

THE CHEMISTRY OF CONVENTIONAL AND ALTERNATIVE TREATMENT SYSTEMS FOR THE NEUTRALIZATION OF ACID MINE DRAINAGE

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Abstract. The objective of this paper is to review the chemical processes which drive the performance of both conventional and passive treatment systems for Acid Mine Drainage and to compare the two. Several decades of research have improved the performance of both yet neither provides an environmentally acceptable, sustainable solution to the problem, which is still a major financial liability of the mining industry. A review of the literature and an examination of the underlying chemical reactions of both approaches suggest that the greatest potential for improvements lies with passive ecological systems. Future research areas are suggested...

Additional Key Words: acid mine drainage, acid rock drainage, passive treatment, lime treatment, ecological engineering.

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Introduction

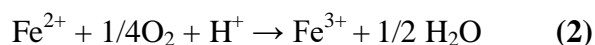
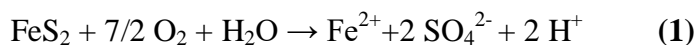
By definition, mining is not sustainable. Yet it is not unreasonable to ask if the treatment of mining wastes can be conducted in a sustainable manner. Ideally, a sustainable solution to any industrial problem is economically viable, generates little or no waste, is energy efficient and is not a source, in itself, of pollution. A growing body of evidence now suggests a causal relationship between the environmental and economic performance of companies since the reduction of pollution enhances profit by increasing efficiency, reducing compliance costs, and minimizing future liabilities (King and Lenox, 2001), economies that should all be of interest to the mining sector.

By general consensus, Acid Mine Drainage (AMD) is the most critical environmental problem created by mining. AMD is unique among industrial contaminants. Because of its leaching capacity, augmented by the activities of the bacteria it attracts, it is self-perpetuating. Nordstrom and Alpers (1999) estimate that without preventative measures the Richmond Mine, at California's Iron Mountain, would generate AMD, with $\text{pH} < 1$ and containing several g/L of dissolved metals, for 3000 years. Kalin (2001) estimated, based on oxidation rates derived from tailings pore water samples, that the site of a small zinc/copper mine in Northwest Ontario, Canada, would generate AMD for 1,000 to 35,000 years. These may be extreme examples but it is not uncommon for base metal mines and their waste products to generate acid for more than 100 years. Since AMD is self-renewing, an ideal solution to it would also be self-perpetuating.

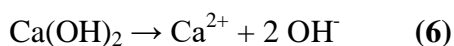
There are two distinct strategies for treating AMD. The conventional solution is to collect and chemically treat acidified effluents in a centralized treatment plant. Alternatively, effluents can be routed through natural or constructed wetlands within which microbial communities perform the same function. Such a passive treatment scenario meets the definition of sustainability. It is economical, non-polluting, and is not a source of secondary wastes. Moreover, a well-engineered passive treatment system is a closed ecological system and hence is self-renewing. But does it work? This paper will discuss the chemistry of both the conventional and alternative approach to the treatment of AMD.

The Chemistry of Conventional AMD Treatment

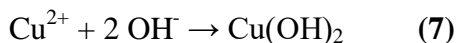
The process of AMD generation is well understood. AMD is formed by the oxidation of metal sulfides, mainly pyrite and marcasite, which have been exposed to air and water during and following mining operations. AMD formation involves iron sulfide oxidation (1), ferrous iron oxidation (2), ferric iron hydrolysis (3), and the enhanced oxidation of ferric sulfide ions (4).



In a conventional treatment system alkaline materials and other chemicals are added to the AMD to neutralize it and enhance hydroxide precipitation. A preferred alkaline material is quicklime, CaO , (5) which forms Ca hydroxide in presence of water (6).



Following dissolution of the hydrated lime, pH increases and metal ions precipitate as hydroxides as shown for Cu in Equation 7.



Each metal in solution contributes a specific metal acidity to the AMD; conversely, the precipitation of specific metals occurs at specific pH levels. For example, hydroxides of Fe^{3+} precipitate at about pH 3, while those of Al at pH 3.7 to 4.5. Divalent metal ions precipitate in the alkaline range, Ni at about pH 8, Fe^{2+} at pH 8 to 9 and Zn at more than pH 9. Further, the change in state of metals, from liquid to solid, is a heterogeneous process and slow by comparison to the neutralisation of hydrogen ions which is homogenous and fast.

