MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF Ni-Cu SULFIDE TAILINGS, THOMPSON, MANITOBA, CANADA[1]

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Abstract. To assess the mobility of metals and consider the geochemical consequences of remediation for exposed Ni-Cu tailings at INCO Ltd., Thompson, Manitoba, Canada, the tailings were described visually, characterized mineralogically, and subjected to sequential extraction and hydraulic conductivity tests. Exposure of the tailings has resulted in the release of metals from sulfides, the acidification of surface and shallow ground waters within the tailings body, and the formation of cemented hardpan layers. Sequential extraction from the solid tailings showed most of the Cu and Zn to be adsorbed by secondary Fe-minerals, while ~15% of the total Ni concentration occurs as water-soluble sulfates in the vadose zone. A rise in water level would result in the dissolution of soluble minerals and the remobilization of metals from the exposed tailings.

The formation and thickness of the cemented hardpan layers on the surface depend on the elevation of the water table and the degree of capillary action as this controls the moisture content of the pore space and hence sulfide oxidation. According to geotechnical measurements, the effect of cementation on reducing water flow through the hardpans to the interior of the tailings is insignificant, but the hardpan could act as a diffusive barrier for oxygen. In the hardpans, from 30 to 50% of sulfides are still not oxidized, and are, therefore, able to generate acid. The high acidity of the water at the surface of the exposed tailings prevents metals from being effectively co-precipitated by the secondary Fe-minerals, jarosite and schwertmannite. Thus, capping exposed tailings with acid neutralizing material is recommended.

Additional key words: tailings, sulfide oxidation, sequential extraction, jarosite, schwertmannite, hardpan, hydraulic conductivity

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Introduction

The Ni-Cu mine at Thompson ($55^{o}38'$N, $97^{o}9'$W, Fig. 1a) has been operated by INCO Ltd. since 1960. The orebody is a deformed, stratabound, sulfide deposit contained within metasediments (SRK, 1984). The ore consists of Ni-pyrrhotite, pentlandite and chalcopyrite with minor pyrite, violarite and mackinawite in an assemblage of gangue minerals, biotite, quartz, and feldspar with minor amphibole and calcite. The processing of the ore includes milling, selective flotation, and smelting of flotation concentrates.

Since 1960 about 40 million tonnes of flotation tailings have been discharged into the tailings management facility. Tailings contain from 4.0 to 15.7 wt% S with a mean net neutralizing potential (NNP) of -460 kg $CaCO_3$eq/t (Klohn Leonoff, 1992). Most tailings are kept submerged, but about 1.6 km^2 of a topographically high area has been left exposed (Fig. 1b). When the tailings are exposed, long-term environmental problems can arise because pyrrhotite is being actively oxidized in the upper, unsaturated region. A hardpan layer, now forming near the surface of exposed tailings, may minimize the infiltration of rainwater and O_2 into tailings stack and reduce the discharge of heavy metals (Chermak and Runnels 1996, Andrew 1998, McGregor and Blowes, 2002). Klohn Leonoff (1992) and SEACOR (1996) recommended that the exposed tailings be capped by a material with low O_2 permeability or kept underwater before possible revegetation. Underwater disposal was found to be less expensive than capping of the tailings (SEACOR 1996).

Objectives

A detailed geochemical, mineralogical and geotechnical study of the exposed tailings was undertaken to (1) estimate the degree of sulfide oxidation and metal speciation in the tailings, (2) describe behavior of metals in shallow ground and surface water, and (3) to recommend potential mitigation techniques. Only shallow groundwater at interface of the saturated and exposed tailings has been studied. Neither deep groundwater within the tailings nor ground water from the silt and clay below or outside of the tailings body was collected. Special attention has been given to estimate the effect of hardpan on the release and transport of metals. In this study, we qualify geochemical consequences of some remediation actions such as submerging of exposed tailings.

Methods

Tailing Sampling

In order to study the tailings deposit, a trench was dug by bulldozers through tailings deposited 5 to10 years ago (Fig. 1c). Trench walls were smoothed at fourteen observation points where the stratification was documented using a Munsell® chart to describe color. At four points (Fig. 1c and 2), representative samples were collected from vertical sections and then sealed in polythene bags. The sample number includes the section number and sample number, starting from the deepest upwards (e.g. 1/6 is the top sample #6 from section TR-1, Fig. 2). A deep sample was collected with a 1.5 m long auger from the saturated zone of each section, where oxidation of sulfides should be minimal. Therefore, there are gaps between the auger samples and the continuous upper part of the sections in Fig. 2. Samples of evaporite minerals were collected from the surface and placed in sealed vials to prevent possible dehydration and oxidation of these highly hydrated phases, which also may contain Fe^{+2} iron.

