2xH^+(aq) \tag{6}$$

$$FeAsS(s) + 2.75O_2(g) + 1.5H_2O(aq) \rightarrow Fe^{2+}(aq) + H_3AsO3(aq) + SO_4^{2-}(aq) \tag{7}$$

$$H_3AsO_3(aq) + 0.5O_2(g) \rightarrow HAsO_4^{2-}(aq) + 2H^+(aq) \tag{8}$$

$$FeAsS(s) + 7/2O_2(g) + 6H_2O(aq) \rightarrow Fe(OH)_3(s) + SO_4^{2-}(aq) + H_2AsO_4^-(aq) + 3H^+(aq) \tag{9}$$

$$2CuFeS_2(s) + 4O_2(g) \rightarrow 2Cu^{2+}(aq) + Fe^{2+}(aq) + SO_4^{2-}(aq) \tag{10}$$

$$2CuFeS_2(s) + 17/2O_2(g) + 5H_2O(aq) \rightarrow 2Cu^{2+}(aq) + 2Fe(OH)_3 + 4SO_4^{2-}(aq) + 4H^+(aq) \tag{11}$$

$$CaCO_3(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) \tag{12}$$

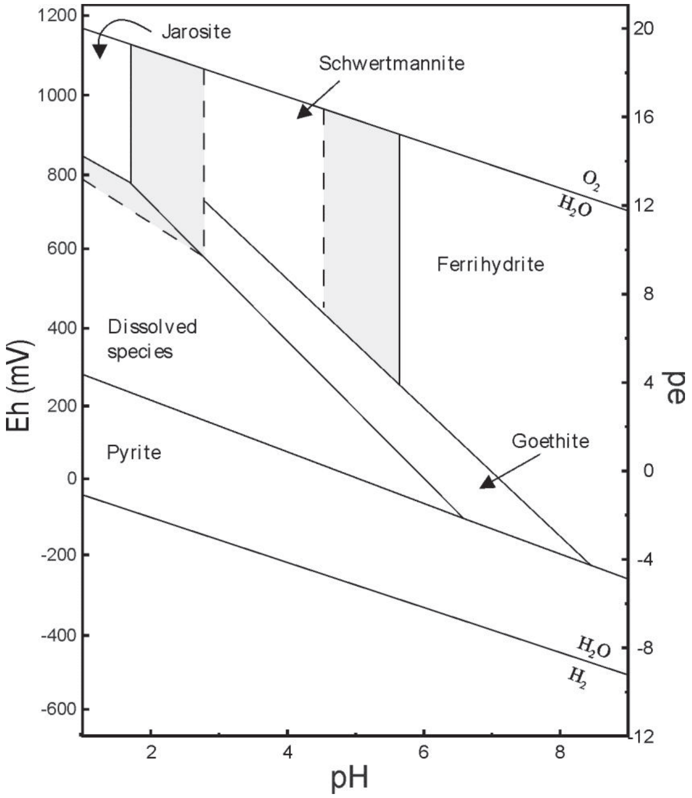

Figure 1. E_h(pe)-pH diagram for the system Fe–S–K–O–H at 25°C and 1 bar pressure, assuming total log activities of $Fe^{2+} = -3.47$; $Fe^{3+} = -3.36$ or -2.27; $SO_4^{-2} = -2.32$, $K^+ = -3.78$. Darker areas show possible expansion of K-jarosite and ferrihydrite fields (Modified from Bigham et al., 1996).

2.3 Geochemistry and stability of arsenic

Arsenic is a metalloid, well known for its toxicity. Arsenic ingestion in drinking water has been linked to many diseases, such as severe skin diseases, various types of cancer, peripheral vascular disease, hypertension and diabetes (Hopenhayn, 2006). It is a common constituent of the bedrock and occurs in sulfides and sulfosalts such as pyrite, arsenopyrite, orpiment [As_2S_3], and realgar [AsS] (Smedley and Kinniburgh, 2002). Even though it is a natural constituent of soils, human activities such as the extraction industry have substantially increased As contamination in the environment. In the natural state under low E_h and high pH conditions, these minerals are relatively stable, but once the ore containing these minerals is extracted, ground, processed, and deposited in tailings impoundments exposed to atmospheric conditions, they are more prone to alteration. Therefore, As is a principal contaminant in many mining areas, especially in gold, copper, and uranium mines (Donahue et al., 2000; Bodénan et al., 2004; Salzsauler et al., 2005; Corriveau et al., 2011b), where As contamination may affect the groundwater and surface water bodies as well as soils and air through dusting.

The most common As species in natural waters are As^{3+} (arsenite) and As^{5+} (arsenate), but organic methylated forms of As may also occur (monomethylated arsenic MMA, dimethylated arsenic DMA). Identifying the As species, for instance in waters affected by AMD, is important because arsenite is more toxic, soluble and poorly adsorbed than arsenate under acidic conditions. Arsenite generally occurs as $H_3AsO_3^o$ under reducing conditions, and the predominant forms of arsenate are $H_2AsO_4^-$ (in weakly acidic ambient) and $HAsO_4^{2-}$ (weakly alkaline ambient) under oxidizing conditions (Fig. 2). The pH and E_h conditions of the water govern the distribution of As species, and they have a tendency to be adsorbed onto mineral phases or to precipitate as arsenates. Arsenate is more strongly held at low pH, as the adsorption maxima is pH 4 to 5, and arsenite is more strongly held at a high pH with an adsorption maxima near pH 9 (Loeppert et al., 2003). The ability of Al, Fe and Mn to remove As from solution is well known (Smedley and Kinniburgh, 2002), and the common Fe(oxy)hydroxides have a positively charged surface area in the wide pH range encountered in the tailings environment (Cheng et al., 2009). In waters with a low pH and high As concentrations, arsenates may precipitate. The most common ferric arsenate is scorodite [$FeAsO_4·2H_2o$], which is also considered as the most stable phase. Scorodite commonly precipitates in acidic environments, and solubility testing on synthesized scorodite has also shown a strong correlation with pH. Paktunc et al.

(2008) report the pH dependence of synthesized (70°, pH 1, 2, 3, and 4.5) scorodite, Fe(III) arsenate and arsenical ferrihydrite: scorodite and Fe(III) arsenates are stable at a lower pH, whereas arsenical ferrihydrite becomes increasingly stable at higher pH levels. In a more recent study, Paktunc and Bruggeman (2010) performed solubility testing on synthetic nanocrystalline scorodite (25°, pH 1, 2, 3, 4, 5 and 7), and the results indicate a higher solubility of scorodite at low and high pH (i.e. <2 and >6), with a minimum solubility of about 0.25 mg/L As around pH 3–4. Their results are comparable to those determined for crystalline scorodite by Krause and Ettel (1989). However, according to Krause and Ettel (1989), the solubility of crystalline scorodite is two orders lower than that of amorphous $FeAsO_4 \cdot xH_2O$. Generally, the stability range of ferric arsenates becomes wider at higher Fe/As ratios, and compounds with an Fe/As ratio ≥ 8 show good stability over a wide range of pH values (3–8) (Krause and Ettel, 1989).

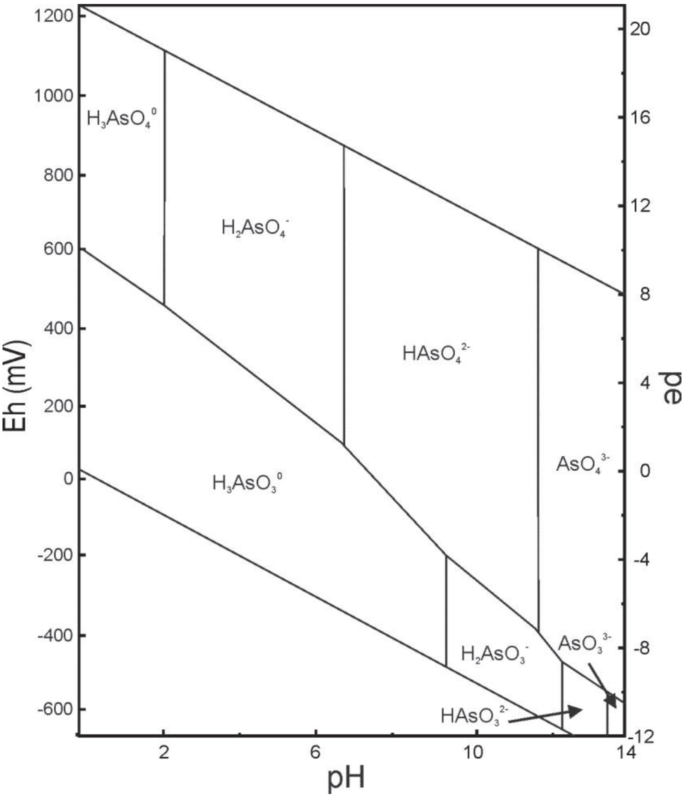

Figure 2. E_h(pe)-pH diagram for aqueous As species in the system $As–O_2–H_2O$ at 25 °C and 1 bar total pressure (Modified from Smedley and Kinniburgh, 2002).

Other arsenates encountered in tailings environments include anabergite [$Ni_3(AsO_4)_2 \cdot 8H_2O$], arseniosiderite [$Ca_2Fe_3O_2(AsO_4)_3 \cdot 3H_2O$], pharmakosiderite [$KFe_4(AsO_4)_3(OH)_4 \cdot 7(H_2O)$], symplesite [$Fe_3(AsO_4)_2 \cdot 8H_2O$], and yukonite [$Ca_7Fe_{11}(AsO_4)_9O_{10} \cdot 24.3(H_2O)$]. Kaňkite [$FeAsO_4 \cdot 3.5H_2O$] is a less frequent ferric arsenate (Čech et al., 1976), although it has been identified in the tailings environment often closely associated with scorodite (Kato et al., 1984; Walker et al., 2009; DeSisto et al., 2011; Kocourková et al., 2011). It is chemically very similar to scorodite, but it contains more water. However, no solubility or thermodynamic data have been reported for kaňkite (Drahota and Filippi, 2009).

3. Material and Methods

3.1 Site description

The study areas described in this doctoral thesis, Haveri Au–Cu and Ylöjärvi Cu–W–As mines, are situated at the western end of the Tampere Schist Belt (TSB) in SW Finland (Fig. 3). The TSB is mainly composed of felsic-intermediate and mafic metavolcanic rocks, turbiditic metasedimentary rocks and plutonic intrusions cutting the supracrustal rocks (Ojakangas, 1986, Kähkönen, 1989, Kähkönen and Leveinen 1994). Characteristic of the TSB, it has ore potential and higher than average concentrations of trace elements. For instance, As concentrations with a median value of 10 mg/kg are encountered in the bedrock of the TSB, whereas the median of the whole country is 0.9 mg/kg (Lahtinen et al., 2005). Even though these mines are located in a geologically comparable region, the ore deposits are very different. Furthermore, the mines are located in the same climate and vegetation zone. The annual mean temperature is +4 °C and rainfall is 600 mm (Finnish Meteorological Institute). The snow cover typically lasts from mid-December to mid-April.

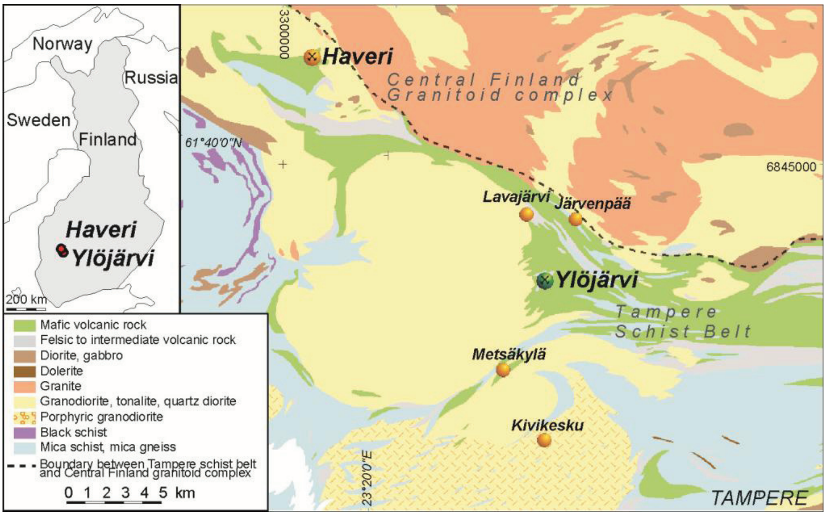

Figure 3. Geological map of the region representing the western end of the Tampere Schist Belt (TBS) and the location of Haveri and Ylöjärvi mines (Modified from Eilu, 2012).

3.1.1 Haveri Au–Cu mine

The Haveri Au–Cu deposit is suggested to be a VMS type setting, chiefly hosted by mafic metavolcanic rocks that are tholeiitic in composition, and to a minor extent by mafic to intermediate tuffs and tuffites (Mäkelä, 1980; Eilu, 2012). Chemical sediments, such as limestone and chert, appear in the Haveri formation (Mäkelä, 1980). Other main rock types described in the surrounding area are calc-alkaline intermediate metavolcanic rocks, graywacke-slate and mica schist and granite. Ore-forming sulfide minerals mainly comprise pyrrhotite, chalcopyrite, and pyrite. Sulfarsenides, cobaltite [CoAsS], glaucodote [(Co,Fe)AsS], gersdorffite [NiAsS], and arsenopyrite are found as accessory minerals (Mäkelä, 1980). Native Au appears as invisible and free grains with sulfides, and as free grains in quartz veins and amphibole gangue (Eilu, 2012). In addition, sphalerite, molybdenite [MoS_2], scheelite [$CaWO_4$], tellurobismutite [Bi_2Te_3], and hessite [Ag_2Te] occur (Paarma, 1947). The only oxide minerals present are magnetite [Fe_3O_4] and ilmenite [$FeTiO_3$]. The mineralogical setting is summarized in Table 1 in Article V.

At the end of 18th century, an iron deposit was discovered in Haveri and was exploited in the mid-19th century for a few decades (Kesti, 1985). However, the mining activity ceased, and in 1935 during re-opened investigations of the iron deposit the noble metal potential was discovered, leading to the inauguration of the Haveri Cu–Au mine some years later. The mine was active from 1942 to 1961. A total of 1.5 million tons of ore containing 2.85 g/t Au and 0.39% Cu were mined from an open pit and underground galleries that are presently inundated (Puustinen, 2003).

