

Effects of iron oxidation on the adsorption of trace elements in systems with low pH and high iron concentrations

Final Report

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1. INTRODUCTION

Metals in surface waters can cause substantial and detrimental effects on plants and on animals. Since metal releases emanating from production and industrial activities have been recognised and partly dealt with, metals from other sources have become increasingly more important. Among the most important sources for metals entering the environment are mine waste (50 % of all the waste produced in Sweden originates from mining activities). The residues from old mining sometimes consist of coarse residues, due to the extraction methods used, and this will increase the penetration of oxygen and water into the tailings, leading to an increase in the rate of oxidation and thus the release of metals to the surroundings.

In order to prevent the release of acidic metal-rich leachates from mining areas, tests with different types of cover of the wastes have been carried out in Canada, Australia and Sweden. In Rum Jungle, Australia a covering project was performed 1982 to 1986. The effects of this cover were monitored. The concept of the cover as a barrier for percolating water worked as expected. Ryan and Joyce (1991), noted however, that no significant trends in metal concentrations in the receiving surface water were detected. In Mount Washington, Canada, covering of sulphidic mine waste took place during 1988 and 1989. Changes in the surface water quality caused by the cover has not been confirmed (Galbraith, 1991). From the same site Kwong, (1991) reports of increased amounts of Fe(II) in the groundwater outlet from the mine waste heaps.

In Bersbo, Östergötland, a full scale covering experiment was carried out from 1987 to 1989. Acceptable or good results have been achieved with respect to the barrier function (oxygen and water) of the cover (Lundgren and Lindahl, 1991). Changes in the hydrochemistry of the outflowing water have occurred as a result of the cover. The most obvious difference is the dramatic increase in iron concentrations from one of the two drainages (Storgruve deposit). Fe(II) is the dominating iron species in the effluent water (Karlsson et al., 1993). The Fe(II) released into the surface waters will oxidise from Fe(II) to Fe(III) that will form sparingly soluble (oxy)hydroxides. This oxidation of Fe(II) and the subsequent precipitation of (oxy)hydroxides takes place in a lake receiving water from three small inlets. The dominating part of the metal load to the lake emanates from the mining area and is a mixture of mine water and leachates from the covered deposit.

The solubility of metals are a function of the hydrochemistry of the soluble phase. Ionic strength, pH, content of soluble humic and fulvic acids are important parameters that affects the solubility. Speciation and thus mobility of metals will also depend on physical or chemical characteristics of the solid phase. Adsorption may occur onto suspended particles, and depending on the size of these particles mobility may either increase (colloids) or decrease (sedimentation). The capacity as well as the rate of which adsorption takes place will also be dependent not only on the type of the adsorbing material at the existing hydrochemical conditions but also on the age of the adsorbing material.

Hydroxides or oxyhydroxides of iron are known to be excellent adsorbents for trace metals e.g. cadmium, copper, lead and zinc (Singh och Subramanian, 1984; Tessier et al., 1985;

Johnson, 1986). Several adsorption studies of trace elements have been described in the literature. Most of the studies, however, have been performed with synthetic solutions of metals, and crystalline material as adsorbents. The effects of an iron phase consisting of freshly formed precipitates on the distribution of trace elements is less known, but of importance in environments where an iron-rich groundwater is exposed to the atmosphere. The pH at which the solids are formed could (together with other factors like organic content, ionic strength) affect the rate of oxidation and precipitation, the character of the formed surfaces and thereby the adsorption of trace elements present in the water phase.

The oxidation and precipitation of iron will on the other hand cause a net production of protons and thereby an acidification of the effluent water. In some systems the precipitation of iron could even be the dominating process that sets the pH. It is also known that a lowering of pH decreases the efficiency in trace element adsorption onto the solid iron(oxy)hydroxides (Tessier et al., 1989; Karlsson et al., 1987).

Two factors with opposite effects on the mobility of trace elements are thus identified; on one hand acidification, which in general decreases adsorption to solid surfaces, and on the other hand production of solid forms of iron that often are excellent adsorbents. Both factors are expected to exist in water systems where releases of soluble iron takes place.

The present report describes the effects of the cover in Bersbo on trace metal retention, especially with focus on the effects of increased iron concentrations in the receiving surface water (lake Gruvsjön). The capacity for trace metal retention of a precipitating iron phase as a function of pH, organic content and temperature are studied. Through a combination of field and laboratory data the distribution between aqueous and solid metal forms is evaluated. The distribution will have effects on the regional distribution of metals.

2. METHODS

2.1 Field studies

The field site Bersbo is situated in the municipality of Åtvidaberg, Sweden, where effective mining for copper took place during a period of 150 years. The main constituent of the ore was pyrite. Since mineral dressing was done manually a coarse waste open for penetration of oxygen and water was produced. Information about geology and mined ores are given in Tegengren (1924). General information of the area and its hydrochemistry are found in Allard et al., (1987).

In order to minimise the amount of covering material several small scattered heaps of mining residues were put together into two major piles. Mining residues were also dumped into the abandoned mine shafts, in order to somewhat decrease the amount of material that needed to be covered. Unexpectedly, a great part, about 1/3 of the total amount of material was contained in the old shafts.

On the eastern pile a dense layer of stabilised coal fly ash covered by 2 m of till was put on the waste material. Description of the covering procedure can be found in Lundgren 1990. Early

follow up of the performance with regard to the cover is described by Lundgren and Lindahl, (1991) and with respect to the hydrochemistry of the leachate by Håkansson, (1991) and Håkansson et al.,(1994).

The leachate from the westward drainage and its effects on the hydrochemistry of the receiving lake (see table 2) are discussed in this report. The sampling point “Outlet” (table 2) refers to a sampling point located at the outlet of the first lake (lake Gruvsjön) and represents concentrations in the lake. The sampling point “Inlet” is situated in a small creek about 200 m downstream of the tailings and the mine and includes water from the mine as well as leachates from the waste and water diverted to ditches during remedial actions. A small increase in evaporation caused by the preservation of moisture in the surficial layers of the cover is expected but transpiration from vegetation and transport of moisture by vegetation is low as long as the vegetation is scarce and the plants are small. This means that although the cover has caused the water to take new paths and less water produces a leachate, the overall effect of water volumes coming from the mine and the tailings are assumed to be similar as previously.