The precipitation process is affected, not only by reaction times, but by the thermodynamic considerations depicted in Figure 1 which provides three-dimensional phase diagrams in the Fe-S-O-H system with $\lg [\text{Fe}]$, $\lg [\text{S}]$ and E_{H} as coordinates at pH 2, pH 5 and pH 7. The concentrations of Fe and S presented here are from the tailings seepages at Copper Cliff, in Northern Ontario, (Kalin, 1993). The figure incorporates thermodynamic data described by various sources (Garrels and Christ, 1965, Stumm and Morgan, 1981 and Weast, 1971). The diagrams are constructed without ionic strength correction as it can be assumed that the inherent uncertainties in the data are larger than any of the correction effects (Meinrath & May, 2002, Meinrath, 2001). For inclusion of $\text{FeCO}_3(\text{s})$, the atmospheric CO_2 partial pressure has been assumed. The drastic change in the relative stability fields of $\text{FeS}_2(\text{s})$ and $\text{Fe(OH)}_3(\text{s})$ between pH 2 (top) and pH 5 (middle) is evident. While in an acidic medium, $\text{Fe(OH)}_3(\text{s})$ is unstable. Its very low solubility product ($\text{pK}_s = 54$) causes a drastic stabilisation at pH 5. At pH 7, other phases, e.g. FeS and $\text{FeCO}_3(\text{s})$, compete with Fe^{3+} and cause the observed decrease of its stability field (bottom). The absolute magnitude of the effects at different values of pH differs in an AMD system depending on the specific Fe and S and H^+ concentrations. However, general tendencies as a function of pH, will persist.

