EFFECTS OF INCREASED IRON CONCENTRATIONS ON THE MOBILITY OF CADMIUM, COPPER AND ZINC IN LEACHATES AFTER REMEDIAL ACTIONS AT AN OLD SULPHIDIC MINE WASTE SITE[1]

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Abstract: The covering of acidic mine waste occured from 1987 to 1989 at a former copper mine site in Bersbo, Sweden. The purpose of the cover was to reduce the weathering of the sulphidic ore residues (pyrite, sphalerite, chalcopyrite, galena).

Analysis of water quality data shows that in one of the two drainages from the covered area, comparatively minor decreases of cadmium, copper, and zinc (30% - 65%) have occurred after completion of the remedial actions. The concentration of sulphate on the other hand, has increased from 600 mg/L to 1 000 mg/L, and iron concentration from 6 mg/L to more than 200 mg/L.

The hypothesis is that these changes are caused by the reduction of iron(III)oxyhydroxides to iron(II) in the mine shafts and subsequent oxidation of sulphides. That is, a possible change from oxygen to iron as an oxidant for the sulphidic minerals.

The effects of the high iron(II) load on the recieving lake and the changes in hydrochemical conditions when this iron is oxidized anew is discussed. Water quality data before and after remedial action and effluent titrations at different (constant) pH have been combined to indicate the effects of metal sorption on iron oxyhydroxides and metal removal by sedimentation.

The amount of iron hydroxides deposited in the mine shafts and thus the potential capacity for weathering is estimated from analysis of the solid waste and concentrations in the leachates before and after restoration.

Additional Key Words: acid mine drainage, iron oxidation,

Introduction

Although the principal mechanisms of oxidation of pyrite are known (Stumm and Lee 1961; Stumm and Morgan 1981; Kelly and Tuovinen 1988), no uniform strategy of disposal of mine tailings has been developed. Thermodynamic calculations and laboratory tests are important tools to assess the impact of different parameters. Empirical studies of pilot- or full-scale projects are, however, a necessary complement to such investigations, since practical difficulties will influence the success of restoration projects.

The starting point of this study is the observed differences in the composition of the leachates, and water quality in adjacent surface waters, especially with regard to iron concentrations, of an old mine tailings deposit before and after a dry deposition covering project. The contrasting effects of iron on the adsorption of trace elements in scavenging of metals are discussed; 1 The formation of an important adsorbent for metals, 2 The lowered pH during oxidation of Fe(II).

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Field site

Bersbo is a former copper mine about 250 km south of Stockholm, Sweden. The bedrock is leptitic with younger granitic and amphibolic intrusions containing hornblende, augite, and calcium-rich plagioclase (Tegengren 1924; Allard et al. 1987). The ore veins contain pyrite, magnetic chalcopyrite, and sphalerite and, to some extent, galena. The same rock types constitute the primary fractions of the tailings on the site. A detailed description of the area is found in Allard et al. (1987).
The most intensive mining period in Bersbo started around 1760, with the highest production between 1850-70. Mining ceased around 1900, although minor extraction continued until 1930.

The waste material was piled near the shafts and covered before reclamation about 0.2 km^2. The leachates discussed in this work emanates from the western part of the tailings deposit (figure 1) and drains into the small lake (Gruvsjön). Since the ores were separated manually from the extraneous material, the mine waste consists of coarse material. Oxygen measurements in the dumps (Lundgren and Lindahl 1991) showed that the material was well ventilated, and oxidative weathering would proceed in the pile. It has been estimated that 700 000 m^3 of mine waste have been produced (Lundgren 1990).
A continued high weathering rate and the possibility to use Bersbo as a full-scale test site for other old sulphidic mine waste sites were some of the objectives for the reclamation project that took place from 1987 to 1989. The aim was to reduce the releases of Cd, Cu, Pb, and Zn associated with the pyrite with 90% [Länsstyresen 1986, (County board)].

Tailings were piled together in two heaps to minimize the area to be covered. To further minimize the area, 200 000 m^3 of tailings were dumped into the old shafts (Lundgren and Lindahl 1991). Areas where tailings had been removed were treated with lime. For a detailed description of the covering procedures and technical specifications, see Lundgren (1990) or Lundgren and Lindahl (1991).