2.2 Solid phase studies

Samples of mine waste from the Bersbo site (Storgruvan) was collected and the samples were carefully examined in order to confirm that only residual material from the mining operations were obtained. Depending on a visual inspection on the degree of weathering the waste was divided into two fractions less weathered (LW) and more weathered (MW) The mine waste was sent to a mining company (Boliden) for grinding.

2.2.1 Humidity cells

Different designs have been proposed to test the potential of sulphidic mine waste to form acid rock drainage. Humidity cells where the waste is exposed to moisture and oxygen in different cycles are widely accepted as a practical way to test this potential. However, the number of cycles, suitable time required for each cycle and surface area exposed to oxidation and leaching are a matter of discussion. In the present case an experimental setup proposed by Corporacion minera de Bolivia (1995) was used, but for practical reasons the number of cycles were limited to two. Humidity cells were constructed according to Lundgren (pers. comm. 1995). The grounded waste material was sieved and 250 g of the fraction between 1 and 2 mm was used for the tests. The material was mixed with glass beads, 3 mm in diameter, put in the cells, then exposed to dry air for 72 h (ambient humidity in the laboratory), exposed to humid air (air passing a water filled chamber) for another 72 h. The sample was put in distilled water for 1 h and allowed to drain for 10 min, then again put in freshly distilled water for 15 min, allowed to drain for 10 min and put back in the cell for a new cycle. The rinsing water about 3 l per cycle (giving a total L/S ratio of 24) and the water was saved for analysis of Fe, Cd, Cu, Zn and pH.

2.2.2 Leaching with reducing agent

A reducing agent is required in order to solubilise the metal species that are associated with the oxidised parts of the waste (predominantly (oxy)hydroxides of iron). The use of hydroxylaminehydrochloride has been proposed by several authors in sequential leaching

procedures (Tessier et al., 1979; Kersten and Förstner, 1986) in order to dissolve amorphous oxides and hydroxides of Al, Fe and Mn. In a study examining the reductive dissolution of weathered mine tailings, Ribet et al. (1995) proposes the use of a 2M solution during 24 h for the extraction of reducible iron with a liquid solid ratio (L/S) of about 30. However, the information from Ribet et al. was not available during the time of the experiments and instead, in the present work, a leaching solution of 0.1 M was used. Five cycles were performed giving a total L/S of 100 and a total leaching time of 288 h. Analysis of Fe, Cu and Zn was done on the leachates.

2.3 Pilot scale test

Initial tests were undertaken in order to examine the water quality of leachates with or without contact with oxygen from the air. The same material as described above was used for the tests. Two barrels of PVC containing 360 l were used for the tests. One of the barrels was open to the atmosphere, and the other was covered with a tight lid with a vent equipped with a water lock. A perforated disk was placed close to the bottom of the barrels (0.1 m). A filter cloth was placed on the disk and 285 kg of mine waste was put on the filter. The barrels were filled with tap water (in the "anaerobic" barrel oxygen was removed by purging with nitrogen). In order to cover the mine waste 143 l of tap water was sufficient. During the tests two pumps circulated the water and N₂ was continuously bubbled in the closed barrel. Oxygen was sampled and analysed on the air above the leaching water, and in the water phase, oxygen and pH was measured and samples for metal analysis (Fe and Zn) were taken.

2.4 Adsorption studies

A well characterised leachate from Bersbo was used in the adsorption-precipitation experiments, modified by additions of fulvic acid and pH-adjustment. Water was taken from the tailings at the Bersbo mine (Storgruvan) on different occasions. The water represented a mixture of mine water and leachates. Concentrations of Fe, Cd, Cu and Zn and pH were determined on the samples. The experiments were performed as titrations at constant pH (pH-stat between pH 4 and pH 5.4). This was considered to be the pH-interval in the receiving lake (see table 2). Prior to further treatment to some of the samples were added Cu or fulvic acid (Table 1). To achieve phase separation (removing precipitates during storage) samples were centrifuged at 20 000 g at 5 °C for 15 min in an ultracentrifuge (Beckman J2-21M). Analysis with PCS (Photon Correlation Spectroscopy) on lake water samples confirm that this procedure is equal to the removal of particles by filtration through a filter with a nominal diameter of 0.40µm (Ledin, 1993). The low temperature was chosen in order to minimise the temperature dependent oxidation of iron during the centrifugation. The centrifuged sample was divided into two or three subsamples, one of them was acidified with HNO₃ (Merck, Suprapure 2 ml/l sample). For some experiments TOC was determined and one subsample was thus withdrawn and stored at 8 °C for later analysis. The rest of the sample was used for the titration which commenced immediately after centrifugation and was performed open to the atmosphere in vessels equipped with a magnetic stirrer. Titrations were performed at constant pH and temperatures ranging from 10 to 25 °C (Table 1) using a water cooling/heating system. pH-values were recorded and kept constant during the titration. The samples were weighed to check for differences due to evaporation before and after titrations. Titrations of

the samples were performed with Radiometer VIT 90. A combination electrode was used to record and monitor pH-values (GK 2402B). A Radiometer Sample Station, SAM 90 kept pH constant by the addition of 0.1 M NaOH at the same rate as the oxidation/precipitation rate. Recordings of the additions of NaOH with time would show the rate of the overall reaction.

Disturbances in the performance of the titrations occurred during some of the experiments. Precipitates of iron were formed at the tip of the byrette preventing the base to react with protons. The ceramic connection between the solution and the reference electrode showed signs of clogging and the electrode was thus cleaned twice a day. The additions of the base were stopped when about 50 % of the iron had precipitated in the first tests (A1 - A10). Some of the most time-consuming tests were, however stopped earlier. In the later tests (Fe2 -Fe13)the aim was to have a 25 % decrease of soluble Fe after the titrations. The concentrations of soluble Fe before and after titration agreed very well with the formation of a solid (oxy)hydroxide of Fe(III) from a soluble Fe(II) specie.

After completion of the titrations, the sample was again centrifuged and decanted into plastic vessels. Subsamples for metal analysis and TOC when applicable, was withdrawn. Cd, Fe, Cu and Zn were analysed with AAS on Perkin-Elmer 1100 with flame technique, on an air - acetylene flame. Analysis of Al (Table 5) was done with the similar technique but with nitrous oxide as oxidant.

