NATURAL IRON HYDROXIDE PRECIPITATES: THEIR ACID GENERATION POTENTIAL IN GROUND WATER ASSOCIATED WITH TAILINGS[1]

Margarete Kalin[2], Andrew Fyson[2], and Günther Meinrath[3]

Abstract. Iron hydroxide precipitates, generated from acid mine drainage adhere to surfaces in tailings and waste rock piles and accumulate as sludges in ditches and in pond sediments in mine waste management areas. Such precipitates undergo a series of transformations which lead ultimately to the stable mineral goethite. Ground water from piezometers in an below tailings containing 41 % pyrite were stored for 4 years unpreserved in their original, un-sterilized sampling bottles reached pH values around 1. The stored water with the iron precipitates have been able to support Fe-oxidizing and Fe-reducing bacteria and similar microbial populations were identified on slides which were immersed into the piezometers from the same tailings site. A clear relationship between microbial activity and Fe(III) mineral compositions in the iron precipitates from the stored samples and from sludges accumulating in a ditch precipitating from the effluent from underground workings at the same site, could not be established. The relevance of the microbial activity in the formation of secondary minerals occurring in ground water in and below tailings and accumulating on the surface is discussed. The high variability of the output of geochemical modelling (PHREEQC) to the modelling input allowed a wide variety of possible interpretations.

Additional Key Words: microbial activity, iron hydroxides, alteration, acid generation potential, geochemical modelling

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[2] Margarete Kalin, President, Boojum Research Ltd. 139 Amelia St., Toronto, Ontario, Canada, Andrew Fyson, Researcher, Boojum Research Ltd., [3] Günther Meinrath, Adjunct Professor, Bergakadmie, Freiberg, Germany and RER Consultants, Schiessstattweg 3a Passau D-94032, Germany.

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Introduction

Amorphous to poorly crystalline Fe(III) (oxy)hydroxides are products of pyritic mine waste oxidation. A driving force for this process is the extreme contrast in solubility of Fe(II) and Fe(III) hydrolysis products. The net result of $Fe(OH)_{3(s)}$ precipitation is a release of three formula units of H^+ per formula unit of precipitated Fe(III) following the idealized net equation (1):

$$Fe^{+2} + 3\ H_2O <==> Fe(OH)_{3(s)} + 3\ H^+ + e^- \qquad (1)$$

It is understood that the commonly rapid, heterogeneous precipitation process does not result in the thermodyamically most stable Fe(III) compound. Instead intermediate phases are formed which tend to alter into more stable products slowly, as expressed by Ostwald's step rule. The initially formed heterogeneous sludge contains metastable compounds such as ferrioxide and other intermediates such as schwertmannite ($Fe_8O_8(OH)_6SO_4$) and jarosites ($XFe_3(SO_4)_2(OH)_6$, (X being a monovalent cation) (Jambor and Dutrizac, 1998). Goethite (commonly given as $FeOOH_{(s)}$) is understood as a final, thermodynamically stable product of the aging process of these natural sludges. Hydrogen ions and SO_4^{-2} may be released during aging. Microbiological activity in the sludges may change the oxidation state of Fe and affect the mineralogy.

Schwertmannite (Kawano and Tomita (2001) and ferrihydrite (Ferris et al., 1989; Ferris, 2005) are found in close association with microorganisms. Microorganisms have a role in the formation and accumulation of these Fe compounds and also their reductive dissolution (Lovley et al., 2004). Depending on culture conditions, the best known acidophilic Fe oxidizer *Acidothiobacillus ferrooxidans* can produce schwertmannite (Duquesne et al., 2003) or jarosites (Sasaki and Konno, 2000) during oxidation of Fe^{+2}. These non- or poorly crystalline Fe precipitates reportedly form in different pH ranges, jarosites at pH <3 and (oxy)hydroxides at pH >3. The more crystalline the precipitates are more resistant to both chemical and microbial dissolution (Lovley et al., 2004). Hence, the highly aspired predictability of AMD by numerical simulation tools faces considerable obstacles by thermodynamical non-equilibrium, microbial interferences, rapid precipitation, slow aging and site-specific effects.

Insight into the relationship between water, sediment chemistry and the spectra of microorganisms present comes from German coal mining lakes. Iron enters lakes in groundwater predominantly as Fe^{+2}, oxidizes in the water column and precipitates predominantly as schwertmannite (Peine and Peiffer, 1998; Peine et al, 2000; Küsel, 2003; Blodau and Peiffer, 2003). Precipitation of this compound is favoured by the oxic conditions, low pH (2.5-4) and high SO_4^{-2} concentrations (Bigham et al., 1994). With increasing depth in the sediment, the proportion of Fe in the form of goethite increase as oxygen concentrations decrease. The highest Fe reduction rates occur near the sediment surface where schwertmannite is the predominant Fe precipitate and most likely substrate for microbial growth (Peine et al., 2000). The changes, attributed to E_H/pH changes in the sediment, can however also be due to aging.

High SO_4^{-2} concentrations are typical for AMD-affected systems due to the microbial oxidation of pyritic sulfide into SO_4^{-2}. Iron reducers can out-compete SO_4^{-2} reducers for electron donors (organic compounds or H_2). Iron reduction may even be limited by the availability of such electron donors as is the case for the ground water in the present study. A large number of studies on Fe reducers have concentrated on neutrophilic organisms (e.g., Lovely et al., 2004). Particularly *Shewanella* is a species which favours reduction of dissolved Fe(III) and *Geobacter* spp which favors direct reduction of Fe(III) solids, e.g. goethite. These organisms are uncommon under acidic conditions. However, acidophilic Fe reducers have now been characterized, in particular *Acidophilium* spp I believe Johnson, have to check. Therefore, if these species are present in a system, their effect on sludges and in pore water of tailings is relevant to acidification.

