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TECHNICAL ARTICLE

Tailings Mineralogy and Geochemistry at the Abandoned Haveri Au–Cu Mine, SW Finland

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Abstract Fourteen samples from the Haveri Au–Cu mine tailings were studied by reflected-light microcopy, scanning electron microscopy, X-ray powder-diffraction, and sequential extraction methods, and 12 water samples were analyzed for total and dissolved elements to delineate the extent of sulfide oxidation and its impact on nearby surface waters. Water-soluble, adsorbed-exchangeable-carbonate (AEC), Fe (oxy)hydroxides, Fe oxide, and Fe sulfide fractions were extracted sequentially. The oxidation layer was found to vary from 50 to 140 cm: the upper part was nearly depleted in primary sulfides, especially pyrrhotite [$Fe_{(1-x)}S$] and pyrite (FeS_2); in the lower part, discontinuous cemented layers were detected. Secondary Fe (oxy)hydroxides and Fe oxyhydroxysulfates were abundant in the oxidation layer and were slightly enriched in trace elements, including As (up to 80 mg/kg), Cu (300 mg/kg), and Zn (150 mg/kg). Almost half of the As (average 25 mg/kg) were present as secondary minerals susceptible to redissolution. The pH of the vadose tailings varied from 2.46 to neutral, and the total sulfur content varied from 1 to 6.5% (average 2.9%). *Aqua regia* extraction showed that the Haveri tailings are characterized by low concentrations of the elements Cd, Cr, Pd, and slightly elevated concentrations of As, which are present at very low concentrations in the surface water (<6 μg/L). However, runoff that flows on top of the tailings and discharges into the nearby lake carries Co, Cu, Ni, and Zn (concentrations of each range from 500 to 1,800 μg/L). Additionally, dissolution of sulfides and Fe precipitates may mobilize trace metals in the ground water. Thus, overall, there is a small continuous release of AMD into Lake Kirkkojärvi, but the environmental impacts to the lake are presently small.

Keywords Acid mine drainage · Geochemistry · Mineralogy · Mine tailings · Sulfide oxidation

Introduction

Acid mine drainage (AMD) caused by oxidative weathering of sulfide minerals in mine tailings poses a contamination risk to surface water, ground water, and soils. Sulfide oxidation releases acidity, ferrous iron, trace metals, and sulfate. The contamination potential of mine tailings is affected by many factors, including the type of ore, primary mineralogy, tailings pile geometry, remediation measures, and prevailing physico-chemical conditions. Cemented layers or hardpan formations may contribute to the natural attenuation processes within tailings impoundments (Blowes et al. 1991; Graupner et al. 2007; Moncur et al. 2005), since they contain secondary iron precipitates that can adsorb and co-precipitate trace metals and arsenic. However, these accumulations may be transitory, leading to subsequent release of potentially toxic elements. Tailings that contain pyrrhotite [$Fe_{(1-x)}S$] are more likely to form cemented layers than pyrite (FeS_2)-rich tailings because of the greater reactivity of pyrrhotite (Alakangas and Öhlander 2006, and two references therein: Agnew and Taylor 2000; Ahmed 1995).

Selective and sequential extraction methods are widely used in studying mine tailings (Alakangas and Öhlander 2006; Carlsson et al. 2002; McGregor and Blowes 2002; Heikkinen and Räisänen 2008; Ribet et al. 1995). Their accuracy and selectivity have been criticized (Hall et al.

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1996; McCarty et al. 1998), as they depend on many factors such as chemicals applied, the procedure conditions (time, temperature, and exposure to light), and the sample to volume ratio. However, Dold (2003) compared the results of a detailed mineralogical study by X-ray diffraction (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.

The abandoned Haveri Au–Cu mine was chosen as study site because no prior studies had been conducted at this site and because it is located near Lake Kirkkojärvi and the village of Viljakkala. The aim of the work was to clarify the mineralogy and geochemistry of the Haveri tailings and the mechanism of metal transport to the surrounding surface waters. The geochemical characteristics of the tailings 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 and also on the neutralization potential of the primary mineralogy of the tailings.

Site Description

The Haveri formation consists of tholeiitic metabasalts, mafic metatuffs, and intermediate metatuffites. The ore is considered to be a volcanic-exhalative Cyprus-type sulfide deposit (Mäkelä 1980; Nironen 1994). The Haveri Au–Cu mine was active from 1942 to 1961 and produced over 1.5 million tonnes of mill tailings (Puustinen 2003). The tailings were piled in a bay of Lake Kirkkojärvi between the mining area and the small former island of Peltosaari (Fig. 1). The village of Viljakkala (pop. about 2000) is located less than half a kilometer from the tailings impoundment, which covers an area of 18.4 ha. The average depth of the tailings is 6.5 m, varying from 2 to 9 m, and the underlying lake sediments consist of silt and clay. The impoundment is surrounded by a dam constructed of the topsoil that covered the Haveri ore deposit and the wall rock. While the southern and southeastern parts of the dam are intact, the northeastern edge of the dam is broken at two locations, and during the final stages of mining, the tailings were dumped in Lake Kirkkojärvi outside the dam. Yet a second dam further north was never built. In places, therefore, the tailings are in direct contact with the lake water.

The small ditches on the northern and southern sides of the dam discharge water into the lake. The bottom of the northern ditch contains a mixture of natural subsoil and tailings. Additionally, since the impoundment topography slopes to the northeast, rain and meltwater run toward the lake from the point where the dam is broken. Gullies, a half to one meter deep, have formed on top of the tailings, channeling the meteoric water toward the lake. The central area of the impoundment is backfilled with gravel and is partially covered with asphalt. This area was used as a rally track in the 1980s to 1990s. Some parts of the impoundment are covered by stunted vegetation of birches, willows, and grass, but the major part of the impoundment is barren. 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.

Materials and Methods

Tailings Sampling

Forty drill cores were collected in May 2006 from the 18.4 ha tailings area. Samples were collected at one meter intervals from these cores, from the surface to the underlying silt and clay subsoil. These samples were analyzed for mineralogy and total sulfur content, and were leached using *agua regia.*

Fourteen additional tailings samples were collected for mineralogical and geochemical studies in May 2007 from three test pits at the sites of three of the drill cores (Fig. 1). These samples were collected in sealed 15 cm long, 5 cm diameter plastic tubes at defined intervals (every half meter) or when changes in structure, hardness, etc. were detected, from the surface to the top of the water table. All samples were frozen for transport to the laboratory where they were dried at room temperature. Small amounts of tertiary minerals, mainly soluble salts (Jambor 1994) formed from the drying pore water, may have deposited.