The extracted ore was crushed and ground in various steps, obtaining 75% of -200 mesh grain size. The ore enrichment was performed in three steps with an initial sulfide froth flotation to separate major sulfides, including Au and Cu, from the gangue. Au was then enriched by a cyanide process and Cu by froth flotation (Kesti, 1985). In the first years, the ore was recovered as raw enrichment and refined at the Harjavalta enrichment plant, but in 1949 an enrichment plant for cyanide leach was built at Haveri. Cyanide leach was performed in an alkaline pH, maintaining the pH at 9.5 by liming, in order to prevent the decomposition of cyanide in solution to form hydrogen cyanide gas, which is highly toxic. Once Au was in cyanide dissolution it was precipitated with Zn powder, and Zn was then separated from Au by HCl leach (Kesti, 1985). In this process, the granular Au was dissolved, and the host sulfarsenide minerals of Au may also have been dissolved, ending up in the waste waters together with the reagent Zn.

Copper froth flotation recovers the copper from sulfide ores by chemically attaching the ground copper mineral grains to a chemical bubble and by collecting the copper concentrate separated from the gangue minerals. In the flotation process, the minerals are concentrated mechanically and are not in dissolved form. The process uses various chemicals: collectors (*e.g.* xanthates), frothers (pine oil, alcohols), and pH regulators (lime, acids) (Nagaraj and Ravishankar, 2007). If the Cu concentrate were to be treated in a smelter, it would be dissolved in sulfuric acid and sent to the electrowinning cells for plating onto cathodes, leaving dissolved elements in the waste waters. However, at Haveri, Cu was recovered merely as a concentrate (Kesti, 1985).

At Haveri, the tailings were piled in a bay of Lake Kirkkojärvi in the vicinity of the mining area (Fig. 4), and they lie on natural lake sediments that consist of silt and clay. The tailings cover an area of about 18.4 ha and the average thickness is 6.5 m, ranging from 2 to 9 m. Tailings were constrained by a dam constructed of the subsoil covering the ore and of the wall rock (Fig. 5A). However, in the later stages of exploitation the tailings were piled directly into the lake outside the dam structure, leaving tailings material in direct contact with lake water. The water in the ditches surrounding the tailings impoundment and in the seasonal gullies on top of the tailings flows into Lake Kirkkojärvi (Fig. 6), which is connected to the larger Lake Kyrösjärvi only through a very narrow inlet.

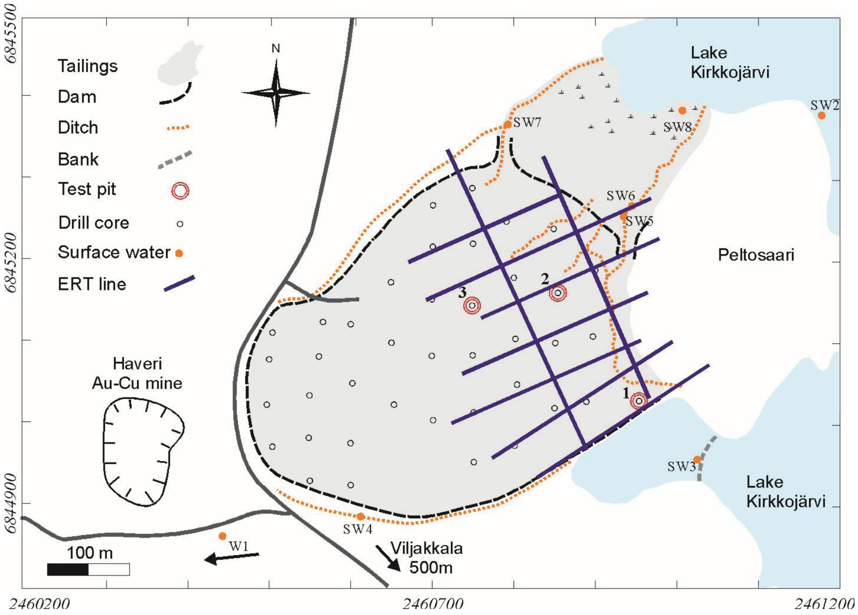

Figure 4. Map presenting the location of the Haveri Au–Cu mine, and the tailings drill core, test pit, and surface water sampling points, as well as electric resistivity tomography (ERT) lines.

After mine closure, rye was planted on the tailings area in order to prevent dusting during drier periods. However, after few failed attempts, no more remediation measures were implemented in the Haveri mine area. The central area of the impoundment was used as a rally track from the 1980s to 1990s and was partially backfilled with gravel and covered with asphalt for this purpose. To the present day, locals have also used the area for driving dirt bikes, even though the regional environmental authorities have prohibited this activity. Currently, an environmental risk assessment is being performed by a consulting company under the supervision of the regional authorities. Research information obtained during this doctoral thesis has proved important in the risk assessment.

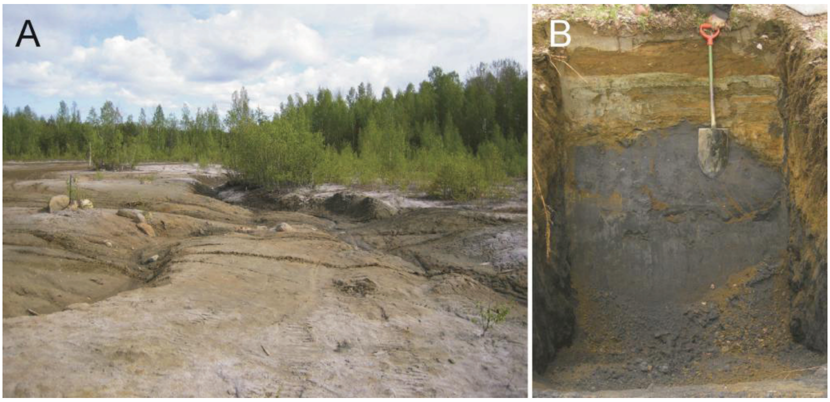

Figure 5. A) The Haveri tailings impoundment is partially constrained by a dam structure on top of which birches are growing; B) an excavated test pit showing layered tailings with a brownish oxidation zone and grayish black transition zone in the vadose tailings.

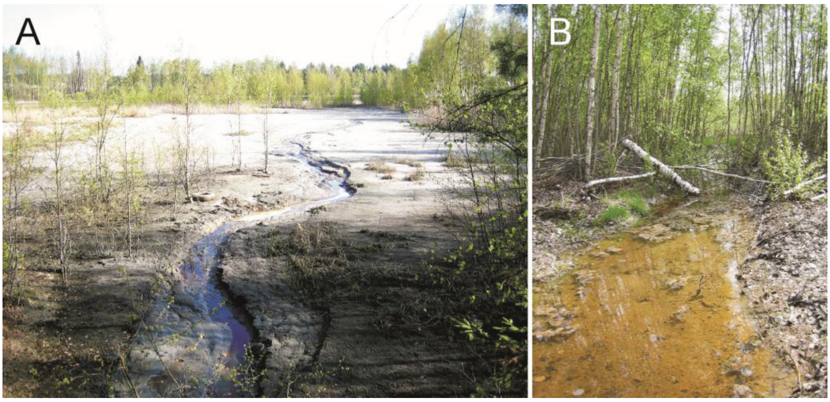

Figure 6. A) Seasonal gullies on top of the tailings pile outside the dam structure at the Haveri tailings impoundment; B) a ditch surrounding the tailings impoundment receiving ADM.

3.1.2 Ylöjärvi Cu–W–As mine

The Ylöjärvi deposit is hosted by a tourmaline breccia, and the surrounding rocks are mainly tuffites with plagioclase porfyrite intercalations (Himmi et al., 1979). The main ore minerals in the breccia matrix, pyrrhotite, chalcopyrite, arsenopyrite, and scheelite, are associated with minor sulfides (pyrite, sphalerite, galena, cubanite [$CuFe_2S_3$], mackinawite [$(Fe,Ni)S_{0.9}$], molybdenite), oxides (magnetite, ilmenite, cassiterite [SnO_2]), and minute concentrations of uraninite [UO_2], native bismuth, silver and gold (Himmi et al., 1979, Table 1 in Article V). The gangue minerals consist of tourmaline, quartz, chlorite, epidote, plagioclase, and hornblende. Carbonates are merely a minor constituent of the mineralization, and the presence of siderite [$FeCO_3$] and ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$] was described (Himmi et al., 1979).

The Ylöjärvi Cu–W–As mine was active from 1943 to 1966 and produced 4 million tons of tailings and sludge. Tailings were first piled in a smaller tailings area of 4 ha at the southern end of Lake Parosjärvi, and in 1952 a larger tailings area of 17 ha was inaugurated south of the mine in a topographical depression (Figs 7 and 8). The average thickness of the tailings heap is approximately 9 m. The natural subsoil below the heap and in the surroundings consists of glacial till and peat bog. Tailings were partially backfilled, but the central uncovered area is barren (Fig. 8A). Copper concentrate was the main product and was extracted by froth flotation. The WO_3 concentrate was enriched by flotation in the course of 13 years from 1948 to 1961, while As concentrate was recovered only during five years from 1949 to 1953, because the demand for the As concentrate drastically declined (Kukkonen et al., 1967). HCl was used for the elimination of apatite from the WO_3 concentrate, whereas $CuSO_4$ activator was applied under acidic conditions in As concentrate flotation (Kukkonen et al., 1967). After As production was stopped, large quantities of arsenopyrite-bearing tailings were discarded in the larger tailings areas. Mining activities left behind two open pits and underground galleries, where coarser tailings (approx. 1.1 Mt) were also deposited in the last years of operation. Water from Lake Parosjärvi was used in processing the ore in a closed cycle, and the first open pit as a clarification pool. As the mining works proceeded under the lake, it was dewatered, and water from the adjacent Lake Saarijärvi was used. After closing the mine, Lake Parosjärvi filled up again with water, and as a result, part of the smaller tailings area, the open pits and the underground galleries were flooded, leaving a large amount of material containing sulfides subject to leaching by surface and groundwater. Reductive conditions prevail at the bottom of the lake, but

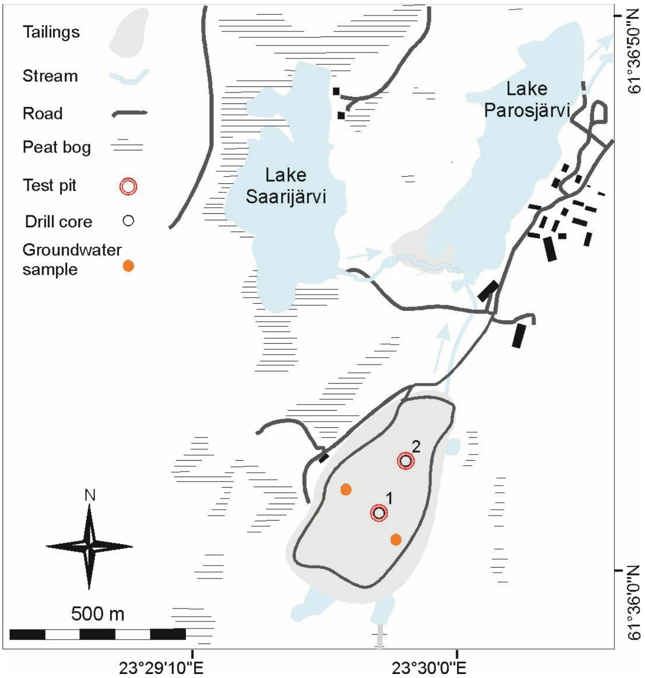

Figure 7. Map presenting the location of the Ylöjärvi Cu–W–As mine, and the tailings drill core, test pit, and groundwater sampling points.

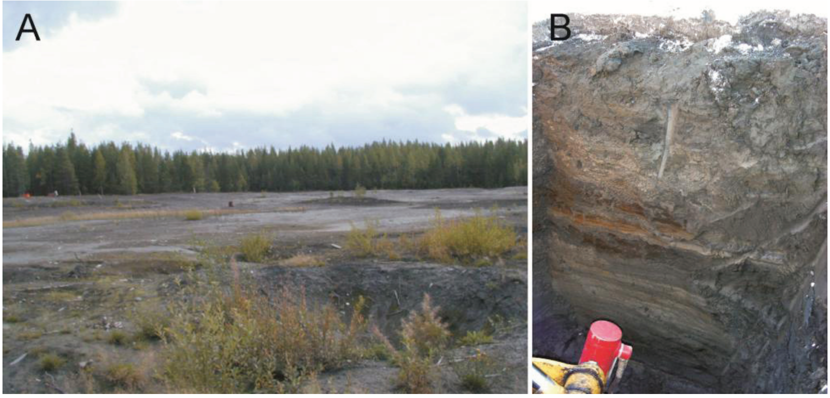

Figure 8. A) Ylöjärvi tailings area (Photo Kati Vaajasaari); B) layering of the surface tailings in an excavated test pit.

two times a year seasonal temperature changes of the water mix the oxidative surface water with the hypolimnetic water, causing degradation and dissolution of the material. However, the main arsenic source in the surface waters is the arsenopyrite grains in the tailings areas. The surface waters originating from the mining area are transported in a 7-km-long watercourse: Lake Parosjärvi in the immediate vicinity of the Ylöjärvi mine is connected to Parosjärvenoja stream, which flows into Lake

Vähävahantajärvi. From there, the surface waters flow through Vähävahantajärvi stream to Lake Näsijärvi (Fig. 9).

No comprehensive remediation measures have been undertaken in the Ylöjärvi mine area. However, over decades the ditch leading from the larger tailings area to Lake Parosjärvi (Fig. 7) has been limed in order to increase the pH and enhance the precipitation of Fe(III) hydroxides. The mining area is currently the property of Metsähallitus (the Finnish Forest and Park Service), which has rented the old mining premises to the Technical Research Centre of the Finnish Defence Forces. The larger tailings area is implemented as a test field for explosives.