*At. (Acidothiobacillus) ferrooxidan*s has been shown to be capable of Fe reduction coupled to oxidation of elemental sulfur, S° (Brock and Gustafson, 1976; Das and Mishra, 1996; Ohmura et al., 2002). However, in the German coal pit lakes, S^o is not abundant at the sediment surface and the *At. ferrooxidans* present is assumed to be involved in Fe(II) oxidation (Küsel, 2003). *Acidiphilium* spp. are acidophilic heterotrophs which are capable of Fe(III) reduction in culture with glucose as electron donor (Küsel et al, 1999). Their isolate could reduce a wide range of Fe(III) compounds in micro-aerophilic conditions with glucose as electron donor (Johnson and McGinness, 1991).

Rates of Fe reduction decreased with increasing crystallinity of the substrate. The highest rates were reported on ferric hydroxide and lower rates on jarosite. Schwertmannite was unknown at that time and not tested. In the time after schwertmannite description the microbial isolate JH-5 produced highest rates with schwertmannite, intermediate rates with ferric hydroxide and lowest rates with goethite. Much higher Fe reduction rates at pH 3 than at pH 5 were reported. Interestingly, the sediment surface from which this isolate was prepared had a low pH and schwertmannite as the dominant precipitate (Roth and Küsel, 2000).

There is clearly a substantial diversity in the capacity and characteristics of Fe(III) reduction by the *Acidiphilium* group. Bridge and Johnson (2000) proposed that under acidic conditions, the *Acidophilum* reduces dissolved Fe(III). Acidic conditions favour dissolution of Fe hydroxide precipitates. Schwertmannite can have various substitutions. Regensburg et al. (2002) reported that arsenated schwertmannite was reduced at a much lower rate than pure schwertmannite by JH5 and no arsenic was released into the culture medium. Küsel et al. (1999) reported that Fe(III) reduction by *Acidiphilium cryptum* JH5 was not inhibited by oxygen. This is important as it suggests that in oxic surface sediments, Fe(III) reduction can occur. Bridge and Johnson (2000) found that *Acidophilum* SJH reduced Fe(III) at high rates in microaerophilic conditions but at low rates in the complete absence of oxygen.

In general, available microbiological studies indicate that Fe(III) reduction can occur in acidic conditions with or without the presence of oxygen. A wide variety of non- or poorly crystalline Fe compounds are utilized by the microbes directly or indirectly (following dissolution) as substrate. Such conditions are widely associated with pyritic mining wastes in pit lakes and in lakes with natural sediments which receive contaminated groundwater.

These microbiological and geochemical considerations shed light on the complexities associated with secondary precipitates. From a remediation perspective however it is important to address the question of whether or not natural Fe hydroxide sludges, which accumulate in various locations in mine site, can, due to instability or transition of the secondary precipitates result in a further source of acid or re-release of metals. Geochemical and mineralogical considerations do not consider microbiological activity. The pH values of waters collected from groundwater in and below tailings of a former Cu/Zn mine in northern Ontario were measured intermittently for a period of over four years in their original collection bottle.

Methods and Materials

Site description

A former Cu/Zn Mine in northern Ontario Canada operated between 1970 and 1981 and generated about 1 million ton of tailings and underground workings producing AMD. The tailings consist of 41 % pyrite and 4 % pyrrhotite and are expected to generate AMD for anywhere between 1000 to 35,000 years, estimated based on the Fe and suphate concentrations determined in the ground water in and below the tailings (Kalin et al 1992). At the site, natural Fe hydroxide sludge also referred to as yellowboy is generated from water emerging from the underground workings and from ground water flowing out of the tailings surfacing in a shallow lake. Yellowboy accumulates in a ditch, constructed to divert the effluent towards a lake and in the outflow of the shallow lake receiving the groundwater discharge from the tailings. A detailed description of the site is given in Kalin (2001).

Ground water sampling , storage and analysis

Groundwater samples were taken from piezometers installed at various locations in the tailings. Samples were collected on September 10, 1996 after the piezometers were bailed and collected in 250 ml polyethylene bottles with screw caps containing a foam liner. Within five to 30 minutes, the pH, E_m, electrical conductivity (EC) and temperature of the samples were analyzed, in a field laboratory and the samples were then placed into a cooler with ice.

In the laboratory, an aliquot of the water was removed to determine elemental composition after filtration (0.45 µm) and acidification. The unpreserved water was re-measured for pH, E_m, EC and temperature and stored at 20 °C in coolers in the dark. The bottles were not airtight and an air space was present above the water. The pH, redox potential (E_m) and temperature of the samples were re-measured over a period of 4 years. On each occasion, 50 ml of each sample was poured into a 120 ml container so that all three electrodes were submerged in the sample simultaneously. After measurements were taken the water was returned to the original sampling bottle for further storage.

The concentrations of Fe and SO_4 in of the groundwater ranged from 700 mg/L to 14,500 mg/L and 3,000 mg/L to 32,000 mg/L. The major cations are Ca and Mg along with Mn. The major contaminant in the water is Zn. The anion/cation balance of the water was calculated as a check on the accuracy of the analysis. The errors range from 0.5 % to 3 % for most samples, with the exception of errors as high as 7 % to 11 % for four samples. The first re-measurements of pH were carried out in 1999, three years after the samples were collected. Measurements were continued periodically until 2000.