Mineralogical Study

Fifteen rock samples were selected from cores drilled into the Haveri formation bedrock (which were available at the National depot for diamond drill core, which is operated by the Geological Survey of Finland). These, along with 20 of the samples collected from the 2006 tailings cores and 27 samples selected from the tailings collected from the test pits in 2007 were studied with an optical microscope under reflected-light, a scanning electron microscope equipped with energy dispersive spectrometry (SEM–EDS), and electron microprobe analyses (EMPA). Six test pit samples were also studied using step-scan X-ray powder-diffraction (XRD). 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 LEO 1450 SEM–EDS was equipped with a W-cathode, and a

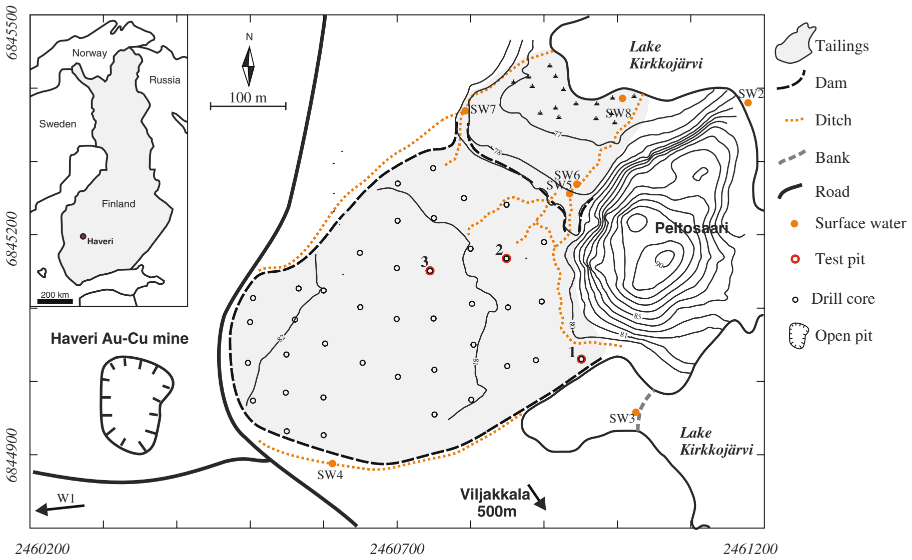

Fig. 1 Map of the Haveri mine area presenting the surface water, test pit, and drill core sampling points (*SW* surface water, *W* ground water)

four-quadrant solid state backscatter detector at the Helsinki University of Technology. For EMPA with a Jeol JXA-8200 electron microprobe with five spectrometers at Bayerisches Geoinstitut at the University of Bayreuth in Germany, the acceleration voltage was set to 20 keV and the beam current to 20 nA. The counting time was 30 s on the peak position and 15 s on the background. The polished sections were carbon coated. 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°. Grain size distribution and specific surface area of four samples were studied with a Malvern 2000 laser diffractometer and by BET, respectively.

Geochemical Study

The tailings pH was measured in test pit samples according to standard method SFS-ISO 10390. Dried tailings solids were mixed with 1 M KCl solution at a ratio of 1:5. The mixture was shaken for 1 h and allowed to settle for 1 h before measurement of pH with a WTW pocket pH meter 340i equipped with a reference Ag–AgCl electrode. Pore water content is expressed as weight percent of the dry mass of tailings versus total mass.

For geochemical studies, the tailings samples were sieved to <0.063 mm fraction. *Aqua regia* leaches (Koljonen 1992) were performed for a total of 20 samples selected from the 40 drill cores to assess the total metal contents and metal distribution in the tailings. This method extracts all fractions except the more inert silicates, and it can be considered as a near total dissolution for most of the sulfide-forming elements. These results can be taken, therefore, as the sum of the elemental contents of the five extraction steps. The *aqua regia* leachates were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sr, Ti, V, and Zn. Additionally, the total sulfur content was measured for 79 drill core samples using an Eltra CS-2000 sulfur analyzer.

Fourteen test pit samples were subjected to sequential extraction (modified from Dold 2003 and Hall et al. 1996).

The five-step extraction procedure was initiated with a water leach ("water-soluble", Table 1). This was done to differentiate secondary gypsum ($CaSO_4{\cdot}2H_2O$) from calcite ($CaCO_3$), which is extracted in the second step. The great neutralization potential of calcite makes its detection important. The second extraction (adsorbed-exchangeable-carbonate, "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 step three ("Fe (oxy)hydroxides"), separately from primary iron oxides. Some residual Fe(III) (oxy)hydroxides were leached together with iron oxides in the fourth step "(Fe oxides"). Primary and supergene sulfides and organics were extracted in the final step ("sulfides"). The samples were analyzed by ICP-AES for the same elements as the *aqua regia* leachates. Ten reagent blank samples and one sample in triplicate were analyzed to evaluate the quality and repeatability of the analytical results.

Table 1 Summary of the five-step sequential extraction

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, secondary sulfates, e.g., gypsum	Dold (2003)
Step 2 "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 3 "Fe(oxy)hydroxides"	Residue 2 + 0.2 M $(NH_4)_2C_2O_4$ shake for 1 h in the dark, at RT	Amorphous Fe(III) precipitates, e.g., schw, fer, jt, go, MnO_2	Dold (2003)
Step 4 "Fe oxides"	Residue 3 + 0.2 M $(NH_4)_2C_2O_4$ in water bath at 80° for 2 h	Residual Fe(III) precipitates (e.g., go, jt) and primary Fe(II) 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)

RT room temperature, *AEC* adsorbed-exchangeable-carbonate, *schw* schwermannite, *fer* ferrihydrite, *jt* jarosite, *go* goethite, *mgt* magnetite, *hem* hematite

The sequential extraction procedure was carried out as follows.

First step: The water leaching step was performed by placing 1.000 g of sample in a 50 mL screw-cap centrifuge tube with 25 mL of deionized water followed by shaking for 1 h at room temperature (RT). After centrifuging, the leachate was transferred into a labeled test tube and the procedure was repeated.

Second step: The residual sample from the first step was mixed with 20 mL of 1.0 M sodium acetate (CH_3COONa, pH 5). The tube was shaken for 6 h at RT and centrifuged, and the leachate was recovered. The solid residue was washed twice with 5 mL of deionized water and the washing water was recovered and added to the leachate.

Third step: 20 mL of 0.2 M ammonium oxalate [$(NH_4)_2C_2O_4$, pH 3] was added to the residue from the second step and shaken in darkness at RT for 1 h. The mixture was then centrifuged and the leachate was recovered. Washing of the sample was performed as in the previous step.

Fourth step: 20 mL of 0.2 M ammonium oxalate (pH 3) was added to the residue from step three and the mixture was heated in a water bath at 80°C for 2 h. The solution was centrifuged, the leachate was recovered, and the residue was rinsed twice.

Fifth step: 750 mg of $KClO_3$ and 5 mL of 12 M HCl were added to the residue from step 4 and then a further 10 mL of HCl was added. After 30 min, 15 mL of water was added, the test tube was shaken, and the mixture was centrifuged. The leachate was removed and the residue was mixed with 10 mL of 4 M HNO_3 and heated in a water bath at 90°C for 20 min. The mixture was centrifuged and the leachate was added to the previous leachate and the residue was again rinsed twice. After each step, the labeled test tubes were filled to 50 mL with water. Before analysis, each solution was filtered through a 0.45 μm membrane filter.

The data from the sequential extractions was used to evaluate the amount of sulfide-bound elements and S already released by weathering of the tailings: the difference in elemental concentration in the sulfide fraction of oxidized tailings with unoxidized tailings was multiplied by the mass of oxidized tailings to date.