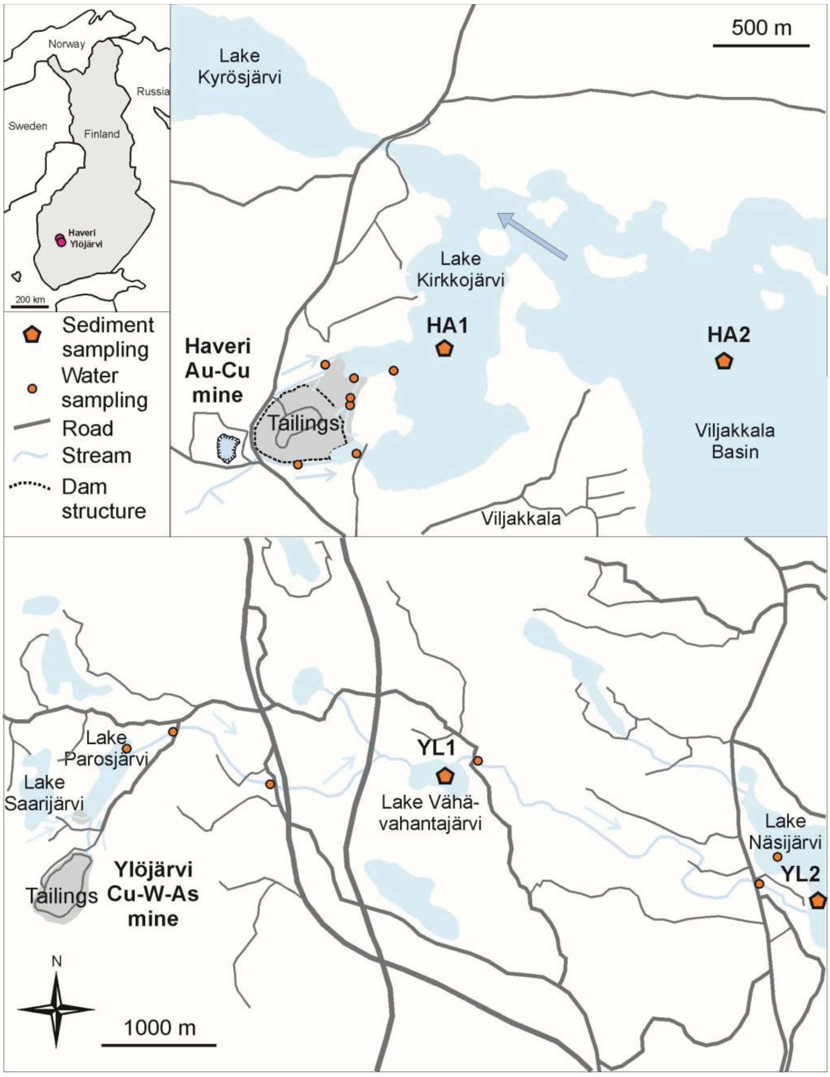

Figure 9. Map presenting the catchment areas, as well as lake sediment and lake water sampling points at the Haveri and Ylöjärvi mines.

3.2 Characterization of the tailings solids

The data studied in this doctoral thesis cover tailings samples from Haveri Au–Cu (Articles I and II) and Ylöjärvi Cu–W–As mines (Articles III and IV), and surface water samples from the former study site (Article I and II), as well as pore water, surface water and groundwater samples from the latter site (Articles III and V). Sampling campaigns were organized between May 2006 and December 2008, and laboratory work was carried out after each campaign, including mineralogical and geochemical studies. Additionally, lake sediment samples collected in March 2005 were investigated (Article V).

Undisturbed tailings solid samples were obtained from excavated test pits (Article I at Haveri and Article IV at Ylöjärvi) and drill core profiles (Articles I and II at Haveri and Article III at Ylöjärvi), frozen for transport immediately after collection and thawed at the laboratory. The samples were cut in half and duplicate samples from different horizons were used for mineralogical and geochemical characterization of the tailings. Additionally, respective ore samples taken from the drill cores collected from the National drill core depot at Loppi, Finland, were studied for primary ore mineralogy. Polished sections of tailings samples and polished thin sections of rock samples were prepared by standard techniques. Water was used only for cutting, not for the flat surface grinding and polishing of the samples.

The mineralogical studies routinely consisted of reflected-light microscopy for preliminary selection of interesting analysis points, SEM-EDS for imaging mineralogical and textural relationships and for preliminary analysis of chemical composition, and EMPA for imaging and quantitative chemical analysis. For the SEM-EDS studies, a LEO 1450 SEM–EDS equipped with a W-cathode, and a four-quadrant solid-state backscatter detector were used at the Helsinki University of Technology (Article I), as well as a JEOL JSM 5900 LV with an Oxford INCA EDS at the Geological Survey of Finland (Articles III and IV). EMPA was performed using a JEOL JXA-8200 electron microprobe with five spectrometers at Bayerisches Geoinstitut at the University of Bayreuth in Germany (Article I). The acceleration voltage was set to 20 keV and the beam current to 20 nA. The counting time was 30 s for the peak position and 15 s for the background. Analyses were also performed using a Cameca SX100 instrument at the Geological Survey of Finland (Article IV). The accelerating voltage and the beam current were set to 20 keV and 10 nA, respectively. Counting times were 10 s for LiF, PET and TAP, and the beam size was 3 µm. The analyzed X-ray lines used were Si *Kα*, Al *Kα*, Se *Lα*, Mg

Kα, As *Kα*, Co *Kα*, Fe *Kα*, Ni *Kα*, Mn *Kα*, Ti *Kα*, O *Kα*, Ca *Kα,* K *Kα*, S *Kα*, and natural minerals and metals were employed as standards. Analytical results were corrected using the PAP on-line correction program (Pouchou and Pichoir, 1986).

Additionally, a set of test pit samples from Haveri tailings were also studied using step-scan powder XRD. The XRD data were collected over the range 3–80°2θ with CoKα radiation on a Siemens D5000 Bragg–Brentano diffractometer equipped with a Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a Vantec-1 strip detector at the electron-microbeam/X-ray diffraction facility at the University of British Columbia. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

Detailed mineralogical studies were performed for the selected test pit samples from the Ylöjärvi tailings using synchrotron-based μ-XRF, μ-XAS and μ-XRD on GeoSoilEnviroCARS beam line 13-BM-D at Argonne National Laboratory (Argonne, IL, USA) in July 2009 and April 2010. Characterization of As oxidation states and bonding was performed by μ-XAS for the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regimes of the As *K*-edge, respectively. Two-dimensional μ-XRD patterns were collected in transmission geometry using a mar345 image plate detector (Marresearch GmbH, Germany).

In addition to the detailed mineralogical study, the tailings solids were investigated for the geochemical distribution of the elements in the duplicate samples to be able to compare the results with mineralogical observations. Selected drill core samples from the Haveri tailings were used for general characterization of the tailings, and they were analyzed for total sulfur content using an Eltra CS-2000 sulfur analyzer, total carbon content with a LECO carbon analyzer, and for total elemental concentrations by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The metal concentrations were obtained using *aqua regia* digestion (Koljonen, 1992) (Article I) and hydrofluoric–nitric acid digestion (for analysis of Co, Cu, Fe, Mn, Ni, Pb and Zn) (Article II). These methods extract all minerals except the more inert silicates, and they can be considered as a pseudo-total dissolution for most of the sulfide-forming elements. These results can therefore be taken as the sum of the elemental contents of the five extraction steps described below.

The most important geochemical characterization of the tailings samples consisted of a five-step sequential extraction procedure, because this method allows assessing the distribution of the potentially toxic elements in different mineral fractions. Tailings samples were subjected to a stepwise extraction scheme that successively targeted water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe (oxy)hydroxide, Fe oxide, and sulfide phases (modified from Hall et al., 1996, and Dold, 2003). Two slightly different schemes were used, but the modified second extraction step targeted the same mineral groups in both schemes, and no significant differences were observed (Table 2). The five-step extraction procedure was initiated with a water leach ("water-soluble", Table 2). This was done to extract water-soluble phases (e.g. efflorescent salts) and to differentiate secondary gypsum from calcite, which is extracted in the second step. The great neutralization potential of calcite makes its detection important. The second extraction ("AEC") leached adsorbed and exchangeable ions held on the exchange sites of negatively charged surfaces through electrostatic attraction, as well as carbonates. Extraction steps one and two commonly reveal only a small fraction of the total element concentrations. Amorphous Fe(III) (oxy)hydroxides and Mn hydroxides were extracted in the third step ("Fe (oxy)hydroxides"). Primary iron oxides were leached in the fourth step ("Fe oxides"), together with some residual Fe(III) (oxy)hydroxides. The extraction method is not As specific, but the Fe(III) arsenates are expected to be leached in the reducing ammonium oxalate leaches together with other secondary Fe(III) minerals. However, Corriveau et al. (2011b) suggest that crystalline scorodite can be more resistant than other Fe(III) arsenates and that it behaves in the extractions more like a sulfide mineral. In this doctoral dissertation, the third and fourth extraction steps are referred to as "Secondary Fe(III) minerals' fractions" when discussing the combined value of secondary minerals in both extraction steps. Primary and supergene sulfides and organics were extracted in the final step ("sulfides"). The residual sample was discarded. The samples were analyzed by ICP-AES. For the studies at Haveri, ten reagent blank samples and one sample in triplicate were analyzed to evaluate the quality and repeatability of the analytical results.

For the general characterization of the tailings and the prevailing conditions governing AMD generation, the tailings pH was measured at the laboratory from test pit samples from Haveri tailings according to standard method SFS-ISO 10390 using 1 M KCl solution at a ratio of 1:5 and a WTW pocket pH meter 340i equipped with a reference Ag–AgCl electrode. Additionally, grain-size distributions of tailings from both study sites were determined by laser diffraction (Mastersizer 2000; Malvern Instruments Ltd., UK) and specific surface areas were measured using the BET $N_{2(g)}$ absorption method (Brunauer et al., 1938). The pore water content (%) of the vadose tailings samples was calculated on the basis of the wet weight and dry weight after drying the samples. Pore gas sampling was intended at the Haveri tailings in September 2008. The GA 2000 analyzer by Geotechnical Instruments Ltd gauges CH_4 and CO_2 by infrared adsorption and O_2 and H_2S by electrochemical measurement. The analyzer was connected to a sampling pipe that was introduced to the desired sampling depth in the tailings. However, thorough gas sampling could not be performed due to moist tailings caused by rainfall events prior to sampling. At one sampling point in the central tailings, the pore gas concentrations were measured in the intervals of 0.10 m from surface to the depth of 0.60 m, at which depth pore water was pumped through the sampling pipe. The pore water content of the Ylöjärvi tailings proved too high to perform pore gas analysis.

3.3 Characterization of the water samples

Surface water (Articles I, II and V), groundwater (Article I, III) and pore water (Article III) sampling and analysis were performed in order to evaluate the water chemistry affected by low-quality mine drainage and the mobilization of elements. At the Haveri mine site, the water samples were collected from an adjacent groundwater well, ditches surrounding the tailings, seasonal gullies on top of the tailings and from Lake Kirkkojärvi. According to the local environmental authorities, the sampled groundwater well at Haveri receives its water from another aquifer and is not influenced by the watershed affected by mining. In the Ylöjärvi tailings area, the groundwater samples were collected from two existing monitoring wells installed during previous environmental studies (Hp4 and Hp5; Carlson et al., 2002) (Fig. 7). The sampling depth was just beneath the tailings pile in the underlying bedrock/soil interface at 12.7 m from the tailings surface in monitoring well Hp4 and at 8.4 m in Hp5. The monitoring wells were pumped the day before sampling and allowed to settle for 24 hours. The groundwater level was found at 3.7 and at 2.7 m from the pile surface, respectively. The pore water was extracted from duplicate tailings drill core samples, as used for mineralogical and geochemical investigations from the Ylöjärvi tailings, with a squeezing technique using a vacuum pump, and the extracts were filtered with a 0.45 µm membrane filter.

Three sets of surface samples were collected: (1) filtered water samples (0.45 µm membrane filter) for analysis of dissolved metals, (2) non-filtered samples for total metal concentrations, and (3) non-filtered water samples for anion analysis. Two sets of groundwater samples were collected: 1) filtered and acidified samples for elemental analysis and 2) non-filtered and non-acidified samples for anion analysis. The samples for metal analysis were acidified to pH <2 with HNO_3 (Suprapur) in the field, except for the samples for total metal concentrations collected in 2006 at Haveri and the pore water samples collected in 2008 at Ylöjärvi, which were digested with HNO_3 in a water bath at 90° before analysis. The surface water samples were analyzed for anions (Cl, F, PO_4, SO_4, NO_3) by ion chromatographic (IC) determination with suppressed $NaCO_3/NaHCO_3$ eluation, for $KMnO_4$ by manual titration with $KMnO_4$ to the equivalent point, and for alkalinity by end-point titration with 0.05 M HCl to pH 4.5. Additionally, the pore water samples that were extracted in sufficiently large quantities (> 15 ml) and groundwater samples were analyzed for Cl, SO_4, and alkalinity. Trace metal concentrations were determined by ICP-MS/AES.

The redox potential (E_h) and pH were measured *in situ* with a Mettler Toledo MP125 portable pH/ E_h meter and an InLab combination pH sensor equipped with an ARGENTHAL™ Ag™ trap in KCl as a reference system (redox potentials corrected to standard hydrogen electrode, SHE). Electrical conductivity (EC) and the dissolved oxygen (DO) content were measured with a WTW multiline P4 Pocket Meter.

All of the geochemical analyses were performed at the accredited chemical laboratory Labtium Oy (www.labtium.fi).

The geochemical equilibrium model PHREEQC (versions 2.17.5 and 2.18.00) (Parkhurst and Appelo, 1999) was used in the interpretation of the pore water and groundwater samples (Article III) using the Wateq4f and Llnl databases. Additionally, thermodynamic calculations with PHREEQC are presented here for the Haveri surface water samples, which are in close association with oxidized tailings. The model was used to determine the aqueous species and saturation indices (SI) of relevant mineral phases in the pore water and groundwater samples. SI values <0 indicate that the mineral is undersaturated and should dissolve in solution, while minerals with SI >0 are stable and expected to precipitate (oversaturated with respect to the solution). Schwertmannite is not included in the databases used, but it was included in the calculation using thermodynamic data acquired from Yu et al. (1999). Furthermore, many important As minerals (e.g. kaňkite, pharmakosiderite, yukonite) are not included, and the results of PHREEQC do not account for As associated with Fe(III) oxyhydroxides.

