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Layers rich in Fe- and Mn-oxyhydroxides formed at the tailings-pond water interface, a possible trap for trace metals in flooded mine tailings

Henning Holmström[a], Björn Öhlander[b,*]

[a]Envipro Miljöteknik AB, Repslagaregatan 19, SE-58222 Linköping, Sweden
[b]Division of Applied Geology, Luleå University of Technology, SE-97187 Luleå, Sweden

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Abstract

Geochemical field studies of the flooded sulphide-rich mine tailings at Stekenjokk in northern Sweden have been performed. Minor diffusion of elements from the tailings to the pond water is occurring. The diffusion rate is higher where tailings that were oxidised before the flooding have been deposited. Layers rich in Fe-and Mn-oxyhydroxides have been developed close to the tailings surface, and a layer of natural sediments rich in organic material have developed on the tailings surface since the flooding. The oxyhydroxides adsorb and/or co-precipitate metals and function as a trap for released metals at the tailings-pond water interface, thereby decreasing the diffusion rate from the tailings pore water to the pond water at the sediment-water interface. This study shows that it is possible for a deposit of flooded tailings to reach a state when it almost functions as a natural lake in northerly areas, with Fe-and Mn-oxyhydroxide layers controlling the diffusion of metals into the overlying pond water, within a relatively short time after remediation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: flooding; remediation; tailings; sulphides; trace metals; oxyhydroxides; electron micoprobe analysis

1. Introduction

Flooding is one proposed remediation method of preventing the formation of acid drainage from sulphide mining waste. The purpose is to limit the supply of oxygen by covering the waste with water. Flooding may be a potentially cost-effective remediation method. However, the water cover does not totally stop the diffusion of oxygen into the tailings. Investigations indicate that some sulphide oxidation may occur in water-covered waste (Aubé et al., 1995; Payant et al., 1995; Holmström and Öhlander, 1999). Flooding of tailings may also result in remobilisation of metals due to dissolution of secondary precipitates, especially if the tailings are old and oxidised. This leads to diffusion of metals up into the overlying waters. It is, therefore, preferable if the tailings to be flooded are unoxidised, to reduce the remobilisation. Unoxidised tailings may, however, contain trapped process water which may diffuse upwards.

The sulphide-rich mill tailings of the Stekenjokk Cu–Zn mine in northern Sweden were flooded almost unoxidised in 1991 (Broman and Göransson, 1994).

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* Corresponding author. Tel.: +46-920-91478; fax: +46-920-91697.

E-mail addresses: henning.holmstrom@envipro.se (H. Holmström), bjorn.ohlander@sb.luth.se (B. Öhlander).

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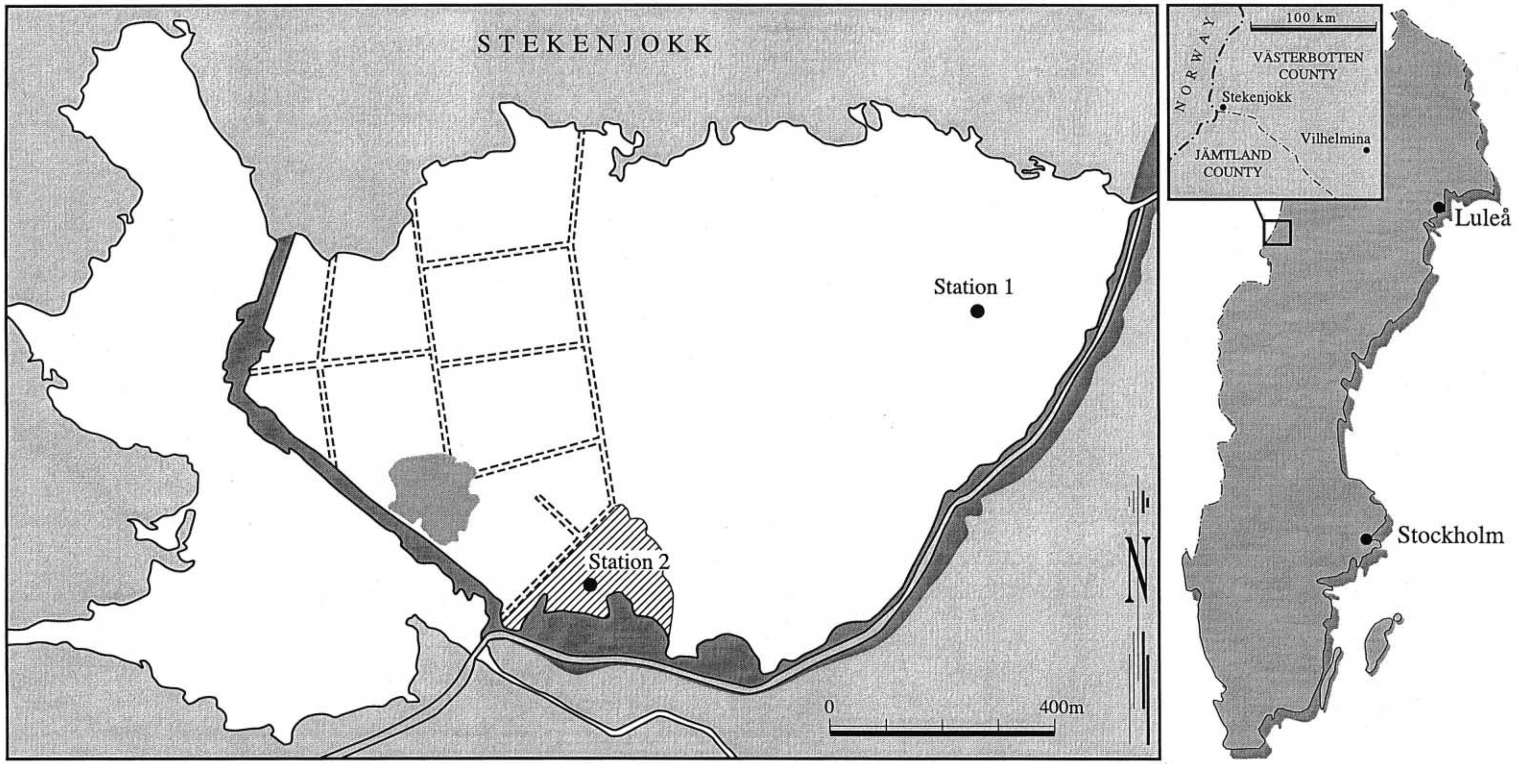


Fig. 1. Map showing the Stekenjokk site. White areas represent water; the raw water pond to the left and the flooded tailings to the right. The breakwater system is indicated and the sampling Stations 1 and 2 are shown. The tailings in the area marked with oblique lines, where Station 2 is situated, were oxidised before the flooding. In the grey area situated 300 m northwest of Station 2, the water is particularly shallow and the tailings were covered by till before the flooding.

Geochemical studies were performed at the site during 1995 and 1997 (Ljungberg et al., 1997; Holmström et al., 1999; Holmström and Öhlander, 1999; Holmström et al., 2000). The results indicated that the dissolved metal concentrations in the pond, especially of Cd and Zn, were elevated compared with the natural background but still rather low. The dissolved metal concentrations in the pond water are to a large extent controlled by precipitation and dissolution of Fe- and Mn-oxyhydroxides in the water column. There were also indications that some sulphide oxidation was occurring in the uppermost part of the tailings. Layers rich in Fe- and Mn-oxyhydroxides were also present in the uppermost sections of the water-covered tailings. These layers were not present when the tailings were flooded. Fish (char) occurs in the pond.