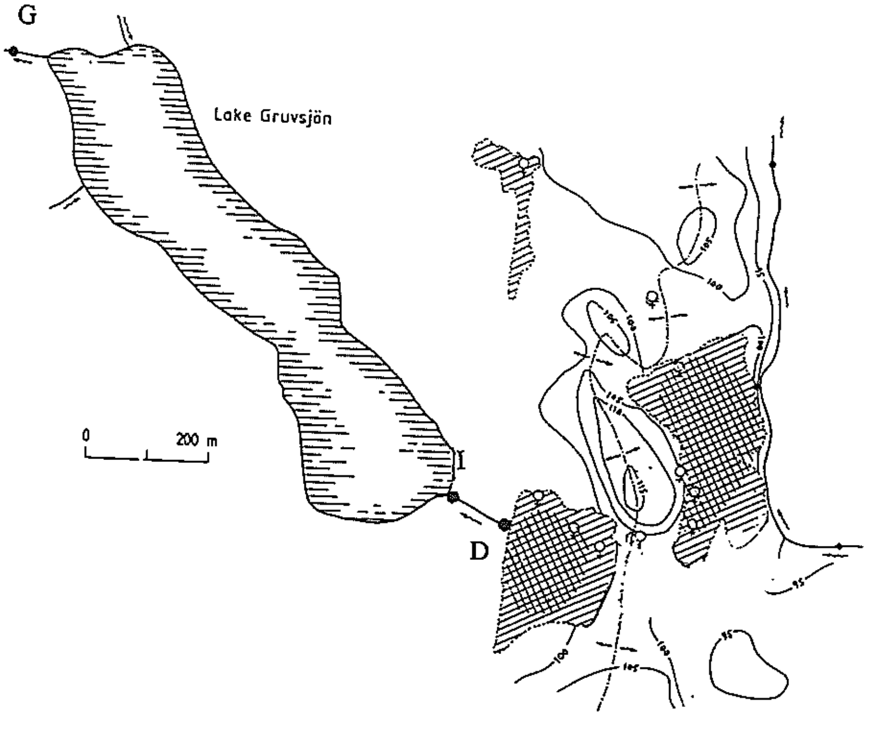

Figure 1. Map over the Bersbo area including sampling locations

Water quality monitoring

A program for water quality monitoring and hydrochemical studies in the area has been conducted since 1983 at up to 15 locations with sampling frequencies from twice daily to monthly. Detailed descriptions of sampling procedures and analytical methods are found in Allard et al. (1987) and Karlsson (1987). Results as well as the effects of hydrochemical and hydrological processes on transformation and redistribution of metals in the drainage system are discussed in Karlsson (1987) and Sandén (1988). The water quality in the drainage from the western part of the tailings is presented in figures 2 and 3 (time series of sulphate and iron) and median values in table 2 (pH, Fe, Cd, Cu, and Zn)

For several reasons, it is difficult to quantify differences in concentration or transport before and after restoration. First, the period after restoration has for some years been unusually dry. These conditions could affect the rate of weathering as well as metal retention in the lake, possibly leading to immobilization of elements. Second, waterflow data are incomplete and missing at locations D and I. Third, data are serially correlated and not normally distributed, indicating that conventional statistical testing is not applicable.