Water Sampling and Analysis

A total of 12 water samples were collected (Fig. 1) during two sampling campaigns in May 2006 (sampling points 1, 2, 3, 4, 5 and 6) and May 2007 (1, 2, 3, 4, 7, and 8). Sample 1 is taken from a 5 m deep ground water well, samples 2, 3, and 8 from Lake Kirkkojärvi, and samples 4–7 from ditches that run to Lake Kirkkojärvi. The ground water well located just less than one kilometer from the mining area is the only domestic ground water supply in the vicinity and it is used only as a supplementary water source. Sampling points 1–4 were the same in the two campaigns. Sampling points 5 and 6 could not be resampled the second year because that small ditch was dry. Alternative samples, 7 and 8, were taken the second year. The water samples from 5 to 8 were in direct contact with the tailings material. Three sets of water 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. 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, which were digested with HNO_3 before analysis. Redox potential (Eh) and pH were measured in situ with a Mettler Toledo MP125 portable pH/Eh 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 dissolved oxygen (DO) content were measured with a WTW multiline P4 Pocket Meter. The 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. Trace metal concentrations were determined by inductively coupled mass spectrometry (ICP-MS) and major elements by ICP-AES. The elements analyzed were Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Th, Tl, U, V, and Zn.

Results

Quality Assurance

The reagent blanks displayed concentrations of major elements and trace elements below detection limits. Repeatability in the analysis of the triplicate samples that underwent the entire sequential extraction procedure was good, with relative standard deviation values, %RSD, generally below 3.0, confirming the quality of the analyses. This also demonstrated that the samples were representative, and that the sequential extraction methods were comparable between samples.

Tailings Characterization

The drill core samples displayed layering with an oxidized upper layer and a less altered lower transition layer in the vadose zone, and a water-saturated layer roughly below 200 cm. The oxidation zone occurred from the surface to a depth of 50 cm in test pits 1 and 2, and to 140 cm in test pit 3. The oxidized surface layer was characterized by yellowish brown, ochreous colors at the top and greenish or grayish brown colors below. The transition zone and the water-saturated tailings were grayish black. Discontinuous cemented layers 2–5 cm thick were detected at the lower part of the oxidation layer. In test pit 2, the cemented layer was situated at a depth of about 40 cm, while in test pit 3, cemented layers were detected at depths of about 40, 135, and 155 cm (Table 2). The layer at 135 cm was most consolidated. The samples from test pit 1 had the highest pH values, 7.11 and 7.29 in samples 1c and 1d, respectively; samples from test pits 2 and 3 had an average pH of 3.10, ranging from 2.46 to 3.86 (Table 2).

The grain size of the four tailings samples ranged from 1 to 850 μm, with silt and fine sand fractions most abundant. The silt fraction of the samples from the oxidation zone (3a, 3c, and 3d) constituted the major part of the grain size distribution (41% on average), while in the sample from the transition zone (3f), it merely added up to 10%. Sample 3f consisted mainly of very fine to medium sand. Grain size separation and stratigraphic layering was present throughout the tailings. Specific surface area data for these samples are presented in Table 2.

The drill cores collected from the southern and southeastern parts of the impoundment, close to the dam, had the highest moisture content. The samples from test pit 1 contained an average of 25 wt% pore water; samples from test pit 2 contained 21 wt% pore water (Table 2). The samples from test pit 3 had 12 wt% pore water, with the lowest water content found in the cemented layer at 135 cm depth. The water table was the lowest in the central area around test pit 3, where it was encountered below 2 m (Table 2). At the bottom of the impoundment, the tailings are in contact with the natural soil (consisting of silt and clay), which hinders water flow and isolates, to some extent, the impoundment from beneath.

Tailings Mineralogy

The main sulfides found in the Haveri tailings were pyrrhotite and pyrite. Chalcopyrite ($CuFeS_2$) was scarce, and magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$) were the only oxides found. Sulfides exist primarily as separate grains, but are also intergrown with silicates. According to Paarma (1947, cited in Mäkelä 1980), minor ore minerals occurring in the Haveri formation include cobaltite (CoAsS), glaucodote [(Fe, Co)AsS], gersdorffite (NiAsS), arsenopyrite (FeAsS), sphalerite (ZnS), molybdenite (MoS_2), tellurobismutite (Bi_2Te_3), and hessite (Ag_2Te). The XRD data demonstrated that the main gangue minerals are hornblende, albite, quartz, microcline, and clinochlore, while biotite appeared only in three less altered samples. Titanite, epidote, apatite, zircon, and chert appear as accessory minerals in the Haveri formation (Paarma 1947), yet they were not detected in the mineralogical studies. Calcite occurs as thin layers and vein fillings in the Haveri formation (Mäkelä 1980), and small amounts of calcite and dolomite [$CaMg(CO_3)_2$] were detected by XRD in the tailings sample from test pit 1. Sulfide minerals are almost depleted in the upper oxidized zone of the tailings; the secondary iron precipitates are responsible for the brownish to yellowish color. The middle cemented layer contains altered sulfide grains that have been replaced by Fe (oxy)hydroxides and Fe oxyhydroxysulfates, varying in composition from a sulfur-rich core to sulfur-poor and iron-oxygen-rich rims (Fig. 2a–c). Secondary iron precipitates also appear as coatings on other grains. In the transition zone, pyrrhotite and pyrite show slight alteration on grain boundaries, and Fe precipitates coat the grains. Sulfides in the saturated zone do not show alteration rims. The mineralogical studies failed to identify the iron (oxy)

Table 2 Sample depths, pH, water content, and specific surface area of the tailings samples from the test pits

Sample	Depth, cm	pH	Pore water, %	Specific area, m^2/g	X-ray diffraction	Notes
1a	5–20	4.29	22.96			Oxidation layer 50 cm
1b	50–65	4.27	25.47			Ground water level 170 cm
1c	100–115	7.11	24.53		x	
1d	150–165	7.29	25.31			
2a	0–15	2.99	19.69		x	Oxidation layer 40 cm
2b	35–50	3.29	21.46		x	Cemented layer 40 cm
2c	100–115	3.86	21.26			Ground water level 180 cm
2d	150–165	3.50	20.00			
3a	0–15	3.08	11.67	7.78		Oxidation layer 140 cm
3b	35–50	2.46	10.68		x	Cemented layers 40, 135, and 155 cm
3c	100–115	2.88	13.39	13.25	x	Ground water level 215 cm
3d	135–145	2.79	9.81	1.38	x	
3e	150–165	3.24	14.46			
3f	200–215	2.99	12.00	0.28		

hydroxides; the hydrous character of these minerals makes microanalysis difficult and the poor crystallinity and very fine grain size obscures the XRD spectrum of these minerals. However, gypsum, jarosite [$KFe_3(SO_4)_2(OH)_6$], and elemental sulfur were detected by XRD. Euhedral gypsum crystals, visible to the naked eye in the field, were detected in test pits 2 and 3 (Fig. 2d). During drier periods, gypsum also precipitates on top of the tailings as a white coating due to capillary transport of Ca to the surface. Jarosite was detected in samples 2a–b and 3b–d, though the XRD data suggested the presence of hydronium jarosite [$(H_3O)Fe_3(SO_4)_2(OH)_6$] in sample 3d, indicating hydronium substitution by K. Scarce secondary covellite, CuS, was detected using a reflected-light microscope and by SEM (Fig. 2c). Study of the tailings samples by SEM and EMPA demonstrated that arsenic does not appear in either pyrrhotite or pyrite; it is present only in sulfarsenides, such as arsenopyrite, cobaltite, glaucodote, and gersdorffite. The mineralogical composition of the tailings samples varies laterally and vertically because of the variation in the exploited and enriched ore.