Natural lake sediments consist mainly of partially decomposed organic material, detrital material such as different primary rock and mineral fragments and material that has formed in situ, e.g. different secondary minerals such as Fe- and Mn-oxyhydroxides. Fe- and Mn-rich layers consisting of different oxyhydroxides in natural sediments are common (e.g. Shaw et al., 1990; Ingri and Widerlund, 1994; Widerlund and Ingri, 1996). Secondary oxides, especially Fe-oxyhydroxides, are also common in mine wastes (e.g. Boorman and Watson, 1976; Blowes and Jambor, 1990; Herbert, 1995; Lin, 1996). Heavy metals have a strong tendency to be adsorbed onto such oxyhydroxides, or may be co-precipitated (e.g. Alpers et al., 1994; Tessier et al., 1996; Herbert, 1996; Banks et al., 1997; Donahoe and Liu, 1998). Organic material is known to sorb metals (Kerndorff and Schnitzer, 1980) and to form metal complexes (e.g. Schnitzer, 1986). Oxyhydroxide-rich layers and organic material on top of flooded tailings may, therefore, partly control the concentration of metals in the pore solutions and change the diffusion rate of metals into the overlying waters, as they do in natural lakes.

The aim of this study was to investigate a tailings repository a few years after remediation. Of particular interest was the tailings-pond water interface with its thin layer consisting of natural sediments deposited after the flooding, and layers rich in Fe- and Mn-oxyhydroxides in the uppermost parts of the tailings, and whether these oxyhydroxides work as a trap for metals diffusing from the tailings pore water.

2. Site description

Stekenjokk was a stratabound volcanogenic Zn–Cu deposit of Caledonian age (Zachrisson, 1971), situated in northern Sweden (Fig. 1), close to the Norwegian border. The average grade was 3.2% Zn, 1.4% Cu, 0.3% Pb and 40 g/tonne Ag (Juve, 1974). Main sulphides were pyrite, sphalerite and chalcopyrite. Galena, pyrrhotite, covellite and minor amounts of arsenopyrite also occurred. The gangue minerals were quartz, feldspars, sericite, chlorite and carbonates. Operations by Boliden Mineral AB lasted from 1976 to 1988, during which 8.08 million tonnes were mined mainly by underground cut and fill operations. A minor volume was mined from an open pit. Mining left waste rock dumps and some 4.4 million - tonnes of tailings containing about 20% sulphur, mainly occurring as pyrite (FeS_2). The tailings deposited in the tailings and clarification pond consisted of 71% silt and clay (<60 μm grain diameter), and 29% of the material had grain diameters between 60 μm and 2 mm (Boliden Mineral AB, 1989).

A decommissioning programme based on flooding was completed in 1991 (for a detailed description, see Broman and Göransson, 1994). Flooding was achieved by raising the water level in the tailings and clarification pond by raising the existing dykes. Some parts of the tailings were re-deposited to lower the surface of the upstream tailings area. A small area of the tailings deposit consists of material which has been oxidised and weathered before the flooding, but the major part of the tailings was unoxidised. The previously oxidised material is richer in sulphides and is more coarse grained than the normal tailings. A breakwater system was built to prevent re-suspension from the tailings surface. The pond has an area of 1.1 km^2 and a water volume of about 2 Mm^3. Water depth varies between 0.6 and 9 m, with an average of about 2 m.

Stekenjokk is situated in the Caledonian mountains at an altitude of roughly 800 m above sea level. The climate is harsh, with an annual mean temperature of 0°C, and an annual precipitation of about 1100 mm (Boliden Mineral AB, 1989). The area is situated above the tree line, and strong winds are common. The pond is covered with ice and snow from October to June. Surface run-off enters the dam via two minor streams on the western side, and the outlet is located on the north-eastern side. The annual water volume discharged through the outlet is about 2 Mm^3. Thus, the hydraulic residence time of the pond is approximately one year.

3. Material and methods

Two cores were sampled from the tailings at two different locations (Stations 1 and 2 in Fig. 1) using a modified Kajak gravity corer with a Plexiglass® tube (∅85 mm). The core from Station 1 was sampled where the tailings were unoxidised and the core from Station 2 was sampled in an area where oxidised tailings were deposited during remediation. In order to minimise the disturbance of the tailings-pond water interface, a diver slowly pressed the corer into the tailings and sealed the Plexiglass® tube. Only cores with an undisturbed surface were accepted. The cores were divided under an Ar-atmosphere immediately after collection into 0.5 cm subsamples for the first 5 cm, and 1 cm subsamples thereafter. The tailing samples were stored in acid-washed polyethylene plastic bags that were subsequently stored in Ar-filled two-litre plastic bottles.

At both locations pH, temperature, depth and dissolved oxygen were measured in situ in the water column of the pond using a Hydrolab® Surveyor II water quality probe. Bottom water samples were collected 2 cm above the tailings surface using an acid washed syringe. The bottom water samples were stored in acid washed bottles and filtered through 0.22 μm Millipore® filters.

Microelectrodes manufactured by the Institute of Biological Sciences, University of Aarhus, Denmark, were used for measuring dissolved oxygen in the sampled cores after retrieval. Microelectrodes have been used earlier to measure oxygen profiles in natural sediments (e.g. Gundersen and Jørgensen, 1990; Gundersen and Jørgensen, 1991; Rasmussen and Jørgensen, 1992). For a more thorough description of the microelectrodes and the procedure used, see Holmström and Öhlander, 1999.

Pore water was extracted within a few hours after collection of the cores using a glove-box filled with Ar to prevent the samples from oxidising. The pore water was extracted by vacuum filtration using a portable Millipore® vacuum pump and an acid washed Nalgene® filterholder. The pore water was filtered through 0.22 μm Millipore® filters and collected in double acid washed test tubes. The test tubes were filled with 0.14 M nitric acid that was poured out prior to use. Two to 10 ml of pore water were extracted from each sample.

In order to avoid contamination all equipment used was acid-washed in 5% nitric acid. Blanks were taken before and after pore water extraction. A blank was also taken from the Milli-Q® water used. The blanks showed no traceable contamination. pH was measured in wet solid tailings using a special Metrohm® pH-electrode calibrated with pH 4 and pH 7 Titrisol® buffers.

Solid tailings were analysed for Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Nb, P, Pb, S, Sc, Si, Sn, Sr, Ti, V, W, Y, Zn and Zr using ICP-AES (ARL 3560 B). Cd, Hg and Ni were analysed using ICP-MS (VG Elemental Plasma Quad). Due to the small amount of pore water, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analysed using High Resolution-ICP-MS (Finnigan MAT ELEMENT). Ca, K, Mg, Na, S, Si and Sr were analysed by ICP-AES (ARL 3560 B). All samples were analysed at SGAB Analytica AB, Luleå, Sweden. No analyses of organic matter in solid tailings were made.

Electron microprobe analysis was performed on two polished thin sections made from material from the surficial tailings at each Station. The one made of material from Station 1 was plated with carbon and the other from Station 2 was plated with gold. The analyses were performed with a Cameca SX 100 WDS-scan operating with a voltage of 20 kV and a current of 12 nA. The spot size was 1–2 μm. Both single semi-quantitative analyses of spots and one mapping were performed. The counting time per pixel during mapping was 200 ms.