The suitability of the total reflection X-ray fluorescence (TXRF) spectrometer was assessed for the determination of As and trace metals in the mine tailings leached with *aqua regia* and in water affected by AMD at Haveri (Juvonen et al., 2009). TXRF is a time- and cost-effective analytical method, although some challenges were encountered in the analysis of samples with high metal concentrations.

3.4 Geophysical characterization of the tailings

Electric resistivity tomography (ERT) measurements were performed at the Haveri tailings impoundment to investigate the relationships between the electrical resistivity of the tailings measured in the field and the mineralogical, physical, and geochemical conditions governing the AMD generation, and to delineate areas that could be directly affected by acidic and metal-rich leachates flowing through the tailings impoundment (Article II). The interpretation and analysis of the inverted resistivity data on tailings were based on the mineralogy and geochemistry of the tailings and surface water samples, and the inverted resistivity sections were compared with previous geological studies to correlate the structural features of subsoil and bedrock below tailings.

The ERT lines in Figure 4 and a more detailed description can be found in Figure 1a in Article II. The *in situ* resistivity measurements were performed in May 2007 with an ABEM Terrameter SAS300C with Booster SAS2000 equipment using the roll-along technique to connect each spread along the measuring lines. A Wenner electrode configuration with 2.5 and 5 m electrode spacing was used in eight lines with distances between them of 50 (L1–L6) and 100 m (L7, L8). In addition, a dipole–dipole array was used in lines L3, L4, and L9 (L9 lies outside the impoundment) to enhance the lateral resolution and to increase the depth of the investigation. The inversion of data for interpretation was carried out with Res2Dinv software (Loke and Barker, 1996) using the robust method with widths of half-unit spacing in the model cells. The model residuals in the inverted sections were ~1–3% for the Wenner configuration and ~2–5% for dipole–dipole. The average depth of investigation was 25 m, which was sufficient to delimit the tailings thickness, the underlying sediments and the structural features of the bedrock. To characterize the internal structure of the tailings, horizontal resistivity maps at different depths were constructed by modifying the data on inverted resistivity sections (*i.e.*, the Res2Dinv files) with IPI2Win and X2IPI software (Bobachev, 1994, 2003). The resistivity maps provide a spatial resistivity distribution model in horizons at different depths defining the geoelectrical structure of the tailings.

3.5 Characterization of lake sediment records

Lake sediment cores were collected in March 2005 from the recipient lakes at Haveri and Ylöjärvi mine sites using a Kajak-type gravity corer (66 mm inner diameter, 500 mm tube length; Renberg and Hansson, 2008)

(Article V). At Ylöjärvi, two cores were collected from separate lakes: Lake Vähävahantajärvi (core YL1, water depth 2 m, 3 km downstream from the mine) and Lake Näsijärvi (core YL2, 11 m, 7 km) (Fig. 9). At Haveri, one coring site was located in the basin immediately outside the tailings area in Lake Kirkkojärvi (core HA1, 7 m, 0,5 km), while another one was located in the deepest part of the Viljakkala basin (core HA2, 24 m, 2.3 km from the mine) (Fig. 9). The Haveri results have previously been used to explain changes in the sediment biota by Kihlman and Kauppila (2010).

The short cores were sliced in the field into 1 cm slices (2 cm slices below 10 cm for HA2) and analyzed for sediment chemistry with ICP-AES and ICP-MS after microwave-assisted HNO_3 digestion (modified US EPA method 3051). The method does not provide a complete digestion of the sediment samples, but is designed to extract the contaminated fraction of the samples. The digestion is suitable for mine impact studies because it does not dissolve major silicates but breaks down sulfides, carbonates, most salts, certain micas, and clay minerals. Analytical quality control was based on the practices and standards of the laboratory (Labtium Ltd., Finas accreditation T025). No project standards or field duplicates were inserted.

The lake sediments were dated with the ^{137}Cs method, which is based on locating the current depth of the distinct 1986 Chernobyl nuclear fallout in the sediment profile. The cesium activity was determined with an Ortec gamma spectrometer equipped with a four-inch NaI(Tl) crystal, two amplifiers and a 2048 channel pulse height analyzer (Äikäs et al., 1994). The final dating was based on linear extrapolation without correcting for sediment compaction, because the focus was on recent events. The samples collected for Article V represent sediments deposited before, during and after the operation of the mine. Hence, the mining impact can be compared with the background values of deeper pre-mining sediments. The background values further provide an idea of the natural contamination potential in areas with ore potential where, for instance, As concentrations in the bedrock and topsoil may be elevated.

4. Results

4.1 Haveri mine

The Haveri Au–Cu mine tailings have remained unremediated for five decades since mining activities ceased, and have subsequently undergone alteration processes. The findings of the mineralogical, geochemical, and geophysical investigations reported here provided information on the contamination processes and pathways, possible attenuation mechanism and also on the neutralization potential of the primary mineralogy of the tailings (Articles I and II).

The Haveri tailings can be considered as contaminated soil and are a source of AMD. The pseudo-total concentrations after *aqua regia* digestion (Table 3 in Article I) demonstrated that Cd, Cr, and Pb (average values of 3, 42, and 10 mg/kg, respectively) only existed at fairly low concentrations in the Haveri tailings, whereas As and Cu (158 and 831 mg/kg, respectively) exhibited concentrations above the upper guideline value for contaminated soils (100 and 200 mg/kg, respectively) set in the Degree of the Finnish Council of State. In places, the concentrations of Co and V exhibited higher values than the upper guideline value, and Ni and Zn exceeded the lower guideline value. The total sulfur content of the tailings varied from less than 1 to 6.5%, with an average of 2.9%.

The exposure to atmospheric conditions and meteoric water had provoked extensive sulfide oxidation in the vadose zone of the tailings above the groundwater table, located at a depth of approx. 2 m from the surface. The brownish oxidation layer was distinguished from the grayish black transition layer at the field in the excavation pits (Fig. 5B). Variation in sulfide oxidation grades was observed, and the oxidation layer generally extended from the surface to a depth of 0.5 m, and up to 1.4 m in the central area of the tailings. The most extensive alteration was observed in the surface samples up to the depth of 0.15 m, where the sulfide minerals were completely depleted. The deeper samples of the oxidation layer showed gradually decreasing signs of alteration as a function of depth, and only pyrrhotite showed extensive oxidation up to the depth of 1.35 m (Figs 10 and 11).

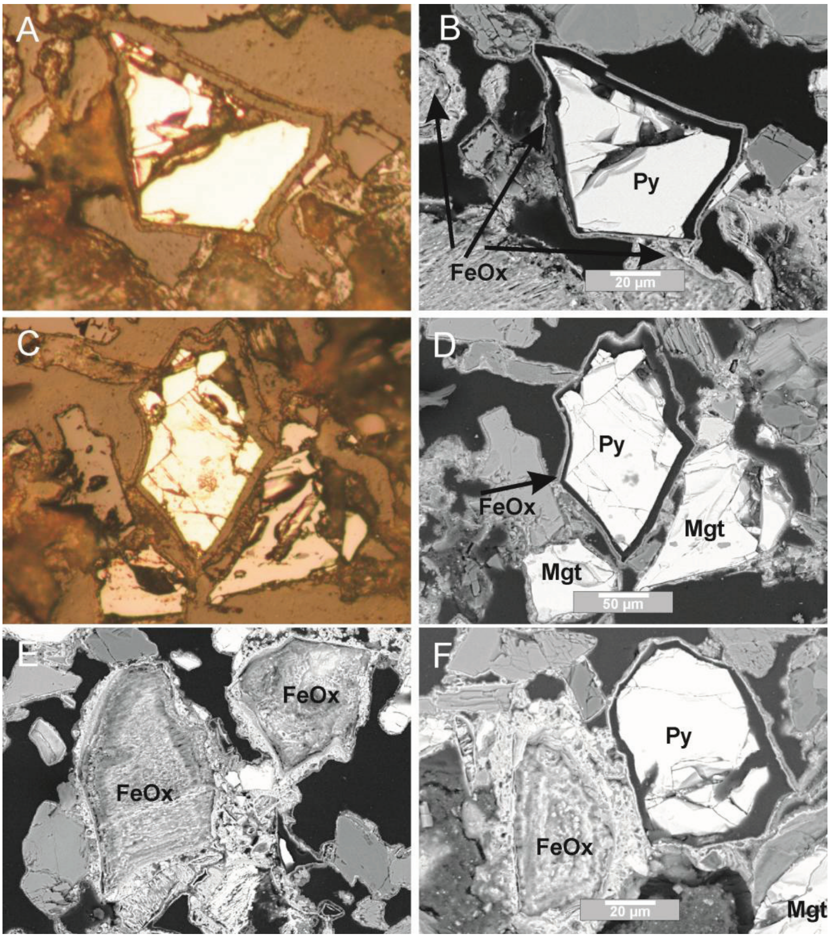

Figure 10. A) Reflected-light microscopic image and B) back-scattered SEM-EDS image of slightly altered pyrite (Py) and Fe(III) hydroxides (FeOx) replacing pyrrhotite; C) reflected-light microscopic image and D) back-scattered SEM-EDS image of slightly altered pyrite and magnetite (Mgt); E) and F)a completely weathered pyrrhotite grains transformed into Fe(III) hydroxides at 1 m depth in the Haveri tailings.

The oxidation of the main sulfide minerals, *i.e.* pyrrhotite, chalcopyrite, and pyrite, from the surface samples was observed in the mineralogical studies, and the sequential extraction results also highlighted the depletion of sulfide-related elements in the sulfide fraction (Fig. 3 in Article I). The oxidation processes described in Reactions 1-11 of Table 3 lowered the pH in the vadose tailings, and consequently in the surface waters in close association with the impoundment. Low pH conditions and a lower moisture content within the shallow tailings further promoted the oxidation processes. Sulfide oxidation had progressed deeper (Figs 10 and 11) and the pH had decreased more (ranging from 2.5 to 3.1) in the vadose layer of the

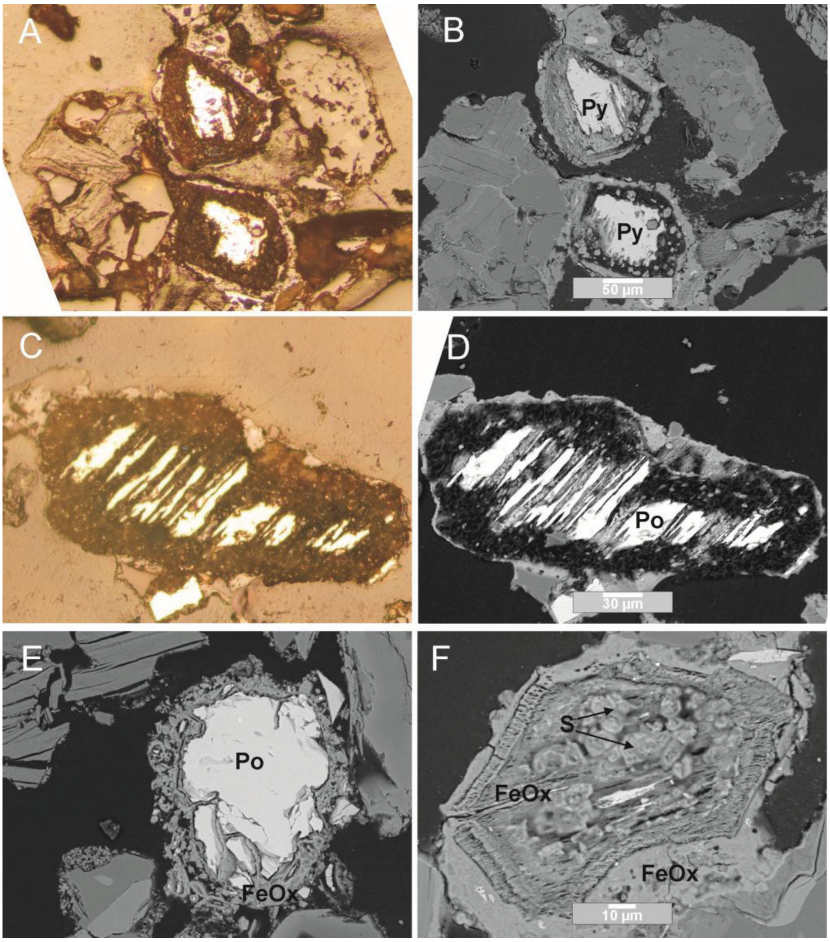

Figure 11. A) Reflected-light microscopic image and B) back-scattered SEM-EDS image of altered pyrite (Py); C) reflected-light microscopic image and D) back-scattered SEM-EDS image of highly altered pyrrhotite (Po); E) back-scattered images of altered pyrrhotite grain embedded by Fe(III) hydroxides (FeOx) and F) almost completely weathered pyrrhotite grain transformed in to Fe(III) hydroxides and native sulfur (S) at 1.35 m depth in Haveri tailings.

central area, where the pore water content was lower (12 wt.% in test pit 3; *i.e.* higher oxygen diffusion to pore spaces), whereas tailings with a higher moisture content (average 25 wt.% in test pit 1) presented fewer signs of alteration at a shallower depth (approx. 0.5 m) and only a slight decrease in pH (ranging from 4.3 to 7.3). Sequential extraction results and bulk powder XRD analysis also revealed that the samples with a higher moisture content contained some remaining calcite, which on the other hand had entirely dissolved in the low-pH tailings presenting a higher oxidation grade. This phenomenon was also detected during the field studies using ERT (Article II). The ERT lines allowed the delineation of areas having a high sulfide oxidation grade with higher electric conductivity and deeper anomalies. The conductivity anomaly in the tailings with a more advanced oxidation grade suggested a descending plume of low quality waters originating from sulfide weathering (Fig. 5 in Article II). The ERT also demonstrated that areas with a lower oxidation grade exhibited lower elemental mobilization, and the moderate conductivity anomalies were restricted to the surface layer of the tailings.