The pH was measured with a Corning 315 pH/Ion pH meter equipped with a combination electrode (Corning #33221-034). A Corning M103 redox instrument with an inert platinum electrode and a standard Calomel probe was used to determine E_H. Redox potential readings were recorded as E_m and transformed to E_H where $E_H = E_m + [241 \text{ mV} – 0.66 * (T (^oC) - 25 ^oC)]$. The analysis of sludge samples was carried out on digests of nitric perchloric acid by the Saskatchewan Research Council Analytical Services (SRC) Laboratory in Saskatoon, Saskatchewan, an accredited laboratory. Both water and sludge elemental composition was determined by ICP.

Microbiological isolation and enumeration

Water from the stored samples with particulates was shipped to B. Johnson Laboratory at the University of Bangor, Wales, U.K. The samples were processed after Johnson (1995) using a medium for enumerating acidophilic bacteria. Glass slides from four sites (M7S, M7N, M27C and M27S (cf. Table 1)) were shipped immediately after collection in the field in their original water. For each slide an area of 55 mm by 26 mm was cleaned using sterile cotton wool swabs. These were placed into 5 ml of sterile basal salts solution (pH 5.8) and "vortexed" thoroughly to release the trapped bacteria.

A dilution series (10^0 - 10^{-4}) was prepared from each suspension, and 100 μL aliquots were used to inoculate solid media that are selective for extremely and moderately acidophilic Fe-oxidizing and heterotrophic bacteria (Johnson, 1995; Hallberg and Johnson, 2001). Plates were incubated for 4-6 weeks at 20 ^{o}C, before colonies were counted and preliminary identification made of isolates.

The pH and E_H of hydroxide sludge collected from immediately below the discharge area of the underground workings were measured in the laboratory within 24 hours. A sub-sample was transferred to centrifuge tubes (50 mL) and shipped to the University of Freiberg, Germany for X-ray powder diffraction analysis (XRD). With the Freiberg equipment, samples in contact with solution could be analysed.

Mineralogical analysis of sludge and groundwater precipitates

The ground water samples, analyzed for their microbial populations, were subsequently shipped to the Center for Minerals at the University of Lausanne, Switzerland. Precipitates which had formed in the stored groundwater were collected on filter paper as a cake. All samples were characterized by XRD using a 3020 Philips diffractometer with Cu K_α radiation (40 kV, 30 mA) and a diffracted beam with monochromator. Solid and supernatant SO_4^{-2} concentrations in these precipitates were not determined.

Mineralogical analysis of the underground working sludge was carried out at the University of Freiberg, Germany. The SO_4^{-2} concentration in the supernatant which had formed in the centrifuge tubes was determined by ion chromatography in a total of 6 samples. An aliquot of the solid sludge was oven dried and the Fe phases digested with HCl. Sulfate was separated from Fe by precipitating Fe hydroxide with NH_3. The SO_4^{-2} in the sludge was determined by turbidity measurement after precipitation as $BaSO_4$. Components other than SO_4^{-2} have not been determined. The elemental composition of the sludges accumulating in the ditch was determined by ICP after digestion in nitric acid at SRC. Fe concentrations were found from 1 to 23 %, S at 1 to 3 %, Zn at 0.1 to 23 %, Cu at 0.5 to 8 %, Al at 2 to 4 % and Ca at 0.5 to 1 %.

Results and Discussion

Geochemistry and mineralogy

Table 1 presents the pH of the groundwater samples measured in the field in 1996, and re-measured in 1999 and 2000. The pH predicted from geochemical modelling is also given. The pH values measured in the field in 1996 ranged initially from pH 5.6 to pH 3.0. Three years later the range of pH had narrowed with values of pH 2.3 to pH. By the year 2000 even lower values of 1.9 to 1.6 were reached in all ground waters of this data set.

The samples had oxidized in storage associated with a significant drop in pH. Values of pH predicted by various assumptions, depending on the type of precipitate forming, were as low as pH 0.3. None of the samples reached this simulated, extremely low pH value. All piezometers in Table 1 were sampled again in May 2001, stored for 2 years and re-measured in February 2003. The pH values ranged from pH 2.8 to pH 2.2.

Table 1. Actual measured and estimated pH development in groundwater (last column modeled by PHREEQC).

Piez. #	pH History			Potential pH Development				
				IF all original [Fe] was Fe^{2+} then pH could drop to pH units due to				pH after PHREEQC equilibrium with CO_2 O_2 and goethite Unit
	pH field '96	pH '99 from '96	pH '00 from '96	oxid.& precipitates of Jarosite	oxid.& hydrol. to $Fe(OH)_3$	precipitation of Jarosite	hydrolysis to $Fe(OH)_3$	
H5	4.6	2.3	1.9	1.6	1.3	1.3	1.1	1.6
H8	4.8	2.2	1.8	0.8	0.5	0.5	0.3	1.1
M24W	5.1	2.0	1.8	1.4	1.1	1.1	0.9	1.4
M27N	3.6	2.2	1.8	0.9	0.6	0.6	0.4	1.1
M27S	5.1	2.2	1.8	0.9	0.6	0.6	0.4	1.2
M4	3.8	2.1	1.9	1.6	1.3	1.3	1.1	1.6
M40A	3.0	2.2	2.0	1.9	1.6	1.6	1.4	1.2
M5E	5.6	2.3	1.9	1.7	1.3	1.3	1.2	1.6
M5W	5.0	2.0	1.6	0.6	0.3	0.3	0.1	1.1
M7N	4.2	2.3	1.8	1.1	0.8	0.8	0.7	1.3
M7S	3.7	2.2	1.8	1.1	0.8	0.8	0.6	1.3
H6	5.4	2.2	1.8	1.0	0.7	0.7	0.5	1.2
H7	5.5	2.2	1.9	1.6	1.3	1.3	1.1	1.6

Laboratory resources, e.g. storage space, are scarce and precious, and ultimately the observation period with the repeated measurements of pH and E_H had to be terminated. To ascertain a reasonable conclusion on the long term observations, the samples H5, H7, H8, M5E and M40A were stirred in October 2000 (sampled 1996) for 9 days at 50 rpm on a magnetic stirrer intermittently (night off day on). The pH values did not change from those reported in Table 1 for 2000.