Tailings Geochemistry and Metal Release

Aqua regia leaching indicated that total metal concentrations in the tailings vary as follows: As 29–510 mg/kg, Cd 1.5–7.0 mg/kg, Co 24–329 mg/kg, Cr 28–74 mg/kg, Cu 246–3,280 mg/kg, Fe 4–18 wt%, Ni 25–145 mg/kg, Pb 6–22 mg/kg, Ti 2,670–5,380 mg/kg, V 132–329 mg/kg, and Zn 24–323 mg/kg. The values show that Cd, Cr, and Pb (average values of 3, 42, and 10 mg/kg, respectively) do not exist in high concentrations in the Haveri tailings. However, As and Cu concentrations (average values of 158 and 831 mg/kg, respectively) are above the upper guideline value for contaminated soils, 100 and 200 mg/kg, respectively, set in the Degree of Finnish Council of State (Table 3). At places, concentrations of Co and V exhibited higher values than the upper guideline value (Table 3). The results of *aqua regia* leach and the total sum of sequential extractions for sample 1c are compared in Table 4. The total sulfur content of the tailings varied from less than 1–6.5% with an average of 2.9%.

The elemental distributions of the sequential extractions are presented in Fig. 3. On average, the amount of elements leached in the first step was 7 g/kg; in the second step, 3 g/kg; in the third step, 9 g/kg; in the fourth step, 33 g/kg; and in the fifth step, 133 g/kg. The sequential extraction data clearly shows the weathering of sulfide minerals from the near-surface samples. The calculated amount of sulfide-bound metals and S leached from the oxidized tailings so far is approximately 690 kg As, 70 kg Cd, 4,500 kg Co, 210 kg Cr, 14,700 kg Cu, 1,330 t Fe, Mo 220 kg, Ni 4,330 kg, 110 kg Pb, 6,000 kg Zn, and 2,070 kg S. The true amount is probably much higher because this calculation represents the uppermost 15 cm, which is depleted in most sulfide-bound metals, while sulfide oxidation has progressed deeper in the central area of the tailings.

Iron is present as secondary precipitates, primary oxides, and sulfides. The highest iron concentration in the Fe (oxy)hydroxide fraction occurs in the cemented layer in sample 3d. In general, the surface samples contained less Fe in the sulfide fraction than did the deeper samples. Sulfur was also depleted in the primary sulfide fraction in sample 1a, and signs of S depletion were seen in near-surface samples 1b, 2a–b, and 3a–b. The proportion of S in the sulfide fraction was generally over 10 times greater in the deeper samples than in the surface samples. S was also present in the water-soluble fraction, primarily from

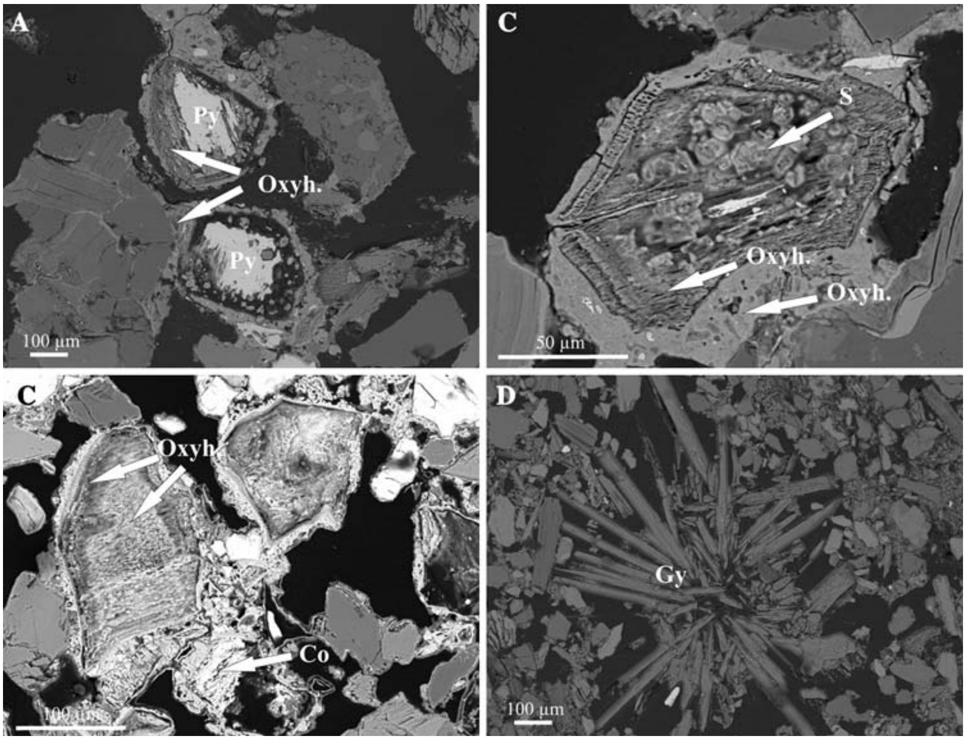

Fig. 2 Backscattered images of: **a** altered sulfide grains replaced by secondary iron precipitates in sample 3d; **b** sulfide grain almost completely replaced by secondary Fe precipitates and by elemental sulfur in sample 3d; **c** secondary iron (oxy)hydroxides and covellite; and **d** euhedral gypsum crystals in sample 3b; *Co* secondary covellite, *Gy* gypsum, *Oxyh* Fe (oxy)hydroxides, *Py* pyrite

Table 3 Comparison of the results of the *aqua regia* dissolution and the lower and upper guideline values for contaminated soils set in the Degree of Finnish Council of State

Element	*Aqua regia*, mg/kg				Lower guideline value, mg/kg	Upper guideline value, mg/kg
	Min	Max	Average	Median		
As	29	510	158	113	50	100
Cd	1.5	7.0	3.1	2.0	10	20
Co	24	329	115	90	100	250
Cr	28	74	43	41	200	300
Cu	246	3,280	831	679	150	200
Fe	40,000	180,000	107,000	98,000	–	–
Ni	25	145	79	88	100	150
Pb	6.3	22	10	9.7	200	750
V	132	329	208	201	150	250
Zn	24	323	140	141	250	400

extraction of gypsum, and to some extent in the AEC fraction in test pit 3.

Water-soluble Ca was present in all samples as gypsum, and was most abundant in samples from test pit 3. Ca and Mg extracted from calcite and dolomite in the AEC fraction, in turn, were present in significant amounts only in samples from test pit 1. In general, Mg and Mn occur in the less soluble fractions, but in test pit 1 they are also present in the AEC fraction. The presence of Ca, Mg, and Mn in the sulfide fraction shows that some silicate minerals are dissolved together with primary sulfides in the final extraction step.