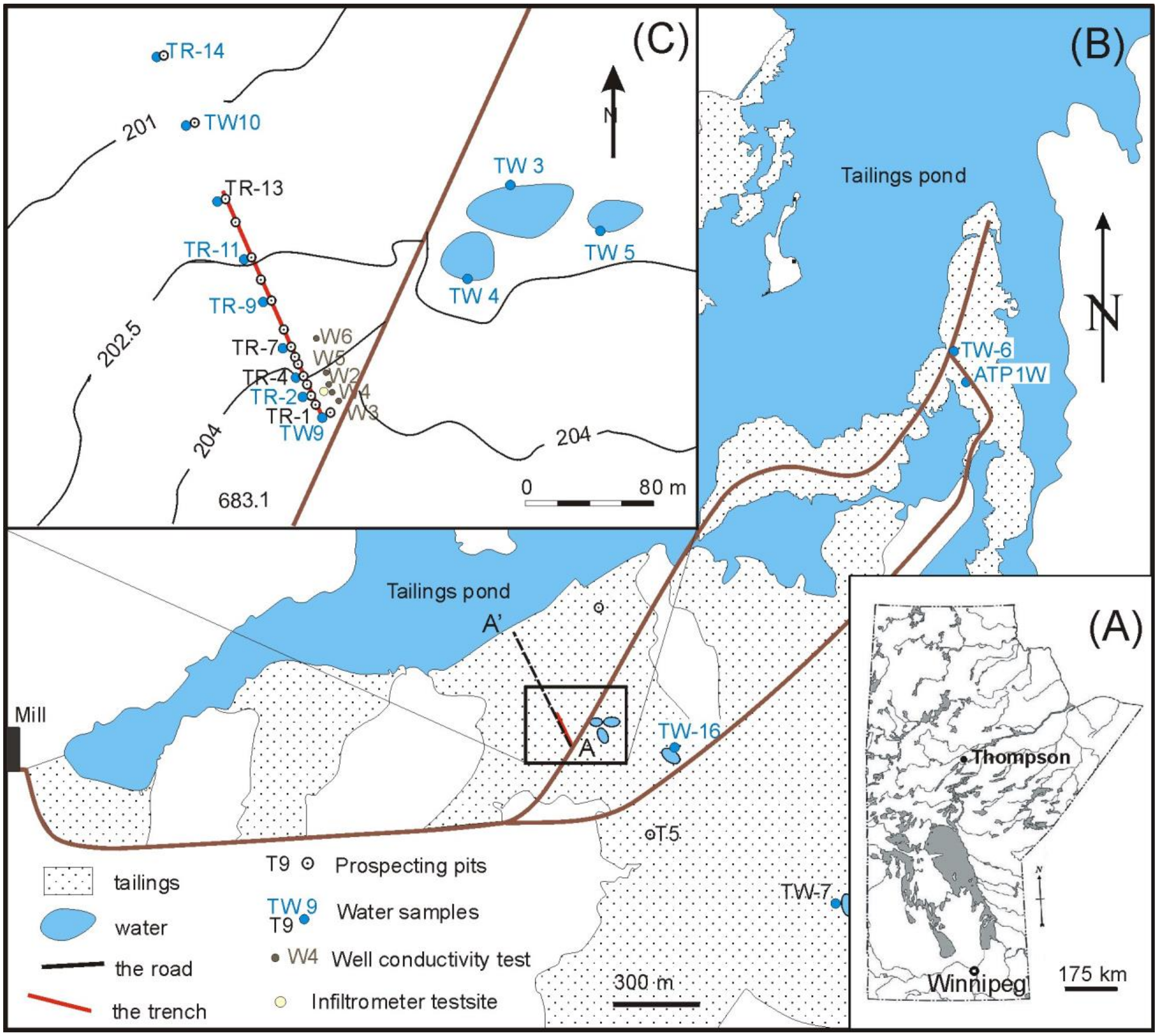

Figure 1. (a) A map showing the location of the INCO Ltd. Ni-Cu mine in Thompson, Manitoba, (b) a plan of the tailings showing trench and (c) the sampling points.

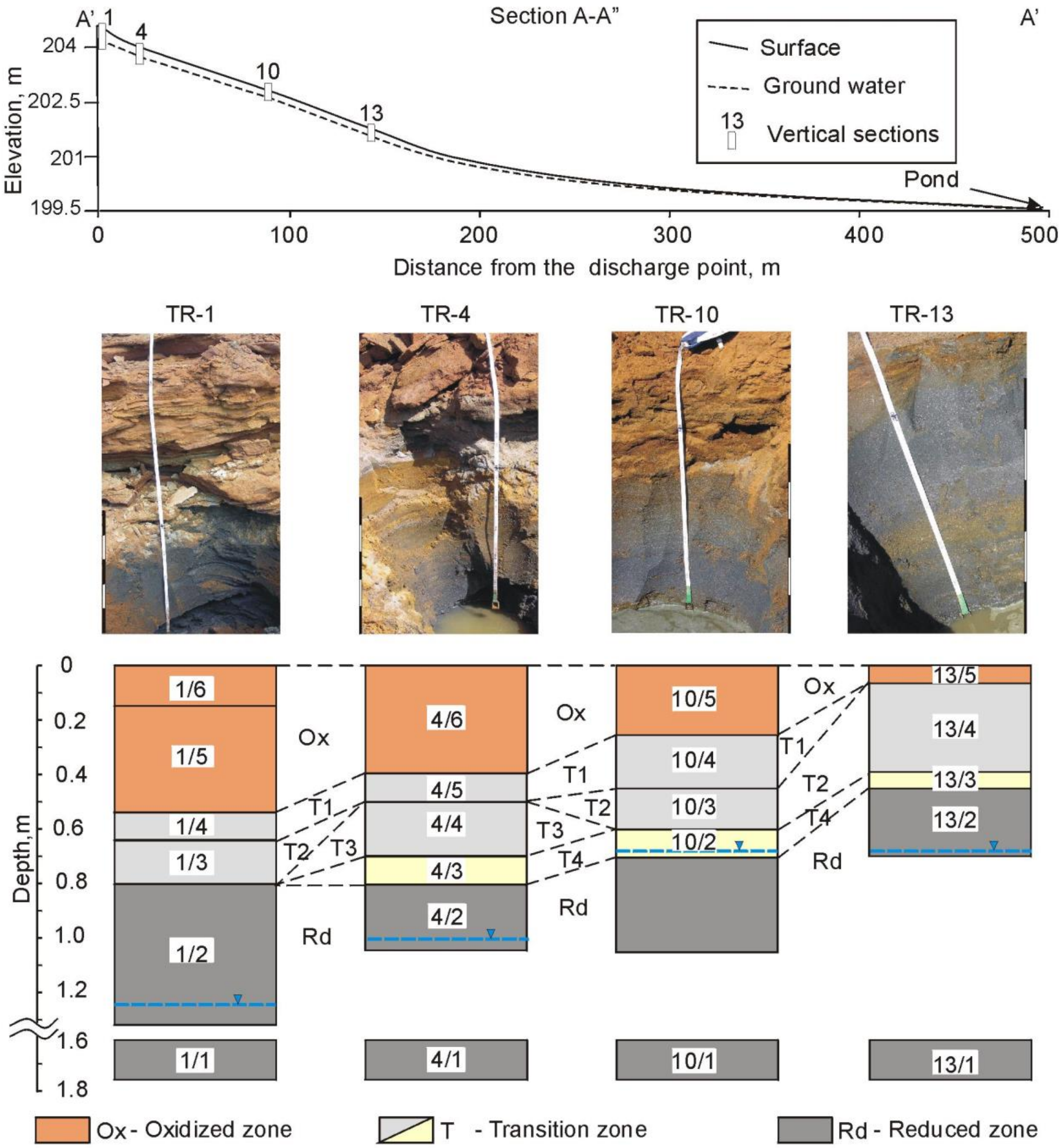

Figure 2. The position, and photographs of the vertical sections and the location of samples in these sections. Zones are correlated between different sections of the trench. Zone names: Ox – Oxidized zone, T1-T4–Transition zone, Rd – Reduced zone. The dashed line with triangles shows the level of the water table. The scale bar of the photographs is 0.5m.

Water Sampling

Samples of surface water from the tailings pond and small isolated pools and of shallow ground water from pits dug in the trench to the saturated zone were tested for pH, Eh, conductivity and total dissolved solids in the field. The water was passed through a 0.45 μm filter before being divided into three aliquots. The first was acidified with 2 mL concentrated HNO_3 (per 1 L) to preserve metals in solution, the second with 1 mL 6M HCl (per 60 mL) to preserve the speciation of iron and the third stored unacidified for anion analysis. All samples were stored at 10°C until analyzed.

Chemical and Mineralogical Analyses

Water samples were analyzed at Envirotest Ltd. Winnipeg, for cations (with ICP-MS), Fe^{+2}, and Fe^{+3} (with IC-UV/VIS) and the following anions SO_4^{-2} Cl^-, NO_2/ NO_3^- (with colorimetry), and alkalinity (by titration). Accuracy of each type of analysis is within 10%, but the total error of all elements may cause charge imbalance for some samples. Unacidified water samples were stored for two months open to air in the refrigerator. During this time precipitates of Fe oxyhydroxides formed by the oxidation of dissolved Fe^{+2}. These sediments were separated from the solution by filtration and the solutions reanalyzed. Metal attenuation was calculated from the differences in concentration from the original analyses. The mineralogy of the precipitates and solid samples was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron microprobe (EMP) with an energy dispersive spectrometer (EDS). A sequential extraction procedure was used to determine the speciation of Fe, S, Ni, Cu, and Zn in samples of tailings. This technique included five stages of leaching developed for mine waste (McGregor et al.1995; Ribet et al. 1995; Fanfani et al. 1997; Dold and Fontboté 2001). Each step preferentially dissolves the minerals given in the brackets:

1) water-soluble (sulfates of Ni, Mg, Fe),

2) exchangeable (phyllosilicates) and carbonates,

3) easily reducible (poorly crystalline and amorphous Fe),

4) moderately reducible (crystalline phases of Fe),

5) residual fraction (primary minerals, mainly sulfides).

