Weathering mechanisms and composition of effluents from a sulphide mine waste deposit after covering – Twenty years of field data

Stefan Karlsson[1,2], Bert Allard[1], Mattias Bäckström[1]

[1]*Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden*
[2]*Project Bergskraft Bergslagen, Harald Ols Gata 1, 714 31 Kopparberg, Sweden*

Abstract In 1988 a deposit with some 500,000 m^3 of coarse sulphidic mine waste at Bersbo, Sweden, was covered with compacted illitic clay or cement stabilised coal fly-ash (CeFill) to prevent weathering and the transport of metals. Theoretically, oxidation of pyrite would give a sulphate/iron ratio in solution exceeding 2, if oxygen is the electron acceptor, but below 2 if Fe(III) is the oxidizing agent. The effluents had ratios of 35—50 and 2—0.8 before and after covering, respectively, why it is concluded that weathering continued. The altered hydrological regime contributes to changes in metal concentrations in the surrounding surface water.

Key Words Sulphidic mine waste, weathering, Fe(III), Fe(II)

Introduction

Covering historical pyritic mine waste with dense sealing layers has been used in order to reduce metal loading to the environment. This strategy is based on the principles that excluding oxygen will limit the weathering and the transport of mobile elements will be at a minimum if precipitation is likewise excluded. In this paper we focus on the use of surface water quality data to evaluate the mechanisms of weathering. The data presented here, refers to the composition of acid rock drainage (ARD) immediately adjacent to the deposits under study.

Theory

The weathering of pyrite is well known (Stumm and Morgan, 1981) and in the presence of oxygen the first step would be:

$$FeS_2(s) + 3.5O_2 + H_2O \rightarrow Fe^{2+}(aq) + 2SO_4^{2-} + 2H^+ \tag{1}$$

In oxidizing environments this reaction is accompanied by oxidation of Fe(II) to Fe(III) where the latter species hydrolyses to ferric hydrous oxides. The rate of oxidation/precipitation is rather slow at low pH but increases significantly at pH exceeding some 3.5 and is almost instantaneous at circumneutral pH.

Exclusion of atmospheric oxygen does not prevent oxidation of pyrite if trivalent iron is present. Under such conditions, Fe(III) serves as an electron acceptor according to reactions 2 or 3:

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

$$FeS_2(s) + 14Fe(OH)_3(s) + 26H^+ \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 34H_2O \tag{3}$$

By calculating the SO_4^{2-}/Fe ratio in the ARD as it leaves the deposit it should be possible to identify the principal weathering mechanism. It is of course necessary that neither of the species is lost from the solution through precipitation or adsorption. In an anaerobic system reaction 1 gives a SO_4^{2-}/Fe ratio of 2. If the resulting Fe(II) is oxidised and forms ferric hydrous oxides then the SO_4^{2-}/Fe ratio would be much higher than 2. In anaerobic systems with Fe(III) as the oxidizing agent this ratio would be 0.13.

Since this approach relies on the ratio of two elements other reactions where they are involved should be considered. They include for instance formation of gypsum, if the site has been limed, precipitation of solid iron phases and reductive dissolution of ferric hydrous oxides without pyrite oxidation. Release of these elements from the sealing layers must also be evaluated, as well as the contribution from groundwater that might enter into the deposit.

Materials & Methods

Site description

Mining for copper began in the 14th century but rational operations took place from 1765. The peak production occurred in 1855—1870 when the mine was the major producer of copper in Sweden for a few years, but the ore ceased and mining closed in 1902. The total copper production has been estimated to 32,000 tonnes. The waste site contained some 1.4 Mton of coarse sized material that covered 0.5 km^2. In 1987—89 the waste was covered with either cement stabilised fly ash (East side) or compacted illitic clay (West side) to prevent intrusion of oxygen and water and hence minimize weathering as well as transport of metals.

The bedrock consists of leptitic granite with amphibolitic intrusions and mica schists with late intrusions of young alkaline granite. Sulphidic ore veins (pyrite, chalcopyrite, sphaelerite and galena) were found at the granite amphibolite interface. The ore used for further refining contained some 20% Fe, 0.5—3% Cu, 1—3% Zn and 1% Pb (Allard et al., 1987).

The waste deposit was divided by a ridge into two surface water catchments. One of them leading to Lake Gruvsjön in the East and the other consisting of a small creek. The soil in the area is dominated by moraine on top of glacial clay with calcareous shells. Higher vegetation contains coniferous stands with some deciduous species. Upstream the waste site there are a few minor bogs and downstream some agricultural fields.