The elements associated with sulfide and sulfarsenide minerals (Cu, Zn, Co, and Ni) were generally depleted in near-surface samples in the oxidation zone. Copper did not show a clear trend, but it appeared mainly as a primary phase, probably chalcopyrite. In test pit 3, however, a notable proportion of Cu was present in the water-soluble fraction (up to 623 mg/kg) and bound to Fe (oxy)hydroxides (295 mg/kg). Cu (<1 wt%) was also detected in the Fe (oxy)hydroxides by SEM. The primary phases of Co, Ni, and Zn are oxidized in the near-surface, and are almost depleted in samples 1a, 2a, and 3a–c. Co and Ni exhibit similar trends in the sequential extraction data: they are extracted primarily in the water-soluble and sulfide fractions and appear in highest concentrations in the lower levels of test pit 3 (total values >400 mg/kg). The maximum values of Co and Ni in the secondary iron precipitates

Table 4 Comparison of the results of the *aqua regia* dissolution and the total sum of sequential extractions for sample 1c

	Aqua regia, mg/kg	Sequential extractions, mg/kg	Difference %
Al	15,800	8,600	+46
As	115	21.1	+82
Ca	13,200	15,400	−17
Cd	2.73	1.02	+63
Co	99.4	60.8	+39
Cu	303	287	+5
Fe	42,100	40,700	+3
Mg	11,500	9,024	+22
Mn	317	347	−9
Ni	86.8	85.6	+1
Zn	141	150	−6

(in both Fe (oxy)hydroxide and Fe oxide fractions) were 44 and 68 mg/kg, respectively.

Arsenic was not present in the water-soluble or AEC fractions, but appeared mainly in the primary phases. The portions of As in the Fe (oxy)hydroxide fraction were generally less than 20% of the total concentration, yet As content in this fraction was most abundant (50%) in the b-samples of the test pits, which were taken from a depth of about half a meter. As with the *aqua regia* leach, Cd, Cr, and Pb appear only in minor concentrations in the sequential leach solutions of the Haveri tailings. Maximum concentrations in the sulfide fraction were 2.8 mg/kg of Cd, 36 mg/kg of Cr, and 35 mg/kg of Pb.

Potassium was present in secondary phases in the Fe (oxy)hydroxide and Fe oxide fractions (average 2,500 mg/kg), particularly in the oxidized zone and in the AEC fraction (average 730 mg/kg) in the transition zone.

Surface Water Geochemistry

The dissolved and total concentrations of elements and the physico-chemical conditions in the ground and surface water samples are presented in Tables 5 and 6, respectively. Sample 1, from the ground water well, displayed low metal concentrations. Despite its proximity to the mine site, the well is not affected by the mining activities as it obtains its water from a different aquifer. Samples 2–4 also exhibited relatively low metal concentrations (Cd, Cr, As, Pb were less than 2 µg/L, and Co, Cu, Zn were less than 26 µg/L). Total concentrations of Ni were slightly elevated (33.8 µg/L) in the ditch at sampling point 4. Sampling points 5 and 6 are seasonally dependent; there is active transport of contaminants to the lake only during rainy periods. Especially in spring, the melt waters channel through the break in the dam, and flow in small rivulets atop the tailings. Relative to samples 2-4, samples 5 and 6 showed higher dissolved concentrations of Co (736 and 722 µg/L, respectively), Cu (1,670 and 1,660 µg/L), Fe (6.62 and 8.21 mg/L), Mn (5,740 and 5,670 µg/L), Ni (692 and 708 µg/L), Sr (288 and 331 µg/L), Zn (753 and 763 µg/L), and SO_4 (1,030 and 1,170 mg/L). Similarly, samples 7 and 8 contained higher dissolved concentrations of Co (583 and 843 µg/L, respectively), Cu (1,110 and 946 µg/L), Fe (5.61 and 47.3 mg/L), Mn (7,230 and 2,560 µg/L), Ni (520 and 913 µg/L), Sr (309 and 267 µg/L), Zn (918 and 821 µg/L), and SO_4 (778 and 1,150 mg/L). In general, the total concentrations of metals were higher than the dissolved concentrations. However, Zn repeatedly had lower total than dissolved concentrations (Table 5). Concentrations of As, Cd, Cr, and Pb (<6 µg/L) were very low, even in samples 5–8, which are characterized as AMD. Sulfate content was slightly elevated in samples 3 and 4 (113–417 mg/L), and much higher in samples 5–8 (up to 1,170 mg/L).

Discussion

Oxidation Zone and Mineral Alteration

According to the mineralogical and geochemical studies, sulfide oxidation is active in the vadose zone of the tailings, especially in the surface layer. The oxidation zone has progressed deeper in the central areas of the impoundment where the tailings are drier, whereas oxygen penetration is inhibited in the moister tailings closer to the dam. In the upper oxidation zone, the pyrrhotite grains have been replaced by secondary Fe precipitates, giving a brownish to yellowish color, and pyrite shows extensive alteration (Fig. 2). The alteration rims around remnant sulfide grains showed zoning in composition with a sulfur-rich core to sulfur-poor and iron-oxygen-rich rims, as was observed by Craig (1990) and Heikkinen and Räisänen (2008). Primary oxides and scarce chalcopyrite do not show signs of alteration in this zone. Sequential extractions showed total Fe and S concentrations to be lower in the surface samples, and both S and Fe are depleted in the primary sulfide fraction (Fig. 3). S is bound to secondary Fe precipitates in the samples from the oxidation zone (samples 1a, 2a–b, and 3a–d). S concentrations in the AEC fraction can be explained by the adsorption of SO_4 to goethite at low pH (Bigham et al. 1996). On average, 13% of the total iron was found in the Fe (oxy)hydroxide fraction in the transition zone where the sulfides present alteration on grain boundaries.

Ca concentrations in the AEC fraction of samples 1c and 1d, approximately 2 wt% of calcite, was confirmed by

Table 5 Concentrations of relevant elements of filtered and unfiltered samples in two ground water samples and ten surface water samples; the metal concentrations in the filtered samples are presumed to be dissolved, while the unfiltered samples, highlighted in italics, provide total concentrations