A more detailed description of the procedure is given in Sidenko et al. (in press).

The bulk carbonate content was determined to calculate the net neutralizing potential, assuming that all carbonate is bound to calcite. Carbonates were dissolved in 6N HCl, with the evolved CO_2 being passed through an Ascarite® mixture where the carbonates were precipitated as Na_2CO_3.

Hydraulic Conductivity Tests

In-situ hydraulic conductivity tests of the hardpan were conducted using two methods at two site locations (near T9 and T5 observation points, see Fig. 1a, b) to measure vertical and horizontal hydraulic conductivities. Horizontal hydraulic conductivity might differ from vertical because of such anisotropies as layering and preferentially oriented fractures. The variable head, or slug test, was used to assess the horizontal hydraulic conductivity of the hardpan. This method involved boring a vertical hole into the hardpan, installing a 5.08 cm diameter piezometer screen over a definitive length with an end cap into the bored hole, filling the piezometer with water, monitoring the rate of drop in the water level with time, and deducing the hydraulic conductivity using Hvorslev's (1949) equation. The vertical hydraulic conductivity was assessed by using an open, single-ring infiltrometer. The infiltrometer was constructed from a piece of polyethylene pipe (cross-section area of about 0.78 m^2) placed on end onto the hardpan and cemented around the pipe perimeter to seal the pipe to the hardpan. The pipe was than filled with water mixed with a dye and the rate of water level drop was measured. The depth of fluid infiltration was deduced by excavating the hardpan after the test and measuring the migration distance of the dye. The hydraulic conductivity was deduced using equations described in Daniels (1989).

Boulder-size samples of hardpan were collected from sites T5 and W3, trimmed to size, and tested for their laboratory measured hydraulic conductivity using a modified falling head test (described in Domenico and Schwartz 1997). The hardpan was gently trimmed by a rock saw to a size of about 50 mm x 25 mm x 25 mm in dimensions. The trimmed sample was positioned into a 3" diameter pipe, sandwiched between a porous ceramic disk, sealed with end caps with influent and effluent valves to permit water from entering and leaving the sample, and subjected to water infiltration. Wax was used to fill the void between the trimmed sample and the inner pipe wall to force water to flow only through the hardpan. Additionally, silicon was used to seal the hardpan to the ceramic disk. The porous ceramic disks are used to facilitate uniform fluid flow from entering the sample. In the falling head test, a column of water is placed on top of the hardpan sample and the rate of fall of water is recorded over time and the hydraulic conductivity is deduced using equations provided in Domenico and Schwartz (1997).

Results and Discussion

Mineralogy and Lithology of Exposed Tailings

The following zones are based on the observations of physical properties and the degree of mineral alteration from fourteen cross-sections. Three principal zones were identified: reduced, transition, and oxidized according to widely accepted criteria, which were suggested by Blowes and Jambor (1990).

The Reduced Zone (Rd) is usually below the water table (Fig. 2). In this zone, the tailings are loose and saturated with water (Fig. 2) and vary in color from dark bluish grey (GLEY2 4/1) to bluish black (GLEY2 2.5/1). Microscopic studies show that some pyrrhotite grains have been replaced by marcasite (Fig. 3a), and thin films of iron hydroxides surround some sulfide grains, which is typical pattern for early stage of pyrrhotite alteration in the sulfide tailings (Jambor, 1994). Products of sulfide oxidation, such as jarosite and S, were identified in samples collected at the level of the water table. Calcite grains are angular and do not show dissolution features, but occasionally they are coated by a thin red film of Fe_2O_3 (Fig. 3b).

The Transition Zone (T) extends a maximum of 1 m above the water table (Fig. 2). The transition zone contains several continuous layers distinguished by macroscopic features and labeled T1 through T4 (Fig. 2). Material of this zone is loose and less saturated with water than the reduced zone. There are often different colored layers. Olive-yellow (2.5Y 6/6) T4 or brownish-yellow (10YR 6/6) T3 beds usually observed at, or just above, the level of the water table, mark the precipitation of goethite, lepidocrocite and sulfur. Bluish grey (GLEY2 6/1) T2 layers and light bluish grey (GLEY2 8/1) or very pale brown (10YR 8/3) T1 layers are found as the top sequence in most sections.