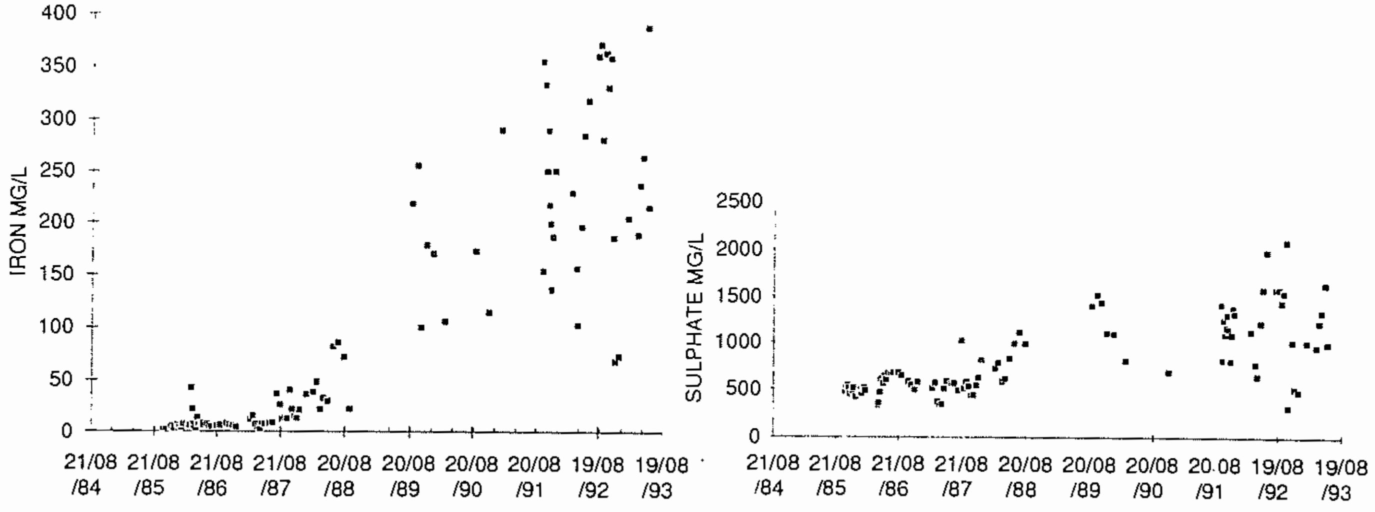

Figure 2. Time series of iron and sulphate at location I

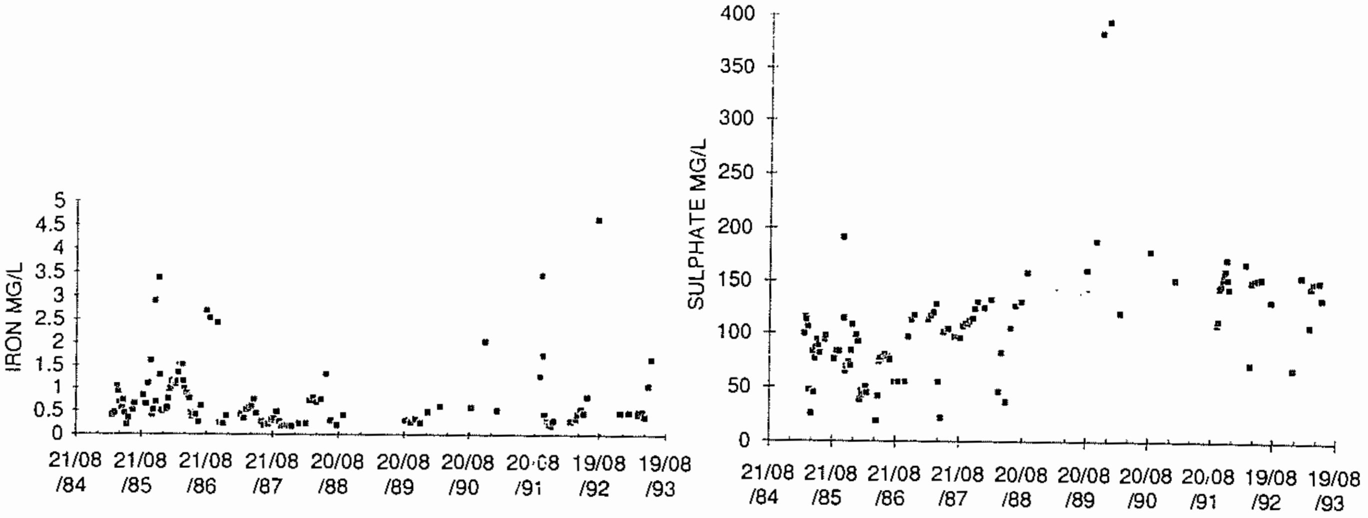

Figure 3. Time series of iron and sulphate at location G

However, the increase in iron concentrations after covering is most probably not only caused by reduced water volumes released from the engineered deposit as an effect of the protective cover (concentrated leachates). It is also observed that increases in concentrations of sulphate, calcium, and sodium at the inlet to the lake (location I) are correlated with increases of these constituents at the outlet (location G). The increases could partly be explained by the reduced precipitation (evaporation effect) 1991-92, but preliminary transport estimates, with simulated waterflow, (Sandén 1993) for these parameters support that the drainage from the mine still is an important source of metals to the lake.