Table 1. Conditions for the laboratory adsorption studies.

Nr	Sample vol. (ml)	NaOH (ml)	pH	Temp (°C)	Added HFA (mg/l)	Added Cu (mg/l)	Time (min)
A1	50	3.20	4.6	25	0	0	1451
A2	50	3.17	4.6	25	0	2.65	712
A3	50	2.06	4.6	25	0	5.30	424
A4	50	3.18	5.0	25	0	0	185
A5	50	3.72	5.0	25	0	2.65	158
A6	50	3.21	5.0	25	0	5.3	116
A7	50		5.4	25	0	0	
A8	50	3.22	5.4	25	0	2.65	60
A9	50	3.20	5.4	25	0	5.3	38
A10	50	0.713	4.1	25	0	0	2760
Fe2	75	2.40	5.0	25	0	0	158
Fe5	75	2.38	4.6	25	0	0	623
Fe6	75	2.40	4.6	15	0	0	1789
Fe7	75	2.40	5.0	10	0	0	722
Fe8	75	2.39	5.0	25	0	0	299
Fe10	75	2.24	4.6	25	10	0	583
Fe11	75	2.40	5.0	15	0	0	1059
Fe12	75	2.40	4.6	25	100	0	279

Fe13 75 2.40 4.6 25 100 0 90

2.5 Storage studies

Samples from the hydrochemical monitoring program were filtered, analysed and then stored at 8 °C. After several months of storage under air the samples were taken out and again filtered and analysed with respect to Fe, Cu, pH and electrical conductivity. Samples were collected from the immediate outlet from the mine waste (D), from the inlet to the lake (I) and from the outlet of the lake (G). Analysis was done as in 2.4.

3. RESULTS AND DISCUSSION

3.1 Hydrochemical monitoring

A monitoring program has been going on for more than 10 years in the Bersbo area. The results for some key parameters regarding the hydrochemistry in the western drainage is presented in table 2 and in figures 1 and 2 below.

Table 2. Median values of some parameters at the mine drainage inlet to lake Gruvsjön and outlet of lake Gruvsjön in Bersbo (Cd µg/l, others mg/l). For each of the parameters n = 70 - 75

Location	pH	SO4	Fe	Mn	Cd	Cu	Zn
Inlet before	3.95	514	6.7	3.35	198	10.6	81.6
Inlet after	3.73	1080	204	8.15	138	3.94	58.0
Outlet before	4.96	86	0.55	0.59	16	0.53	7.58
Outlet after	4.7	138	0.46	1.14	8.5	0.21	4.52

before = before remedial actions (85 -87)

after = after remedial actions (89 -95).

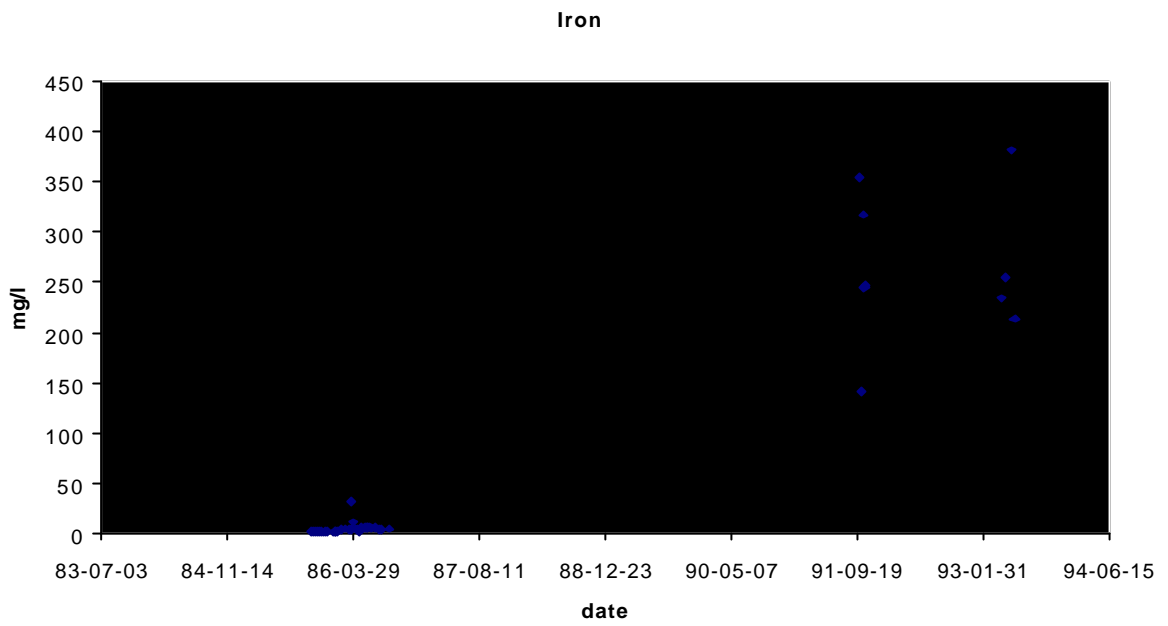


Figure 1a. Concentrations of iron as a function of time at the inlet of Lake Gruvsjön