Figure 1 shows a correlation of experimentally measured E_H/pH solution conditions with a calculated redox diagram of Fe. Considered have been the solid phases K jarosite (K-Ja, lg $K_s = -9.34$), schwertmannite (Sh, lg $K_s = 18$), ferrihydrite (Fh, lg $K_s = 4$), goethite (Gt, lg $K_s = 1.4$) and pyrite (Py).

As relevant aqueous species have been included Fe^{+2}, $FeCO_3°$, Fe^{+3}, $FeOH^{+2}$, $Fe(OH)_2^{+}$, $Fe(OH)_3°$ and $Fe(OH)_4^{-}$ (Meinrath and May, 2002). These species define the stability of the Fe(III) redox state towards reduction, but contribute only a marginal amount of the total Fe(III). At the given total Fe concentration (lg ([Fe_{tot}] / [mol dm^{-3}]) = -3.5, pyrite precipitation is (thermodynamically) favoured as soon as SO_4^{-2} reduction sets in. Hence, the stability limit of pyrite coincides with the S(-II)/S(VI) boundary within the limits of Fig. 1. The boomerang-shaped field represents the limits of natural aqueous environments. The right hand side grey field represents a pH region which is physically inaccessible due to excess of ionic strength from CO_2 dissolution ($[HCO_3^-] > 0.1$ mol dm^{-3}).

Figure 1a presents the E_H/pH measured in 85 groundwater samples (after bailing) after 5 min to 30 min upon recovery of the water from the piezometers. Figure 1b presents the E_H/pH values after 0.5 to 4 years storage. The sample bottles display intense formation of Fe precipitates. While the samples showed rapid acidification due to exposure to ambient air, the acidification process continued during a laboratory storage time of 0.5 years to 4years. Figure 1b shows E_H/pH data for a set of 45 samples (a subset of samples given in Fig. 1a measured either already of 0.5 years or finally after 4.6 years when the observations were terminated. All 85 samples were observed and measured until the end of the experiment. Figure 1 represents those samples where the pH difference between field measurement and final pH measurement was greater than 2 pH units. The other 40 samples showed differences of less than 2 pH units at the end of the observation of 4.6 year period (not shown). The water from the piezometers in Table 1 was used for the microbial identification.