Effects of iron

Principal reactions for the oxidation of pyrite are the following (Stumm and Morgan 1981)

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

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \tag{2}$$

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

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

Other sulphide minerals could also be oxidized by Fe^{3+} e.g.:

$$ZnS(s) + 8Fe^{3+} + 4H_2O = Zn^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \tag{5}$$

Ferrous forms are dominating in the effluent water from the tailings as well as in the lake (Karlsson et al. unpubl.). In contact with atmospheric oxygen it is oxidized, and precipitates of ferrous hydroxides are formed (especially noticable in the creek beween locations D and I). According to equations 2 and 3, this would lead to a net release of two protons, thereby increasing the acidity in the system. These conditions are in fact observed in the data series from locations D and I. As a result, increased loadings would decrease pH. It is noticed in several studies (for Zn e.g. Tessier et al., (1989)) that generally in natural waters and for many elements the solid/solution ratio decreases with decreasing pH. The same effect of pH is reported for Cd, Cu, Pb, and Zn in the Bersbo area (Karlsson et al. 1987). This general pattern is in some waters complicated by the tendency of humic and fulvic acids (HFA) to form complexes with metals (Pettersson et al. 1993) and adsorb onto fresh ferric hydroxides (Davis 1984). The maximum observed concentration of HFA is, however, only 0.3 mg/l in Lake Gruvsjön.

On the other hand, it is found that sorption-coprecipitation of trace elements on hydrous oxides of iron are important, and it is suggested that they regulate concentrations of trace elements in water and sediments (Singh and Subramanian 1984; Tessier et al. 1985; Johnson 1986).

To estimate the net effects on trace metal mobility of iron oxidation, ferrous iron was allowed to oxidize at different pH relevant for these acidic systems.

Material and methods

Water was sampled from location D on three occasions. The concentrations of Fe, Cd, Cu, and Zn is found in table 1.

The experiments were performed as titrations at constant pH (pH-stat) (4.1, 4.6, 5.0, and 5.4). Preliminary studies of kinetics of the oxidation were performed on one sample by the addition of copper (0, 2.65 and 5.30 mg/l) in the form of $CuSO_4$ (nine titrations). All titrations were performed in stirred vessels open to the atmosphere and at 25 °C.

Prior to titration, pH was adjusted on 100 ml of sample with NaOH (0.1 M). Phase separation was performed by centrifugation at 20 000 g in 15 min in an ultracentrifuge (Beckman J2 - 21M) to remove any precipitates formed during storage. The solution was carefully decanted into new vessels. A subsample of 30 ml was acidified for subsequent analysis of metals.

The additions of base to the 50 ml sample started immidiately after centrifugation. For the samples from 1992, the release of protons were monitored and pH kept constant with Radiometer PHM84. A combination electrode (GK2501C) was used. The rate of reaction was recorded by measuring the additions of NaOH with time. Base addition was stopped well before concentrations of Fe or Cu were limiting factors for the rate of reaction. The sample was then centrifugated and decanted into plastic vessels and acidified for metal analysis.

Titration of the sample collected 931019 was performed with Radiometer VIT 90 and measured by combination electrode GK2402B. This test was stopped after 2760 min for pH 4.1, respectively. Evaporation losses during titration was measured (weighing) and corrected for.

Fe, Cd, Cu, and Zn were analyzed on Perkin-Elmer 1100 with flame techniques. Humic material in the lake Gruvsjön was isolated according to Pettersson et al. (1989).

Calculation method

The weathering of Fe is calculated by comparisons of Zn and Fe in the leachates at location I (table 2), before and after remediation (I_{bZn}, I_{bFe} and I_{aZn}, I_{aFe}, respectively) and from data of the content in the waste material (Zn_s, Fe_s). The weathering rate of iron before remediation (Fe_{wb}) is expressed as $I_{bZn} * Fe_s/Zn_s$, and after remediation $Fe_{wa} = I_{aZn} * Fe_s/Zn_s$. Accumulation of iron in the tailings before and after remediation is calculated from the difference in the measured concentrations in the leachates ($Fe_{wb} - I_{bFe}$) and ($Fe_{wa} - I_{aFe}$). The difference in accumulated amounts is a measure of the total amount of iron available for oxidation by the mechanism described by equation 4.