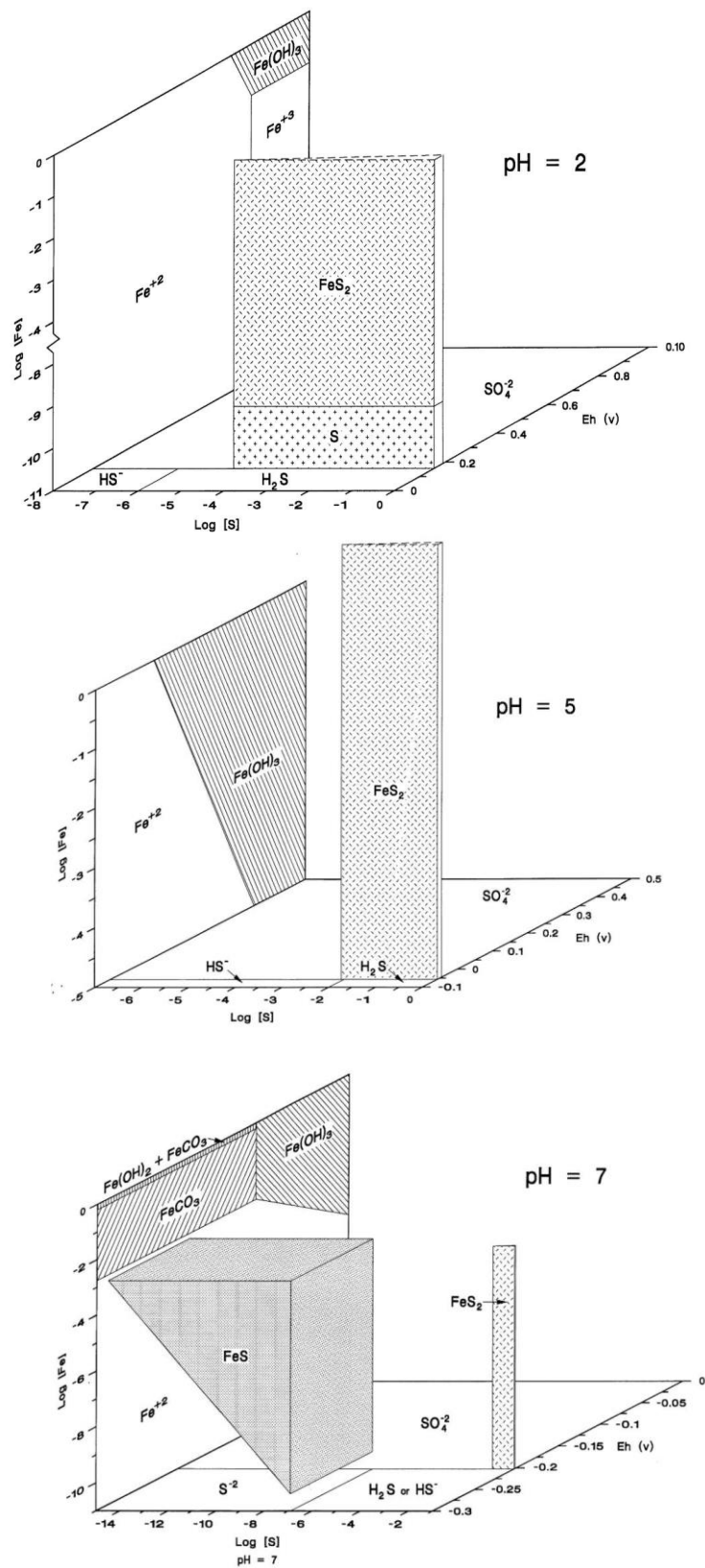


Figure 1. Three-dimensional phase diagrams in the Fe-S-O-H system with $\lg [\text{Fe}]$, $\lg [\text{S}]$ and E_H as coordinates at the pH 2, pH 5 and pH 7.

It is possible to extrapolate, from the data in Figure 1, the value of pH required to induce precipitation. However, despite the general importance of pH in an AMD system, it is not the only important factor in metal removal, as also ionic strength, temperature, E_H , and concentrations of suitable complexing agents (e.g. humic substances) play a role and other interactions with the precipitated solids (Uhlman et al 2004). For the formation of solid phases, the Ostwald Step Rule holds, suggesting that in a fast process the thermodynamically less stable phase is formed primarily while the thermodynamically more stable end-member phases may slowly transform from these initially-formed phases. Sludges therefore include the well-known crystalline form of goethite but consist mainly of highly amorphous oxy and hydroxy iron oxides.

Brown et al. (2002) reviewed lime treatment methods used in the U.K.; Vachon et al. (1985), Kuyucak et al. (1991a) and Aubé and Zinck (2003) reviewed Canadian systems, and Skousen et al. (1998) and Costello (2003) reviewed U.S systems. The common denominators of lime-based systems is that they remove metals as hydroxides, and that the neutralized water leaving them contains sulfates, mainly as Mg and Ca sulphate or gypsum (Rose and Ghazi 1997). The resulting hardness of the water can be detrimental to the receiving environment (Charles et al. 2002, Moni and Dhas 1989).

In summary, AMD is a buffered system of such complexity that the addition of lime, in itself, will not bring about the complete precipitation of iron and other metals based on its stoichiometric equivalence

Secondary waste characteristics

In a conventional treatment plant, hydrated lime is added to the AMD as slurry. The effluent is then aerated, and flocculents are added to carry the precipitates to the sludge at the tank bottom. The content of solids in the sludge has traditionally been about 2% to 7% but modern High Density Treatment (HDS) plants recycle sludge to more efficiently utilize the lime in it and apply more efficient flocculation processes to achieve densities of 30% or better. All sludges contain calcite (CaCO_3). HDS sludges are especially high in gypsum (CaSO_4) (Aubé and Zinck, 2004).

In Canada, an estimated 6.7 million cubic metres of sludge are produced each year (Zinck et al., 1996). Since the long-term stability and environmental acceptability of these sludges are of great concern, numerous characterization and leaching studies have been conducted (Kuyucak et al., 1991b; Payette et al., 1991, Zinck et al., 1996, Zinck, 1997, Fiset et al 2003, Zinck, 2004). Zinck examined sludges with densities as low as 2.4 % and HDS sludges as high as 32.8 %. She concluded that with time the alkalinity of the sludges decreases while the cycles of freeze-thaw and natural dewatering increase density, that HDS sludges had a higher metal content, improved crystallinity and a reduced potential for metal leaching, and that with time the calcite and gypsum content in HDS sludges increases. Sludges produced through the conventional AMD treatment process require appropriate disposal to prevent the re-release of metals and much work remains to be done to optimize the neutralization process and minimize long term environmental consequences (Zinck 2004). As Ledin and Pederson (1996) conclude, lime effectively removes metals and hydrogen ions from AMD, but it also creates abundant and unstable secondary wastes. It is no panacea and cannot be considered environmentally sustainable.