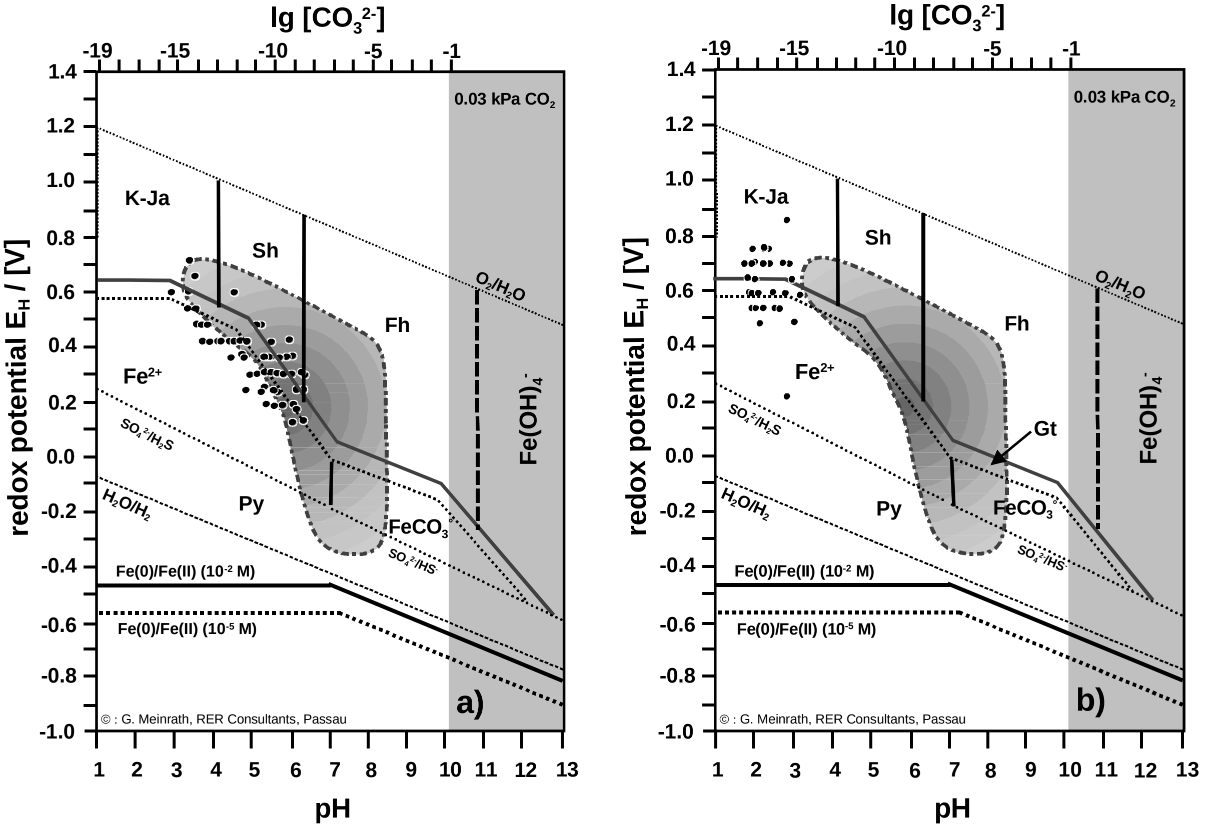

Figure 1a and 1b: E_H/pH diagram of Fe_{tot} $3 \cdot 10^{-4}$ mol dm^{-3}, $S_{tot} = 0.05$ mol dm^{-3}, and $1.6 \cdot 10^{-5}$ mol dm^{-3} in equilibrium with the CO_2 partial pressure of air, 12 °C ambient temperature, 1013 kPa pressure and an ionic strength of 0.1 mol dm^{-3}. The solid phases potassium jarosite (K-Ja), schwertmannite (Sh), ferrihydrite (Fh), goethite (Gt) and pyrite (Py) are considered. The boomerang-shaped field represents the stability limits of natural aqueous systems (Baas-Becking et al. 1960). The grey shaded region at pH >10 is physically not accessible because the ionic strength would exceed its limit because of carbonate dissolution.

The comparison with the limits of natural aqueous environments (Baas-Becking et al. 1960) immediately indicates that the acidification process leads to physicochemical conditions far outside these limits. The stability limits of natural environments are found to account well for the natural undisturbed aquatic ecosystems (Kalin et al., 2005, Meinrath et al., 1999). The interesting aspect shown by the pH values is the long time span over which the pH decreases. These decreases cannot be explained solely by slow mineral precipitation/transformation processes.

Figs. 1a, and 1b have been created with respect to similar graphs given by Bigham et al. (1996). The motivation for these modeling efforts was the higher SO_4^{-2} concentration in the present samples than those of Bigham et al. (1996). The simulations indicated a very high sensitivity of the size and even the very existence of the stability fields for the solids K-jarosite, schwertmannite and ferrihydrite to the selected conditions. Even the selection of an ionic strength correction approach was able to squeeze the stability field of schwertmannite out of the diagram. This observed instability of the stability field prediction for solids has been indicated by Bigham et al. (1996). It is increased by the uncertainty of the schwertmannite solubility lg $K_s = 18.0 \pm 2.5$ (Bigham et al., 1996) and lg $K_s = 10.5 \pm 2.5$ (Yu et al., 1999), the general uncertainty on the chemical composition of schwertmannite and the available estimates for the solubility of potassium jarosite ($-9.21 >$ lg $K_s > 12.51$) (Bigham et al., 1996). The variability in ground water composition in water in and below tailings of this high pyrite tailings deposit, adds to the challenge to account for acid mine drainage by numerical modelling (Meinrath et al., 2000). In addition, the comparability of published thermodynamic data is highly debated along with the numerical predictions under revision (Meinrath and Kalin, 2005).

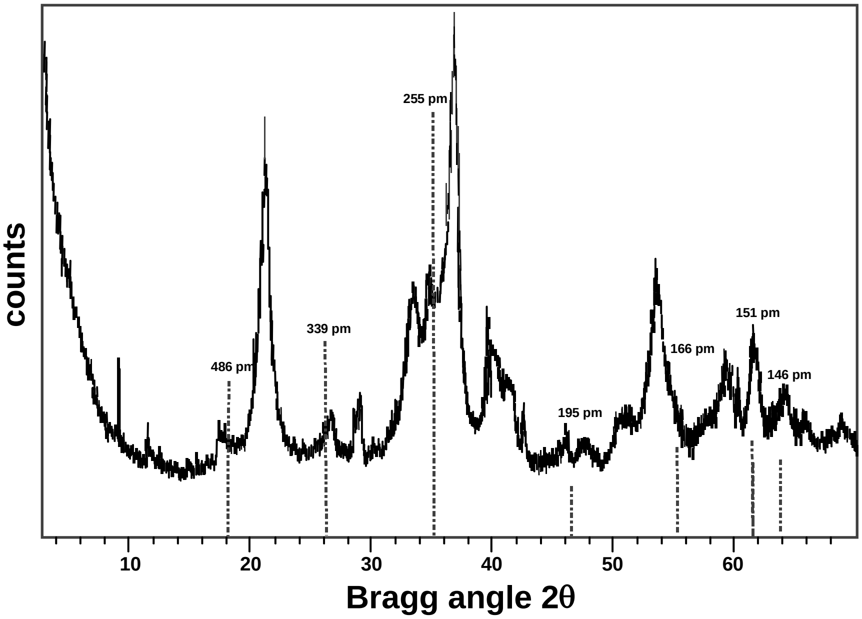

Figure 2: X-ray powder diffraction pattern (Cu K_α)) of a solid Fe sample precipitated from aqueous solution sampled from piezometer. The dashed lines give signals indicative for schwertmannite (esp. lines at 486 pm and 339 pm). The main crystalline component is jarosite.