Results

The concentrations of humic and fulvic acids in sample 920930 from the lake was 0.18 mg/l.

Results for metal concentrations in solutions are presented in table 1, together with total amount added NaOH and elapsed time for the titrations. It is found that 1.8 moles of NaOH corresponds to 1 mole of precipitated iron. This is a resonable number since there are also other species present. Dissolved Al probably exceeds saturation with respect to $Al(OH)_3(s)$

Kinetics for the overall reactions will be described elsewhere. The dependence of $[H^+]$ on the rate is, however, in accordance with findings from Millero (1985), who found that the dependence of rate on the hydrogen concentration was $[H^+]$ raised -2 for pH > 5 and -1 for pH < 4. In the present experiments it was found to be between -1.9 to -1.5.

Results for the metal concentrations (Cd, Cu, and Zn) in table 1 are plotted as quotients of the relative amount of sorbed/coprecipitated metal and the relative amount of precipitated iron as a function of pH (figure 4a). It is found for Cu that the efficiency for metal removal accounted for by the precipitation of iron decreases with pH. For Zn, however, this is not the case. By plotting the relative removal of metals from the solution, (figures 4d) with time in a logaritmic scale, a clear dependence is found, and it seems as if time could be an important parameter in the removal of zinc.

Table 1. Results from the pH-stat tests and metal analysis

		NaOH, ml	time, min	Fe, mg/L	Cd, ug/L	Cu, mg/L	Zn, mg/L
920318	start			538.3	261	4.47	121.4
pH 5.0	end	[1]1.25	286	326.2	246	2.31	99.2
920930	start			380.8	122	1.66	62.01
pH 4.6	end	3.20	1451	212.1	118	1.055	50.20
920930	start			380.8	122	4.308	62.01
pH 4.6	end	3.17	712	169.7	110	3.82	51.51
920930	start			380.8	122	6.956	62.01
pH 4.6	end	2.06	424	182.8	110	6.680	49.19
920930	start			375.7	123	1.67	61.61
pH 5.0	end	3.18	185	195.9	118	0.645	52.156
920930	start			375.7	123	4.318	61.61
pH 5.0	end	3.72	158	144.4	111	2.595	52.02
920930	start			375.7	123	6.966	61.61
pH 5.0	end	3.21	116	179.8	112	4.235	53.93
920930	start			330.3	116	1.190	57.47
pH 5.4	end			152.5	110	0.285	51.71
920930	start			330.3	116	3.838	57.47
pH 5.4	end	3.22	60	144.4	110	1.340	51.51
920930	start			330.3	116	6.486	57.47
pH 5.4	end	3.20	38	148.5	109	5.010	52.72
931018	start			188.87	327	11.135	124.53
pH 4.1	end	0.713	2760	157.56	320	9.95	115.14

[1] Sample volume 25 ml

Discussion

Will the increase in iron concentration affect the scavenging of metals? It is indicated that mobility from sediments are low, especially if the organic content of the sedimenting material is high (Håkansson et al. 1991; Pedersen et al. 1991 and Robertson 1991). (It is suggested that formation of sulphides by sulphate- reducing bacteria or binding of metals to surfaces coated with organic matter could be the explanation). Reactions that occur before sedimentation could thus be important regulators in the scavenging of metals.

The transport of iron to the lake under study was estimated with location I as the reference point (table 1). At this location, the specific effects of the cover will not influence waterflow (with the exception of a small decrease caused by the evaporation of water from an introduced but not vegetated soil layer). Ditches draining the surface layers of the deposit meet the main drainage near location D.
Through a comparison of the drainage areas of locations I and G a tentative estimate of the increase in transport of iron to the lake from the tailings can be done.