4. Results and discussion

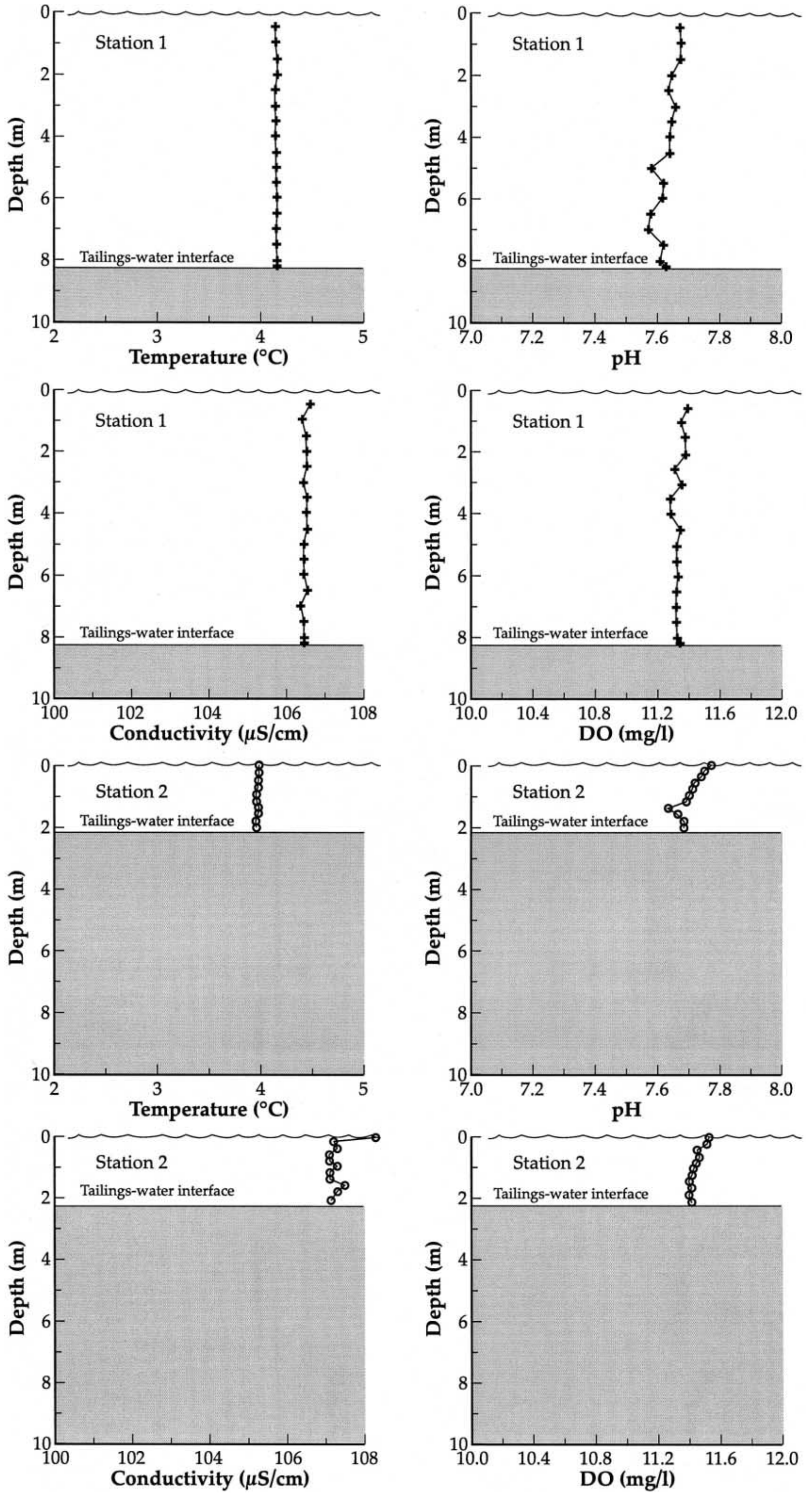
Two cores were sampled. The core sampled at Station 1 had a length of 26 cm, and the core sampled at Station 2 was 12 cm long. Both cores consisted of dark-grey tailings with a fluffy c. 0.5 cm thick layer on top, probably consisting of sediments rich in organic matter deposited after the flooding. This sediment layer seemed to be composed partly of living (green) algae and other black–brown unidentified materials. In the core sampled at Station 1, red alternating layers, a few millimetres thick, were visible below the layer rich in organic matter and above the dark-grey tailings. On top of the tailings in the core sampled at Station 2, small red nodules, a few millimetres in diameter, were visible instead of continuous red layers. The sulphide grains in the tailings were coarser in the core sampled at Station 2, suggesting the possibility that the smaller particles have been flushed away and settled in deeper parts of the tailings pond. This may also be a relict of the position of the spigotting points during tailings discharge.

The pond water was well mixed and well oxygenated with oxygen concentrations of around 11 mg/l O_2 during the sampling. The temperature of the pond water at the sampling sites was about 4°C and the pH varied between 7.57 and 7.78. The conductivity of the pond water varied between 106.5 and 108.4 μS/cm (Fig. 2). These results agree with the results of an extensive study of the pond water at Stekenjokk performed during 1995 (Ljungberg et al., 1997). The tailings are oxygenated down to depths of 11–17 mm (Fig. 3). The metal concentrations are rather low in the pond water (Table 1).

The content of most elements in the cores from both Stations 1 and 2 is rather constant at deeper levels in the tailings, but varies at the tailings surface (Figs. 4 and 5). The content of As, Ca, Cd, Co, Cu, Fe, Mo, Pb, S and Zn increases with depth from the tailings surface, whereas the content of Al, K, Mg, Mn, Na, Si and Ti decreases. The heavy metal concentrations are generally somewhat higher at Station 2 than Station 1. The average chemical composition of the tailings is shown in Table 2. The concentration difference between the surficial tailings and the tailings at depth for As, Cd, Co, Cu, Mo, Pb, S and Zn cannot be explained by oxidation of sulphides at the tailings surface as the mass difference is too large. The explanation is dilution with detrital material (mainly silicate minerals), organic material and Fe- and Mn-oxyhydroxides which lowers the concentration of heavy metals. The increasing amount of detrital material in the surficial sediments has resulted in increased contents of Al, K, Mg, Si and Ti. This is illustrated in Fig. 4 for Mg, Si and Ti. The detrital material has been received from the surroundings since the flooding, during snowmelt each year. The area around Station 1 is probably also affected by excavations and workings on the impoundment performed by Boliden AB during the remediation and during 1996, when the outlet from the impoundment was rebuilt.

There are well developed layers richer in Fe and Mn in the uppermost part of the tailings, as shown in Fig. 5, which corresponds well to the depth of oxygen penetration. These layer most likely are rich in poorly crystallised Fe- and Mn-oxyhydroxides. Studies of two polished thin sections from the surficial tailings show that the oxyhydroxides occur as aggregates as well as surface precipitates on mineral grains. It can also be seen from Fig. 5 that there is a close relationship between solid and dissolved Fe and Mn. Peaks in pore water concentration occur below the peaks in solid concentration. This is clearly seen for Mn at both Stations and for Fe at Station 1. It is evident that the Mn-rich layer is situated on top of the Fe-rich layer. This is due to the fact that Mn-oxyhydroxides are more sensitive to low redox than Fe-oxyhydroxides, i.e. Mn-oxyhydroxides tend to dissolve at higher redox than Fe-oxyhydroxides (e.g. Davison, 1993).

Although the concentrations of As, Cd, Co, Cu, Fe, Mo, Pb, S and Zn are lowest in the uppermost solid sample in both cores, the highest concentrations occur in the samples richest in Fe (illustrated in Fig. 6 for Cu, Zn and S). Pore water concentrations of the metals are highest in the layers richest in Fe, or just below. Since Fe-oxyhydroxides are known to have the capability to retain many trace elements by adsorption or co-precipitation (e.g. Alpers et al., 1994; Tessier et al., 1996; Banks et al., 1997), these results indicate that the Fe-oxyhydroxides to a large extent control the trace metal concentrations in the pore water. The lowest metal concentrations occur in the deepest pore water samples. There is good correspondence between the concentrations in the uppermost pore water samples and the bottom water samples at both Stations. For Ni (not shown here), the uppermost solid sample has the highest concentration for Station 1, and no obvious pattern for Station 2, possibly indicating a stronger correlation to Mn-oxyhydroxides. Although S has similar concentration pattern in the solid material as metals such as Cu and Zn, the pore water concentrations for Station 2 steadily increases with depth, and there is a concentration peak between 2 and 4 cm for Station 2. The deepest samples have


Station 1
Tailings-water interface
Depth (m)
0
2
4
6
8
10
Temperature (°C)
2
3
4
5
pH
7.0
7.2
7.4
7.6
7.8
8.0
Conductivity (μS/cm)
100
102
104
106
108
DO (mg/l)
10.0
10.4
10.8
11.2
11.6
12.0
Station 2