The Chemistry of Ecologically-Based AMD Treatment

A variety of passive AMD treatment systems have been developed in the last 20 years (Wildeman et al., 1993, Kalin et al., 1995a, 1999, Skousen et al., 1998, Costello 2003). Aerobic wetlands, anaerobic or compost wetlands, vertical flow wetlands, AMD treatment ponds, bio reactors and permeable reactive barriers have been applied widely. Some passive systems utilize the dissolution of limestone in ponds or channels to neutralize AMD. Typically, they incorporate anoxic limestone drains, limestone ponds or open limestone channels (Skousen et al., 1998, Waters et al., 2003). These systems work for a few years (Ziemkiewicz et al., 2003) but inevitably limestone is coated by Fe and Al hydroxides. These coatings are stable enough to reduce limestone dissolution and to plug the system. Since the limestone must be renewed, such systems are not truly passive or self-sustaining. Aerobic and surface-flow wetlands are widely employed in the U.S. for the treatment of alkaline, neutral and weakly acidic coalmine drainages primarily by inducing the precipitation and adsorption of iron hydroxide. In these systems, anaerobic reduction processes, which are the key to biomineralisation and metal fixation, play a minor role.

Treatment systems such as anaerobic wetlands (Machemer and Wildeman, 1992, Wieder 1990, 1993), Sequential Alkalinity Producing Systems (Kepler and McCleary 1994, 1997), bioreactors (Jones and Gusek, 2004; Tsukamoto and Miller, 2004), and permeable reactive barriers (Blowes et al., 2000) all require the addition of biodegradable organic substances to provide carbon for anaerobic alkalinity-generating processes. These can include hay and straw (Bechard et al., 1994), potato waste (Fyson et al., 1995; Kalin et al., 1995b), used mushroom compost (Machemer and Wildeman, 1992), lactate and cheese whey (Oleszkiewicz and Hilton, 1986; Herrera et al., 1991), molasses (Maree and Hill, 1989), highly refined organic substances such as ethanol and methanol, (Tsukamoto and Miller, 2004; Jones and Gusek, 2004) and animal waste slurries (Ueki et al., 1988). This list is far from exhaustive.

In general, highly refined organic substances are the most effective per unit addition, but organic wastes are more attractive environmentally and can supply organic substrates for sulfate reduction over a longer time period as well as such other nutrients as phosphate and nitrate. Moreover, suitable organic wastes are often available locally at little or even no costs (Grossd et al., 1993). On the other hand, the organic substrate will periodically need replacement if it is not re-generated on an annual basis from within the system, e.g., by the debris of vascular plants. Systems incorporating flourishing populations of primary producers of organic carbon, can be considered truly sustainable due to photosynthesis, which in turn supports other life processes which maintain themselves in the sediment.

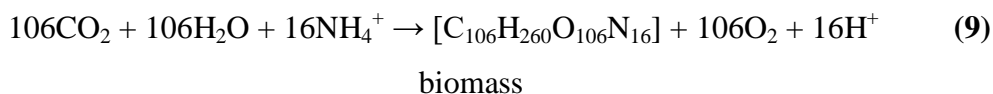
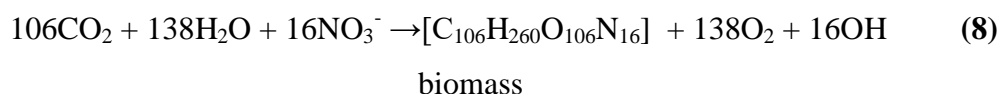
The longevity of passive AMD treatment systems has been recently reviewed (Eger and Wagner, 2003; Sjöblom 2003). The projected long-term performance and cost-effectiveness of 137 passive systems in the Eastern U.S. were assessed and compared to conventional systems by Ziemkiewicz et al. (2003) who found that, in general, they performed poorly due to the exhaustion of degradable carbon sources. Nevertheless, there were exceptions, systems that were both economic and effective within the prospected 20-year life span. Most of the evaluated systems had been operated for less than five years. Eger and Wagner (2003) observe that the effective life span of such systems is determined by the availability of degradable organic carbon. It can be concluded that this was due to the failure of the systems to self-generate the necessary carbon through primary production.