The oxidation of sulfide minerals in the oxidation layer led to elemental mobilization and to the precipitation of secondary Fe(III) minerals, which formed discontinuous cemented layers in the central area of the impoundment. In the area with a thicker oxidation layer, up to three consolidated layers were detected with varying composition. Two of the cemented layers were detected in the oxidation layer and the third in the upper part of the transition layer. Jarosite and Fe(III) (oxy)hydroxides (probably goethite) were detected in Haveri tailings (Article I). Based on the calculation with PHREEQC, the surface water samples in direct contact with tailings material (sampling points 5 and 6 in 2006, and 8 in 2007, Table 6 in Article I) were oversaturated with respect to goethite, jarosite and schwertmannite, showing good agreement with the mineralogical findings from the highly oxidized tailings. The sequential extraction results showed that trace elements were both adsorbed on mineral surfaces (minor component) and existed as co-precipitates in the structure of the secondary Fe(III) minerals. In particular, As, Cu, and Zn originating from the oxidative dissolution of sulfarsenides, chalcopyrite, and sphalerite, respectively, were enriched in the secondary Fe(III) mineral fractions. In the Haveri tailings, arsenic was effectively retained in the secondary Fe(III) minerals in the two shallowest samples (to the depth of 0.35–0.5 m), with concentrations corresponding to 40–100% of the total concentrations of As in the sequential extractions (Fig. 3 in Article I). The highest concentrations (up to 80 mg/kg) were recorded in samples 2b and 3b, which represented cemented layers. The accumulation of divalent cations in Fe(III) minerals was promoted in the deeper samples (up to 300 mg/kg Cu, 150 mg/kg Zn, and to a lesser extent 50 mg/kg Co and 70 mg/kg Ni). The formation of cemented layers is also an indication of high metal concentrations in the pore waters.

Precipitation of efflorescent salts was detected in the oxidation layer of the central tailings, and also due to capillary action at the tailings surface during drier periods in the summer (Fig. 12). The euhedral gypsum grains were visible to the naked eye in the field, and were also detected under reflected light and the electronic microscope (Fig. 12).

Trace elements (As, Cu, Zn) and SO_4 were retained to some extent in the secondary Fe(III) minerals. However, elevated trace metal (except As) and SO_4 concentrations were observed in low-pH (varying from 3.4 to 4.4, average 3.8) surface water samples (up to 736 µg/L Co, 1,670 µg/L Cu, 8.21 mg/L Fe, 708 µg/L Ni, 763 µg/L Zn, 1,170 mg/L SO_4) in the vicinity of the tailings area (Table 5 in Article I). This suggested that elemental mobilization from the Haveri tailings still occurred at the time of this study. The investigation of lake sediment records revealed the long-term trends in elemental mobilization during the active mining period from 1942 to 1961 and after decommission of the mine. The metal accumulation in the sediments during mining was moderate but increased gradually, whereas the highest metal peaks were detected after mine closure. The tailings started to dry up when a cover of fresh tailings was no longer deposited in the impoundment. This led to intensive sulfide oxidation and AMD. The highest peaks in metal mobilization and accumulation in the lake sediments were observed in sediments dated five to fifteen years after mine closure (Fig. 4 in Article V). At the same time, elements derived from silicate minerals peaked, implying very intensive sulfide oxidation and acidification of the tailings. Elements (*e.g.* Ag, As, Cu, Ni, and Zn) derived from the oxidation of chalcopyrite and accessory sulfides exhibited a short-lived peak, whereas Fe and S derived from the oxidation of major sulfides (pyrrhotite and pyrite) maintained elevated values for a few decades. The metal peaks were also observed in the more distant sediment core in Viljakkala Basin (Fig. 5 in Article V). Thereafter, the metal concentrations gradually decreased, with only Fe and S exhibiting higher values over a longer period, and in the recent top sediments concentrations slightly higher than the pre-mining values were recorded for many elements. Copper was the most abundant sulfide-bound element, apart from Fe, in the sediment records, showing 6-fold higher concentrations during mining and 200-fold higher concentrations during the most intensive sulfide oxidation period in comparison to pre-mining values (Fig. 13). Copper also persisted in the recent top sediment layers with 17-fold higher values, illustrating that the environmental impact of mining still persists. The quantities of elements leached from the superficial tailings due to sulfide oxidation were approximated at 70 kg Cd, 110 kg Pb, 210 kg Cr, Mo 220 kg, 690 kg As, 4,330 kg Ni, 4,500 kg Co, 6,000 kg Zn, 14,700 kg Cu, 1,330 t Fe, and 2,070 t S (Article I). A similar order of element abundance was detected in the post-mining lake sediments (Article V).

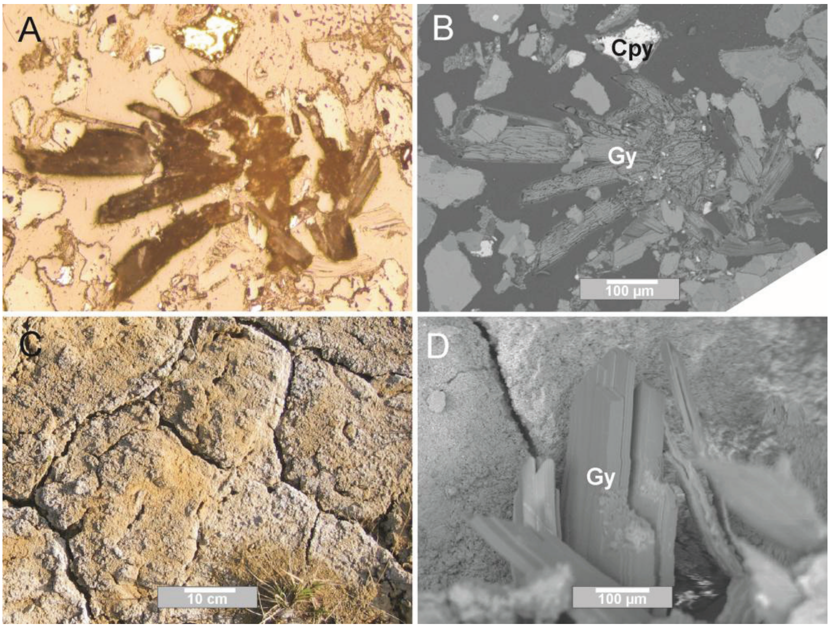

Figure 12. A) Reflected-light microscopic image and B) back-scattered SEM-EDS image of gypsum (Gy) grains in a sample at 1 m depth in test pit 2; C) photograph of white gypsum crystals and desiccation cracks on top of the tailings; and D) back-scattered SEM-EDS image of a euhedral gypsum grain from top of the Haveri tailings. (Cpy = chalcopyrite).

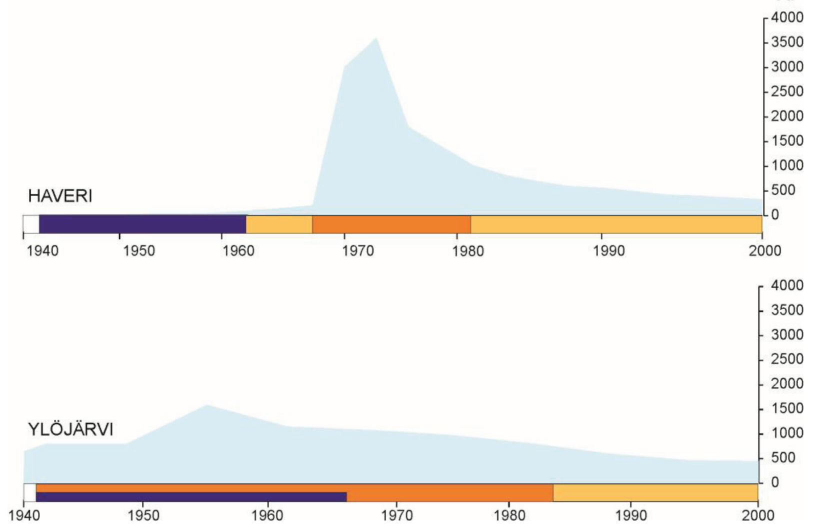

Figure 13. Concentrations of Cu (mg/kg) in lake sediment samples from Haveri and Ylöjärvi representing the tendencies in the evolution of elemental mobilization and consequent accumulation in lake sediments during and after mining. Blue areas represent the active mining period, and dark orange and light orange represent periods of intensive and moderate contamination, respectively.

4.2 Ylöjärvi mine

Mineralogical and geochemical investigations were performed on samples taken from two profiles in the vadose zone of the larger (17 ha) of two tailings areas at the Ylöjärvi mine. The tailings heap, rising approx. 9 m above the surrounding topography, had undergone oxidation processes and elemental leaching in the surface layers of the pile. The results provided detailed information on the origin of the As contamination in the surface waters and groundwater in the Ylöjärvi mining area described by Carlson et al. (2002) and Kumpulainen et al. (2007), and also further insights into the stability of the secondary As-bearing ferric precipitates acting as an important As attenuation mechanism (Articles III and IV).

Field observations showed that the vadose layer varied in thickness, and the groundwater level was detected at depths of 2.7 and 3.7 m in two groundwater wells. The moisture content was high in the tailings samples, ranging from 23 to 32% (average 28%). The oxidation layer in the Ylöjärvi tailings was not as well defined as in the Haveri mine tailings, although brownish layers of varying thickness were distinguished within the shallowest approx. 0.65 m (Fig. 8B). Oxidation of arsenopyrite (Reactions 7–9 in Table 3), which is the only primary As-bearing sulfide mineral in the Ylöjärvi tailings, was the source of As contamination. The sulfide oxidation had been most extensive from the surface to the depth of 0.15 m, leaving no remnant sulfide grains including arsenopyrite, and the signs of oxidation decreased downwards (Fig. 14). In profile 2, below 1.10 m (in the 2007 sampling, and below 1.24 m in the 2008 sampling), a sharp change in grain size was detected (Fig. 15). The samples from profile 1 and the shallower layer in profile 2 were composed of silt, and the layer below 1.10 mm of fine sand. The upper part of the coarser layer had undergone extensive sulfide oxidation, and arsenopyrite presented advanced sings of alteration (Fig. 14D). Thereafter, the signs of oxidation gradually decreased again, and only pyrrhotite and pyrite presented alteration on grain boundaries (Fig. 16). Characteristic of this highly altered layer, which also contained the lowest moisture content (approx. 23%), secondary As-bearing Fe(III) minerals were abundant (Fig. 17), and a cemented layer was detected at the interface of the grain-size boundary (samples 2h at 1.24 m in Article III and sample at 1.10 m in Article IV). As-bearing Fe(III) (oxy)hydroxides and Fe(III) arsenates were detected in the samples representing the cemented layer under SEM-EDS and during EMPA studies. More detailed mineralogical investigation using synchrotron-based methods in Article IV revealed that Fe(III) (oxy)hydroxides corresponded to arsenical ferrihydrite-type mineral and Fe(III) arsenates to hydrous ferric arsenate (HFA), scorodite and kaňkite types. The calculations in PHREEQC supported the precipitation of ferrihydrite and goethite (Table 3 in Article III), and Fig. 18 suggested the precipitation of ferrihydrite at pH >5.0 (E_h varied from 212 to 362 mV, Table 2 in Article III). The pore water samples were also oversaturated with

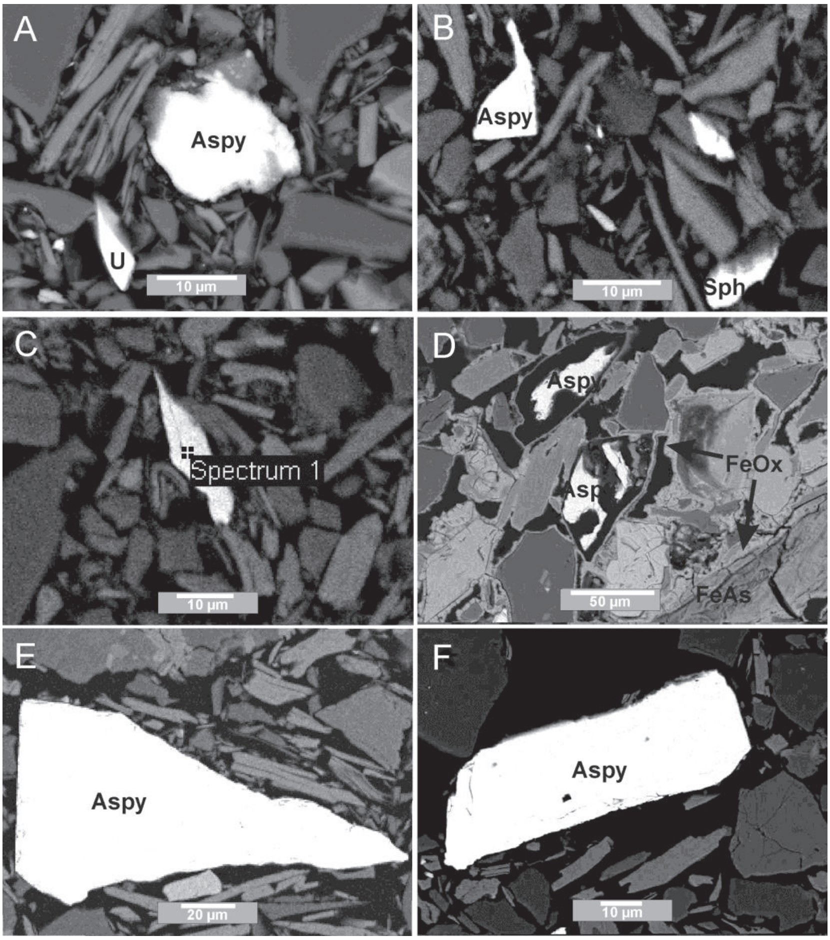

Figure 14. Back-scattered SEM-EDS images of arsenopyrite (Aspy) from profile 2 at A) approx. 0.5 m depth; B) 0.5 m; C) 1.0 m; D) 1.1 m; E) 1.5 m; and F) 2.3 m in Ylöjärvi tailings. (FeAs = ferric arsenates, FeOx = Fe(III) (oxy)hydroxides, Sph = sphalerite, U = uraninite).

respect to schwertmannite, but Fe(III) (oxy)hydroxysulfates were not detected in microanalytical work, and its precipitation was not suggested by Figure 18. Scorodite was undersaturated or near equilibrium, implying its metastability. More detailed interpretation of the modeling results can be found in Article III.

The sequential extraction results also demonstrated that the secondary As-bearing Fe(III) phases were most abundant in the highly altered shallow samples and in the samples taken from the cemented layer. These phases were dissolved in the reducing NH_4-oxalate leaches, *i.e.* secondary Fe(III) minerals' fractions, which are shown as high concentrations of Fe and As in these fractions (Fig. 2 in Article III and Fig. 7 in Article IV). The proportion of As in these fractions ranged from 82.5–93.7% (up to 3,685 mg/kg) of the total As in the sequential extractions in the highly oxidized samples (Article IV). Arsenic showed a wide range of concentrations in the sulfide fraction,

Figure 15. Drill core sample from profile 2 (sample 2h at 1.15-1.32 m depth in Article III) in the Ylöjärvi tailings.