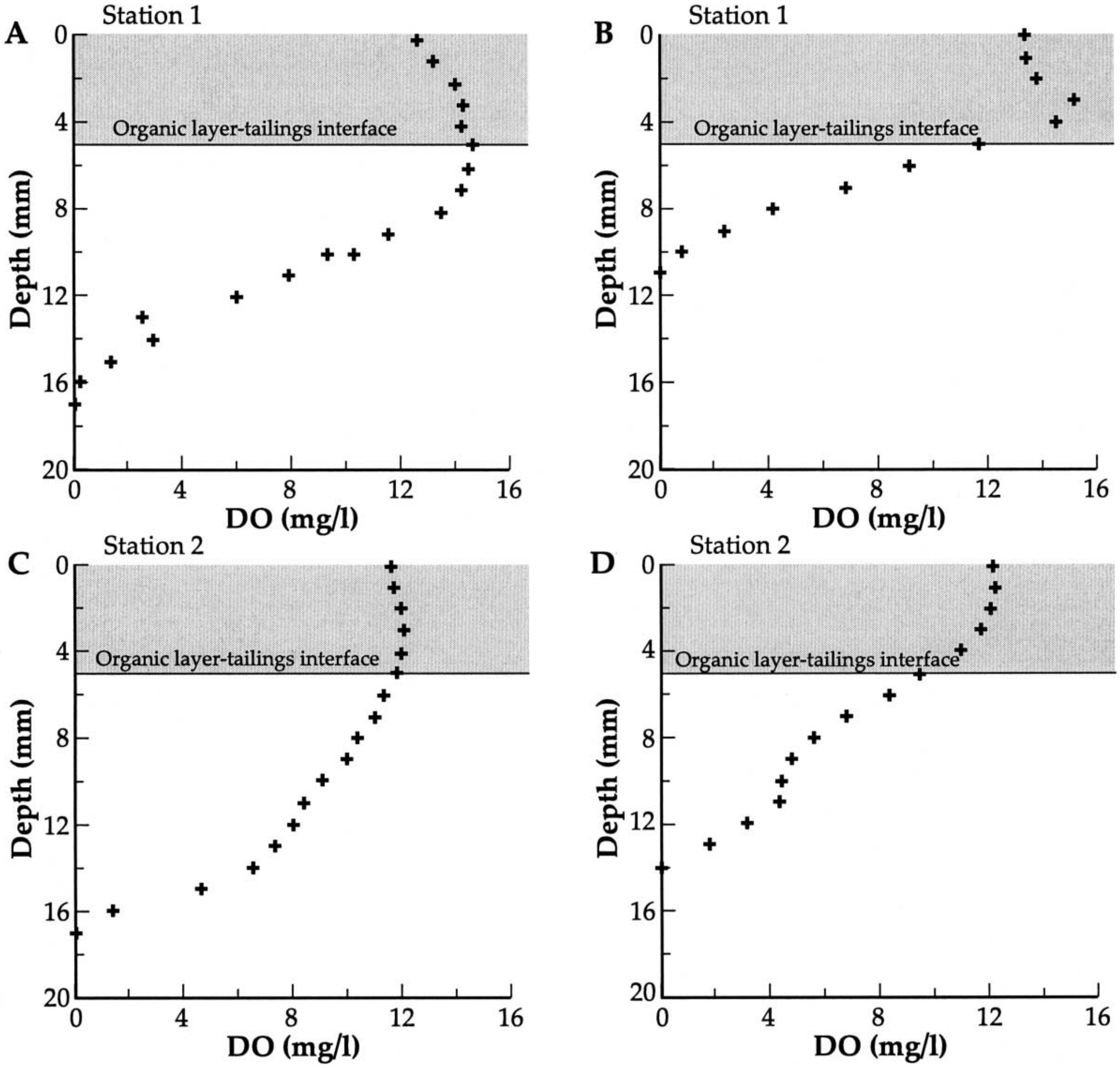


Fig. 3. Dissolved oxygen profiles in the sampled cores. Note the scale in millimetres. (A) and (B) are two different profiles in the core sampled at Station 1. (C) and (D) are two different profiles in the core sampled at Station 2.

higher concentration than the uppermost one also for Station 2.

Electron Microprobe analysis was performed on polished thin sections from the surficial tailings in order to study the Fe-oxyhydroxides, and to determine if they contain heavy metals. Mapping of a pyrite grain from Station 2 covered with Fe-oxyhydroxides and five point analyses of Fe-oxyhydroxides from Station 1 were performed. The results from the mapping and single spot analyses of Fe-oxyhydroxides are shown in Fig. 7 and Table 3.

Fig. 7 shows that the pyrite grain is covered with Fe-oxyhydroxide presumably formed by oxidation. This supports the conclusion of Holmström and

Fig. 2. Temperature, pH, conductivity and dissolved oxygen in the water column of the pond above the tailings sampling points. Note the scale in metres.

Table 1
Average composition of the water column (dissolved phase) during 1995. From Holmström et al. (2000) (b.d: Below the detection limit)

Element	Winter/Spring (May) 38 samples	Summer (July/ August) 107 samples	Autumn (September) 50 samples
(mg/l ± SD)			
Ca	32.0 ± 1.2	19.7 ± 1.0	21.8 ± 0.8
Fe	0.009 ± 0.005	0.042 ± 0.013	0.011 ± 0.004
K	0.51 ± 0.13	0.58 ± 0.34	0.35 ± 0.09
Mg	1.12 ± 0.04	0.68 ± 0.06	0.78 ± 0.03
Na	1.30 ± 0.18	1.00 ± 0.24	0.85 ± 0.10
S	18.1 ± 0.5	10.9 ± 0.5	12.2 ± 0.4
Si	0.33 ± 0.14	0.96 ± 3.40	0.26 ± 0.19
(μg/l ± SD)			
Al	1.04 ± 0.73	3.97 ± 0.68	2.01 ± 0.71
As	0.44 ± 0.11	0.34 ± 0.09	0.34 ± 0.11
Ba	2.85 ± 0.13	1.89 ± 0.27	1.99 ± 0.16
Cd	1.07 ± 0.20	0.69 ± 0.06	0.65 ± 0.06
Co	0.07 ± 0.03	0.16 ± 0.05	0.13 ± 0.02
Cu	2.03 ± 0.44	1.71 ± 0.18	1.57 ± 0.20
Hg	0.25 ± 0.03	b.d	b.d
Mn	7.9 ± 7.8	24.5 ± 8.9	8.0 ± 1.2
Ni	2.21 ± 0.24	1.38 ± 0.35	2.17 ± 0.22
Pb	0.23 ± 0.16	0.18 ± 0.06	0.16 ± 0.06
Sr	66.6 ± 2.8	43.7 ± 2.3	47.7 ± 1.4
Zn	268 ± 53	142 ± 15	150 ± 8

Öhlander (1999), that minor oxidation is occurring also after the flooding. Cu and Zn are evidently enriched by the Fe-oxyhydroxides covering the grain. It was, however, impossible to further analyse heavy metals, due to the fact that the high currents used seemed to evaporate the matrix of the polished thin section, but it is likely that elements like Cd, Co, Ni and Pb are also enriched. The single spot analyses showed that Cd, Co, Cu, Pb and Zn are present in the Fe-oxyhydroxides. It can be concluded that Fe-oxyhydroxides adsorb and enrich heavy metals at Stekenjokk.

Simple diffusion calculations suggest that diffusion of metals is occurring from the surficial sediments up

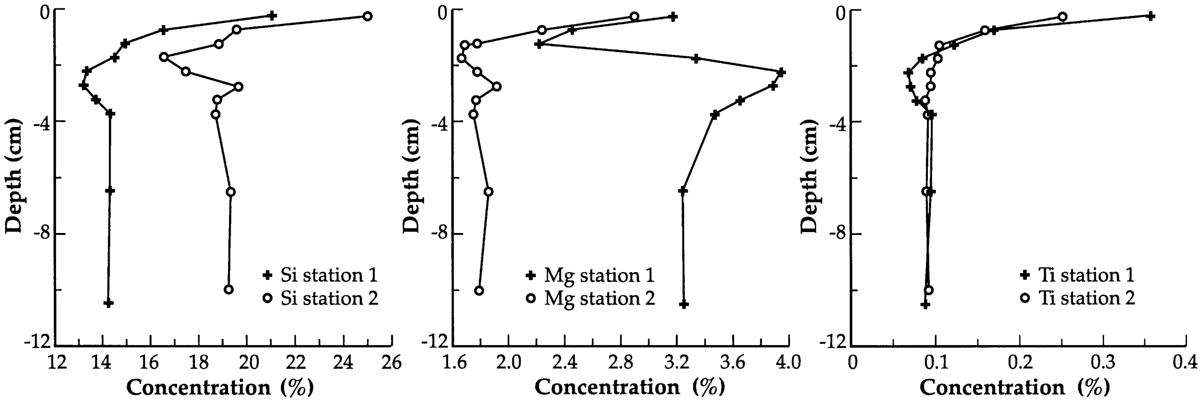


Fig. 4. Concentration profiles showing the contents of Si, Mg and Ti in solid tailings at both Stations. Note the scale in centimetres.