Bioreactors utilize SRB inoculants to treat effluents both in situ (Jones & Gusek, 2004) and ex situ (Adams et al., 2004). Such systems treat effluents and capture commercial grade metals, exploiting the capacity of AMD to mobilize and transport hydroxides. The value of the resultant metals makes these systems more economical than conventional treatment plants (Adams et al., 2004). Similarly, the biosulphide process, currently employed at three sites, uses hydrogen sulfide generated by SRB to remove metals from AMD in bioreactors (Lawrence et al., 2003, Marchant 2004).

German researchers have taken an acute interest in the potential of passive remediation techniques to restore hundreds of acidic Tagebauseen (pit lakes) created in the former East Germany by the flooding of open cast lignite coal mines Nixdorf, B. et al., 2001, Totsche, O et al., 2003). Willscher (2001) compiled a list of procedures commonly practiced worldwide to neutralize AMD including the exclusion of water and air, inhibition of microbial oxidation, and the promotion of sulphate reducing bacteria. In 2003, Willscher again summarized at least seven different ways to utilize limestone in combination with wetlands, concluding that passive and semi-passive treatment methods need to be improved. Totsche and Steinberg (2003) reviewed the natural alkalinity generating processes associated with photosynthesis and concluded, sadly, that, there is no economically practical way to treat the Tagebauseen. Their conclusion was based on the inability of photosynthesis in such waters to generate alkalinity.

Photosynthesis in the water column or controlled eutrophication

Phytoplankton and meadows of periphytic algal/moss in acidic systems generate alkalinity, when photosynthesis is coupled to the uptake of nitrogen as nitrate (Equation 8). But when photosynthesis is coupled with the uptake of ammonium-N, usually the prevailing form of nitrogen in AMD acidity is generated instead (Equation 9).



Microcosm studies of the Tagebauseen suggest that the addition of nitrate or ammonium will stimulate phytoplankton growth and induce eutrophication but that the resulting growth does not substantially generate alkalinity (Totsche et al., 2002). Similarly, the net effect of fertilization by N and P is small. This is due to the fact that primary productivity in the open water column in ponds or lakes below pH 4.5 is limited since inorganic carbon or CO₂ becomes insoluble and hence is unavailable to photosynthesis. In such waters, alkalinity generation through photosynthesis occurs only in the algal mats that draw upon the inorganic carbon generated by decomposition within the sediment where the pH is elevated.

Another key component of biological AMD treatment processes is the availability of phosphate which is required both by primary producers and all other organisms for growth. Phosphate however is scarce in AMD due to its adsorption to iron hydroxide particles. Phosphate availability, due to its co-precipitation with iron hydroxide was found to be the limiting factor in the biological productivity of the Tagebauseen (Krumbeck et al., 1998). Studies of an English lake, acidified by acid rain, showed that the addition of phosphate stimulated biological alkalinity generation (Davison et al., 1995). In these lakes, iron is not abundant. In anoxic sediments, phosphate is released with the reductive dissolution of iron hydroxides and

becomes available as a nutrient for organisms. The availability of phosphate is critical to the biologically-mediated treatment of AMD.

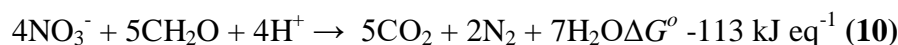
In other microcosm experiments with waters of the Tagebauseen, nutrients and organic substrates were added to induce eutrophication in the water column and so provide carbon for alkalinity generating microbes in the sediment. This, in fact, led to the removal of acidity and iron and increased alkalinity to near-neutral conditions in the water column which persisted for the two year duration of the experiment (Fyson et al., 1998, 1999; Steinberg et al, 2000; Fyson and Gelbrecht, 2004). In a comprehensive summary of biogenic processes in the Tagebauseen, Nixdorf and Deneke (2004) concluded that the decomposition of phytoplankton, periphyton, and aquatic vegetation, the detritus of the controlled eutrophication of the water column, sustained biogeochemical cycling processes in the sediment. Clearly, the benefit of eutrophication in the water column is that it ultimately enriches the sediment the key driver of neutralization

Microbial Reduction reactions in sediments

Most sediments are essentially anoxic with the redox potential decreasing with depth. Following the reduction of oxygen by aerobic respiration, Equations 10-13 (shown below) occur in the order given with decreasing redox potential (Mills et al., 1989; Stumm and Morgan, 1996). The thermodynamic driving force, expressed by the Gibbs free energy of the reactions, (given for conditions pH 7, 25 °C and 25 °C) is most negative for de-nitrification and least negative for sulfate reduction, indicating that nitrate reduction is the prevailing process.