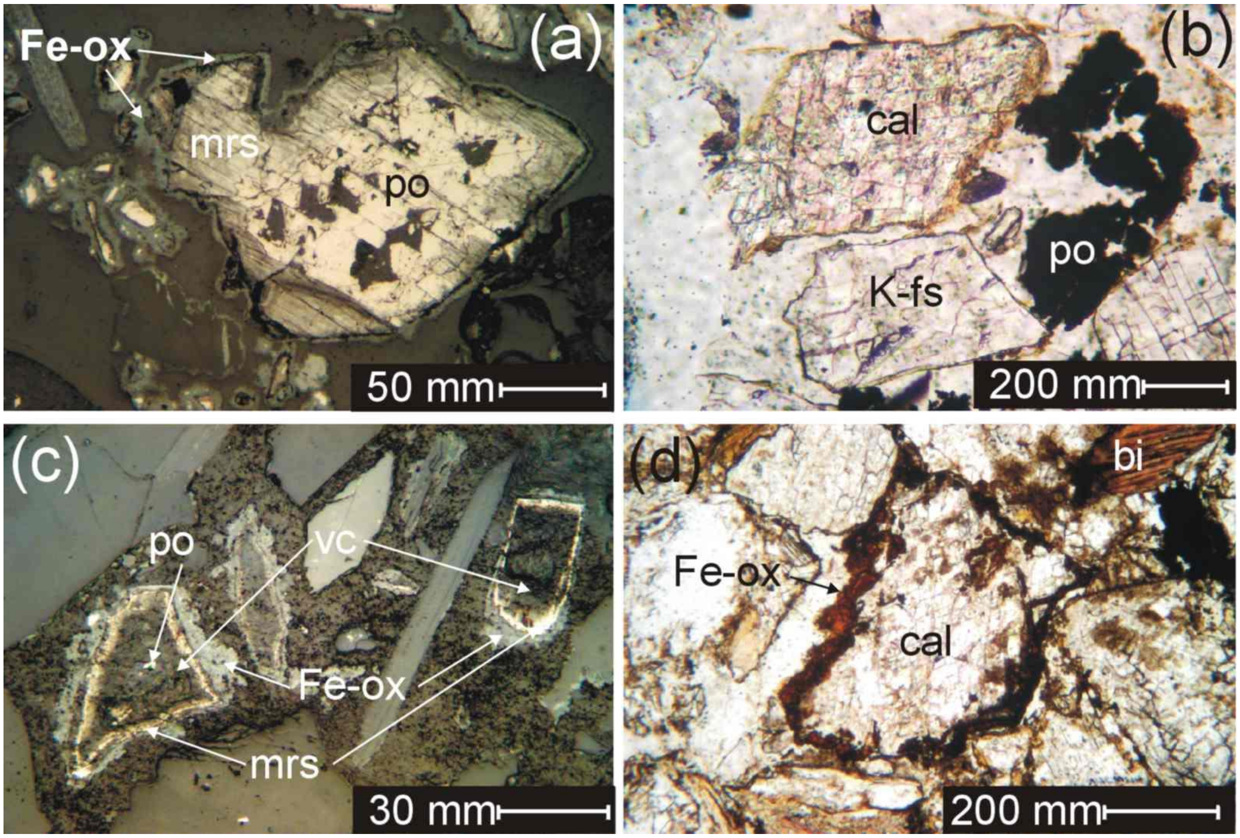

Figure 3. Photomicrographs of polished thin sections in (a, c) reflected and (b, d) transmitted plane polarized light, showing: (a) pyrrhotite (po) partially replaced by marcasite (mrs) and Fe-oxyhydroxides (Fe-ox) in sample 4/2; (b) an unaltered calcite (cal) grain in contact with pyrrhotite and K-feldspar (K-fs) from sample 4/2; (c) the atoll-like texture of pyrrhotite grains almost surrounded by vacant zone (vc), marcasite and Fe-oxyhydroxides in sample 4/3; (d) a corroded calcite grain is surrounded by Fe-oxyhydroxides in sample 4/3.

In the transition zone, about 50% of pyrrhotite is replaced by secondary minerals. The rims become more complex. The sequence "pyrrhotite – vacant zone (epoxy filled) – marcasite – iron oxide" found from the core to the outer rim of oxidized pyrrhotite (Fig. 3c) is similar to zoning observed by Jambor (2003). There is evidence of pentlandite and sphalerite alteration, while pyrite and chalcopyrite grains do not show any evidence of oxidation. Calcite grains are very corroded and surrounded by thick rims of iron hydroxides (Fig. 3d).

The Oxidized Zone (Ox) consists of reddish (5YR 5/4) to yellowish-brown (10YR 5/6), usually cemented, hardpan layers from a few cm to 0.5 m thick. The total thickness of the oxidized zone has an inverse relationship to the depth to the water table. The elevation of the water table is apparently controlling the moisture content in the pore space, and hence the diffusion of O_2 and rate of sulfide oxidation.

The few marcasite and vacant zone rims observed around the pyrrhotite grains in the oxidized zone are very thin due to faster oxidation of marcasite in the oxidized zone than in the transition zone. Iron hydroxide rims, however, are thicker than in the transition zone and consist of inner rims replacing pyrrhotite and outer ones representing the cement (Fig. 4a). An EMP profile shows a decrease in the concentration of Ni from 0.56 wt% in the core of a pyrrhotite grain through an inner rim of $Fe_2(OH)_3$ to 0.16 wt% in the cement (Fig. 4b). Most of the pyrrhotite grains are replaced by secondary Fe phases, and pyrite is altered along fractures (Fig. 4c). Pentlandite and chalcopyrite show minor replacement by Fe-oxyhydroxides. Goethite and/or lepidocrocite, identified by XRD in the >75 µm fraction, are probably from the cement of the hardpan. Jarosite was mainly found in lower part of the hardpan, while goethite and lepidocrocite were distributed irregularly (Kavalench, 2004). There was no calcite found in this zone using mineralogical methods. However geochemical data indicate the presence of dolomite.

The formation of green, white and yellow colored crusts of evaporate minerals were observed on the surface of tailings during dry weather. Morenosite $(Ni,Fe,Mg)SO_4{\cdot}7H_2O$ and melanterite $(Fe,Ni,Mg)SO_4{\cdot}7H_2O$ were identified by powder XRD and SEM-EDS analyses. These sulfates are transient forms of the metals because they can be easily dissolved during a rainstorm (Jambor et al., 2000).

Geochemistry of Solid Tailings

The speciation of Fe, S, Ni, Cu, Zn has been determined in the samples collected from TR1, TR4, TR10, and TR 13 vertical sections (Fig. 5 and Fig. 6).

Fe and S speciation. The mean concentration of Fe varies from 11.5 to 17.8 wt% between different sections (Fig. 5). The mean proportions of Fe in the residual fraction of different sections indicate that from 63 to 66% of Fe remains in sulfides, mainly in pyrrhotite. The vertical distributions of total Fe differ between sections and do not display a regular pattern (Fig. 5). In all sections, the highest concentrations of crystalline Fe-oxyhydroxides are in the uppermost oxidized zone, which correlates with mineralogical study. High proportions of amorphous Fe-hydroxides in the T4 layer just above the water table, in sections TR4, TR10, and TR13, result from the precipitation of these phases due pore-groundwater interaction. The sum of water-soluble, carbonate and exchangeable fractions does not exceed 3.1% of total Fe content.

The mean S content varies from 5.5 to 7.5 wt% among sections. Sulfur is mainly present in the water-soluble and residual fractions with mean proportions varying from 7 to 11% and from 87 to 90 %, respectively (Fig. 5). The distribution of water-soluble S does not display a clear pattern with depth among sections because the tailings were deposited under water at different times.

Speciation of Ni, Cu, Zn. The levels of metal concentration in different sections are 1600 - 2900 ppm Ni, 120-220 ppm Cu, 81 – 92 ppm Zn. Similar proportions of metals are left unoxidized (in the residual fraction) in different sections; Ni 60 - 73%, Cu 52 - 69 %, and Zn 60 - 67% of the total content. The affinity of metals to co-precipitate with well crystalline secondary Fe-phases decreases in the order Cu (18-34%) > Zn (17-21%) > Ni (8-13%). The mean proportions of the metals in the exchangeable and carbonate fractions in all sections are low and do not exceed 5% of the total concentration (Fig. 6). Significant Ni was found in the water-soluble fraction (up to 23 % of the total content) with the highest values in the transition zone (Fig. 6). Concentrations of water-soluble Cu and Zn are too low (<2.2% of total) to be significant. Amorphous Fe-oxyhydroxides accumulate 8 - 11% of Ni, 8-11 % of Cu, and 12 – 15 % of Zn. The highest concentration of metals bound to well crystalline Fe-phases is found in the oxidized zone of tailings. The highest values of Cu and Zn bound to amorphous Fe-phases were detected in the T4 (Fig. 6) marking the precipitation of Fe-phases Thus, sequential extraction shows that the affinity of metals to more stable secondary Fe-phases decreases in the order Cu>Zn>Ni, indicating that Ni has the highest ability to migrate. The significant concentration of soluble Ni above the water table indicates that flooding of the tailings might result in rapid Ni mobilisation. Thus the results of sequential extraction can be used to evaluate water quality if the flooding of exposed tailings is chosen as the effective option at mine closure.