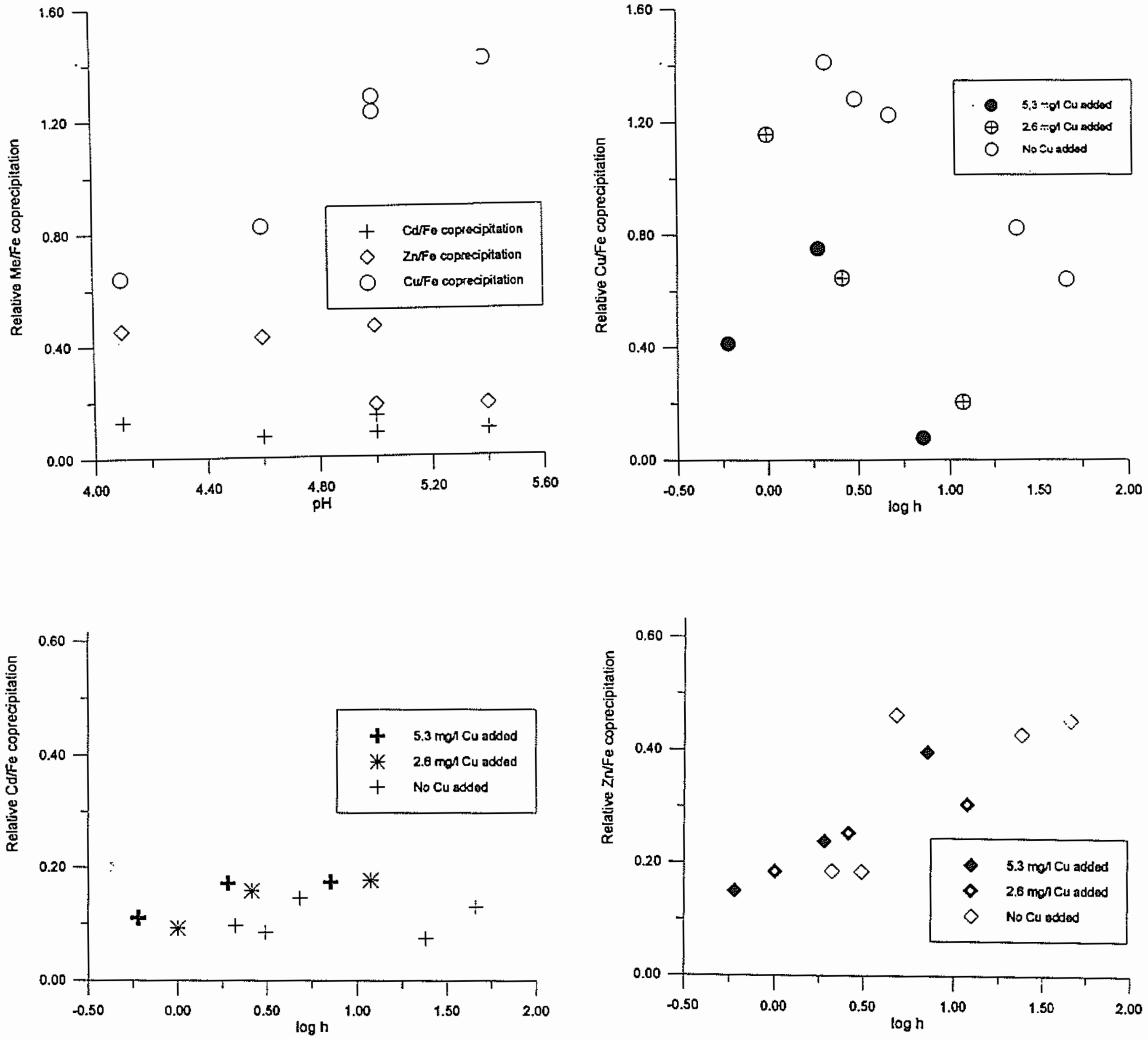

Figure 4. Sorption/coprecipitation of a) the metals Cd, Cu, and Zn as a function of pH $[Me_s/Me_{tot}]/[Fe_s/Fe_{tot}]$.
b) Cu as a function of time (log h) $[Cu_s/Cu_{tot}]/[Fe_s/Fe_{tot}]$,
c) Cd as a function of time (log h) $[Cd_s/Cd_{tot}]/[Fe_s/Fe_{tot}]$,
d) Zn as a function of time (log h) $[Zn_s/Zn_{tot}]/[Fe_s/Fe_{tot}]$

The estimated contribution of water from I based on drainage areas is estimated to be about 8% of the contribution at location G. Median values at location I and G for some constituents are given in table 2.