The groundwater is of the Ca - SO_4^{2-} - CO_3^{2-} - type and has a pH 7.1—7.8, alkalinity of 2.5—3 meq/l and a salinity of 500 mg/L. The composition of the unpolluted surface water is of the Ca-Na,SO_4^{2-}- type, with pH 4.9—4.3 and salinity around 100 mg/L. It also contains dissolved organic carbon in the range of 15—25 mg/L. The ARD typically contained SO_4^{2-} 500—1000 mg/L, Fe 3—10 mg/L, Zn 60—90 mg/L and Cu 8—15 mg/L at pH of 3.2—3.9.

Analytical

The data set used here comes from a number of studies in the area, from weekly sampling of surface water at some 15 locations during 1983—89 to more sporadic measurements in 2002—2004. The database contains more than 50,000 water quality observations. Here, we focus on the two sampling locations at each deposit where ARD was collected as it entered into the streams. Analytical parameters included pH, alkalinity, electrical conductivity, chloride, sulphate, dissolved oxygen and organic matter as well as principal and trace metals (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn). Chemical analyses were performed with standardised analytical methods.

Results & discussion

The covers performed as expected since the oxygen concentration in the air inside the deposits went down from 21% to less than 0.1% within 6 months after the covers were in place (Lundgren 2000). Metal concentrations (notably Zn, Cd, Pb, and Cu) were lowered and pH increased after one year, particularly in effluents from the illite covered westerly deposit (Karlsson and Bäckström 2003). Large increases in sulphate and iron concentrations were observed, especially at the CeFill side. The development of Fe and SO_4^{2-} concentrations with time are given in fig. 1 and the corresponding mean values of the SO_4^{2-}/Fe ratio in tab. 1. Before the waste was covered this ratio indicates aerated conditions, as supported by previous observations of extensive and progressive

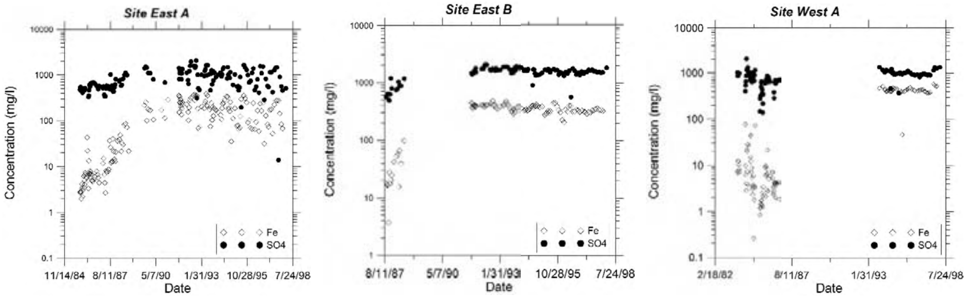

Figure 1 *Concentrations (mg/L) of Fe and SO_4^{2-} as a function of time*

Table 1 *Mean values for concentrations of iron and sulphate, pH and the corresponding SO_4^{2-}/Fe ratio*

Parameter	**East Site A**		**East Site B**		**West Site A**		**West Site B**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Fe (mg/l)	34.3	366	14.2	191	8.9	431	5.0	-
SO_4^{2-} (mg/l)	790	1619	567	1028	737	1026	602	-
pH	4.60	4.51	4.17	3.87	3.42	4.91	3.39	-
SO_4^{2-}/Fe	22.0	2.61	48.6	3.54	122	1.50	89.2	-
n	23	76	47	105	73	47	61	-

oxidation and hydrolysis of Fe(II) in the downstream area (Karlsson et al. 1988). When the deposits had been covered there was a significant increase in the concentrations of iron and sulphate in the ARD (fig. 1, tab. 1). The increase of iron was at least ten fold while the sulphate concentrations were doubled. The concentration relationship between the species would indicate different mechanisms of either mobilisation or immobilisation.

Both covers were impermeable to rainwater (Lundgren 2000) but there is still a net outflow of groundwater that has been in contact with an unknown fraction of the waste. This was most evident in the easterly sub-catchment. Assuming a constant weathering rate the new hydrological conditions would favour increased concentrations, but a lower mass transport.