In nature, the kinetics of these processes, are slow. All four reactions, are mediated by indigenous micro-organisms in anoxic environments where appropriate electron acceptors (nitrate, Mn^{4+} , Fe^{3+} , sulfate) and electron donors (usually a simple organic substance, represented in the equation as CH_2O) are present. These processes consume hydrogen ions (H^+) raising the pH, and promoting metal precipitation.

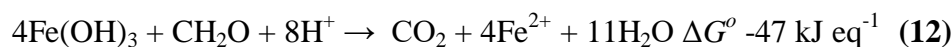
Nitrate Reduction (Denitrification)



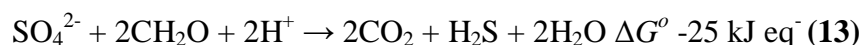
Manganese Reduction



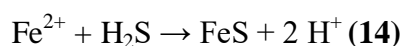
Iron Reduction



Sulfate Reduction



The generated sulfide (Eq. 13) can react with Fe^{2+} (or other metal ions) to form metal sulphides according to Eq. 14, thus re-generating a metal-containing solid, biogenic pyrite or, in the presence of other metals, minerals.



Precipitation of FeS generates hydrogen ions, but removes iron from the system, which decreases metal acidity completing the remediation cycle.

These remediation processes occur spontaneously in nature. Alkalinity variations occurring over the past century in poorly buffered Connecticut lake sediments have recently been studied using algal material (chrysophytes and diatoms) as indicators (Siver et al., 2003). Despite the high rates of acidic precipitation in a region with poorly buffered soils and crystalline bedrock some lake waters retained a neutral pH. Over the last 40 to 70 years a substantial increase in sedimentary sulfur has occurred on the surface of the sediment in the neutral-pH lakes, corresponding to an average alkalinity generation of 78-145 meq m⁻² yr⁻¹, far in excess of the 45 – 48 meq m⁻² yr⁻¹ of acidity being transported into them. The major sulphur sink in the lakes was not organic sulphur but Fe sulphides, most likely generated by dissimilatory bacterial reduction of sulfate.

A detailed investigation of Lake 239 in the Experimental Lakes Area of Northwest Ontario found an alkalinity generation 4.5 times higher than acid deposition. Amounting to 118 meq m⁻² yr⁻¹ (Schindler et al., 1986). More than half of the in situ alkalinity production was found to have come from the biological reduction of SO₄²⁻ reduction (35%) and NO₃⁻ (26%) with the ion exchange between H⁺ and Ca²⁺ accounting for the remainder.

Sulphate reducers are clearly important to the generation of alkalinity and their role in constructed wetlands has been well studied (Postgate, 1984, Widell & Hansen, Widdel 1993, Odom and Singleton, 1993, Barton, 1995). Moreover, many strains have been isolated and cultured for use in industrial processes, as noted above.

When considering all the microbial reactions in the sediment, it becomes evident that it is combination of the hydrogen sulphide produced by SRB with the Fe²⁺ that generates iron sulphide and alkalinity and maintains the reducing conditions necessary for the stable deposit of metal sulphides in the sediments. From the thermodynamic relationships, it further follows that iron is also a relevant component in alkalinity production – provided the oxidation of Fe²⁺ and Fe³⁺ can be prevented.

The work on passive systems places undue emphasis on sulfate reduction at the expense of iron reduction which is at least as important. Typically, when both dissolved iron and sulfate are abundant in AMD, bacteria that reduce Fe³⁺ at a higher redox potential out-compete SRB for electron donors (Stumm and Morgan, 1996). Although the biogeochemical iron cycle in acidic aquatic ecosystems and the role of microorganisms have been studied in detail (Sulzberger et al., 1990; Peine and Peiffer, 1996, 1998; Blodau and Peiffer, 2003; Lovley et al., 2004), the potentially beneficial role of the iron reduction process in AMD treatment has not yet been appreciated or exploited. Thermodynamics dictates that only when Fe³⁺ is fully reduced will sulfate reduction come into play. But, in natural sediments, both processes can occur simultaneously (Blodau and Peiffer, 2003). The reduced iron produced through Fe³⁺ reduction combines with sulfides from sulfate reduction to produce the desired stable precipitates. A better understanding of the relationship between iron and sulfate reduction is essential for the effective employment of these processes for AMD treatment.