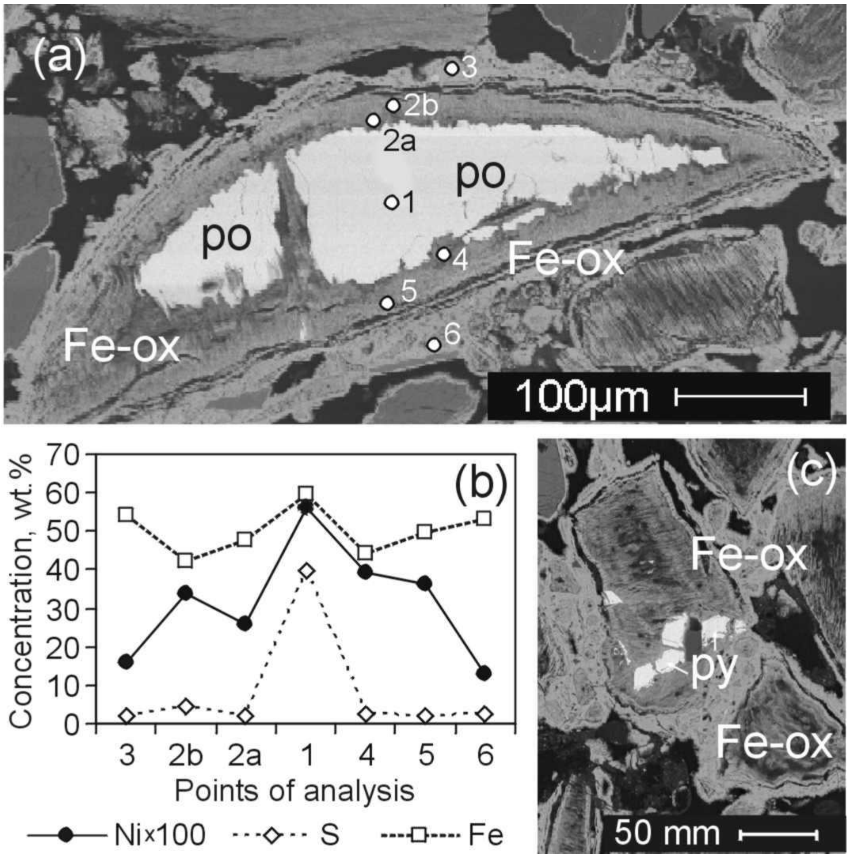

Figure 4. Scanning electron microscope images in electron backscattered mode and the results of EMP analyses showing: (a) pyrrhotite grain surrounded by Fe-oxyhydroxides with points of analyses through a rim-core-rim profile; (b) the concentration of Ni, S and Fe across the profile; (c) a grain of pyrrhotite almost completely replaced by Fe-oxyhydroxides containing inclusions of pyrite, sample 1/5.

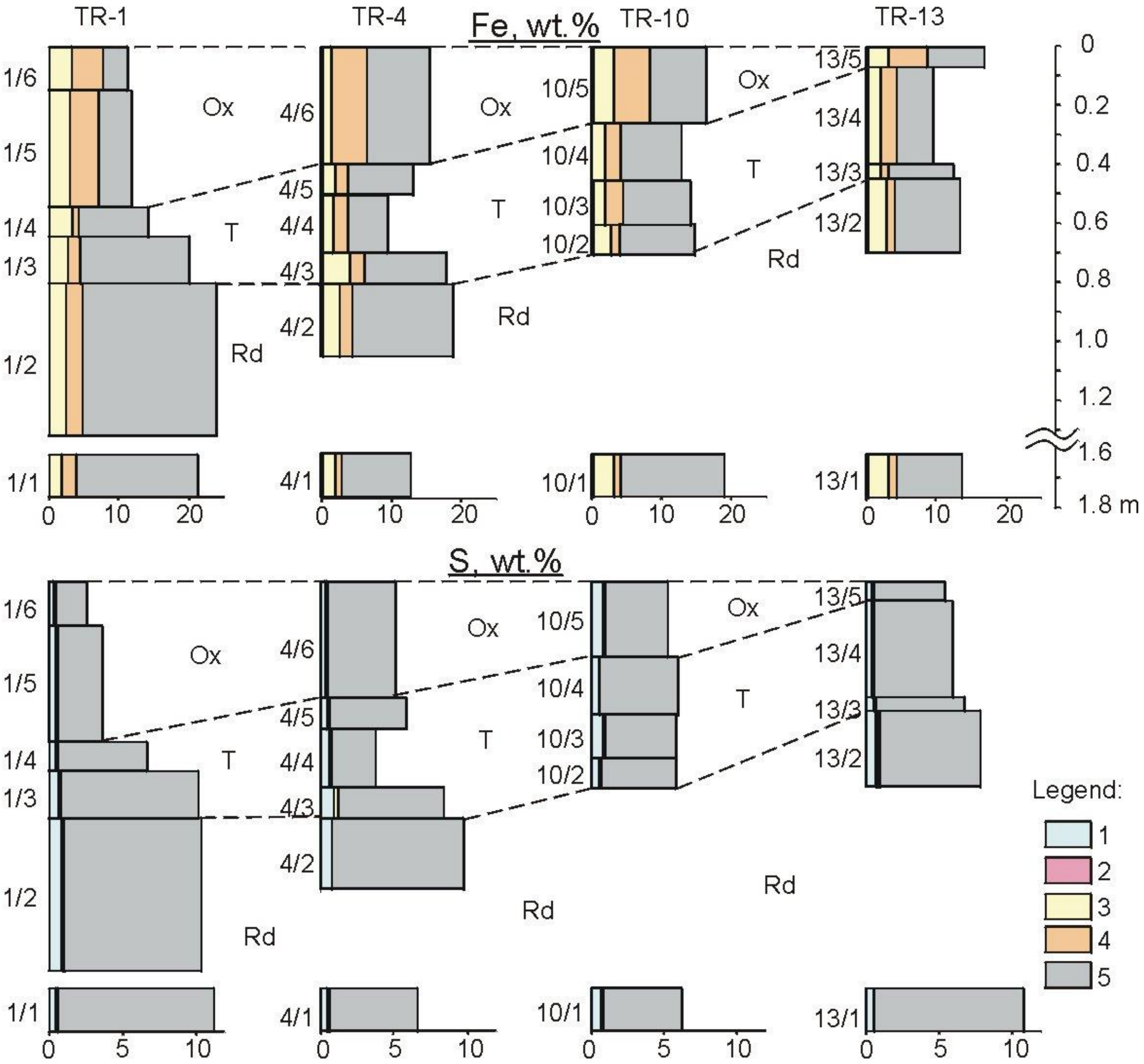

Figure 5. The speciation of Fe and S in the tailings solids from sequential extraction. The fractions are (1) water-soluble fraction (2) exchangeable and carbonate, (3) bound to amorphous and poorly crystalline Fe-oxyhydroxides and oxyhydroxysulfates, (4) bound to crystalline Fe-oxyhydroxides and oxyhydroxysulfates, (5) residual.