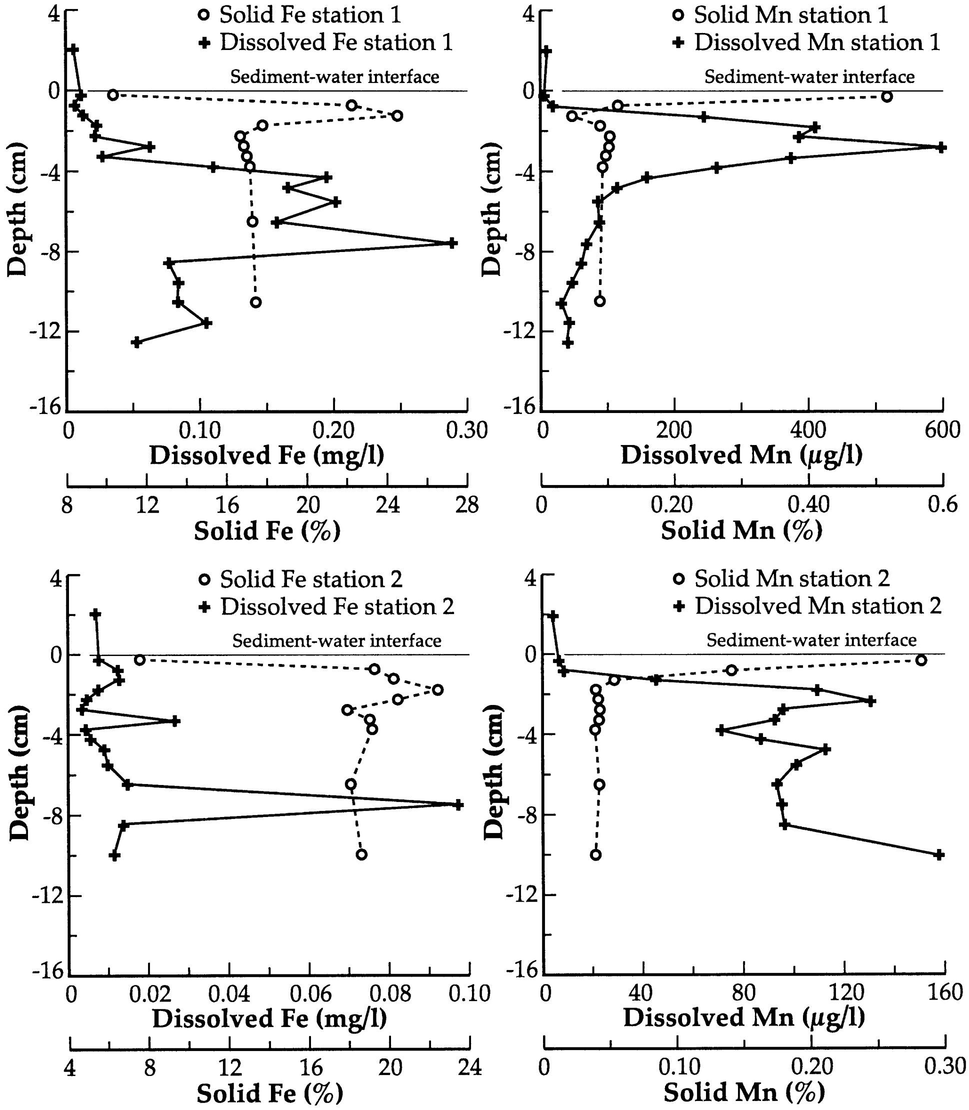


Fig. 5. Concentration profiles showing solid and dissolved Fe and Mn at both Stations. Note the scale in centimetres.

into the pond water despite the layers rich in organic matter and Fe- and Mn-oxyhydroxides. The flux of elements across the tailings-water interface has been estimated using Fick's First Law (Eq. (1)):

$$F_{\mathrm{d}} = -\varnothing D \frac{\mathrm{d}C}{\mathrm{d}z} \qquad (1)$$

where F_{d} is the diffusive flux (g/cm^{2}y), $\varnothing$ the sediment porosity, determined from the two cores' taken, c. 81 and c. 62% in the surficial tailings at Stations 1 and 2, respectively (these are high values but not unrealistic considering the fluffy nature of the surficial tailings at Stekenjokk), D the sediment diffusion coefficient corrected for tortuosity and temperature (4.15 and 3.97°C at Station 1 and Station 2, respectively) according to Ullman and Aller (1982). Diffusion coefficients from Li and Gregory (1974) have been used and $\mathrm{d}C/\mathrm{d}z$ is the concentration gradient measured across the tailings-water surface, approximated here as $\Delta C/\Delta z$ where ΔC is the difference in concentration

Table 2
Average composition of the tailings at Stekenjokk. 33 analyses from Ljungberg et al. (1997) are included. Major elements expressed as oxides

Element	Stekenjokk unoxidised tailings (53 samples)
(weight% ± SD)	
SiO_2	35.5 ± 6.4
Al_2O_3	5.89 ± 2.27
CaO	5.73 ± 2.38
Fe_2O_3	28.0 ± 4.6
K_2O	0.79 ± 0.26
MgO	4.60 ± 1.91
MnO	0.11 ± 0.09
Na_2O	0.42 ± 0.27
P_2O_5	0.22 ± 0.04
TiO_2	0.17 ± 0.08
LOI	17.0 ± 4.6
(ppm ± SD)	
As	1139 ± 351
Ba	252 ± 110
Be	1.68 ± 0.40
Cd	31.9 ± 15.7
Co	61.4 ± 19.5
Cr	31.1 ± 16.7
Cu	2266 ± 806
Mo	48.6 ± 11.7
Ni	24.3 ± 9.7
Pb	1458 ± 389
S	177757 ± 55907
Sc	6.01 ± 3.36
Sr	81.9 ± 32.3
V	156 ± 30
Y	14.0 ± 4.09
Zn	6829 ± 3001
Zr	51.1 ± 20.6

between the uppermost pore water analysis and the bottom water analysis (2 cm above the sediment surface), and Δz the vertical distance between the two analyses. Similar approximations have been used by e.g. Carignan and Nriagu (1985). It is assumed that D is equal to the molecular self-diffusion coefficient D_0. Advective flux, flux due to bulk movement of fluid, e.g. caused by bioturbation, wave and current stirring is neglected and only diffusion flux is taken into account.

The results of the diffusion rate calculations in this study for some important elements are shown in Table 4. According to the calculations, all elements except Pb at Stations 1 and 2, Co and Mn at Station 1 and A1 at Station 2 diffuse up from the tailings to the bottom-waters and the water column of the tailings pond. The diffusion rate is higher for the heavy metals Cd, Co, Cu and Zn at Station 2 compared with Station 1. The explanation for this is that although the highest concentrations of both solid and dissolved concentrations of these metals are similar for both Stations, the dissolved concentrations in the uppermost pore water sample is higher at Station 2 (Fig. 6) resulting in a higher $\Delta C/\Delta z$ value. However, the diffusion rate of the main elements Ca, Fe, Mg, Na and S is higher at Station 1.

At Station 2 previously oxidised material was dumped, and it seems as if this location is a hot spot for heavy metals. Larger proportions of the total concentrations of metals are in a more easily soluble state, e.g. secondary precipitates, and may dissolve and be released.