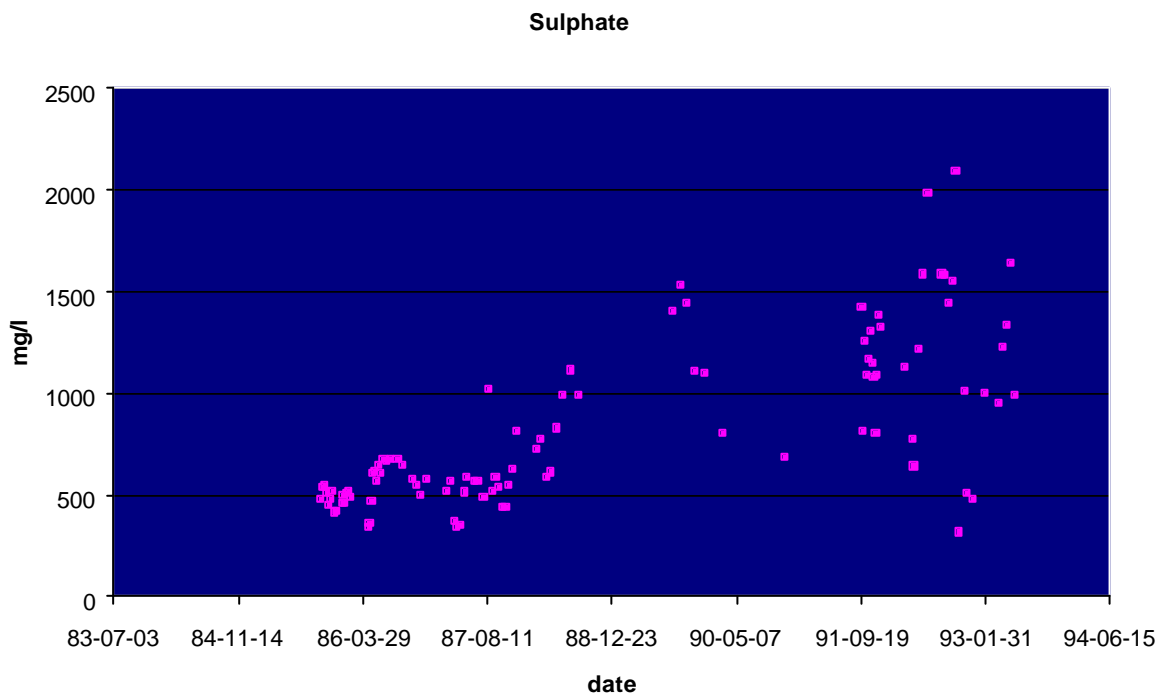


Figure 1b. Concentrations of sulphate at the inlet to the lake Gruvsjön

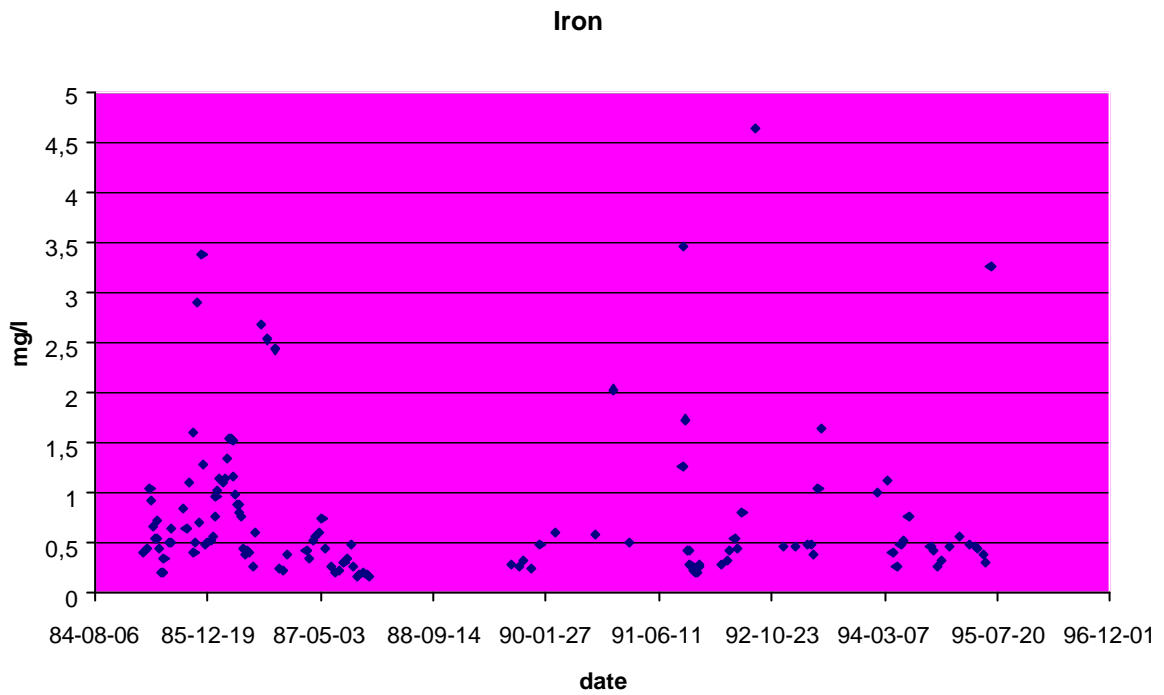


Figure 2a. Concentrations of iron as a function of time at the outlet of Lake Gruvsjön