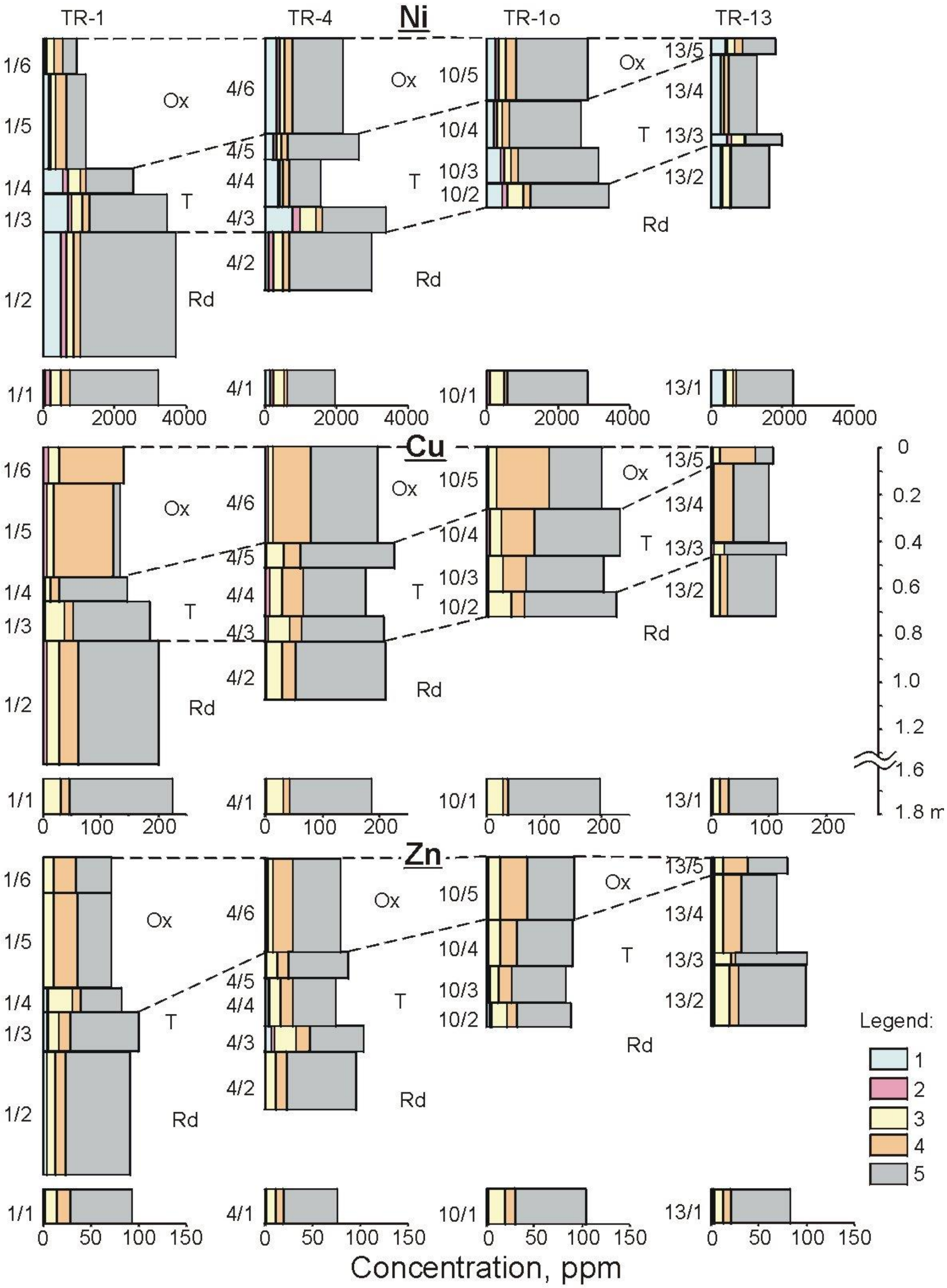

Figure 6. The distribution of Ni, Cu and Zn in vertical sections of the tailings. The fractions are (1) water-soluble fraction (2) exchangeable and carbonate, (3) bound to amorphous and poorly crystalline Fe-oxyhydroxides and oxyhydroxysulfates, (4) bound to crystalline Fe-oxyhydroxides and oxyhydroxysulfates, (5) residual.

Net neutralizing potential (NNP). The NNP was calculated using the measured concentrations of carbonate and the concentration of residual sulphide, because this form of sulphur contributes to future acid generation (Table 1). All samples collected from the trench are potentially acid generating with NNP varying from –55 to –319 kg $CaCO_3$ eq/ton. NNP decreases upwards from

Table 1. Concentrations of total carbonate (as calcite in wt%), residual S in wt% and calculated NNP in kg calcite eq/t.

Sample	Thickness, cm	Zone*	S	$CaCO_3$	NNP
Section 1					
1/6	0-15	Ox	2.2	1.3	-55
1/5	15-55	Ox	3.0	1.1	-82
1/4	55-65	T1	6.0	1.8	-170
1/3	65-80	T2	9.5	2.3	-272
1/2	80-130	Rd	9.5	1.3	-283
1/1	160-175	Rd	10.7	1.5	-319
Section 10					
10/5	0-25	Ox	4.8	1.4	-135
10/4	25-45	T1	5.4	1.2	-156
10/3	45-60	T2	6.1	1.3	-178
10/2	60-70	T4	6.9	2.2	-193
10/1	160-175	Rd	10.3	1.8	-303
Section 4					
4/6	0-40	Ox	4.6	0.8	-136
4/5	40-50	T1	5.3	0.9	-155
4/4	50-70	T3	3.0	1.2	-82
4/3	70-80	T4	7.2	1.9	-204
4/2	80-100	Rd	8.9	1.7	-261
4/1	160-175	Rd	6.1	1.5	-176
Section 13					
13/5	0-7	Ox	4.3	1.1	-125
13/4	7-40	T2	4.4	0.9	-127
13/3	40-45	T4	4.8	1.2	-139
13/2	45-60	Rd	5.1	1.6	-144
13/1	160-175	Rd	5.4	1.4	-154

* See abbreviations in the text

reduced zone in sections TR-1, TR-10 and TR-13 (Table 1), which could be due to changes in chemistry of the mill discharge with time. Also, changes in sulfide/carbonate ratio could be caused by the migration of acid produced in oxidized zone downwards and the leaching of calcite from reduced zone. Hardpan layers are acid generating with NNP ranging from –55 to –136 kg $CaCO_3$ eq/ton.