Sample	Al µg/L	As µg/L	B µg/L	Ba µg/L	Ca mg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Fe mg/L	K mg/L	Mg mg/L	Mn µg/L	Na mg/L	Ni µg/L	Pb µg/L	Rb µg/L	Si mg/L	Sr µg/L	U µg/L	Zn µg/L
DL	1.0	0.05	0.5	0.05	0.1	0.02	0.02	0.2	0.1	0.03	0.01	0.1	0.1	0.2	0.05	0.05	0.01	0.06	0.1	0.01	0.2
1/2006	59.3	0.1	9.3	26.2	12.9	0.04	0.8	<0.2	14.7	0.2	3.5	6.4	172	6.1	12.6	0.1	0.3	10.2	64.6	0.3	14.3
_1/2006*_	_29.7_	_<0.2_	_10.7_	_29.0_	_12.3_	_<0.1_	_0.6_	_<1.0_	_8.7_	_0.8_	_3.4_	_6.4_	_196_	_6.1_	_121_	_1.0_	_0.3_	_8.8_	_71.3_	_0.3_	_9.6_
2/2006	88.8	0.5	8.0	10.6	6.4	0.0	0.4	<0.2	8.2	0.1	2.4	3.0	29.2	2.8	3.3	0.1	2.7	1.5	32.7	0.1	2.5
_2/2006*_	_507_	_0.3_	_7.7_	_14.3_	_6.5_	_<0.1_	_1.6_	_<1.0_	_9.5_	_0.7_	_2.1_	_3.1_	_96.9_	_2.9_	_4.4_	_<0.6_	_3.4_	_2.6_	_33.5_	_0.1_	_3.1_
3/2006	57.8	1.7	12.4	52.1	31.5	0.0	3.6	<0.2	8.9	0.2	6.1	15.3	108	6.4	13.1	0.1	4.1	2.0	90.8	0.2	17.3
_3/2006*_	_<10_	_0.3_	_12.7_	_53.7_	_30.9_	_<0.1_	_0.8_	_<1.0_	_13.4_	_0.0_	_6.0_	_15.7_	_0.9_	_6.3_	_19.6_	_<0.6_	_4.4_	_2.2_	_98.8_	_0.1_	_9.3_
4/2006	300	0.3	14.0	33.3	45.4	0.1	3.5	0.5	16.1	0.7	6.0	19.2	324	6.1	11.7	0.1	3.4	5.4	113	0.1	14.7
_4/2006*_	_1480_	_0.3_	_14.9_	_42.9_	_45.4_	_<0.1_	_8.5_	_1.8_	_25.5_	_2.3_	_6.1_	_21.9_	_525_	_6.2_	_33.8_	_0.8_	_5.4_	_6.5_	_123_	_0.2_	_13.2_
5/2006	24300	0.8	23.5	9.6	189	5.2	736	3.3	1670	6.6	65.9	62.0	5,740	17.2	692	0.5	59.2	27.7	288	14.0	753
_5/2006*_	_29,300_	_0.4_	_30.5_	_10.7_	_185_	_6.1_	_866_	_3.2_	_1,880_	_3.9_	_73.6_	_64.5_	_6,810_	_17.4_	_775_	_0.8_	_64.6_	_23.0_	_317_	_13.6_	_749_
6/2006	23,600	0.9	23.1	9.3	201	5.3	722	3.1	1,660	8.2	63.1	70.4	5,670	25.3	708	0.5	58.7	27.5	331	15.9	763
_6/2006*_	_26,300_	_1.4_	_30.7_	_16.0_	_201_	_6.1_	_834_	_3.5_	_1,830_	_7.8_	_71.0_	_75.7_	_6,190_	_26.4_	_774_	_0.8_	_63.6_	_23.4_	_368_	_15.6_	_755_
1/2007	117	0.2	13.1	20.6	8.6	0.0	0.4	0.4	11.3	0.4	3.6	4.1	107	4.2	14.3	0.2	0.6	9.02	50.7	0.5	55.8
_1/2007_	_216_	_0.3_	_15.4_	_19.5_	_9.3_	_<0.1_	_0.5_	_1.0_	_10.7_	_0.7_	_3.2_	_4.1_	_137_	_4.5_	_14.8_	_<0.6_	_0.7_	_8.4_	_46.2_	_0.5_	_45.9_
2/2007	51.2	0.5	10.5	9.4	5.1	0.0	0.1	0.3	6.5	0.1	2.4	2.5	2.0	2.7	2.5	<0.1	3.1	1.4	38.6	0.1	2.6
_2/2007_	_312_	_0.5_	_12.6_	_11.0_	_5.3_	_<0.1_	_0.6_	_1.1_	_7.8_	_0.4_	_2.2_	_2.6_	_29_	_2.9_	_3.5_	_<0.6_	_3.2_	_1.7_	_37.0_	_0.1_	_15.4_
3/2007	23.1	1.4	12.8	43.4	27.7	0.0	5.9	<0.2	6.7	0.3	4.6	13.4	103	5.8	15.7	0.1	4.0	0.6	86.1	0.1	18.1
_3/2007_	_819_	_2.0_	_13.7_	_53.9_	_28.8_	_<0.1_	_7.4_	_1.5_	_21.3_	_1.6_	_4.9_	_14.1_	_126_	_6.1_	_18.1_	_0.9_	_5.4_	_2.1_	_89.8_	_0.2_	_23.1_
4/2007	457	0.6	46.9	28.2	174	0.1	8.8	<1.0	41.4	2.9	14.8	60.2	1,370	13.7	15.6	<0.1	5.9	7.5	370	0.3	24.3
_4/2007_	_1920_	_0.9_	_79.5_	_42.8_	_220_	_0.2_	_19.1_	_1.3_	_117_	_6.1_	_25.2_	_83.1_	_1,800_	_15.5_	_28.9_	_0.8_	_10.5_	_8.6_	_655_	_0.9_	_43.7_
7/2007	22,500	0.6	68.5	29.1	140	4.1	583	1.8	1,110	5.6	9.1	56.0	7,230	12.4	520	0.1	11.6	20.1	309	5.7	918
_7/2007_	_23,100_	_1.0_	_69.1_	_36.4_	_142_	_4.1_	_636_	_2.3_	_1,200_	_6.6_	_9.1_	_57.9_	_7,640_	_13.1_	_563_	_0.9_	_12.8_	_19.6_	_334_	_6.4_	_831_
8/2007	17,700	2.3	38.5	17.5	177	5.3	843	1.4	946	47.3	27.0	97.2	2,560	19.7	913	0.2	55.3	21.1	267	6.8	821
_8/2007_	_18,500_	_3.0_	_39.4_	_38.4_	_182_	_5.2_	_881_	_2.5_	_1,100_	_52.8_	_26.2_	_102_	_2,750_	_20.6_	_956_	_1.3_	_56.3_	_21.0_	_276_	_9.0_	_746_

The detection limits (DL) are shown, though they were slightly higher for the samples digested with nitric acid (*)

Table 6 In situ measured physico-chemical parameters, anion concentrations, and alkalinity and $KMnO_4$ value of samples in two ground water samples and ten surface water samples

Sample	pH	EC µS/cm	Redox mV	O_2 mg/L	Br mg/L	Cl mg/L	F mg/L	SO_4 mg/L	NO_3 mg/L	Alk mmol/L	$KMnO_4$ mg/L
1/2006	6.4	167	410	5.2	<0.1	8.1	0.1	27	1.8	0.6	6.2
2/2006	7.7	82	423	9.2	<0.1	3.6	<0.1	15	1.9	0.3	28
3/2006	7.2	316	423	9.6	<0.1	3.9	0.2	131	0.8	0.3	26
4/2006	6.5	406	389	5.7	<0.1	3.9	0.2	191	1.0	0.2	24
5/2006	3.4	1,880	701	9.6	<1.0	30	<1.0	1,030	<2.0	<0.02	18
6/2006	3.5	2,020	675	6.4	<1.0	31	1.0	1,170	<2.0	<0.02	18
1/2007	6.0	115	368	4.1	<0.1	3.2	0.1	14.9	3.3	0.6	20
2/2007	7.8	71	373	7.5	<0.1	3.7	<0.1	10	1.0	0.3	36
3/2007	7.0	289	389	8.1	<0.1	3.8	0.3	113	<0.2	0.3	37
4/2007	5.9	1,440	388	6.9	<0.1	5.4	<0.5	417	0.3	0.4	51
7/2007	4.4	1,590	464	3.0	<0.2	13	1.6	778	1.9	<0.02	18
8/2007	3.9	1,330	661	5.2	<0.2	13	1.1	1,150	<0.4	<0.02	27