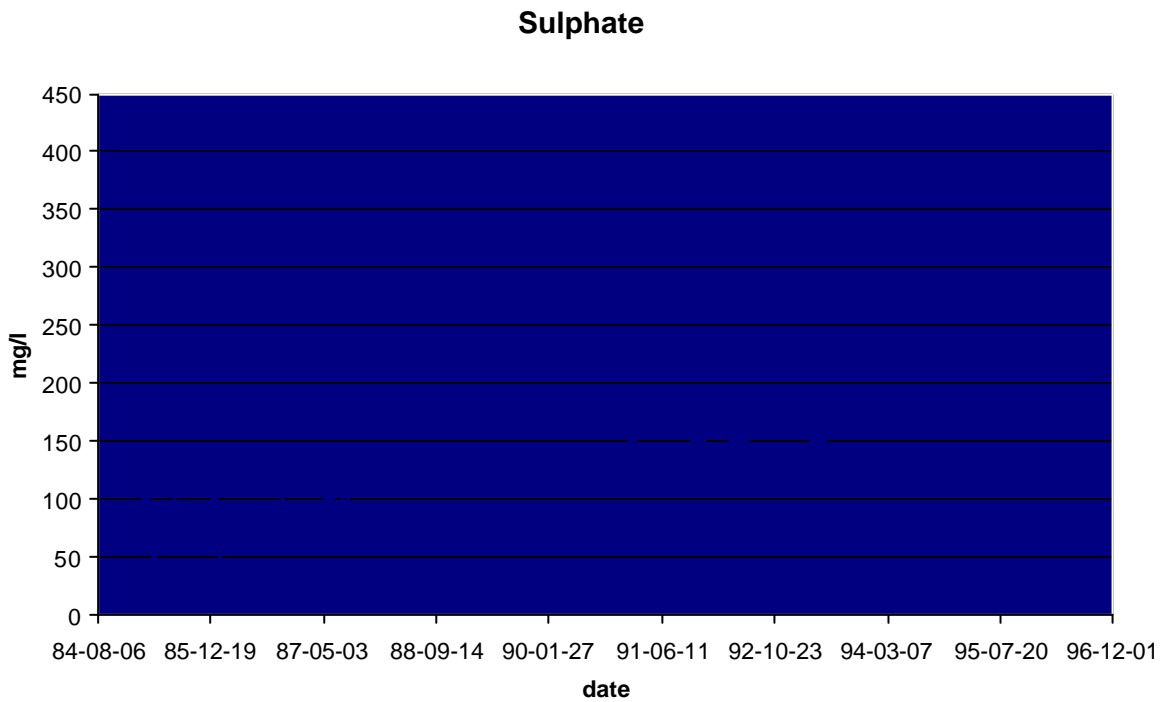


Figure 2b. Concentrations of sulphate as a function of time at the outlet of Lake Gruvsjön

As can be seen in table 2, the concentrations of the heavy metals Cd, Cu, and Zn have decreased at the inlet after covering. At the outlet (representing concentrations in the lake) decreasing concentrations are also found. The change in pH and the high input of Fe to the lake may however have changed the conditions in the lake resulting in either a decrease or an increase in the ability of the lake to act as a sink for heavy metals. In order to calculate the effect of the lake, an estimation of the metal transport has to be done. The transport of metals out of the lake can be determined relatively accurate since recordings of the water flow are available. The effect of the cover on water flow can however not directly be seen since no recordings of the flow of water coming in to the lake are available. The contribution of flow at the outlet emanating from the inlet can however be made, using conservative parameters and assuming that the share of the flow from mine water plus leachates i.e. "Inlet" has not changed due to the remedial actions (Håkansson, 1991) and that the contribution from the surroundings are constant. Below is an example for potassium.

$$IK_b * X + (1 - X) * YK = OK_b \quad (1)$$

$$IK_a * X + (1 - X) * YK = OK_a \quad (2)$$

where

$IK_{b,a}$ refers to concentrations of K (potassium) at the inlet before and after remedial actions

$OK_{b,a}$ refers to concentrations of K (potassium) at the outlet before and after remedial actions.

X is the share of the water originating from the inlet and passing through the lake.

YK is the concentration of K in the water from the rest of the drainage area.

These estimations as above were made for Na, K, SO_4 , and Mn with median values.

X (above) became for Na 0.235, for K 0.091, for SO_4 0.092 and for Mn 0.115.

The high value for Na could be caused by a high leaching from surrounding areas due to ion-exchange with Ca. A substantial part of the area was treated with limestone. In several mining areas the precipitation of jurbanite is reported. It has not been found here though, but if it is the case this would result in that e.g. concentrations of potassium at the outlet after remedial actions (OK_a) are low and thus the a higher proportion of water would originate from the mining waste area. Carignan and Nriagu (1985) reported that acidification could release Mn from sediments by diffusion. A lowered pH in the lake is observed (table 3) and may be one of the causes for the high outlet concentrations of Mn.

The contribution from the inlet sampling point is thus set to contribute with 0.1 of the water flow at the outlet or equivalent constitute 0.1 of the drainage area.

When we put this value in eq. 3

$$ICd_b * 0.1 + 0.9 * YCd = OCd_b \quad (3)$$

and in eq 4

$$ICd_a * 0.1 + 0.9 * YCd = OCd_a \quad (4)$$

we find a contradiction giving negative values of the concentrations from the surroundings (YCd) The explanation is that Cd is not conservative and that the lake acts as a sink for Cd both after and before covering. Even if we do not know the concentrations (or average

concentration) of Cd from the other sources contributing to the outlet concentration, we can see that differences are higher after covering.

Before covering the retention in the lake is higher than 3.8 µg per L of outlet water ($0.1 \cdot 198 + 0.9 \cdot Y_{Cd} = 16$), while after covering the retention is higher than 5.3 µg per L of outlet water ($0.1 \cdot 138 + 0.9 \cdot Y_{Cd} = 8.5$). This means that the lake probably retains Cd more efficiently after covering than before. The same reasoning is applicable to Zn and Cu and by the same arguments Zn is also found to be more efficiently retained in the lake, and while the lake still act as a sink for Cu, this metal is less efficiently retained after the remedial actions.

3.2 Solid phase studies

The leachates from the humidity cells gave a pH of between 3 and 4 for both materials. No clear trends were found, possibly due to the low number of cycles (2) that was not sufficient for a substantial weathering.

The total leached amounts for both the humidity cells and reducing tests are presented in table 3 below.

Table 3. Leached amounts from humidity cells and reducing tests on different types of weathered mine waste (mg/kg of total weight).

Treatment/ waste type	Humidity cells		Reducing agent	
	LW	MW	LW	MW
Fe	185	588	10 700	11 800
Zn	39	104	314	785
Cu	1.93	3.43	197	131
Cd	0.28	0.66	NA ¹	NA ¹

1 NA = not analysed

The reducing tests were performed with a high L/S (totally 100) with 5 cycles, while oxidation tests were done at a total L/S of 24. In order to facilitate comparisons between the relative amounts of heavy metals leached from the different tests a normalisation with respect to Fe was done and is presented in table 4 below. Since the leachate from the humidity cells were conducted at a relatively low pH, secondary hydroxide precipitates was not expected. No signs of hydroxides were observed neither on the material nor on the vessels.

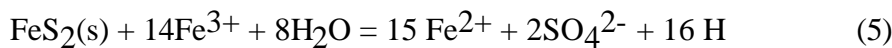
Table 4. Leached amounts from humidity cells and reducing tests normalised with respect to Fe on different types of weathered mine waste.