However, under whatever criticism the numerical output of a simulation tool is seen, two conclusions may be derived from Figs. 1a, and 1b. First, the acidification process in the samples is too persistent to be the sole effect of ambient air oxygen maintaining a thermodynamically favored process of pyrite oxidation. Second, if SO_4^{-2} containing Fe hydroxide phases are formed, these will occur in the acidic range with jarosite being the thermodynamically stable product above pH 3 and schwertmannite (as a representative of SO_4^{-2} containing Fe (oxy)hydroxides) between pH 6 and pH 3.

The empirical observation of pH changes in ground water with their Fe precipitates indicated precipitates holding some schwertmannite along with jarosite and ferrihydrite in agreement with the simulation given in Fig. 1a, and 1b. Schwertmannite was identified by comparison with the patterns provided by the Joint Committee of the Powder Diffraction Society (JCPDS): #47-177 ($Fe_{16}O_{16}(SO_4)_3OH_{10} \cdot 10\ H_2O$ for schwertmannite and #22-0827 ($Fe_3(SO_4)_2(OH)_6$ for jarosite (Fig. 2).

Figure 3 shows pH and E_H values in the sludges collected from the AMD which emerges from the underground working. Hence, these E_H/pH values represent precipitates located on the surface in ambient conditions, in contrast to the precipitate analysed which had formed in the bottles in which groundwater was stored for 4 years from piezometers. The E_H/pH values do not places the sludges accumulating on the surface into mineralogical regions, but indicate a close relationship with the Fe^{+3}/Fe^{+2} redox boundary. This boundary almost coincides with the limit of natural aqueous environments, because this limit is caused by Fe bacteria. This observation is indicative of the importance of microbial activity even in rather acidic waters.

The X-ray powder diffraction analysis was carried out on six sludges collected between the immediate discharge of the underground effluent and its final discharge into the receiving lake. In these samples, no schwertmannite could be identified. The sludges in the ditch had accumulated for about 4 to 5 years in the field when discharge of the underground workings started. If schwertmannite has been present initially, it has been transformed into poorly crystalline Fe (oxy)hydroxides.

Microbiology

Table 2 presents enumerations of the three major, identified, bacterial groups in the piezometers: Fe-oxidising acidophiles, heterotrophic acidophiles and moderately acidic Fe-oxidizers. The most frequently identified Fe-oxidizing group, found in 8 of 12 samples was *At. ferrooxidans*-like.

To determine microorganisms present in situ, microscope slides were suspended within the piezometers for a period of four years from June 10, l998 to July 6, 2002, at the screen depth of the piezometers.

B. Johnson noted that all of the extremely acidophilic isolates from M7S were *At. ferrooxidans*-like, and that no moderate acidophiles were isolated from the slide from this site. *At. ferrooxidans*-like isolates also dominated site M7N, though about 12% of the colonies obtained were *Leptospirillum ferrooxidans*-like. The piezometers M27C was dominated by *At. ferrooxidans*-like Fe-oxidisers. The dominant heterotrophic isolate was a *Frateuria*-like bacterium, previously found in AMD in Norway (Johnson et al., 2001). There are two colony forms of Fe-oxidisers from site M27S, although both appeared to be *At. ferrooxidans*-like bacteria. The dominant heterotrophs were identified as *Acidiphilium*-like.

An overview on the microbial diversity in the groundwater samples is given in Table 3. Both Fe-oxidizing and Fe-reducing bacteria were present. An enumeration is shown in Table 4 for the three prevalent of groups of identified bacteria which show the abundance of bacterial activity in the stored samples even after over four years.

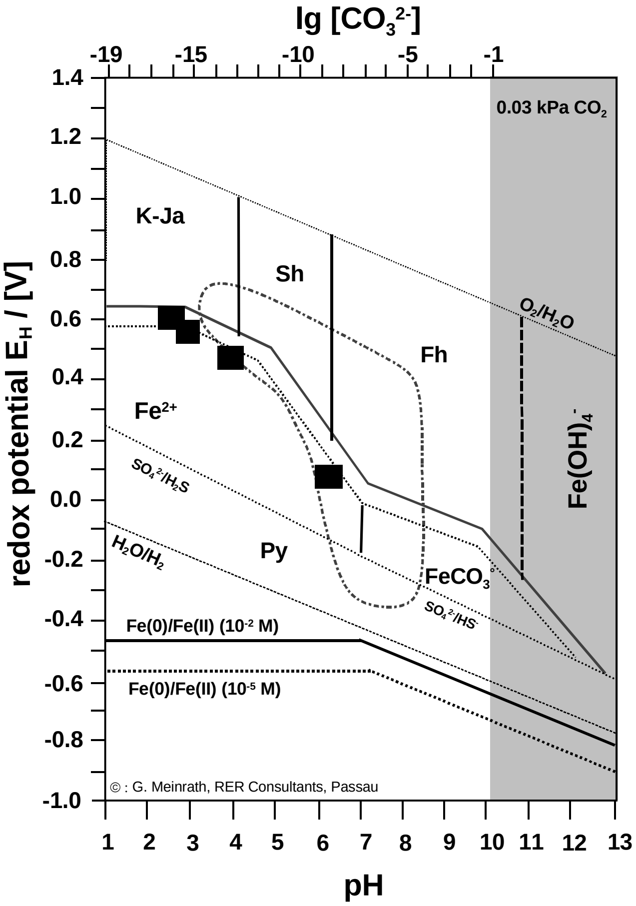

Figure 3: E_H/pH diagram of Fe (cf. Figs. 1a, b). The black squares represent the E_H/pH conditions in the surface ditch at locations where samples for XRD analysis have been collected. These four E_H/pH regions are not associated with special minerals but are located along the E_H/pH redox boundary of the Fe(III)/Fe(II) couple. While the stability regions of the minerals jarosite (K-Ja), schwertmannite (Sh) and ferrihydrite (Fh) are rather uncertain, the redox boundary Fe(III)/Fe(II) is well established.