If the weathering mechanisms had remained unchanged after covering of the waste, the element ratios would also have been unaltered. This is not the case since the mean values for the SO_4^{2-}/Fe ratio are significantly lowered (tab. 1), notably as a response to increased iron concentrations. The minimum values observed were around 0.03. From these magnitudes alone it is not possible to unambiguously conclude if the dominating weathering mechanism is entirely anoxic. If pyrite oxidation with Fe(III) would dominate the expected ratio should be close to 0.1. These field data also suffers from uncertainties related to the impact of water flow and water pathways and possibly also contribution from reductive dissolution of Fe(III)-phases where the process does not lead to sulphide oxidation. Since no depletion of iron has been observed since 1989, it seems unlikely that that the latter mechanism dominates.

It is also evident that the concentration of alkaline and alkaline earth metals increased in the ARD after covering, except for Mg in the westerly pathway (tab. 1). The true magnitude of the increase remains unknown because available estimates of how the water balance has changed are uncertain. It is however evident that there was no identical increase between the elements as would have been the case if groundwater dominated the run-off composition. Thus, there are reasons to assume that the cover materials contributed to the altered elemental composition of the ARD. The two materials would result in different ionic contributions where water passing the CeFill would be enriched in alkaline, alkaline earth's and sulphate, among the species included in the study. Illitic clay in the area releases rather limited amounts of most ions, possible with the exception of potassium, when exposed to large volumes of water.

In quantitative terms the contribution of ions from the sealing layers should be low, if not negligible. Their permeabilities were below 10^{-9} cm^2/sec and the fraction of water at the sampling sites that that passed through them should therefore be very limited. One possibility behind the altered ionic composition is that the groundwater level in the covered deposits increased. Under those circumstances the contact between the groundwater and the cover materials would be higher. Consequently, seeps of groundwater coming in contact with these materials within the deposit are therefore suspected to be the principal way of these ions getting into the ARD.

The fractions of principal elements at the two sites are only slightly different before and after the covering (fig.2). It should be noted that there was a difference between the sites already before they were covered. The easterly drainage had a larger contribution of groundwater in the ARD, which is reflected by higher fractions of Ca and Cl. The surface water at the westerly side was more influenced by rainwater that is low in all elements.

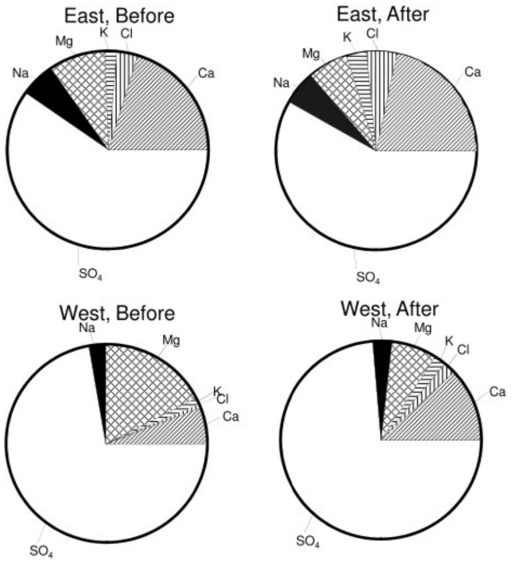

Figure 2 *Relative distribution of principal species in the ARD*

Conclusions

This study shows that although the SO_4^{2-}/Fe ratio can be biased by several processes its numerical values still indicate aerobic weathering before the cover was in place, which conforms with the general theory. When the cover was in place the ratio was lowered to values close to, and under periods identical with, pyrite oxidation with Fe(III) as the electron acceptor.

Acknowledgments

The authors express their gratitude to all colleagues who took part in sampling, analysis and data evaluation from 1983 to 2010.

References

Allard B, Bergström S, Brandt M, Karlsson S, Lohm U, Sandén (1987) Environmental impacts of an old mine tailings deposit – Hydrochemical and hydrological background. Nordic Hydrology 18:270—290
Karlsson S, Allard B, Håkansson K (1988) Characterization of suspended solids from a stream receiving acid mine effluents. Applied Geochemistry 3:345—356
Karlsson S, Bäckström M (2003) Surface water quality in Bersbo, Sweden – Fifteen years after amelioration of sulphidic waste. Mining and the Environment III, Sudbury, Canada (CD)
Lundgren T (2000) The Bersbo Pilot Project – Follow up studies 1989—1999. Envipro Miljöteknik AB
Stumm W, Morgan JJ (1981) Aquatic Chemistry. Wiley Interscience, 780 pp