Treatment/ waste type	Humidity cells LW	Humidity cells MW	Reducing agent LW	Reducing agent MW
Fe	100	100	100	100
Zn	21.1	17.7	2.9	6.6
Cu	1.0	0.58	1.8	1.1

1 NA = not analysed

It can be seen from the table that the material dissolved by the reducing agent have comparatively low concentrations of Zn. This is an indication that the hydroxides of Fe that will be dissolved by the reducing agent contain less Cu and Zn than what is contained in the pyrite. Since the tests with the humidity cells were conducted during a relatively short period, the proportion between the metals Zn and Cu may be different in a situation with a high weathering rate and possibly more extreme pH-values. A mechanism where pyrite is oxidised by Fe(III) instead of O₂ which is indicated in the reducing tests above is more corresponding to the situation after remedial actions than before (Table 2).

The oxidation of pyrite by Fe(III) can be described by:



where Fe³⁺ comes from the dissolution of (oxy)hydroxides

3.3 Pilot scale test

The results presented here refers to the initial phase when the experiment was set up and does not represent long-time performance of a (water)-covered mine waste.

Oxygen concentrations in the air were low for the anaerobic system during the whole experiment (0.45 %). It seems however that the duration of the experiment was not sufficient to lower the oxygen content in the water below 1 mg/l (see figure 3). It is also possible that concentration in the water are kept high by diffusion of oxygen that can take place through the walls of the vessel. pH in the leachate water showed the same development in both the studied systems (from pH 5 to pH 3).

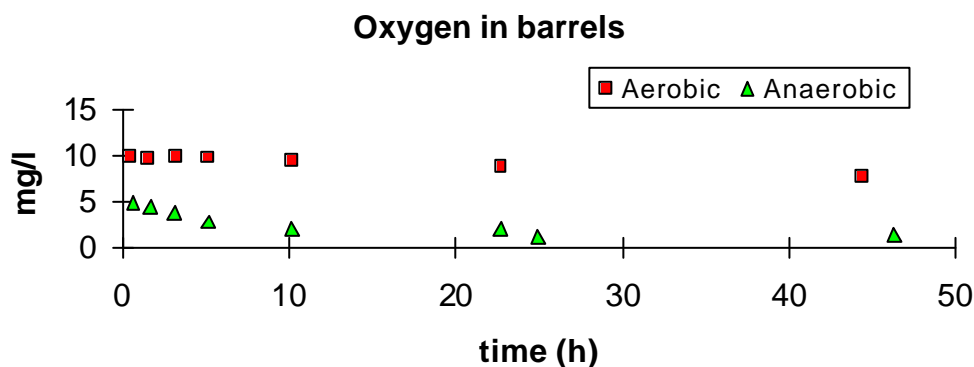


Figure 3. Concentrations of oxygen in two differently treated barrels for pilot scale testing of mine waste leaching

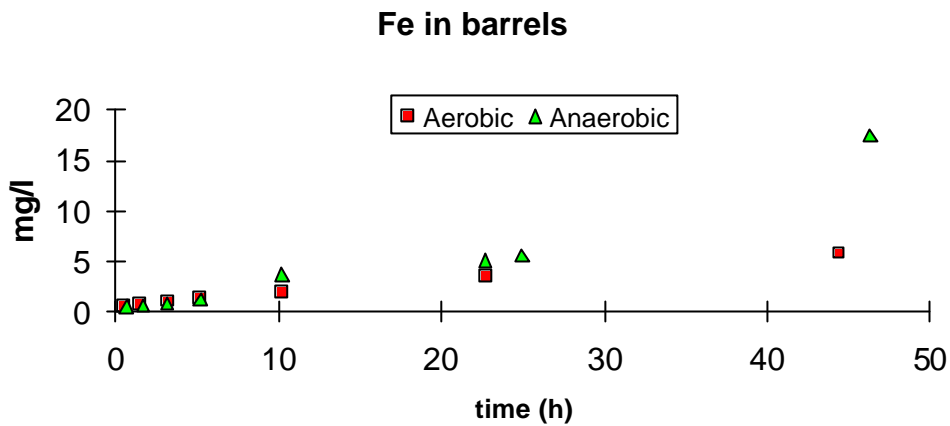
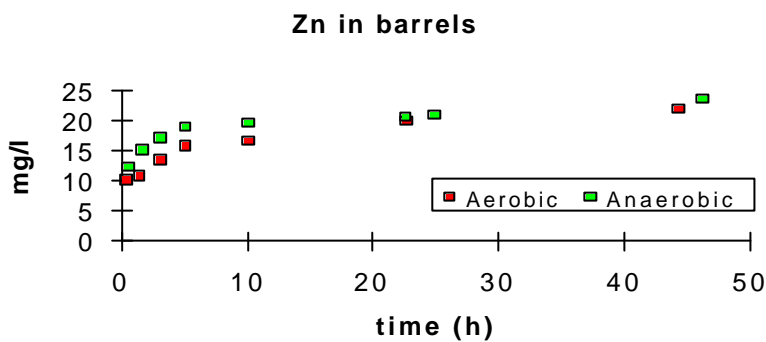


Figure 4. Concentrations of iron in two differently treated barrels for pilot scale



testing of mine waste leaching.

Figure 5. Concentrations of zinc in two differently treated barrels for pilot scale testing of mine waste leaching.

In figure 4 the build up of Fe concentrations are presented. The concentrations of Fe is increasing in the "anaerobic" system. This is in accordance with the changes in the hydrochemistry of the leachate at the field site after application of the cover.

Zn concentrations are similar in the two systems, with somewhat higher values for the "anaerobic" system. After two years of storage without mixing and with oxygen present the initially aerobic barrel had a zinc concentration of 80 mg/l while the initially anaerobic barrel had a zinc concentration of 58 mg/l.

3.4 Adsorption studies

The concentrations of metals before and after titration at constant pH for the mine and leachate water are presented in table 5. In figures 6 - 8 the amount of metal that adsorbs/coprecipitates is related to the amount of precipitated iron.

Table 5. Concentrations of metals in the soluble phase before and after titrations.