With a dilution in the lake, the increase in iron concentration in the lake water will be (223.6 - 6.68)*0.08 = 17.34 mg/l. This iron (Fe^{2+} is dominant both in the lake and at location I (Karlsson et al. unpubl.)) during oxidation will theoretically produce a water with a pH of 3.2 (equations 2 and 3). However, this pH is not (yet) obtained in the lake, as can be seen in table 2.

At pH 4.6, coprecipitation of Cd, Cu, and Zn is 0.0237 ug, 0.0036 mg, and 0.07mg, respectively, for each mg of precipitated Fe according to table 1. Additions of Fe in the order of 17 mg/l to the lake will thus cause additional amounts of 0.4 ug/L, 0.06 mg/L, and 1.19 mg/L for Cd, Cu, and Zn, respectively, to coprecipitate. However, according to figure 4a, about 50% less of Cu will coprecipitate with the solid phase as pH is lowered from 4.9 to 4.2. The net effect will thus be a decrease of the adsorption of Cu. For Zn an increase in adsorption is expected when pH is lowered, due to the long time needed for oxidation (figure 4d). The effects of the increased iron concentrations on the adsorption of Cd are not clear.

Table 2. Median values of metal concentrations at locations D,I, and G before (- 1987) and after (1989 -) remedial actions. The subscript b and a refers to the situation before and after remedial actions were taken. (n = 10 for most parameters at D_b, n for the other locations see figures 2 and 3).

	D_b	D_a	I_b	I_a	G_b	G_a
pH	4.90	4.57	3.95	3.73	4.93	4.29
Fe (mg/L)	17.71	403	6.68	223.6	0.55	0.44
Cd (ug/L)	204	161	198	145	16	9.4
Cu (mg/L)	8.79	3.50	10.62	4.09	0.533	0.238
Zn (mg/L)	46.5	74.8	81.6	59.4	7.56	5.76

The new hydrochemical conditions in the lake will increase the adsorption/coprecipitation of metals, on a solid phase, in the order Zn > Cd > Cu.

It is possible that oxidation of pyrite still proceeds despite the lowered oxygen content in the tailings (equation 4) This reaction means that weathering may continue with Fe(III) as a substrate for oxidation. The purpose of the calculations below are to give a rough estimate of the longevity of such a mechanism.
Assuming that all sulphides weather at the same rates and that no secondary minerals of Zn are formed, the quotient Fe/Zn in the solid phase could be taken as a measure of the weathering of iron. The covered solid phase have been analyzed by a prospecting company (Vieille Montagne): Fe 10.7%, Zn 0.7%, Cu 0.29%. The calculation method gives the amount of accumulated iron (556 mg/L). According to equation 5 it is required 406 mg/L of iron to oxidize the present amount of released Zn (59.4 mg/L). Available iron will be 1/3 of the accumulated, since that is the part dumped in the shafts and thus exposed to water. It is assumed that a more or less constant weathering and accumulation of iron has been going on for 150 years (Håkansson et al. 1991), indicating that a time scale for the continued weathering could be constructed. Weathering with this mechanism could thus continue for (556/406*1/3)*150 = 70 years.
This estimation is valid if <u>no</u> oxygen is present to regenerate the storage of Fe^{3+}.

Concluding remarks

The estimated maximum time for a continued weathering of pyrite with Fe^{3+} as a substrate for oxidation in the Bersbo area is 70 y.
Adsorption studies indicate that a lowered pH caused by Fe oxidation will decrease the retention of Cu in the receiving lake and increase the retention of Zn.
In relatively acid systems with a fast hydrological response, the net effect of high Fe concentration is likely to be an increased mobility of several elements.

References

Allard, B., S. Bergström, M. Brandt, S. Karlsson, U. Lohm and P. Sandén. 1987. Environmental impacts of an old mine tailings deposit - Hydrochemical and hydrological background. Nordic Hydrol. 18:279-290.

Davis, J. A. 1984. Complexation of trace metals by adsorbed natural organic matter. Geochim. Cosmochim. Acta 48:679-691. http://dx.doi.org/10.1016/0016-7037(84)90095-4

Håkansson, K., S. Karlsson, L. Lundman and B. Allard. 1991. Redistribution of metals from a contaminated drainage system - Accumulation in sediments estimated from surface water quality and sediment analysis (submitted).