Fundamentally the same Fe-oxidizing bacterial groups were present on the slides in the piezometers as those in the stored samples. *At. ferrooxidans*-like bacteria prevailed in the samples and in the piezometers. While the population variations are certainly intriguing, confirmation that the bacteria are, in fact, present not in a dormant but active form even after 4.6 years of storage has been a surprising observation in this study.

Table 2: Densities of microbial groups on slides in piezometers (after bailing)

Piez. #	Stratigraphy	Depth (m)	Fe-oxidizing acidophiles $x\ 10^3/cm^2$	Heterotrophic acidophiles $x\ 10^3/cm^2$	Moderately acidophilic Fe-oxidizers $x\ 10^3/cm^2$
M7N	Tailings	4.4	59.2	15.7	69.6
M7S	Sand	10.3	139	1.4	<0.1
M27C	Gravel	11.3	0.35	0.7	0.7
M27S	Peat	4.5	8.7	1	3.5

slides installed in June 1998, collected in July 2002 and analyzed in August 2002

Table 3: Microbial diversity in 4.6 year stored groundwater from tailings

	Iron-oxidizing bacteria			Iron-reducing bacteria				
Piez.#	Sulfur-oxidizing bacteria At. ferrooxidans	L.ferrooxidans	Heterotrophic bacteria Ferrimicrobium	Sulfur-oxidizing bacteria At. thiooxidans	Heterotrophic bacteria Acidiphilium	Moderate Fe-oxidizers	Fungi	Yeasts
H5	-	-	+	-	+	-	+	-
H6	+	-	-	-	-	-	-	-
H8	+	-	-	+	+	-	-	-
M4	+	-	+	+	-	-	-	-
M5E	-	-	+	-	+	-	-	-
M5W	+	-	+	-	+	+	-	-
M7N	+	-	+	-	-	-	-	+
M7S	+	-	+	-	+	+	-	-
M24W	+	-	-	-	-	-	-	-
M27N	+	-	-	-	-	-	-	-
M27S	+	-	-	-	-	-	-	-
M40A	-	-	-	-	-	-	+	-

* samples collected in September 1996, and sent for analysis in May 2001

The microbiological spectrum of the stored samples and that of the glass slides suspended in the contaminated groundwater plume were very similar; both contained microorganisms capable of Fe and sulfur oxidation and Fe reduction. Not only did the microbes sustained exposure to oxygen but also to highly acidic pH < 2 but they also survived. While the precise nature of the microbiologically mediated processes that have occurred in storage is not clear, it is evident that such processes as oxidation and precipitation coupled with the release of H^+ have occurred during storage. Figure 1b gives evidence of a continued generation of H^+ after the initial rather rapid hydrolysis of Fe, as pH values continue to decrease in the samples stored in the dark at room temperature.

The organisms found include autotrophic Fe oxidizers (*At. ferrooxidans*) and heterotrophic Fe oxidizers (*Ferrimicrobium*). These organisms are well known to oxidize Fe and sulfur compounds at low pH. Their activity will cause pH to continue to decline (unless conditions become inhibitory to the microorganisms or alkalinity generating processes, for instance Fe and SO_4^{-2} reduction, come into play. This is an improbable process in these carbon-depleted waters. The isolation of these bacteria from the stored groundwater samples shows that they can survive at these low pH values. The presence of 'moderately acidophilic microorganisms', is interesting as the pH was <2 in all samples at time of analysis. This likely reflects the ability of such microorganisms to survive for a long period in a wide range of conditions. Microorganisms, in particular the autotrophic *At. ferrioxidans* and the heterotrophic *Acidophilium* spp,. were also isolated from these stored bottles (Table 3).

Table 4: Enumeration of acidophilic and Fe-oxidizing bacteria in 4.6 year groundwater

Piez.#	Fe-oxidizing Acidophiles/ml	Heterotrophic Acidophiles/ml	Moderagely Acidophilic Fe-oxidizers/ml
H5	7.4×10^4	2.0×10^3	5.5×10^4
H6	1.1×10^2	30	1.5×10^4
H8	1.7×10^5	$<10^4$	3.0×10^5
M4	4.0×10^6	$<10^4$	$<10^4$
M5E	1.2×10^7	1.0×10^5	$<10^4$
M5W	4.8×10^4	2.0×10^3	3.0×10^4
M7N	1.0×10^6	1.0×10^5	3.0×10^5
M7S	2.2×10^6	$<10^4$	$<10^4$
M24W	1.2×10^4	$<10^3$	$<10^3$
M27N	1.9×10^5	1.0×10^4	1.6×10^5
M27S	2.4×10^5	1.0×10^3	2.0×10^5
M40A	1.6×10^5	$2.0 \times 10_4$	1.4 x 105

*Samples collected in September 1996 and sent for analysis in May 2001

Acidophilium isolates have also been shown to carry out Fe(III) reduction (Küsel et al., 1999, 2002) in low pH conditions and in the presence or absence of oxygen. *At. ferrooxidans* has been identified in previous studies (McGinness and Johnson 1993; Johnson et al 2001, Léveillé, 2001) as a dominant species. The species *Leptospirillum ferrooxidans*, another often described acidophilic Fe oxidizer (Walton and Johnson, 1992; Edwards et al., 1999; Bond et al, 2000, Druschel et al., 2004) was notably absent in this study. The 16s rDNA study on piezometer samples from the same site in northern Ontario was carried out by Lau et al (2001) and this species was not reported. A variety of other Fe oxidizers may be present in more moderate pH levels (Johnson, 2003, Johnson and Hallberg, 2003).