It is likely that the diffusion rates would have been higher if the layers rich in Fe- and Mn-oxyhydroxide layers and organic matter had not existed. It is probable that minor amount of metals still are released by sulphide oxidation in the uppermost, oxygenated tailings (Holmström and Öhlander, 1999), but the pore water concentrations of metals such as Cd, Co, Cu and Zn are much lower in the surficial tailings than below the oxyhydroxide-rich layers. If significant parts of the metal masses occur as metal-organic complexes in the fluffy surface sediment rich in organic matter, it is possible that the calculated diffusion rates are too high. The actual diffusion rates for metal-organic complexes may well be several orders of magnitude lower than the calculated ones (e.g. Elderfield, 1981; Burdige and Homstead, 1994; Burdige and Homstead, 1994). However, we have no data on the importance of metal-organic complexes at Stekenjokk.

The layers rich in Fe- and Mn-oxyhydroxides thus probably function as a trap for heavy metals, thereby lowering the amount of elements that are moving up into the pond water by diffusion. This is difficult to see directly from the concentration profiles due to the high sulphide content of the tailings, and due to the large content of detrital material in the uppermost part of the tailings. A normalisation with S can be used to understand the behaviour of the metals. It is assumed that S only occurs in sulphide minerals. One problem is that S, especially as SO_4^{2-}, is commonly adsorbed by oxyhydroxides (e.g. Karltun, 1995). This may be

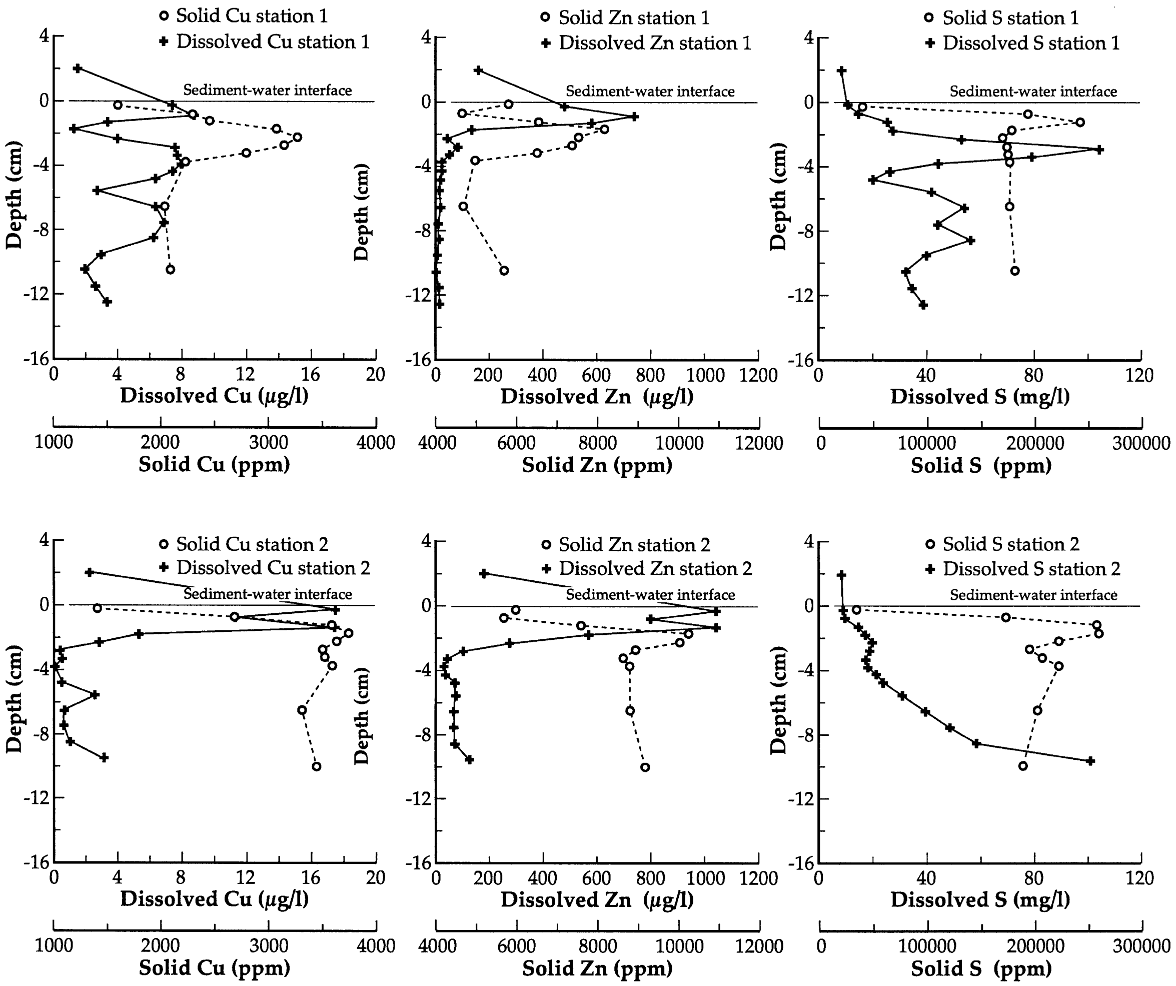


Fig. 6. Concentration profiles showing solid and dissolved Cu, Zn and S at both Stations. Note the scale in centimetres.

the reason why the S content reaches a peak value at depths of about 1.5 cm in both cores (Fig. 6); the same depth at which Fe concentration peaks caused by Fe-oxyhydroxides are situated. This peak may also be due to the existence of some secondary mineral s such as gypsum, which, however, has not been verified. This may give rise to a degree of error which is considered relatively small since most of the S occurs in sulphides. When normalised with S, elements such as As, Cd, Co, Cu, Mo, Ni, Pb and Zn all show high and increasing ratios towards the tailings surface (Fig. 8), although the concentrations of the metals are lowest in the uppermost sample (Fig. 6). If all metals were contained in sulphides the ratios would be rather constant through the whole profile, due to the relative homogeneity of the tailings at Stekenjokk. The homogeneity can be seen towards the depth in both cores at which the ratios are almost constant. This means that in the surficial tailings, the content of heavy metals is higher relative to S, i.e. to the sulphide content, and that the heavy metals must be correlated to other phases, presumably Fe- and Mn-oxyhydroxides and organic material. Regression analysis shows that between 84 and 99% of the total variation of As/S, Cd/S, Co/S, Cu/S, Mo/S, Ni/S, Pb/S and Zn/S may be explained by the content of Fe or Mn, i.e. connected to Fe- and Mn-oxyhydroxides.

The amount of non-sulphide bound metals, i.e.