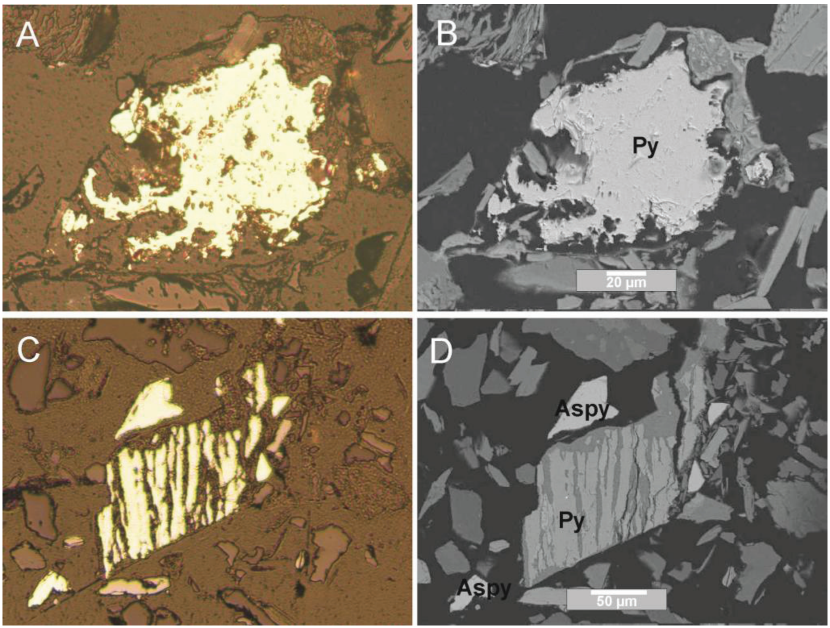

Figure 16. A) Reflected-light microscopic image and B) back-scattered SEM-EDS image of altered pyrite (Py) at approx. 1.85 m depth; and C) reflected-light microscopic image and D) back-scattered SEM-EDS image of unaltered arsenopyrite (Aspy) and pyrite inter grown with silicate mineral at 2.3 m depth in profile 2 in the Ylöjärvi tailings.

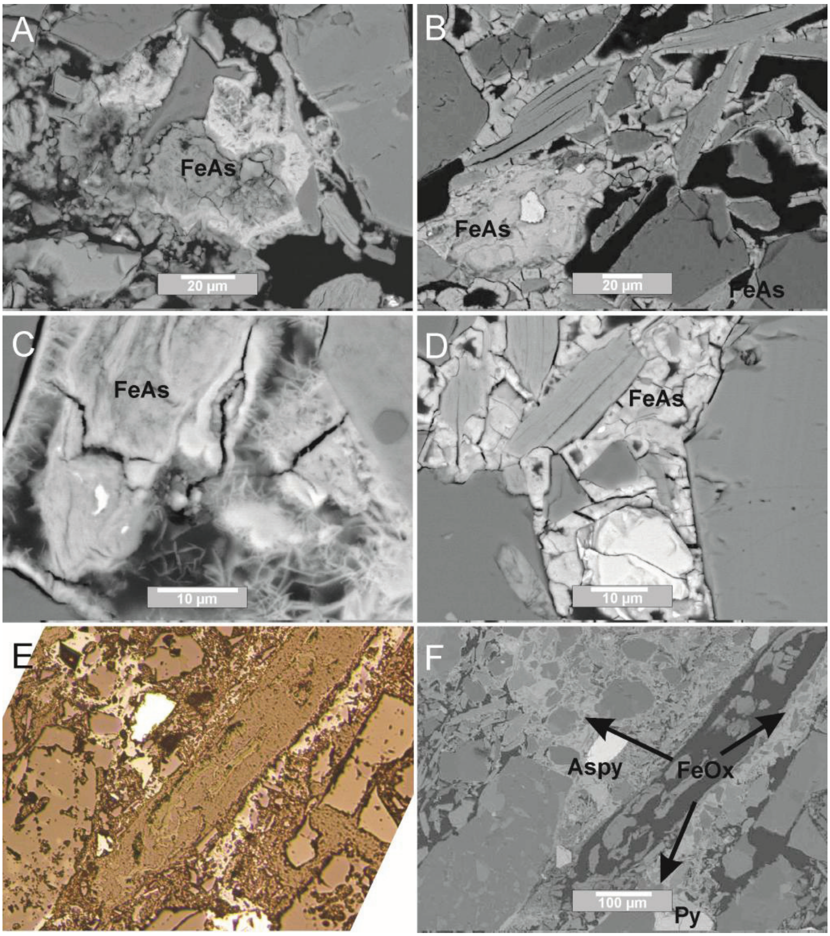

Figure 17. A); B); C); and D) Back-scattered images of secondary Fe(III) arsenate (FeAs) at approx. 1.10 m depth; E) reflected-light microscopic image and F) back-scattered SEM-EDS image of unaltered arsenopyrite (Aspy), pyrite (Py), and secondary Fe(III) hydroxides (FeOx) at 1.50 m depth in profile 2 in the Ylöjärvi tailings.

from 25 mg/kg (<3% of the total As content) in the shallow, highly oxidized samples to up to 6,900 mg/kg (97.6 % of the total As content) in the less altered samples at depths of 1.50 m and 2.30 m.

The mineralogical setting was contrasted with the pore water geochemistry and physicochemical conditions. The pore pH ranged from 4.9 to 8.9, whereas redox conditions varied from 212 to 362 mV (Table 2 in Article III). Pore water and groundwater sampling revealed that elevated concentrations of As were released from the tailings pile, and the As concentration in pore water ranged from 31.9 to 5,140 µg/L (average 1,721 µg/L), and in groundwater below the heap from 4,740 to 14,500 µg/L. Arsenic was accumulated in pore water and transported into groundwater, despite the precipitation of secondary As-bearing Fe(III) minerals in the oxidation layer. However, in the shallow tailings, As concentrations in pore water were controlled by the precipitating Fe(III) minerals and the pH. The

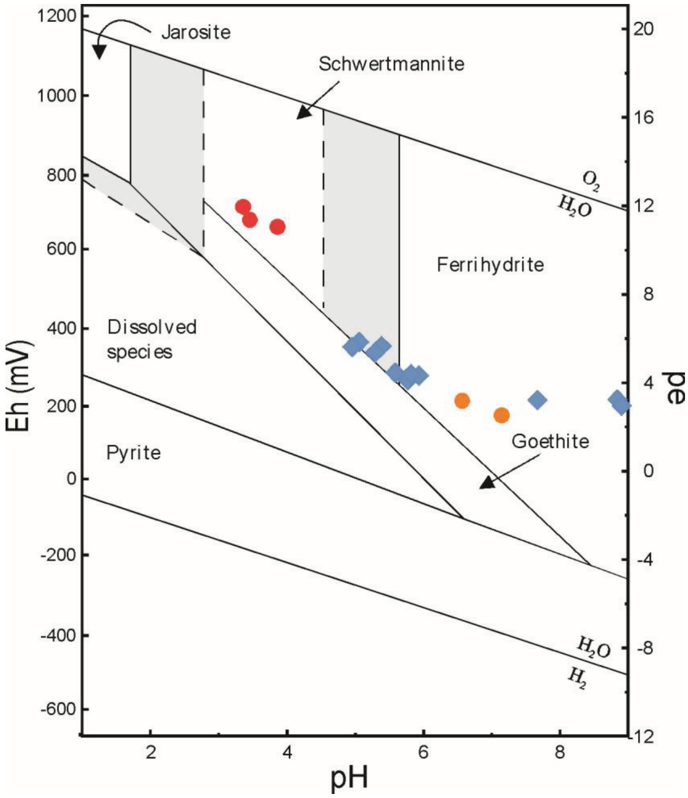

Figure 18. Eh(pe)-pH diagram for the system Fe–S–K–O–H at 25 °C and 1 bar pressure (see details in Figure caption 1). Darker areas show possible expansion of K-jarosite and ferrihydrite fields; red circles represent surface water samples from the Haveri tailings; blued diamonds denote pore water samples from the Ylöjärvi tailings; and orange circles groundwater samples below the Ylöjärvi tailings (modified from Bigham et al., 1996).

highest As pore water concentrations were detected in samples where unaltered arsenopyrite remained, whereas the lowest concentrations were recorded in highly oxidized samples with abundant secondary Fe(III) minerals. Highly oxidized samples were also the samples presenting the lowest pH (ranging from 4.9 to 5.8). Besides As, Fe, and W presented higher average concentrations in groundwater than in pore water samples. The pore water concentrations for Fe varied from 0.09 to 159 mg/L (average 13.4 mg/L), whereas the groundwater concentrations ranged from 23.1 to 31.6 mg/L (average 27.4 mg/L). Other elements (*e.g.* Co, Cu, Ni, U, Zn, and also SO_4) generally presented higher concentrations in the pore water samples than in the groundwater samples, and seem to be retained along the descending pathway (Table 2 in Article III).

Previous surface water analysis (Carlson et al., 2002; Parviainen et al., 2006; Bilaletdin et al., 2007a; Kumpulainen et al., 2007) and the systematic monitoring since 1975 (HERTTA database, unpublished data) have demonstrated that the catchment area of the Ylöjärvi mine is affected by AMD, and several seepage points around the tailings pile reduce the quality of surface waters. Nearly half a century after mine closure, As (3–2,650 µg/L) and other elements show elevated concentrations in surface water samples. The study of ^{137}Cs-dated lake sediment records demonstrated that modern element transport was also reflected in the recent top sediments. The concentrations of Ag, As, Cd, Co, Cu, Ni, Zn, and U were above the pre-mining concentrations, implying that drainage waters from the mining area still contaminate the catchment area (Fig. 2 in Article V). The lake sediment records from the Ylöjärvi catchment also showed that many elements already peaked in concentration during the active mining period (*e.g.* Ag 61-fold higher concentrations in comparison to the pre-anthropogenic impact, As 11-fold, Cu 37-fold, Co 15-fold, U 10-fold, and Zn 4-fold higher) maintaining elevated concentrations through the end of operations and immediately after mine closure (Fig. 13 for Cu). Thereafter, the concentrations gradually began to decrease as a consequence of attenuation mechanisms (*e.g.* precipitation of secondary Fe(III) minerals) and because the downward-moving oxidation front caused the migration of the contaminant plume to also percolate in the tailings pile instead of surface runoff. Unlike the Haveri mine, clear post-mining peaks originating from sulfide oxidation in the tailings pile could not be detected in the lake sediment records from Ylöjärvi, probably because of the dispersive character of the drainage waters from the Ylöjärvi tailings facility (Fig. 13). At Ylöjärvi, the lake sediment cores sampled deeper pre-mining sediments, which revealed that changes in land use patterns may mobilize metals in a region with mining potential. In this case, the impact of agricultural activity was detected as an increase in the concentrations of both silicate and mining-derived elements.

5. Discussion

The decommissioned Haveri Au–Cu and Ylöjärvi Cu–W–As mines have a history of over half a decade of environmental impact derived from the mining processes during exploitation, and from the weathering of tailings generating AMD. In many other active and closed mining areas, low-pH drainage waters carrying heavy metals have been recorded (Moncur et al., 2006; Nieto et al., 2007; Heikkinen et al., 2009; Nordstrom, 2011). The type of ore deposit, ore processing methods, waste management, dam structure and permeability, remediation measures, climate and other variables influence the discharge rates and quality of drainage waters (Plumlee, 1999; Plumlee et al., 1999). After mine closure, the generation of AMD is the principal cause of contamination, which is also dependent on many factors: the mineralogical setting, grain size, specific surface area, prevailing pH-E_h conditions or changes in them, precipitation of secondary Fe(III) minerals, and formation of cemented layers. As reported in Article V, the contemporaneous and post-mining drainage waters derived from Haveri and Ylöjärvi mines have varied in composition and intensity in the course of time. In the Haveri tailings impoundment, the flow path of runoff ends up in Lake Kirkkojärvi, and the lake sediment records clearly illustrate that the Haveri mine tailings experienced a climax in AMD generation approximately 5 to 15 years after mine closure, implying that the surface water concentrations were much higher than at the time of these investigations. Kihlman and Kauppila (2010) also report that in the lake sediments dating the time of post-mining metal peaks, ecological effects on the lacustrine biota are observable. The impact of AMD waters on arcellaceans and diatoms has been detected over a large area, including Viljakkala Basin. At present, metal concentrations in the surface lake sediments moderately exceed the pre-mining background values. At the Ylöjärvi mine, highest metal accumulations were reported in lake sediments deposited during mining, especially after the mid-1950s, and during two decades after mine closure. Thereafter, the lake sediment concentrations have decreased to a level slightly exceeding the pre-mining concentrations. Hence, as demonstrated in Article V, both mines have passed the maximum contaminant loading in the drainage waters, and the metal concentrations in the sediment load have now decreased significantly from the peak levels, but nevertheless present values affected by AMD. Based on Articles I–V, several factors related to AMD generation in tailings influence the quality of mine drainage waters, which will be discussed in the following sections.

5.1 Attenuation mechanisms in oxidized tailings

Articles I and III described the advanced stages of sulfide oxidation and processes affecting the attenuation mechanisms in low-quality mine drainage at the Haveri and Ylöjärvi tailings facilities, respectively. At both sites, secondary Fe(III) minerals showed a retention capacity for trace elements. Additionally, the As-bearing Fe(III) mineral phases in the Ylöjärvi tailings were studied in detail in Article IV.