Johnson, C. A. 1986. The regulation of trace element concentration in river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. Geochim. Cosmochim. Acta 50:2433-2438. http://dx.doi.org/10.1016/0016-7037(86)90026-8

Karlsson, S. 1987. Influence of hydrochemical parameters on the mobility and redistribution of metals from a mine waste deposit. (Diss.) Linköping Studies in Arts and Science 10. Linköping University.

Karlsson, S., P. Sandén and B. Allard. 1987. Environmental impacts of an old mine tailings deposit - Metal adsorption by particulate matter. Nordic Hydrol. 18:313-324.

Kelly, B. C. and O. H. Tuovinen. 1988. Microbiological oxidations of minerals in mine tailings. In Salomons, W. and U. Förstner, Chemistry and Biology of Solid Waste, Dredged Materials and Mine Tailings. pp. 33-53. Springer.

Länsstyrelsen, Östergötlands län, Planeringsavdelningen Beslut 1986-12-19. *County Board, Östergötland (in Swedish).*

Lundgren, T. 1990. The first full scale project in Sweden to abate acid mine drainage from old mining activities. In Proceedings of the International Conference of GAC-MAC. Vancouver.

Lundgren, T. and L-Å. Lindahl. 1991. The efficiency of covering the sulphidic waste rock in Bersbo, Sweden. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. Montreal.

Millero, F.J. 1985. The effect of ionic interactions on the oxidation of metals in natural waters. Geochim. Cosmochim. Acta 49:547-553. http://dx.doi.org/10.1016/0016-7037(85)90046-8

Pedersen, T. F., B. Mueller, J. J. McNee and C. A. Pelletier. 1991. Diagenetic reactivity of mine tailings in mesotrophic and oligotrophic lakes in Manitoba and British Columbia. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. Montreal.

Pettersson, C., I. Arsenie, J. Ephraim, H. Borén and B. Allard. 1989. Properties of fulvic acids from deep groundwaters. Sci. Tot. Environ. 81/82:287-296. http://dx.doi.org/10.1016/0048-9697(89)90135-6

Pettersson, C., K. Håkansson, S. Karlsson and B. Allard. 1993. Metal speciation in a humic surface water system polluted by acidic leachates from a mine deposit in Sweden. Wat. Res. 27:863-871. http://dx.doi.org/10.1016/0043-1354(93)90151-7

Robertson, J. D. 1991. Subaqueous disposal of reactive mine waste: An overview of the practice with case studies. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. Montreal.

Sandén, P. 1988. Dynamics of metal concentrations and mass transport in an old mining area. (Diss.) Linköping Studies in Arts and Science 22. Linköping University.

Sandén, P. 1993. Övervakning av ytvattenkemi i Bersbo. Rapport från verksamheten 1992/1993. SMHI *Monitoring of surface water chemistry. Report. Swedish Meteorological and Hydrological Institute (in Swedish).*

Singh, S. K. and V. Subramanian. 1984. Hydrous Fe and Mn oxides - Scavengers of heavy metals in the aquatic environment. CRC, Critic. Rev. Environ. Control 14:33-90. http://dx.doi.org/10.1080/10643388409381713

Stumm, W. and G. F. Lee. 1961. Oxygenation of ferrous iron. Industrial and Engineering Chemistry 53:143-146. http://dx.doi.org/10.1021/ie50614a030

Stumm, W. and J. J. Morgan. 1991. Aquatic Chemistry. Wiley, New York, 2nd ed.

Tegengren, F. R. 1924. Sveriges ädlare malmer och bergverk. SGU. Ser Ca 17:313 - 329. Norstedt, Stockholm. *Swedish Geological Survey (in Swedish).*

Tessier, A., F. Rapin and R. Carignan. 1985. Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochim. Cosmochom. Acta 49: 183 - 194. http://dx.doi.org/10.1016/0016-7037(85)90203-0

Tessier, A., R. Carignan, B. Dubreuil and F. Rapin. 1989. Partitioning of zinc between the water column and the oxic sediments in lakes. Geochim. Cosmochim. Acta 53: 1511-1522. http://dx.doi.org/10.1016/0016-7037(89)90234-2