XRD data and is in accordance with the high tailings pH values (7.11 and 7.29, respectively). There was some remaining calcite in samples 1a and 1b, and the pH averaged 4.28 (Fig. 3; Table 2). Elsewhere, the primary calcite had already dissolved, leading to low pH (from 2.46 to 3.86) with time. Bodénan et al. (2004) and Johnson et al. (2000) report that calcite can maintain a near-neutral pH, even when present in very small amounts. Yet, over time, the neutralizing potential of calcite is expected to be low because of its low concentration in the tailings. Al and Fe(III) (oxy)hydroxides can also contribute to the acid-neutralization processes when carbonates have dissolved (Blowes and Ptacek 1994; Gunsinger et al. 2006; Jurjovec et al. 2002). Dissolution of Al hydroxides buffers the pH at

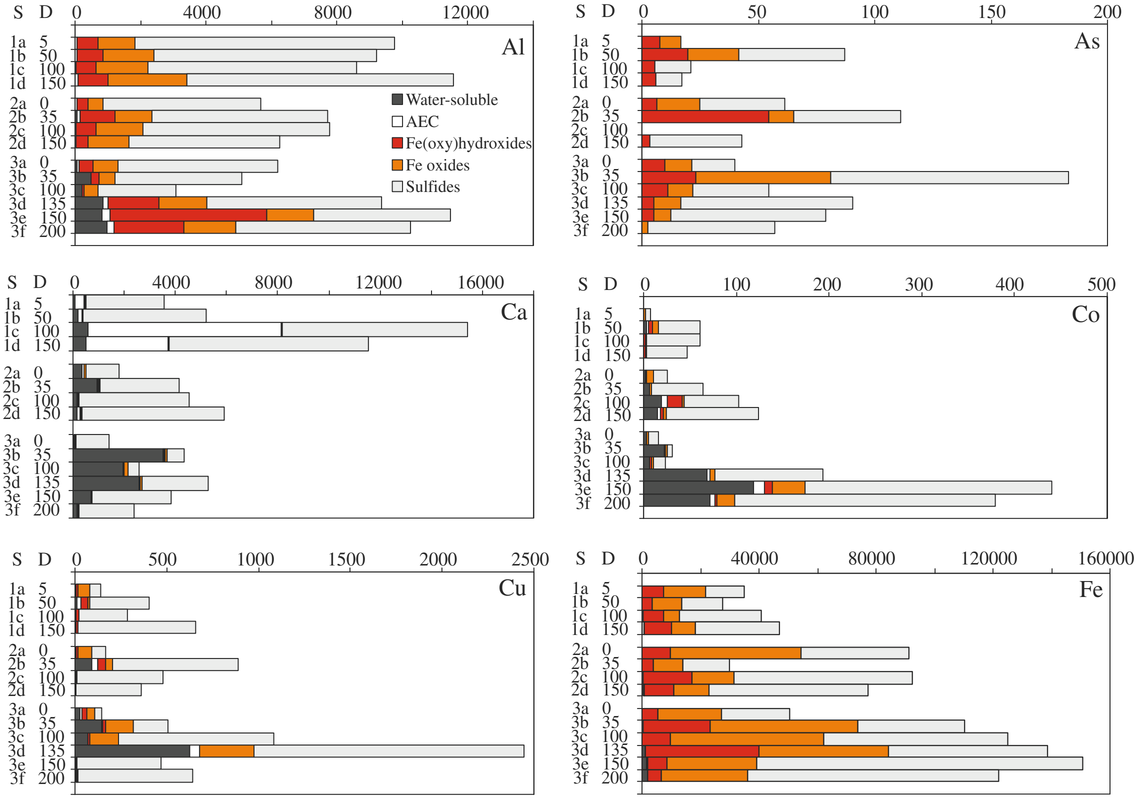

Fig. 3 Elemental distributions (mg/kg) in the five-step sequential extractions (*S* sample, *D* initial sample depth in cm, *AEC* adsorbed-exchangeable-carbonate fraction)

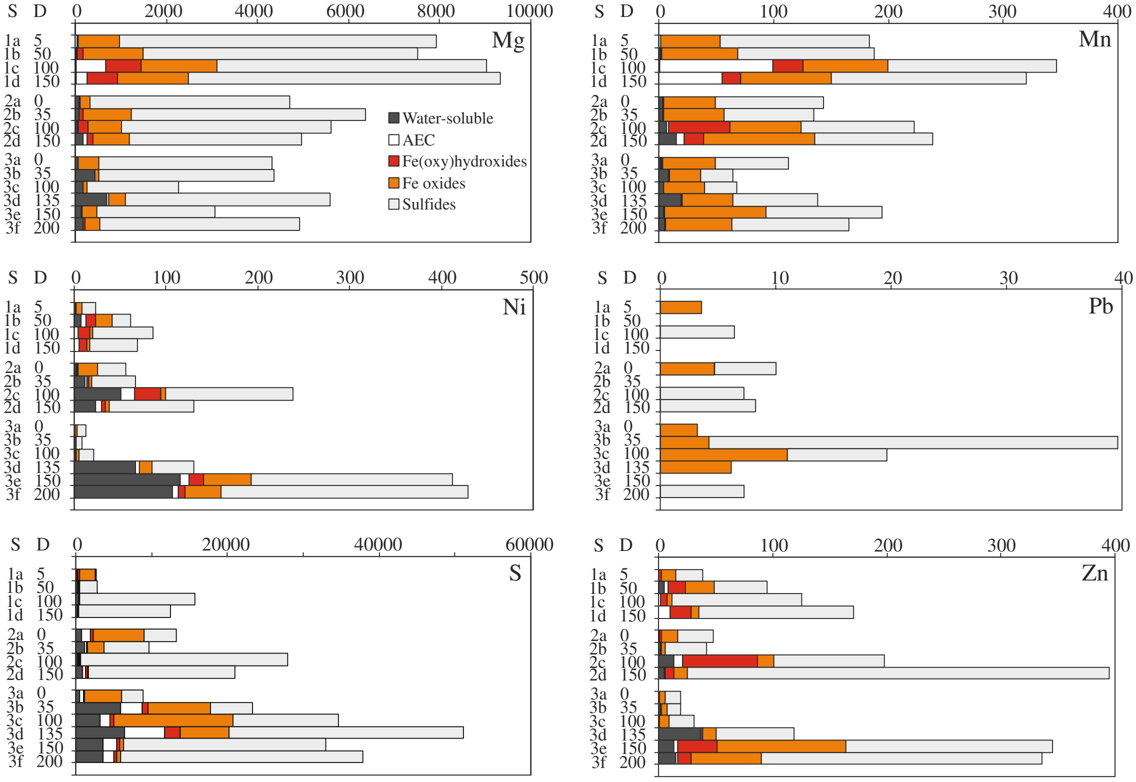

Fig. 3 continued

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 do not exhibit alteration at grain boundaries because aluminosilicates alter and become important in the acid-neutralization processes only at 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).