Previous work has demonstrated that dissolved cations and anion complexes, especially abundant in AMD, have a tendency to act differently according to the pH. In the low pH range, divalent cations are mobile and are not expected to be trapped in Fe(III) (oxy)hydroxides, whereas As and other oxyanions are preferentially retained in secondary Fe(III) minerals (Dzombak and Morel, 1990). This was detected in the highly oxidized layer of the Haveri mine tailings, where As concentrations in the secondary Fe(III) minerals' fractions comprised 40 to 100% of the total As content in sequential extractions, whereas divalent cations showed a relatively low content in these fractions, implying that they remain in solution. Only Cu and Zn presented notable concentrations in these fractions in deeper samples. Sulfur was also detected in the AEC fraction in the deeper samples, which can be explained by SO_4 adsorption on goethite at low pH levels (Bigham et al., 1996). Sulfur in the secondary minerals' fractions is derived from the jarosite precipitations. Furthermore, in Article I, the surface water analysis revealed that, indeed, Co, Cu, Ni, and Zn exhibited the highest concentrations in the modern drainage waters with a low pH (average 3.8), but As was virtually absent from the drainage waters (Table 5 in Article I).

At the Ylöjärvi mine, As was preferentially co-precipitated with ferrihydrite, and ferric arsenates were present in one sample. The arsenical ferrihydrite and Fe(III) arsenates of HFA, scorodite and kaňkite type mineral phases proved to be important carriers of As in highly oxidized samples, and they immobilized As derived from arsenopyrite oxidation, which is the original source.

In many tailings areas, effective sulfide oxidation and subsequent metal release and hydrolysis of Fe have been found to produce cemented layers

(Blowes et al., 1991; McGregor and Blowes, 2002; Alakangas and Öhlander, 2006; Graupner et al., 2007). Accordingly, cemented layers were detected at both studied sites. Furthermore, this study demonstrated that cemented layers can form in low-sulfide and low-carbonate tailings. The data in Articles I, III, and IV indicated that these layers were enriched in Fe and trace elements in the secondary Fe(III) minerals' fractions in comparison to the uncemented samples, implying the higher accumulation of secondary Fe(III) minerals and enhanced retention of potentially toxic elements. In the Ylöjärvi tailings, the cemented layer hosted ferric arsenates that served as an important sink for As. Previous studies on cemented layers have shown that they have the potential for natural attenuation, and their contribution to mitigating the impact of AMD is based on the accumulation of Fe(III) minerals, and consequent adsorption and co-precipitation of potentially toxic elements from solution (Blowes et al., 1991; Lin, 1997; McGregor and Blowes, 2002; Moncur et al., 2005; Graupner et al., 2007). They also work as a hydraulic and diffusive barrier, hindering the infiltration of pore water and pore gases, and slowing down the downward movement of the oxidation layer (Blowes et al., 1991; McGregor and Blowes, 2002). Similarly, lower moisture contents relative to the surrounding uncemented tailings were recorded in the well-defined cemented layers and below them at both mine sites. The findings in Articles I, III, and IV support the conclusion that natural attenuation mechanisms are occurring in the Haveri and Ylöjärvi tailings. However, these accumulations, like Fe(III) minerals in general, may be transitory and subject to variation in pH-E_h conditions (Jurjovec et al., 2002). At pH <3, Fe(III) minerals contribute to the neutralization processes as described in Section 2.2. In particular, the acidic conditions (pH 2.5–3.2) in the central Haveri tailings imply the dissolution and re-precipitation of Fe(III) minerals, and the subsequent formation of the third and lower-most cemented layer below the oxidation layer in the greyish black transition layer. The stability of Fe(III) minerals is discussed in the following Section 5.2.

Despite the formation of secondary minerals and cemented layers in the vadose zone, there are implications of groundwater contamination at both study sites. The downward penetrating high conductivity ERT anomaly reported in Article II was consistent with the geochemical and mineralogical data in Article I, implying a descending low quality plume in the central Haveri tailings. The presence of cemented layers also suggests that tailings pore waters carry abundant dissolved metals. In the Ylöjärvi tailings, the groundwater data demonstrated the accumulation of As and Fe in the groundwater body beneath the heap (Article III). These data emphasized that in tailings areas like the studied ones, which have an advanced stage of sulfide oxidation and where the active weathering occurs at a great depth, the major contaminant plume migrates towards groundwater bodies instead of surface runoff from tailings. Meteoric water has flushed the superficial tailings, transporting potentially toxic elements to surface water bodies over decades and leaving less mobile contaminants in these layers. In general, in humid climates where precipitation exceeds evapotranspiration, the contaminant plume is expected to migrate downward to the groundwater beneath the tailings heap, in contrast to capillary upward transport of contaminants common in arid and semi-arid climates (Plumlee, 1999). However, contaminated groundwater may discharge to an adjacent creek or below the dam structure, affecting surface water quality. This phenomenon and other attenuation mechanisms acting along the flow path are also reflected in the lake sediment records, which show that in the recent top sediments the elemental concentrations have decreased since the concentration peaks.

5.2 Stability of Fe(III) phases and possible implications for remobilization

The above discussion describes the importance of the secondary Fe(III) minerals in mitigating the mobilization of potentially toxic elements from weathering tailings. However, the stability of Fe(III) (oxy)hydroxides and especially Fe(III) arsenates with varying Fe/As ratios is a controversial and complex issue. The stability of these minerals in the oxidation layer may be altered if pH-E_h conditions are changed: acid dissolution or reductive dissolution may remobilize elements trapped in Fe(III) minerals through desorption or dissolution of the mineral itself. Further acidification of the tailings by active sulfide oxidation can destabilize Fe(III) minerals precipitated within a higher pH range, whereas reductive dissolution is triggered when tailings are placed under oxygen deficient conditions, provoking the remobilization of secondary phases stable under oxygenated ambient conditions (Jurjovec et al., 2002; Kocar and Fendorf, 2009; Lindsay et al., 2011).

In the Haveri tailings, jarosite (average pH 2.8) and Fe(III) (oxy)hydroxides (probably goethite in low pH (<5) tailings, and goethite or ferrihydrite in near-neutral tailings) were detected. PHREEQC suggested that jarosite and goethite, as well as schwertmannite, were thermodynamically oversaturated in the surface water samples affected by AMD (average pH 3.9), and according to Figure 18 schwertmannite was the preferentially precipitating phase. If ferrihydrite was present in the less altered tailings, it could undergo dissolution in case of further weathering.

The arsenical ferrihydrite, HFA scorodite, and kaňkite-type mineral phases retain an important amount of dissolved As in the vadose layer of the Ylöjärvi tailings. The Fe(III) arsenates with an Fe/As ratio < 1.5 have the potential for greater As mass attenuation, but ferrihydrite is probably the most important sink, as it was found to be precipitated throughout the studied profile. The tailings pH conditions (4.9–8.9) at the time of the study favored its precipitation (Fig. 18; Bigham et al., 1992, 1996), and thermodynamic calculations by PHREEQC also implied its precipitation. Ferric arsenate compounds with an Fe/As ratio ≥ 8, including arsenical ferrihydrite, show good stability over a wide range of pH values (3–8) (Krause and Ettel, 1989). The precipitation of scorodite and Fe(III) arsenates with a lower Fe/As ratio is promoted at low pH, preferentially ranging from 3 to 4 (Paktunc et al., 2008; Paktunc and Bruggeman, 2010). However, HFA, scorodite, and kaňkite were detected in the sample collected from the cemented layer of the Ylöjärvi tailings. According to PHREEQC, scorodite was undersaturated or near equilibrium. These low-crystalline phases are metastable at pH 5.4 recorded in the pore water sample from the corresponding depth (Krause and Ettel, 1989), and over time scorodite may dissolve incongruently to form ferrihydrite (Bluteau and Demopoulos, 2007). The remobilized As is partly adsorbed onto ferrihydrite, but aqueous As is released upon scorodite dissolution (Bluteau and Demopoulos, 2007). Lowering of the pH of the Ylöjärvi tailings by further acidification of the weathering tailings would favor the precipitation of scorodite and Fe(III) arsenates with a lower Fe/As ratio (Paktunc et al., 2008; Paktunc and Bruggeman, 2010). On the other hand, ferrihydrite, carrying the majority of secondary As, would be subjected to remobilization or transformation at a low pH (Krause and Ettel, 1989; Bigham et al., 1992). However, considering the low sulfide content (generally <1% of S, Article III), relatively high moisture content and decreasing oxygen diffusion in the downward moving oxidation layer, the Ylöjärvi tailings are not expected to experience intensified acidification in the future. Therefore, maintaining the current system and further promoting the precipitation of arsenical ferrihydrite is recommended.

The sequential extractions simulate the solubility of different mineral groups under the specific conditions of each step, and they are highly recommended as a supplementary tool together with mineralogical investigations in mine tailings. The reducing NH_4-oxalate extractions (secondary Fe(III) minerals' fractions) simulate the above-mentioned Fe(III) mineral phases and the associated elements that would dissolve if conditions were to become more reductive in the tailings pile. Hence, considerable amounts of As (40–100% and 82.5–93.7 % of the total As in the highly oxidized samples, respectively) are expected to remobilize in the Haveri and Ylöjärvi mine tailings under reducing conditions. In the Haveri mine tailings, greater concentrations of Cu, Zn, and S (as SO_4) among other potentially toxic elements were also found in the NH_4-oxalate extractions in the deeper samples, whereas in the Ylöjärvi tailings, Cu, U and Co presented elevated concentrations, especially in the cemented layer. Hence, these elements are sensitive to reductive dissolution, besides As.

Although sorption onto Fe(III) (oxy)hydroxides and co-precipitation with poorly-crystalline phases can limit As mobility in pore water, attenuation resulting from co-precipitation with more crystalline phases will probably facilitate greater long-term stability (Foster et al., 1998). Therefore, aging processes involving transformation into a more crystalline phase may have an implication for the long-term stability of elements trapped in the secondary Fe(III) minerals. Adsorbed As can be desorbed during the transformation and recrystallization process of poorly crystalline As-bearing Fe(III) (oxy)hydroxides (Fuller et al., 1993; Waychunas et al., 1993), but As trapped in the structure of aging Fe(III) arsenate, for instance, may be bound more firmly (Krause and Ettel, 1989). Although geochemical modeling suggested the presence of schwertmannite at both study sites, it was not observed in the mineralogical studies. However, if present, schwertmannite is prone to alteration to goethite (and to jarosite as an intermediate phase), and Acero et al. (2006) reported that during the transformation process As is released into solution. In another study, the transformation of schwertmannite to goethite and eventually to hematite through diagenesis was found to release the sorbed As (Pérez-López et al., 2011). Ferrihydrite and jarosite also tend to transform into thermodynamically more stable minerals, namely goethite or hematite (Schwertmann and Murad, 1983). Pederson et al. (2006) reported that the transformation of ferrihydrite or lepidocrocite [γ-FeOOH] to goethite or hematite has the potential to enhance As stability at trace concentrations. Das et al. (2011) confirmed the importance of As in the long-term stability of ferrihydrite in alkaline conditions. However, rates of transformation may decrease for Fe(III) (oxy)hydroxides with lower Fe/As ratios (Das et al., 2011). Considering the above discussion, the transformation of As-bearing (as co-precipitate) jarosite and ferrihydrite in the Haveri tailings, as well as arsenical ferrihydrite at Ylöjärvi to goethite would benefit the long-term stability of As.

Recrystallization of poorly-crystalline Fe(III) arsenates would also increase As stability over time. For instance, the solubility of well-crystallized scorodite has been found to be 100-fold lower than that of amorphous equivalent (Krause and Ettel, 1989). The transformation of poorly crystalline ferric arsenate into crystalline scorodite has been reported to cause the Fe/As molar ratio of the precipitate to decrease from 1.22 to 1 upon recrystallization (Le Berre et al., 2008). These authors also deduced the decrease to result from the stepwise conversion of ferrihydrite, initially precipitated together with poorly crystalline Fe(III) arsenate, to crystalline scorodite. As mentioned earlier in this section (5.2), the poorly crystalline Fe(III) arsenates at the Ylöjärvi tailings are metastable. Therefore, at the current or more elevated pH conditions, their transformation into a highly crystalline scorodite is not expected, whereas transformation into ferrihydrite can occur, implying partial As mobilization (Bluteau and Demopoulos, 2007).

5.3 Implications for remediation planning and recommendations for future investigations

The mining industry produces huge waste streams and faces environmental challenges to ensure a sustainable future (Lottermoser, 2011). For historical mine sites, reuse (application of wastes to a beneficial end), recycling (extraction of elements or converting wastes into value products), and rehabilitation (mitigation of environmental impact) of mine wastes are demanded (Lottermoser, 2011). Reducing the environmental and health impact of mine wastes requires multidisciplinary research and expertise, and geochemistry and mineralogy is central to these (Jamieson, 2011). Evaluating and selecting remediation techniques at abandoned mine sites is a complex task, and many options need to be considered, because some methods used in active or closing sites may not work for sites that have been abandoned for extended periods. Among the various remediation strategies developed for implementation at mine sites are the collection and treatment of contaminated surface water and groundwater, passive treatment of contaminated surface water using constructed wetlands, treatment of contaminated groundwater using permeable reactive barriers or other *in situ* remediation approaches, and the emplacement of covers on tailings impoundments and waste-rock piles to prevent oxygen ingress or infiltration of precipitation (Blowes et al., 2003). At historic and abandoned mine sites, tailings have weathered, and drainage water carrying contaminants is consequently discharged through groundwater, seepage, runoff and flooding after heavy rainfall events, expanding to a vast area from the source. The treatment of contaminated waters is the most common approach, but from a long-term perspective, controlling the source of contamination and inhibiting AMD generation is more appealing. Preventing hydrospheric and atmospheric interaction with sulfide minerals slows down the weathering processes and mitigates the metal loading in drainage waters in the first place. At decommissioned mine sites, liable mining corporations are often difficult to track, and the responsibility falls on the government. Therefore, remediation methods with low costs and requiring low maintenance are demanded.

As in the superficial tailings at Haveri and Ylöjärvi, significant amounts of contaminants, especially As, Cu, Zn, are associated with Fe(III) minerals, and cemented layers host accumulations of secondary Fe(III) minerals, it should be ensured that these layers are not placed under reducing conditions in the future. This sets requirements for optimal remediation to prevent reductive dissolution of the secondary minerals with a capacity to retain potentially toxic elements. For instance, the application of a soil or synthetic cover, raising of the water table or the addition of organic carbon due to re-vegetation can induce the transition to anaerobic conditions, triggering reductive dissolution (McCreadie et al., 2000; Carlsson et al., 2002; Salzsauler et al., 2005; Kocar and Fendorf, 2009; Lindsay et al., 2011). Hence, at Haveri for instance, merely enhancing the surface runoff in the central, highly oxidized areas may be considered to limit the infiltration of meteoric water for sulfide oxidation. In the peripheral and moist areas with less alteration, maintaining the current conditions is to be considered. In pursuance of channeling the runoff, the drainage waters could be limed in order to enhance the co-precipitation of divalent cations, which are present in runoff affected by AMD, together with Fe(III) minerals.