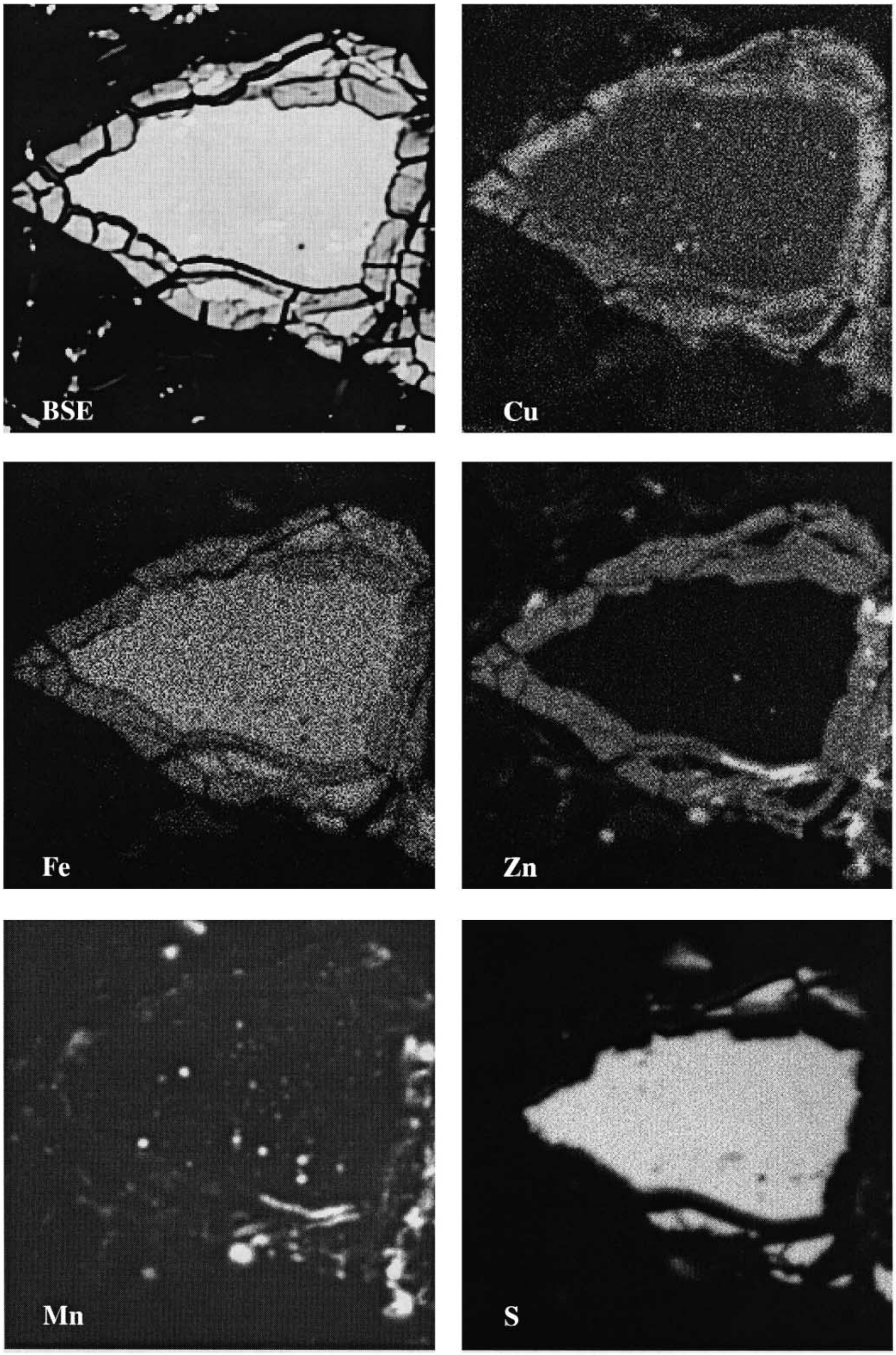

BSE
Cu
Fe
Zn
Mn
S

Table 3
Qualitative results from single spot analyses of Fe-oxyhydroxides from Station 1 made by electron microprobe. Analyses 1, 2 and 3 were done on a Fe-oxyhydroxide rim covering a pyrite grain. Analyses 4 and 5 were made on a Fe-oxyhydroxide aggregate (b.d: The element was below the detection limit)

Element	Analysis no: 1 concentration (wt%)	Analysis no: 2 concentration (wt%)	Analysis no: 3 concentration (wt%)	Analysis no: 4 concentration (wt%)	Analysis no: 5 concentration (wt%)
Cd	b.d	0.03	0.02	b.d	0.02
Co	0.005	b.d	0.04	0.004	0.03
Cu	0.16	0.10	0.17	0.07	0.08
Fe	44.2	20.1	54.3	38.9	39.2
Mn	0.09	0.02	0.06	0.06	0.07
Ni	b.d	b.d	b.d	b.d	0.03
Pb	1.09	1.05	b.d	0.06	0.16
S	0.95	0.27	8.32	0.69	0.75
Zn	2.30	1.72	1.95	1.29	1.34

metals adsorbed or co-precipitated on/with Fe- and Mn-oxyhydroxides or organic material in the uppermost sediments at both Stations can be calculated according to Eq. (2), where X_{total} is the total concentration of the element in question at the particular depth, S_{total} is the total sulphur content at the same depth and $X_{\text{sulphide}}/S_{\text{sulphide}}$, the ratio between the element and sulphur in the original tailings. The ratio between the element and sulphur in original tailings is calculated as an average of the four deepest samples at each Station and is a constant ratio in the calculations. It is assumed that these tailings are unaffected by secondary precipitation of oxyhydroxides.

$$X_{\text{total}} = X_{\text{non sulphide}} + (X_{\text{sulphide}}/S_{\text{sulphide}})S_{\text{total}} \qquad (2)$$

The calculations show that in the uppermost 0.5 cm, where the ratios show maximum values, about 33–42% As, 73–83% Cd, 59–76% Co, 60–72% Cu, 55–66% Mo, 81–91% Ni, 44–69% Pb and 76–81% of all Zn is non-sulphide bound. The amount of non-sulphide bound metals in the surface sediments is higher at Station 1. The amount of non-sulphide bound metals decreases deeper down in the tailings and at depth the metals are sulphide bound.

Table 4
Calculated diffusion rates across the tailings-water interface at both Stations. A negative value means diffusion from the pond water down to the tailings and a positive value diffusion from the tailings up into the pond water (b.d: The element was below the detection limit in the surficial tailings)

Element	Diffusion rate Station 1 (g/cm^2 y)	Diffusion rate Station 2 (g/cm^2 y)
Al	2.5×10^{-8}	-1.2×10^{-8}
Ca	3×10^{-4}	1.9×10^{-4}
Cd	5.7×10^{-8}	1.2×10^{-7}
Co	-4.9×10^{-10}	2.1×10^{-10}
Cu	1.8×10^{-7}	3.3×10^{-7}
Fe	1.7×10^{-7}	1.4×10^{-8}
K	b.d	2.2×10^{-5}
Mg	1.8×10^{-5}	3.7×10^{-6}
Mn	-1.2×10^{-7}	4.5×10^{-8}
Na	1.5×10^{-5}	6.8×10^{-6}
Ni	4.6×10^{-8}	4×10^{-8}
Pb	-3.3×10^{-8}	-1.8×10^{-8}
S	9.6×10^{-5}	2.7×10^{-5}
Zn	9.3×10^{-6}	1.8×10^{-5}

5. Conclusions

The tailings at Stekenjokk were flooded in 1991, and during the years after the flooding thin layers rich in Fe- and Mn-oxyhydroxides have formed in the uppermost part of the tailings, and a thin sediment layer rich in organic material has been developed on top of the tailings. This was seen in both cores sampled. Calculations using a normalisation procedure show that in the uppermost part of the tailings

Fig. 7. Microprobe mapping picture of a pyrite grain from Station 2 showing the back-scattered (BSE) image of the grain and the element distribution of Cu, Fe, Zn, Mn and S. Note the outer ring containing Cu, Fe and Zn. The area size is 100 × 100 μm.

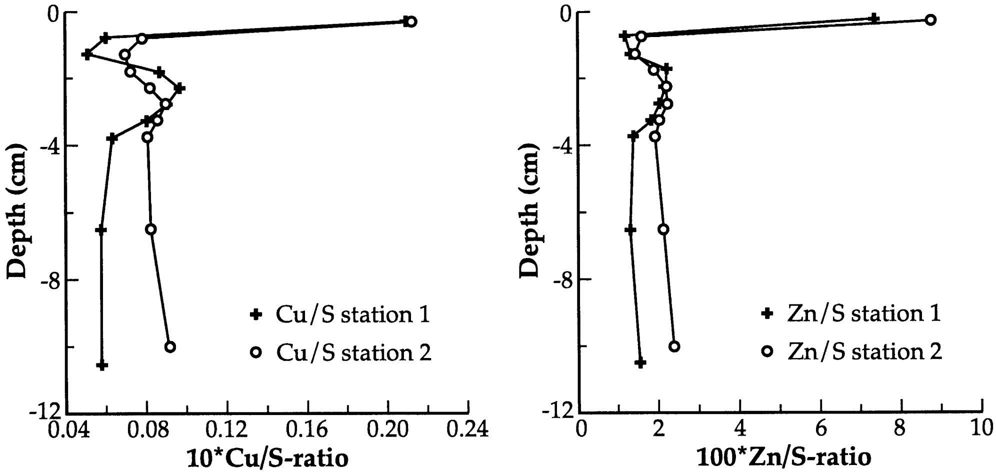


Fig. 8. S-normalised molar ratios for Cu and Zn at both Stations. Note the scale in centimetres.