Fe (mg/l)	Cd μ g/l	Cu (mg/l)	Zn (mg/l)	Al (mg/l)
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Nr	before	after	before	after	before	after	before	after	before	after
A1	380.8	212.1	122	118	1.66	1.055	62.01	50.20	NA	NA
A2	380.8	169.7	122	110	4.308	3.82	62.01	51.51	NA	NA
A3	380.8	182.8	122	110	6.956	6.680	62.01	49.19	NA	NA
A4	375.7	195.9	123	118	1.67	0.645	61.61	52.16	NA	NA
A5	375.7	144.4	123	111	4.318	2.595	61.61	52.02	NA	NA
A6	375.7	179.8	123	112	6.966	4.235	61.61	53.93	NA	NA
A7	330.3	152.5	116	110	1.190	0.285	57.47	51.74	NA	NA
A8	330.3	144.4	116	110	3.838	1.340	57.47	51.51	NA	NA
A9	330.3	148.5	116	109	6.486	5.010	57.47	52.72	NA	NA
A10	188.9	157.6	327	320	11.14	9.95	124.5	115.1	NA	NA
Fe2	300	219.2	327	297	4.9	2.8	138	104.6	3.5	1.2
Fe5	275.7	244.4	333	309	7.2	5.1	135.6	129.3	23.2	8.9
Fe6	301	232.3	327	299	6.9	4.8	144.2	125.4	20.9	10.9
Fe7	285.8	210.1	330	280	5.8	3.2	140.4	102.8	10.4	4.3
Fe8	281.8	178.8	322	302	5.6	2.7	141	121	6.7	1.6
Fe10	277.8	191.9	320	300	6.0	3.6	136.4	120.6	8.5	2.6
Fe11	284.8	204.2	328	281	6.1	3.3	145.6	104.6	8.7	4.1
Fe12	244.4	167.7	293	284	5.3	1.5	128	101.2	11.1	1.5
Fe13	293.4	184.3	296	278	5.7	2.7	129.9	114.1	15.7	2.6

(cont.)

Nr	before	after
Fe5	4.25	4.47
Fe6	4.65	4.65
Fe7	4.40	4.00
Fe8	3.92	3.72
Fe10	4.45	4.14
Fe11	3.79	9.96
Fe12	9.14	7.32
Fe13	10.5	6.65

In figure 6 adsorption is presented as a function of time elapsed for the titrations. It can be seen that adsorption increases with time for up to some hundred minutes. All data have been

used for the plot.

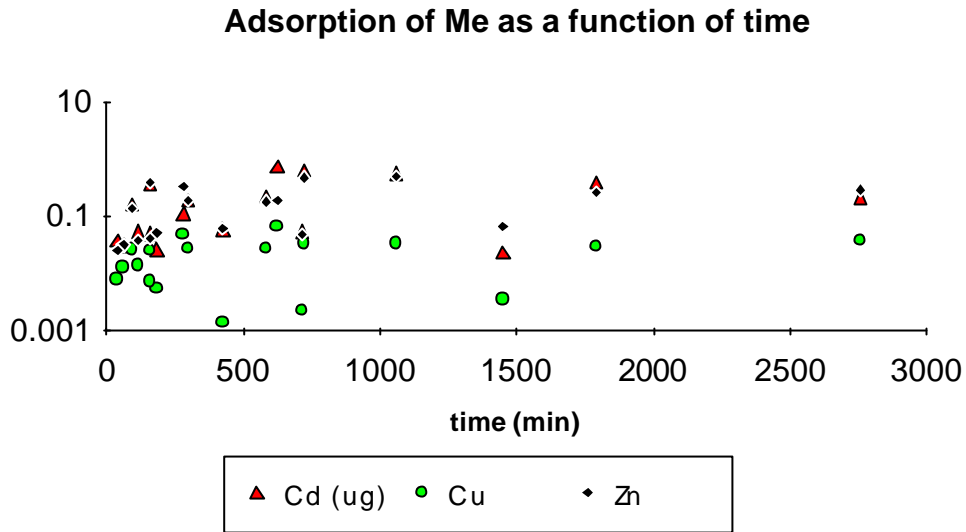


Figure 6. Adsorption of metals expressed as mg Me/mg of precipitated Fe (for Cd μg) expressed as a function of time (min) for titrations.

In figure 7 the relation between pH and time elapsed for the titrations are plotted (data where similar amounts of Fe is scavenged from the solution are used for the plot).

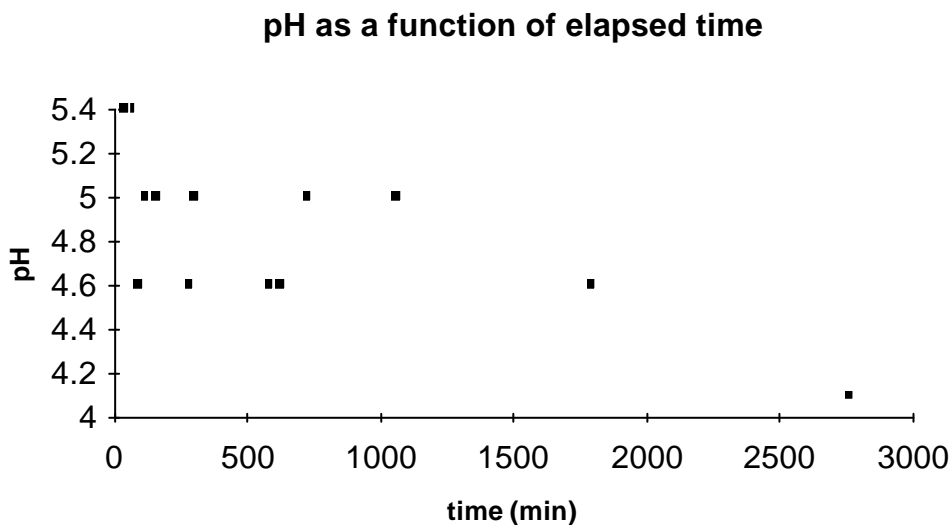


Figure 7. Time (min) required for completion of titrations compared to pH

A correlation between the rate of reaction and pH is found which is in accordance with several studies e.g. Eary and Schramke, (1990); Stumm and Morgan (1991). In figure 8 average adsorption values at each pH are compared for Cd, Cu and Zn. Cu differs from the other metals in that no clear pH-dependence is found. While other metals are increasing their adsorption at low pH Cu has similar adsorption over the studied pH-interval. As noted above this unexpected pH-effect is not unambiguously an effect of pH itself but could rather be an

effect of the longer duration of the experiments performed with low pH, that apparently favours the adsorption of Cd and Zn.