Water chemistry and metal attenuation

Ground water. Shallow ground water travels radially from the top of the tailings delta towards the toe and discharges into the tailings pond (Fig 1). Shallow ground water is classified as Mg-Ca-Fe-SO_4 water with the content of total dissolved solids ranging from 5.6 to 20 g/L. Ground water has a pH of 5.3 - 6.2 buffered by carbonate minerals in the lower zones of the tailings. The dominant anion in all types of water is SO_4^{-2}. The dominant form of Fe in the ground water, Fe^{+2}, has concentrations from 0.1 to 2820 mg/L. K concentrations range from 68 to 253 mg/L. Aluminium concentration varies from 0.01 to 3.4 mg/L. The metal concentrations in the solutions are from 0.01 to 0.05 mg/L Cu, from 2.3 to 886 mg/L Ni, and from 0.24 to 2.5 mg/L Zn. Interaction of ground water (TW10 and TW9) with air was simulated to observe the chemical changes in the solution and to identify the chemical composition and mineralogy of the precipitates. After two months of storage of samples collected in 2003 (TW10F and TW9F), Fe^{+2} decreased and Fe^{+3} increased because of oxidation and the values of pH decreased by 2.6. The total concentration of Fe was decreased by 390 mg/L as the result of the precipitation of Fe-phases. Concentrations of Ni were reduced by 18% and 26% and Zn by 38% and 81% of the initial concentrations because of precipitation (Table 2). Cu concentration did not change within the accuracy of the measurements.

Ground water, collected from the trench after one year of exposure, provides information about the changes in the chemistry of the ground water (Table 2). Ground water in the trench (sample TW9, Fig. 1) has a lower pH (6.0) and much higher Ni concentration (886 mg/L) in 2004 compared to the sample collected at the time of trench excavation in 2003 (pH = 6.2, Ni = 2.3 mg/L). For the sample not collected from the trench (TW10), Ni concentration (~2 mg/L) and pH (~5.8) were the same as in the previous year. Changes observed in the trench were caused by the rapid oxidation of previously unoxidised tailings.

Results from the transect along the trench shows lateral zoning in the groundwater chemistry. The highest acidity, metal and SO_4^{-2} concentrations were observed in the topographically high area (samples TW9, TR2, TR4, TR7, Fig. 1b, Table 2) at the discharge point of the tailings (T9, Figure 1b). These values decrease from the discharge point to the lower area (TR11, TR 9, TR 13) where the groundwater is close to the surface (Fig. 2). The lateral zoning in water chemistry could be caused by different rates of sulfide oxidation at differing elevations. The rate of sulfide oxidation is higher in elevated areas because of the lower moisture content, which is a function of the depth to the water table and capillary action. Oxygen diffuses slower through pores partially filled with water compared to air filled pores (Elberling et al., 1994).

Table 2. Chemistry of water samples: initially and after the formation of precipitates (F after sample number), mg/L. Groundwater samples are in the order along the transect AA'.

Sample	pH	TDS	Eh	Ca	Mg	Na	K	SO_4^{2-}	Fe^{2+}	Fe^{3+}	Cu	Ni	Zn
Ground water 2003													
TW10	5.8	18800	0.27	428	2490	630	188	13000	1380	148	0.05	3.7	0.24
TW10F	3.24	18300	0.71	321	2360	607	182	13100	864	290	0.04	3.0	0.15
TW9	6.22	9100	0.21	411	1150	96	128	6130	1010	38	0.04	2.3	0.42
TW9F	3.64	9300	0.51	304	1080	87	103	6660	510	150	0.08	1.7	0.08
TW1	5.15	12300	0.43	436	820	112	68	7930	2170	208	0.08	75	1.64
Ground water collected from the trench pits in 2004													
TR14	6.62	7400	0.25	373	1190	434	148	4890	0.1	0.05	0	4.6	0.02
TW10	5.8	18000	0.28	379	2550	653	170	11900	859	53.9	0.01	1.7	0.05
TR13	5.36	29300	0.25	401	3160	525	253	17800	3250	187	0.01	3.6	0.07
TR11	5.57	23300	0.23	366	2280	259	215	14200	2820	151	0.01	1.6	0.06
TR9	5.66	23600	0.18	361	2320	221	233	14500	2820	154	0.01	2	0.08
TR7	5.08	7700	0.33	398	1750	44.7	131	n.d.	2440	143	0.01	125	1
TR4	5.29	21700	0.25	402	1990	38.1	111	13300	2220	223	0.01	441	2.55
TR2	4.92	5600	0.34	389	1830	51.8	84.8	n.d.	1140	95.1	0.01	607	2.31
TW9	5.99	14300	n.d.	698	1600	47.1	131	8420	659	65.5	0.01	886	0.18
Surface water from insolated pools on the surface of tailings													
TW3	2.84	12400	0.70	590	1660	275	3.3	9260	9.3	123	0.32	162	1.13
TW4	2.75	17800	0.68	563	2420	460	1.4	13600	41.1	241	1.08	142	1.48
TW5	2.59	13100	0.69	513	1740	233	15	9940	41.5	293	0.30	47	0.47
TW5F	2.54	12500	0.76	458	1690	254	2.5	9620	<0.05	171	0.31	44	0.48
TW6	2.49	6300	0.63	463	433	166	29	4350	419	137	0.04	24	0.30
TW6F	2.49	6000	0.79	453	467	184	32	4320	6.7	148	0.05	23	0.27
TW7	3.2	3300	0.59	457	335	15	3.1	2200	117	12	0.26	9.7	0.16
TW7F	3.09	3500	0.67	402	300	21	4.4	2530	0.05	47	0.27	9.0	0.26
TW16	2.74	13000	0.55	480	1960	274	43	9420	178	210	0.16	107	1.25
TW16F	2.89	13200	0.63	389	1800	288	32	10000	3.7	253	0.13	111	0.96
Surface water from the pool on the surface of rock waste covering tailings													
ATP1W	4.24	4600	0.57	442	242	519	96	2760	0.7	1.5	0.04	7.1	0.05

n.d. – no data

Surface water. In comparison with the ground water, pools from the surface of tailings are acidic (pH = 2.5 – 3.2). This water contains less Fe^{+2}, K^{+} and Al^{+3} (9.3 – 419, 1.4 – 43, 0.8 –23.6 mg/L, respectively) but similar concentrations for other major ions. Surface solutions contain higher levels of Cu (0.04-1.08 mg/L) and Ni (9.7-162 mg/L) than the ground water (Table 2), while concentrations of Zn (0.16-1.48 mg/L) are similar. In the four samples analyzed after the precipitation of solids, the average concentration of Fe^{+2} had decreased from 189 to 3 mg/L, while the levels of Fe^{+3}, SO_4^{-2} and acidity were close to the initial values. The concentration of total Fe decreased by 140-400 mg/L. In most samples, the initial concentrations of Cu, Ni and Zn differed from the final ones by just a few percent (Table 2). This variation could have been due to the precision of the analyses and, therefore, was not used to calculate the quantity of attenuated elements.