33–42% of the As, 73–83% Cd, 59–76% Co, 60–72% Cu, 55–66% Mo, 81–91% Ni, 44–69% Pb and 76–81% Zn is non-sulphide bound, i.e. connected to some other phase, presumably Fe- and Mn-oxyhydroxides and organic material. The layers rich in Fe- and Mn-oxyhydroxides and organic material retain upwards diffusing metals by adsorption and/or co-precipitation, thereby lowering the amount of metals being transported from the tailings into the pond water.

The heavy metal concentrations are somewhat higher at Station 2, where previously oxidised tailings were deposited during the remediation, compared with Station 1. The diffusion of heavy metals from the tailings up into the pond water is also higher at Station 2.

This study shows that it is possible that, after some time, a flooded tailings pond may reach a state where the uppermost part of the tailings will start to function as a natural lake, in which the sediment-water interface controls the diffusion of elements into the overlying pond waters. The time-frame during which this occurs may not always be several decades or centuries, but may be as short as a few years after remediation. However, it must be emphasised that the tailings at Stekenjokk was remediated almost completely unoxidised and that the carbonate content of the tailings is high.

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References

Alpers, C.N., Blowes, D.W., Nordstrom, D.K., Jambor, J.L., 1994. Secondary minerals and acid mine-water chemistry. In: Jambor, J.L., Blowes, D. (Eds.). Short Course Handbook on Environmental Geochemistry of Sulfide Mine-wastes. Waterloo, Ont., pp. 247–270.

Aubé, B.C., St-Arnaud, L.C., Payant, S.C., Yanful, E., 1995. Laboratory evaluation of the effectiveness of water covers for preventing acid generation from pyritic rock. In: Hynes, T.P., Blanchette, M.C. (Eds.). Proceedings of Sudbury'95, Mining and Environment 28 May–1 June 1995, Sudbury, Canada, pp. 495–504.

Banks, D., Younger, P.L., Arnesen, R.T., Iversen, E.R., Banks, S., 1997. Mine-water geochemistry: the good, the bad and the ugly. Environmental Geology 32, 157–174.

Blowes, D.W., Jambor, J.L., 1990. The pore water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. Applied Geochemistry 5, 327–346.

Boliden Mineral AB., 1989. Stekenjokk Efterbehandlingsplan 1989-11-30. Boliden Mineral AB, Boliden, Sweden. Decommissioning plan for Stekenjokk. In Swedish.

Boorman, R.S., Watson, D.M., 1976. Chemical processes in abandoned sulphide tailings dumps and environmental implication for Northeastern New Brunswick. CIM Bulletin 69, 86–96.

Broman, P.G., Göransson, T., 1994. Decommissioning of tailings and waste rock at Stekenjokk, Sweden. Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third Conference on the Abatement of Acidic Drainage, Pittsburgh, USA, 24–29, April 1994. pp. 32–40.

Burdige, D.J., Homstead, J., 1994. Fluxes of dissolved organic carbon from Chesapeake Bay sediments. Geochimica et Cosmochimica Acta 58, 3407–3424.

Burdige, D.J., 1994. Erratum to Burdige DJ, Homstead J. Geochimica et Cosmochimica Acta 1994a. Geochimica et Cosmochimica Acta 58, 5370.

Carignan, R., Nriagu, J.O., 1985. Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario. Geochimica et Cosmochimica Acta 49, 1753–1764.

Davison, W., 1993. Iron and manganese in lakes. Earth-Science Reviews 34, 119–163.

Donahoe, R.J., Liu, C., 1998. Pore water geochemistry near the sediment-water interface of a zoned, freshwater wetland in the southeastern United States. Environmental Geology 33, 143–153.

Elderfield, E., 1981. Metal-organic associations in interstitial waters of Narragansett Bay sediments. American Journal of Science 281, 1184–1196.

Gundersen, J.K., Jørgensen, B.B., 1990. Microstructure of diffusive boundary layers and the oxygen uptake of the sea floor. Nature 345, 604–607.

Gundersen, J.K., Jørgensen, B.B., 1991. Fine-scale in situ measurements of oxygen distribution in marine sediments. Kieler Meeresforschung 8, 376–380.

Herbert Jr., R.B., 1995. Precipitation of Fe oxyhydroxides and jarosite from acidic groundwater. GFF 117, 81–85.

Herbert Jr., R.B., 1996. Metal retention by iron oxide precipitation from acidic groundwater in Dalarna, Sweden. Applied Geochemistry 11, 229–235.

Holmström, H., Öhlander, B., 1999. Oxygen penetration and subsequent reactions in flooded sulphidic mine tailings: a study at Stekenjokk, northern Sweden. Applied Geochemistry 14, 747–759.

Holmström, H., Ljungberg, J., Öhlander, B., 1999. Role of carbonates in mitigation of metal release from mining waste. Evidence from humidity cells tests. Environmental Geology 37, 267–280.

Holmström, H., Ljungberg, J., Öhlander, B., 2000. The character of the suspended and dissolved phases in the water cover of the flooded mine tailings at Stekenjokk, northern Sweden. The Science of the Total Environment 247, 15–31.

Ingri, J., Widerlund, A., 1994. Uptake of alkali and alkaline-earth elements on suspended iron and manganese in the Kalix River, northern Sweden. Geochimica et Cosmochimica Acta 58, 5433–5442.

Juve, G., 1974. Ore Mineralogy and Ore Types of the Stekenjokk Deposit, Central Swedish Caledonides. Sveriges Geologiska Undersökning C 706, Uppsala, Sweden.

Karltun, E., 1995. Sulphate Adsorption on Variable-charge Minerals in Podzolized Soils in Relation to Sulphur Deposition and Soil Acidity. Swedish University of Agricultural Sciences, Uppsala, Sweden. PhD Thesis.

Kerndorff, H., Schnitzer, M., 1980. Sorption of metals on humic acid. Geochimica et Cosmochimica Acta 44, 1701–1708.

Li, Y.H., Gregory, S., 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochimica et Cosmochimica Acta 38, 703–714.

Lin, Z., 1996. Leachate chemistry and precipitates mineralogy of Rudolfsgruvan mine waste rock dump in central Sweden. Water, Science and Technology 33, 163–171.

Ljungberg, J., Lindvall, M., Holmström, H., Öhlander, B., 1997. Geochemical field study of flooded mine tailings at Stekenjokk, Northern Sweden. Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, B.C, Canada, 31 May–6 June 1997. pp. 1401–1417.

Payant, S., St-Arnaud, L.C., Yanful, E., 1995. Evaluation of techniques for preventing acidic rock drainage. In: Hynes, T.P., Blanchette, M.C. (Eds.). Proceedings of Sudbury'95, Mining and Environment, 28 May–1 June 1995, Sudbury, Canada, pp. 485–494.

Rasmussen, H., Jørgensen, B.B., 1992. Microelectrode studies of seasonal oxygen uptake in coastal sediment: role of molecular diffusion. Marine Ecology Progress Series 81, 289–303.

Schnitzer, M., 1986. Reactions of humic substances with metals and minerals. In: Carlisle, D., Berry, W.L., Kaplan, I.R., Watterson, J.R. (Eds.). Mineral Exploration: Biological Systems and Organic Matter. Prentice-Hall, Englewood Cliffs, New Jersey, pp. 409–427.

Shaw, T.J., Gieskes, J.M., Jahnke, R.A., 1990. Early diagenesis in differing depositional environments: The response of transition metals in pore water. Geochimica et Cosmochimica Acta 54, 1233–1246.

Tessier, A., Fortin, D., Belzile, N., Devitre, R.R., Leppard, G.G., 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements. Geochimica et Cosmochimica Acta 60, 387–404.

Ullman, W.J., Aller, R.C., 1982. Diffusion coefficients in nearshore marine sediments. Limnology and Oceanography 27, 552–556.

Widerlund, A., Ingri, J., 1996. Redox cycling of iron and manganese in sediments of the Kalix river estuary, Northern Sweden. Aquatic Geochemistry 2, 185–201.

Zachrisson, E., 1971. The structural setting of the Stekenjokk ore bodies, central Swedish Caledonides. Economic Geology 6, 641–652.