Monitored natural attenuation (MNA) is a remediation method that refers to the reliance on natural processes to achieve groundwater cleanup goals within a reasonable time frame (Ford et al., 2007). These include chemical, physical, and biological processes that act to reduce the mass, volume, mobility, toxicity, or concentration of groundwater contaminants – both organic and inorganic. The effectiveness of monitored natural attenuation has been clearly and routinely documented at petroleum-contaminated sites. However, it may also be an important factor at sites contaminated with chlorinated solvents, inorganics including metals and radionuclides, and mixtures of these contaminants. Natural attenuation pathways for As and divalent cations include the precipitation of sulfide minerals, co-precipitation as trace components in Fe or Mn oxyhydroxides, and adsorption on Fe or Mn oxyhydroxides or other mineral surfaces. MNA requires extensive sampling and modeling efforts to demonstrate that natural attenuation is achieved to meet the site-specific cleanup goals and that the conditions are not changed, leading to remobilization of the potentially toxic elements. In addition, a longer time period is generally required to achieve the cleanup goals than for other remediation techniques. MNA could be considered at Haveri because the site meets the requirements for natural attenuation processes. Multiple line evidence proved that processes supporting natural attenuation, such as the precipitation of secondary Fe(III) minerals and formation of cemented layers trapping potentially toxic elements, have occurred in the Haveri tailings (Article I). However, the extension, mineralogy and physical properties of the cemented layers should be studied in detail to evaluate their long-term capacity as an attenuation mechanism. Additionally, as demonstrated in Article V and by Kihlman and Kauppila (2010), the metal loading and ecological impact derived from AMD at Haveri has decreased since the most active sulfide oxidation peak. Surface water sampling (Article I) indicated that waters in close contact with tailings still carried considerable metal concentrations (Co, Cu, Ni, and Zn), but in the adjacent lake water samples the concentrations had decreased to an acceptable level. At Ylöjärvi, natural attenuation processes trap As within the tailings, but As is nevertheless transported from the area, and MNA may not be recommended. However, Carlson et al. (2002) observed that the peat bog between the Ylöjärvi tailings and Lake Saarijärvi (Fig. 7) retains As and other trace elements, contributing to the immobilization of these elements. Furthermore, Bilaletdin et al. (2007a, b) reported that in the catchment receiving effluent derived from Ylöjärvi mine, As concentrations are controlled by dilution, precipitation and sedimentation, which contribute to the attenuation processes along the pathway. Groundwater sampling at Haveri and also a hydrological study of both tailings areas are recommended to evaluate the water quality, flow direction and possible discharge points in order to assess in detail the feasibility of MNA.

Permeable reactive barriers (PRB) are an effective way to eliminate inorganic contaminates and control the pH of the drainage flowing through them (Blowes et al., 2000). PRB is placed in the path of a migrating contaminant plume, and is designed to remove heavy metals and arsenic from groundwater by promoting microbial-mediated sulfate reduction, sulfide mineral precipitation and arsenic and heavy metal sorption. The reactive material of the barrier can contain a mixture of, for instance, municipal compost, leaf mulch, wood chips, gravel, and limestone (Benner et al., 1999). In another study, a mixture of leaf compost, zero valent iron, limestone, and pea gravel was used, which proved to effectively retain As, Pb, Cd, Zn, and Ni (Ludwig et al., 2009). PRB could be an option at the studied mine sites to eliminate potentially toxic elements from the groundwater, as contaminant plumes have been inferred at both sites. The oxidation and acid-neutralization reactions imply that a plume of low quality waters is forming at the Haveri tailings, but water in the tailings moves slowly. However, groundwater discharge may occur below the dam structure at Haveri. At Ylöjärvi, toe seepage and groundwater discharge have been reported (Kumpulainen et al., 2007; Article III). Both tailings sites have a relatively limited scale, allowing the construction of a PRB surrounding the piles, but prior to the implementation of a PRB a hydrological study is required to delineate the flow directions. Depending on the characteristics of the drainage waters, a PRB can work without any maintenance in excess of a decade before requiring replacement of the reactive material placed in the barrier (Benner et al., 1999; Mayer et al., 2006), and some PRBs installed in the 1990s are still operating, despite approaching 20 years of operation (personal communication of D.W. Blowes). As suggested earlier, groundwater and pore water sampling is also recommended at Haveri to better evaluate the water quality within the impoundment and in its surroundings. Implementation of a PRB requires little short-term maintenance, although periodic groundwater monitoring at both sites is recommended. Major work is only required once the effectiveness of the PRB reduces and the reactive material needs to be replaced and treated as contaminated waste.

The United States Environmental Protection Agency, USEPA, (http://www.epa.gov/) lists *in situ* chemical oxidation technologies for the elimination of organic contaminants from groundwater. For inorganic contaminants, Sen Gupta et al. (2009) describe a technology for subterranean arsenic removal based on oxygenating the infiltrated water. Groundwater oxidation promotes the oxidation and hydrolysis of Fe. The oxidation of Fe(II) and As(III) is enhanced by subsurface bacterial activity, and subsequently As (V) is adsorbed on Fe(III) (oxy)hydroxides. This method does not produce sludge, and As is stored *in situ*, but to prevent the destabilization and desorption of As the system must be maintained under suitable redox conditions. The implementation of groundwater oxidation could be an option at Ylöjärvi, where Fe and As are accumulated in the groundwater beneath the tailings. This method is low-cost and the maintenance efforts are low, though periodic maintenance and monitoring are required over an extended period.

Health and ecological risk assessment, performed at the Ylöjärvi mine during RAMAS project, indicated that health risks arising from the contamination of the water system are expected to be insignificant owing to the lack of significant exposure routes (Sorvari et al, 2007). However, the authors reported that the environmental effects extend over a large area, reaching both terrestrial and aquatic ecosystems. Furthermore, they are not expected to decrease within a reasonable time considering the amount of arsenic stored in the tailings unless risk management actions are undertaken.

In conclusion, detailed assessment of the need for remediation actions and the selection of adequate methods is recommended for the Haveri and Ylöjärvi tailings. The acidity and elevated concentration of divalent metals in surface waters (and probably in the groundwater beneath the impoundment) affected by AMD at Haveri and elevated concentrations of As in the surface and groundwater at Ylöjärvi should be mitigated. In addition, access to, as well as professional and recreational use of the mining premises at both sites should be restricted. At Haveri, dirt biking should definitely be prevented, while at Ylöjärvi, the Finnish Defence Forces ought to consider giving up the testing of explosives in the tailings area to prevent dusting and the transport of particles through air to the surroundings. Swimming in Lake Parosjärvi should be prohibited, especially for children, and the nearby groundwater wells for household use should be regularly monitored to exclude the possibility of ingestion of As-contaminated water.

5.4 Reflections on the research hypotheses

The research hypotheses set at the beginning of the work are analyzed here, answering the research questions listed earlier in Section 1.1.

1. *Mine tailings of limited extension characterized by a low sulfide content and low neutralization capacity produce AMD and they have significant and long-term environmental impacts locally.*

- Tailings facilities with low sulfide and low carbonate contents tend to generate acidic and metal(loid)-rich drainage waters. After half a decade, Co, Cu, Ni, Zn and SO_4 persisted in the effluents of the Haveri tailings, whereas As was the principal contaminant at the Ylöjärvi mine, with concentrations well above (three orders) the threshold values for drinking water.

2. *At decommissioned tailings sites, natural attenuation processes govern the quality of the modern drainage water.*

- Sulfide minerals in tailings areas that have been exposed to air and meteoric water for extended periods tend to oxidize and mobilize potentially toxic elements and sulfate. However, through hydrolysis, Fe(III) precipitates accumulate under favorable conditions, retaining As and divalent cations. The precipitation of these minerals is especially important in superficial, highly oxidized layers retaining potentially toxic elements from surface runoff. However, it was observed in this study that the low quality waters tend to migrate within the pore spaces downwards to the groundwater.

3. Comprehensive mineralogical and geochemical research is crucial to understanding the stability of Fe(III) minerals carrying potentially toxic elements and their impact on the potential for attenuation at abandoned mine tailings.

- The importance of understanding the mineralogy and geochemistry of mine tailings was apparent in assessment of the source of contamination and the secondary phases. Detailed mineralogical observations allow more specific evaluation of the stability of the secondary phases and which elements they carry by adsorption or co-precipitation. Geochemical studies of solid samples also proved important, because they provide insights into the chemical distribution of the potentially toxic elements and their possible mobility. Aqueous geochemistry, on the other hand, is indicative of elements mobilized from the tailings solids and allows thermodynamic calculations for chemical speciation and saturation characteristics. All this contributes to better understanding of the system and its stability.

4. Multidisciplinary and site-specific research is required before selecting appropriate remediation techniques at abandoned mine sites. Mineralogical and geochemical data are mandatory in decision making.

- It was emphasized that site-specific studies are mandatory at mining sites. The Haveri and Ylöjärvi mines are located at same climatic and vegetation zone and even geologically they are situated in a similar belt (TSB), consisting of metavolcanic and metasedimentary rocks cut by plutonic intrusions. Additionally, the tailings material may superficially appear similar, with low sulfide and carbonate contents. However, the ore deposits are very different and the primary mineralogy principally dictates the potential for certain contaminants. Consequently, the characteristics of AMD were very different at each site. *Hypothesis 3* showed the importance of mineralogical and geochemical studies, and when combined with data from other disciplines, such as hydrogeology and geophysics, these give a solid premise for the assessment of rehabilitation requirements and techniques.

5. Decommissioned tailings can be a resource for the future exploitation of valuable elements.

- One of the aims of the EU Raw Material Initiative (Finland's mineral strategy, http://www.mineraalistrategia.fi/) is to promote recycling and facilitate the use of secondary raw materials. The EU Raw Material Initiative lists critical raw materials, and their potential source could be the recycling of abandoned mine tailings. The Haveri tailings were earlier investigated for Au potential by a mining company, but they proved unprofitable at that time. Thus, early in the investigations the research scope was narrowed to environmental aspects of abandoned mine sites, and this hypothesis was not therefore addressed here.

6. Summary and Conclusions

In this doctoral dissertation, the extent and character of tailings oxidation, as a source of acid mine drainage (AMD), and the precipitation of secondary Fe(III) phases, as an important element of natural attenuation, were studied by means of mineralogy and geochemistry at the decommissioned Haveri Au–Cu and Ylöjärvi Cu–W–As mine tailings. A combination of traditional mineralogical methods together with novel synchrotron-based techniques, as well as a description of the geochemical distribution of elements by sequential extractions allowed a comprehensive characterization of the mine tailings. In addition, the chemistry of pore water, surface water and groundwater, and the geophysical characteristics of the tailings, as well as sediment records from lakes receiving AMD were studied to evaluate the mobilization and transport of potentially toxic elements. The geochemical data on water composition and the geochemical code PHREEQC allowed the identification of thermodynamically oversaturated phases. The stability of the Fe(III) minerals and their potential for trapping and/or releasing potentially toxic elements was assessed. As a whole, these investigations illustrated the past events that have led to the contamination derived from the mine tailings, and provide implications for the stability of the present system.

The investigations showed that decommissioned low-sulfide mine tailings may have severe environmental impacts on their surroundings, even though natural attenuation mechanisms mitigate the metal loading of the drainage water transported to adjacent surface water and groundwater bodies. Lake sediment records revealed that elemental mobilization from both Haveri and Ylöjärvi tailings areas has decreased and stabilized at a level slightly exceeding the natural background levels. At both sites, the surface tailings had undergone extensive sulfide oxidation, contributing to the generation of AMD and elemental mobilization. The dissolved elements (As, Cu, Co Zn, SO_4) were partly retained in secondary Fe(III) minerals, and accumulations of these minerals were found in cemented layers. As, in particular, was found to be associated with cemented layers at both sites, proving their importance as a natural attenuation mechanism. In the Haveri tailings, jarosite and goethite were found to trap As, Cu and SO_4 in the acidic (pH 2.5–3.5) environment, whereas in the Ylöjärvi tailings, arsenical ferrihydrite, HFA, scorodite, and kaňkite retained As, Cu, Co in the mildly acidic to neutral conditions (pH 4.9–8.9). Scorodite and kaňkite are metastable under the current conditions.

Despite the attenuating effect of secondary Fe(III) minerals, elevated concentrations of trace metals, As and SO_4 were detected in tailings pore water, surface waters surrounding the tailings areas and in groundwater below the tailings heap. A plume of low quality waters is forming within the central, highly oxidized Haveri tailings, whereas Fe and As have accumulated in the groundwater beneath the Ylöjärvi tailings and are also discharged through toe seepage in all directions from the tailings heap.

Studying abandoned mine sites helps in understanding their evolution and long-term site-specific environmental impact in order to avoid repeating past malpractices in current and future mines. This study also provides crucial information for the planning of a rehabilitation scheme for abandoned mine sites, providing the implications for the current conditions in the tailings and for what measures will keep the system stable and mitigate future contamination.

At the Haveri mine, the elemental mobilization peaked after the active mining period, and contamination was derived from AMD. This finding implies that the environmental effects of mining can be significantly reduced by exhaustive design and maintenance of mine waste facilities. Maintaining tailings saturated with water, or otherwise insulating tailings from oxygen and meteoric water, and constructing an impermeable dam and basal structure is necessary to mitigate the action and consequences of sulfide oxidation processes. A recent Ph.D. dissertation addressing the formation of contaminated drainage waters at two active mine sites in Finland highlights that, even in low-sulfide tailings, sulfide oxidation processes commence producing AMD shortly after continuous disposal ceases (Heikkinen, 2009). Preventing the diffusion of oxygen and altering the groundwater level in tailings areas that have experienced an advanced stage of oxidation may induce the dissolution of secondary Fe(III) minerals due to reductive or acid dissolution. At the Ylöjärvi mine, on the contrary, major contamination peaks were recorded during mining, implying that avoiding malpractice in waste and water management plays an important role in controlling the environmental impacts of the actual mining processes.

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