Cemented Layers and Secondary Minerals

Cemented layers appear in the lower part of the oxidation layer. The well-defined layer at 135 cm in test pit 3 is the most consolidated, has the lowest moisture content, and contains the greatest amount of secondary precipitates. Many authors have suggested that cemented layers or hardpans act as a hydraulic and diffusive barrier, hindering the infiltration of pore water and pore gases (e.g., Blowes et al. 1991; Lin 1997; McGregor and Blowes 2002). Graupner et al. (2007) note that cemented layers can slow the downward movement of the oxidation layer and play an important role in the natural attenuation of As and Pb in secondary phases. Also, Webster et al. (1998) demonstrated that AMD-derived Fe(III) oxyhydroxysulfates can act as a sink for trace elements and sulfate. In the Haveri tailings, Cu, Zn, and As seem to be enriched in the secondary phases of the Fe (oxy)hydroxide and Fe oxide fractions. Total As concentrations varied from 18 to 183 mg/kg in the sequential extractions. Generally, half of the As appeared in the primary sulfide phases, but up to 80 mg/kg was bound to the secondary Fe (oxy)hydroxides. Cu and Zn also seem to be co-precipitated preferentially with secondary minerals in the oxidized tailings, as their concentrations in the AEC fraction is low (Fig. 3). Zn was enriched in the secondary phases of transitional layer as well (Samples 2c, 3e, and 3f). At low pH, bivalent cations are mobile and are not expected to adsorb but to co-precipitate with Fe (oxy)hydroxides (Dzombak and Morel 1990).

Samples 3b to 3f showed the highest concentrations of water-soluble S and Ca, confirming the presence of gypsum, which was also identified by SEM-EDS and XRD. Secondary gypsum is composed of Ca derived from the dissolution of calcite and of SO_4^{2-} from sulfide oxidation (McGregor and Blowes 2002). Some water-soluble Fe, Mg, Mn, Ni, Cu, Co, and Zn were also present, mainly in the samples from test pit 3, but these might have precipitated from the pore water when the samples dried. The samples from test pit 3 presented more advanced sulfide alteration, inferring higher trace metal concentrations in the pore water and the possibility of tertiary mineral precipitation. McGregor and Blowes (2002) suggest that besides gypsum, dissolution of melanterite [$FeSO_4 \cdot 7H_2O$], and copiapite [$(Fe,Mg)Fe_4(SO_4)_6(OH)_2 \cdot 20H_2O$], and the desorption of sulfate from Fe oxides and oxyhydroxysulfates, are other possible sources of soluble sulfur. When present, water-soluble Mg probably exists as epsomite ($MgSO_4$). In the Haveri tailings, the highest concentrations of water-soluble Mg were in the cemented layer in sample 3d.

When pore water pH gradually decreases due to sulfide oxidation, goethite [FeO(OH)] precipitates at acidic to neutral conditions, schwertmannite [$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$] at pH 2.8–4.5, and jarosite, hydronium jarosite, and natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] at $pH < 3$ (Bigham et al. 1996; Jambor 2003; McGregor and Blowes 2002). The low pH (averaging 3.1) of the Haveri tailings around test pits 2 and 3 should favor the precipitation of these minerals. The presence of jarosite in the oxidized tailings was inferred from the high concentrations of K and S in the Fe (oxy)hydroxide and Fe oxide fractions and confirmed by XRD data. Ferrihydrite [$Fe_5O_3(OH)_9$] precipitates at slightly higher pH (>5) (Bigham et al. 1992), and therefore was not expected to be found in the oxidized tailings.

Secondary Cu sulfide (covellite, CuS), identified by mineralogical methods, was not extracted in a separate leach (see Dold 2003) but was extracted together with the primary sulfides. The covellite content could therefore not be estimated.

Leaching of Trace Metals into Surface Waters

Surface waters in the immediate vicinity of the Haveri tailings were investigated to assess the true leaching capacity and the environmental impact of the tailings material. Results in Table 5 show that the Haveri tailings have a relatively minor impact on the trace metal load transported into Lake Kirkkojärvi. The intact part of the dam on the southern and southeastern sides appears to retain leachates. However, on the northern edge of the tailings, meteoric and melt waters flow on top of the tailings, and through the break in the dam. These waters flush the surface tailings, carrying higher concentrations of trace metals to Lake Kirkkojärvi. Yet the water mass of the lake dilutes it, mitigating the impact of surface water runoff from the tailings impoundment. Considerable amounts of unweathered sulfides remain in the vadose tailings, and the acidic conditions within the tailings contribute to mineral dissolution. Thus, sulfide oxidation is expected to continue for decades. A plume of low quality water may be also forming from secondary solids redissolving within the tailings, which would lead to continued transportation of metals over a long period of time. Even though it is out of the scope of this study, it is worth mentioning that the silt and clay subsoil likely hinders the transportation of the low quality waters to underlying ground water because of its low permeability and good metal adsorption capacity. Yet, slow seepage through the subsoil layer could still pose an environmental risk to ground water, and so future subsurface discharge to surface water cannot be ruled out. Future research on the ground water quality of the Haveri tailings area is encouraged.

Sequential Extractions

When combined with the specific mineralogical data of the tailings, sequential extractions can help to assess the distribution, occurrence, and remobilization capacity of trace metals. This method also provides useful information about the degree of sulfide oxidation and clearly shows depletion of S and sulfide-bound metals in surface samples. However, sequential extractions alone cannot accurately define the mineralogical composition.

When comparing the results of *aqua regia* leaches with the total sum of the elements in sequential extractions, sulfide-bound elements correlated well, except for As and Cd (Table 4). The difference between the results of these methods for Cd (63%) can be explained because of the low concentrations (2.73 and 1.02 mg/kg, respectively). Higher Al and Mg concentrations in the *aqua regia* extractions could be a result of partial dissolution of silicates such as biotite. Hall et al. (1996) suggested the possibility that the sulfide extraction step could partially dissolve some silicates, but the trace elements of interest, such as As, Cd, Co, Cu, Ni, and Zn, are not likely to be present in significant amounts in the silicate structure.

Conclusions

Sulfide oxidation occurs in the vadose zone of the Haveri tailings. The oxidized tailings present distinctive geochemical characteristics relative to the underlying transition zone. The topmost 15 cm of the oxidized tailings is depleted in the main sulfides, pyrrhotite and pyrite; the active oxidation layer extends down to 140 cm in the central area of the tailings impoundment. Up to three cemented layers were detected in the central part of the tailings impoundment, but they are not continuous through the tailings area. As, Cu, and Zn are slightly enriched in the secondary phases of the oxidized tailings and the cemented layers. The cemented layers should be monitored and studied in detail to clarify their possible contribution to natural attenuation and to mitigating the downward-moving oxidation process. Most of the readily soluble calcite has dissolved, and the pH presently ranges from 2.46 to 3.86 in the vadose zone of the central tailings, enhancing the sulfide oxidation process. The resulting acidic leachates may dissolve the secondary Fe precipitates in the cemented layers, possibly remobilizing trace elements in the ground water.

Aqua regia extractions showed that the Haveri tailings do not contain significant amounts of Cd, Cr, and Pb, which is reflected by their low concentration in the surface waters (<6 μg/L). *Aqua regia* concentrations of some trace elements (As, Co, Cu, and V) were above the upper guideline values for contaminated soils set in the Degree of Finnish Council of State. In general, all trace metals were only present in moderate concentrations in the lake water samples from the area of the tailings impoundment. Only samples taken from water that was in direct contact with the tailings had elevated concentrations of metals (Co, Cu, Fe, Mn, Ni, and Zn) and sulfate; their pH was about 3.5. However, concentrations of As in water samples were low (<3 μg/L). There is a small continuous release of AMD into Lake Kirkkojärvi, yet the lake water samples showed that the environmental impacts to the lake are presently small.

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