Placing rock waste on the surface of the tailings could improve the water chemistry of the surface ponds. The sample ATP1W was collected from a surface pond on the old road build of waste rock on exposed tailings (Fig. 1b). This sample had lower acidity (pH = 4.2) and metal concentrations (Ni-7.1 and Zn–0.05 mg/L) compared to an adjacent pond on the surface of the exposed tailings (sample TW6; pH = 2.5, Ni-24 and Zn–0.3 mg/L). Neutralisation of acidic surface and pore water by waste rock could result in the attenuation of metals by co-precipitation with secondary Fe – hydroxides. According to historical data (Klohn Leonoff, 1992), the waste rock consists of quartzite (32%), schist and mineralized schist (23%), varieties of skarn (22%), quartz and pegmatite (12%) and amphibolite (12%). The highest contribution to neutralization is expected from skarn with a potential of 88 kg $CaCO_3$/ton. There is a wide range of measured NNP of schist and mineralized schist ranges with average values from 1 to -350 kg $CaCO_3$/ton (Klohn Leonoff, 1992). As proportions of these rocks had not been estimated separately, there is a large uncertainty in estimating bulk NNP. The mean weight NNP for waste rock was -9 kg $CaCO_3$/ton assuming acid generation. The contradiction between these two observations indicates the need for further study of the waste rocks.

Metal attenuation from waters. More Cu, Zn, and Ni was precipitated from the ground water than from surface waters due to higher pH of the ground water (Table 2), resulting in an increase in the effectiveness of metal sorption with Fe-hydroxides (Dzombak and Morel 1990).

Ni, Cu, and Zn co-precipitated from ground water with goethite (FeOOH) and poorly crystalline schwertmannite $Fe_8O_8(OH)_{8-2x}(SO_4)_x \times nH_2O$, while the formation of schwertmannite and jarosite $(K_{0.77},Na_{0.03},H_3O_{0.20})Fe_3(SO_4)_2(OH)_6$ controlled the metal attenuation from surface waters. A detailed description of these precipitates and the results of geochemical modelling of solution are given by Sidenko and Sherriff (2005). Schwertmannite is a metastable phase that can re-crystallize into goethite in just one year. The concentrations of metals bound to highly crystalline (goethite and jarosite) and poorly crystalline precipitates (schwertmannite) were determined. Most Ni and Zn are bound with metastable schwertmannite (Table 3) and could be released back into solution or reabsorbed by new-forming goethite.

Table 3. Total concentration and proportions of total element concentrations bound with (1) poorly (schwertmannite) and highly (2) crystalline Fe-phases (goethite and jarosite) in the precipitates.

Element	**Fraction**	**Units**			**Sample**			
			T10F	**T9F**	**T7F**	**T6F**	**T16F**	**T5F**
			Ground water		**Surface water**			
			Sh+Gt*	**Sh+Gt***	**Sh***	**Sh+Jrs***	**Sh+Jrs***	**Jrs***
Fe	Total	Wt.%	47.2	49.9	42.5	44.5	35.1	31.0
	1	% of total	64	48	98	86	61	4
	2		36	52	2	14	39	96
S	Total	Wt.%	4.5	3.5	6.0	4.2	9.0	10.8
	1	% of total	89	89	97	83	41	5
	2		11	11	3	17	59	95
K	Total	Wt.%	0.08	<0.01	<0.01	0.43	1.9	4.8
	1	% of total	99	d.l.**	d.l.**	0	3	2
	2		1	d.l.**	d.l.**	100	97	98
Ni	Total	ppm	22	24	53	14	197	3.5
	1	% of total	99	99	91	85	92	32
	2		1	1	9	15	8	68
Zn	Total	ppm	8.6	13	8.7	70	25	19
	1	% of total	53	94	85	100	47	20
	2		47	6	15	0	53	80
Cu	Total	ppm	20.9	7.4	6.0	43	9.9	81
	1	% of total	76	33	78	49	3	24
	2		24	67	22	51	97	76

* Sh -poorly crystalline schwertmannite; Gt - goethite and Jrs - jarosite.
**d.l. - concentration of K below detection limit <0.01 wt.%

Concentration factors were calculated to understand the affinity of metals to the precipitates. These factors are the ratios in the precipitate to those in the solution after precipitation. The affinity of metals to secondary Fe phases are in the sequence Cu>Zn>Ni, which is in agreement with the order of the first hydrolysis constants for these metals (Dzombak and Morel 1990; Dutrizac and Jambor 2000).

Geotechnical properties of the hardpan

Limited water access to the interior of the tailings may inhibit the oxidation by transport of O_2 with rainwater and removal of oxidation products. The rate of advective transport of solutes through the hardpan to the interior is controlled by the hydraulic conductivity of the hardpan. The variable head tests provided a measure of the horizontal hydraulic conductivity of the hardpan that ranged from $2x10^{-4}$ to $6x10^{-4}$ cm/s. The infiltrometer test produced a vertical hydraulic conductivity that ranged from $5x10^{-3}$ to $3x10^{-3}$ cm/s. Excavation of the hardpan below the infiltrometer location after testing showed that the dye in the water largely passed through vertical fractures within the hardpan, and to a lesser extent the matrix of the deposit. Thus, the higher vertical than horizontal hydraulic conductivity is probably associated with interconnected vertical fractures within the hardpan providing preferential conduits for water flow in the vertical direction compared the horizontal. Comparing the in-situ and laboratory hydraulic conductivity results shows that the vertical hydraulic conductivity of the hardpan is similar to uncemented tailing material ($8x10^{-4}$ to $2.5x10^{-3}$ cm/s). Laboratory falling head tests on uncemented tailings material had two ranges of hydraulic conductivity values. Measurements of four samples fall between $9.5x10^{-4}$ and $2.5x10^{-3}$ cm/s and represent the conductivity of the hardpan matrix or through fractures not visible to the human eye, while two another samples of hardpan with visible fractures display higher values, $1.5x10^{-1}$ and $2.0x10^{-1}$ cm/s. Thus, the hydraulic conductivity testing suggests that if evaporate minerals on the hardpan dissolve, the metals may be transmitted through the hardpan (via vertical fractures) as readily as through uncemented material.

Conclusions

Sulfide oxidation in the exposed tailings results in the release of metals to pore water and shallow groundwater. Some of the metals may be attenuated by co-precipitation and adsorption to secondary Fe-minerals such as goethite and schwertmannite. The affinity of metals to these minerals decreases in the order Cu>Zn>Ni indicating that Ni has the highest ability to migrate in both ground and surface water. The same conclusion can be made from the results of the sequential extractions which showed most Cu and Zn to be adsorbed by secondary Fe-minerals, while only ~15% of the total Ni concentrations occur as water-soluble sulfates in the Transition and Oxidized zones of the tailings. A rise in water level could result in the dissolution of soluble minerals and the remobilization of metals from the exposed tailings.

The formation and thickness of cemented hardpan layers depend on the elevation of the tailings surface above the water table as this controls the moisture content of the pore space and hence sulfide oxidation. The effect of cementation in reducing water flow through hardpans is insignificant according to geotechnical measurements. However, cementation stabilizes the surface for possible remediation activities that might involve heavy machinery. In the hardpan, from 30 to 50% of sulfides are still not oxidized and able to generate acid. Due to the high acidity of the water at the surface of the exposed tailings, metals cannot be effectively co-precipitated by secondary Fe-phases. As well, the formation of soluble metal sulfates on the surface may result in a flush of the metal into the pond during the rainstorm. Thus, from a geochemical point of view, the capping strategy has less environmental risk then raising the water table. Capping with the acid neutralizing waste rock reduces the acidity of surface water and forms a diffusive barrier for O_2. Further studies should be focused on properties of different capping materials available around the mine site.

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