Adsorption as a function of pH

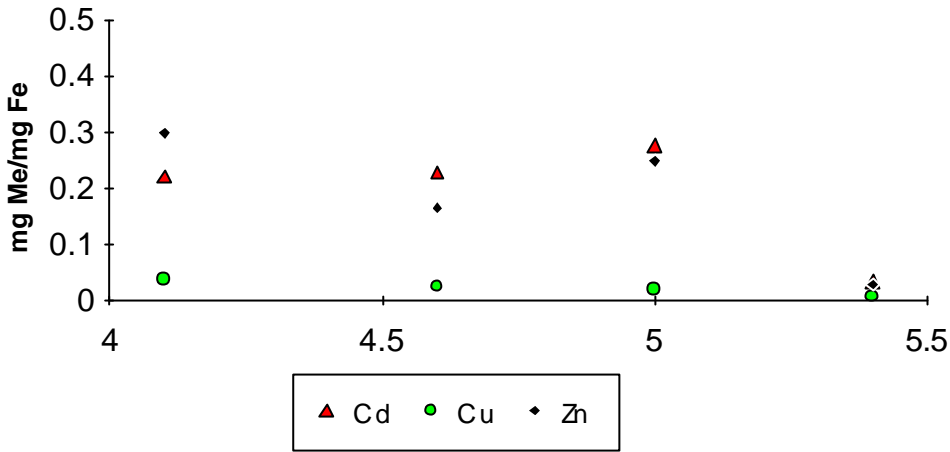


Figure 8. Adsorption of metals (average value at each pH) expressed as mg Me/mg of precipitated Fe (for Cd μg) expressed as a function of pH for titrations.

In figure 9 the average adsorption values are plotted against the temperature. Also for temperature does Cu differ from the other metals with constant adsorption at the studied temperatures, while Cd and Zn have an increased adsorption at low temperature. This could again be an effect of the longer duration of the low temperature experiments giving longer contact times and the opportunity for an efficient adsorption of Cd and Zn.

Adsorption of Me as a function of temperature

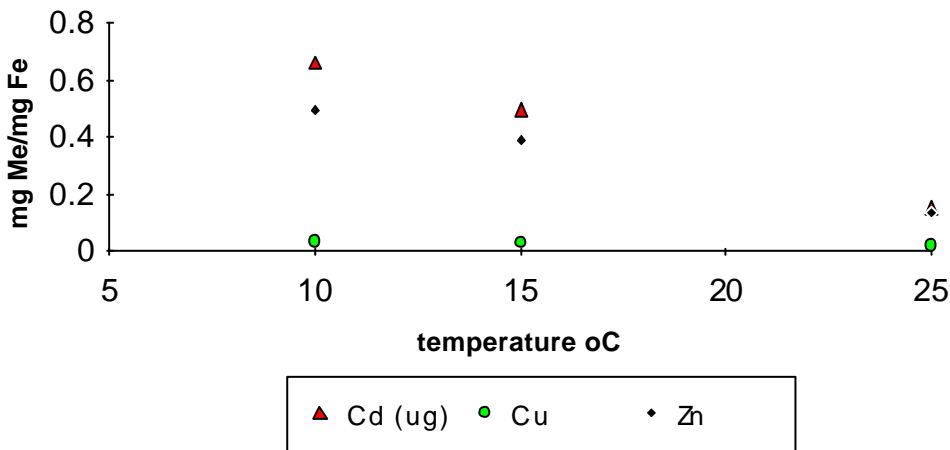


Figure 9. Adsorption of metals (average value at each pH) expressed as mg Me/mg of precipitated Fe (for Cd μg) expressed as a function of temperature for titrations

3.5 Storage studies

Results from the storage of water samples are presented below (Table 6) This was done on samples taken for the hydrochemical monitoring programme. This was done to study the development of the hydrochemistry on the samples.

Table 6. Concentrations in samples from the hydrochemical monitoring program initially (i) and after storage (s)

	Stor. time (d)	pH (i)	pH (s)	El. cond. (i)	El. cond. (s)	Cu (i)	Cu (s)	Fe (i)	Fe (s)
D 1	206	4.6	2.77	2630	3150	3.71	3.49	378	276
D2	192	4.74	2.55	2650	3120	3.19	3.05	398	165
D3	183	4.75	3.09	2630	2840	3.09	2.92	399	307
D4	113	4.83	2.64	2650	2800	3.86	3.73	381	282
Inlet 1	206	3.49	2.53	1870	2550	4.51	4.17	182	37.7
Inlet 2	192	3.49	2.61	1960	2400	3.58	3.39	195	83.8
Inlet 3	183	3.69	2.68	1690	2070	3.11	2.9	162	62.6
Inlet 4	113	4.66	3.16	1213	1440	2.41	2.27	112	69.7
Outlet1	183	4.2	4.12	403	406	0.225	0.22	0.42	0.1
Outlet2	169	4.19	4.15	400	406	0.22	-	0.27	-
Outlet4	113	4.57	4.57	356	187	0.189	0.198	0.47	0.1

D1-D4 are samples of mine and leachate water draining from the Storgruve deposit taken from four occasions.

During storage the pH of the samples decreases. This is most evident for the samples taken from location D and from samples taken from the inlet to the lake. These samples have high concentrations of iron and the pH drop is most likely an effect of the precipitation of Fe(III) after oxidation. The increase in electrical conductivity is an effect of the higher ionic conductivity of hydrogen than of iron. (Hydrogen becomes an important constituent in the water when pH drops below 3). Adsorption of copper does take place on samples from D and the Inlet but to a small extent.

4. CONCLUSIONS

- The concentrations of the metals Cd, Cu and Zn into the lake and out of the lake have decreased after the remedial actions, and most likely also the transported amounts.
- The receiving lake acts as a sink for Cd, Cu and Zn, but Cu is less efficiently retained after covering actions.
- It is strongly indicated that the high input of Fe to the lake causes a further acidification of the lake.
- Laboratory studies show that the secondary oxidation of Fe causes a comparatively less retainement of Cu compared to Cd and Zn.
- Humidity cells and reducing leaching dissolution tests indicates that the formed hydroxides of iron on the waste is a less important source of trace elements than the ore itself.
- If (oxy)hydroxides of iron are formed at low pH then trace elements can still be present in the mobile water phase.

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