Both *At. ferrooxidans* and *Acidiphilium* spp found in the present study may be capable of Fe(III) reduction. *At. ferrooxidans* has been shown to be capable of Fe reduction coupled to oxidation of elemental S (Brock and Gustafson, 1976; Das and Mishra, 1996; Ohmura et al., 2002). *Acidiphilium* spp. are acidophilic heterotrophs which have been shown to be capable of Fe(III) reduction in culture with glucose as electron donor (Johnson and McGinness, 1991, Küsel et al, 1999). The highest rate of reduction produced by the German microbial isolate JH-5 was with schwertmannite, intermediate rates with $Fe(OH)_3$ and the lowest rates with goethite (Roth and Küsel, 2000). These researchers also found very much higher reduction rates at pH 3 than at pH 5. Interestingly, the sediment surface from which this isolate came has a low pH and schwertmannite is the dominant precipitate. Both Küsel et al. (1999) and Bridge and Johnson (2000) determined that their isolates were able to reduce Fe^{+3} in the presence of oxygen.

These studies relate to the present work, since *At. ferrooxidans* and *Acidophilium spp*, capable of Fe^{+3} reduction, are found in oxic and anoxic conditions. Unlike Fe^{+3} reduction, SO_4^{-2} reduction only occurs in anoxic conditions and at a much lower redox potential than Fe^{+3} reduction. In addition, Fe^{+3} reducers will out-compete SO_4^{-2} reducers for electron donors (organics). It is also generally accepted that SO_4^{-2} reduction requires a pH of 5.5 or higher (Johnson, 2003). Such conditions were found in only one (H7) of the 13 piezometers reported in this study (Table 1) and this value represented the initial field measurement after 4.6 years storage when samples were submitted for microbiological studies, a pH < 2 was measured in all samples, conditions which are unlikely to support SO_4^{-2} reduction.

Conclusions

Microbial activity plays an important role in acid mine drainage (AMD). The attempt to describe, simulate and predict AMD solely by geochemical modelling based on the paradigm of thermodynamic equilibrium and numerical algorithms must fail. Notwithstanding the current revision of the (lacking) metrological basis of chemical data (Plzák 2000, de Bièvre 2004, Filella and May, 2005), the observed long-term development of acid generation cannot be explained by purely chemical driving forces. The E_H/pH diagrams presented outline the general geochemical background which can be associated with groundwater discharging to an oxygenated environment from highly pyritic tailings. Their predictive power, however, is poor.

Nevertheless, it would be difficult to explain the continuous and long term pH depression by purely chemical reaction, suggesting therefore indirectly, that the precipitates are growth substrates for bacterial activity. There is no alternative mean to explain the E_H/pH measurements, but to assume microbial activity. The rich bacterial microcosm associated with the precipitates in the stored bottles and determined in fresh ground water collected at the site (Lau et. al. 2001) as well as on the slides suspended in the ground water below the tailings is not surprising, as the literature documents extensively the ability of microbes to use the precipitates as a growth substrate. The feed back mechanisms between chemical changes in the water, resulting from the bacterial populations utilizing the precipitates to grow, and subsequent shortage of growth medium which will result from the growth, will lead to dormancy or death in the microbial populations, but only to create new conditions awaited by other microbial groups which differing abilities.

Tables 2 - 4 show that the precipitates with the groundwater are able to support Fe-oxidizing and Fe-reducing bacteria over a long period of time. The occurrence of bacteria in low pH water has been described by Edwards et al. (1999).

On the other hand, reproducible and comparable pH measurements in the highly acidic pH range are difficult to establish - and to defend (IUPAC 2002). Therefore, the termination of the long-term acidification experiments after 4.6 years of total storage is justified. At the time of termination, the values in the samples ranged between pH 1.6 and pH 2.0.

These observations open up a large number of unanswered questions. Of major interest is the impact of bacterial activity upon the mineralogical composition of the sludges. Unfortunately, numerical simulations are not capable to predict reliably the major solid phases, as the overall quality of chemical thermodynamical data is insufficient. A further reason is the generally metastable state of the initially formed Fe phases which depend on the microscopic conditions during the precipitation process. The thermodynamic equilibrium assumption of most geochemical simulation codes cannot serve as a reliable basis to predict metastable states. Metastable solid phases will transform to the more stable solid compounds according to Ostwald's step rule. If ground water moves from a reducing environment into an environment in which oxygen is present and Fe hydrolyzes with the associated precipitate formation, microbial activity appears to play a role in gradually reducing the pH to a very low value. The initial and rather rapid decline in pH noted, need not to be the final pH which might be expected.

As an example for such alteration processes the presence of sulfate-containing Fe (oxy)-hydroxides has been investigated. The mineral schwertmannite currently attracts considerable attention. In fact, schwertmannite has been observed in XRD studies from precipitates of piezometers M27N in the Cu/Zn tailings, commonly together with jarosite. The numerical simulations on the basis of PHREEQC (Parkhurst et al. 1999) were unable to predict occurence of schwertmannite and jarosites with any reliability. Nevertheless, sulfate-containing Fe (oxy)hydroxides may release further acidity, as soon as the minerals alter – either due to neutralization (jarosites) or due to aging (schwertmannite). In summary, this study has underscored the fundamental importance of biological activity in the mine water environment.

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