Acid Reduction Using Microbiology (ARUM)

A pilot test system to derive design criteria for the construction of microbially active sediments, potentially effective in the treatment of AMD, was constructed in 1990-1993 at the foot of the Copper Cliff tailings in Sudbury, Ontario. The system consisted of an

oxidation/precipitation cell and two reducing cell with a combined area of 2000 sq. m. into which seepage flowed at the rate of 1 to 5 L/min. (Kalin 1993). The work was funded by the Mine Environment Neutral Drainage Program of Natural Resources Canada. It was envisaged that passive treatment could be used in tailings seepage collection ditches and on tailings in remnant ponds or as pre-treatment for conventional water treatment, to reduce lime consumption. This process of Acid Reduction Using Microbiology (ARUM) has since been successfully applied at sites in Canada (Fyson et al., 1995, Kalin et al., 1995b, 1999) and Brazil (Kalin and Caetano Chaves, 2003).

Base metal waste rock piles release Fe^{3+} which forms iron hydroxides and oxyhydroxides as soon as it contacts near neutral rain water, generating hydrogen ions. Waste rock seepages hence emerge at values of $\text{pH} > 3$. Tailings, however, generally release Fe^{2+} . Tailing seepages consequently have a high chemical oxygen demand, similar to plumes of contaminated groundwater plumes when they emerge as surface waters. Fe^{2+} may precipitate as iron oxide and hydroxysulfate when values of pH are above 5. These processes are elementary chemical reactions which cannot be influenced significantly by microbes.

Therefore, depending on the origin of the AMD/ARD, the characteristics of iron varies. However, in seepages containing substantial amounts of Fe^{2+} these chemical precipitation processes can be effectively exploited, since the resulting iron oxy-hydroxides co-precipitate and adsorb other metals. This was done in the oxidation/precipitation cells in the ARUM pilot system. The data used in Figure 2 were previously published in Kalin and Smith (1997). The metal removal for the period from June to September 1996, in the fifth year when the system reached its optimal configuration, is evident. Flow, at that time, was low with receiving seepage at a rate of about 1 L/min. The pH of the inflow to the oxidation/precipitation cells ranged from 5 to 6 and of the outflow from 3 to 4. A considerable reduction in iron and metals had occurred.

Considerable work has been carried out in recent years on the characteristics of the natural precipitation products of iron. In the acidified lignite coal pit lakes in Germany, surface sediments were found to be dominated by intermediate iron precipitate species oxyhydroxy, oxyhydroxysulfate or amorphous to crystalline oxyhydroxides with Schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) and Goethite ($\text{Fe}(\text{OH})_3$) being prominent phases. Intermediate phases like Schwertmannite may be slowly transformed into the more stable Goethite in agreement with the Ostwald Step Rule. This transformation process may compete efficiently for electron donors with sulphate reduction. Schwertmannite reduction does not generate alkalinity and maintains a value of 3 for the sediment surface pH (Blodeau and Pfeiffer 2003, Regenspurg, 2004). The relationship of iron precipitate transformation to biological alkalinity generation needs to be investigated in more detail.

In Goethite-dominated sediments, reduction of iron and sulphate coexist at the sediment surface. Under these conditions, values of pH are in the neutral range and sulphides are abundant throughout the sediment core. Neutralization rates in the Tagebausen were found to vary by orders of magnitudes (Peine & Pfeiffer, 1996, 1998). The fermentation of organics and the sum and balance of iron- and sulphate-reduction rates and the re-oxidation of H_2S are controlled by their respective Gibbs free energies. The thermodynamics of such systems are described in detail in Blodau and Pfeiffer (2003). These authors concluded that in AMD affected lakes where Fe^{3+} precipitates as Schwertmannite, there is little accumulation of sulfides, and that the addition of decomposable organic matter would not lead to neutralization. The universality of this is not yet clear, but it is an important consideration for passive treatment systems and their natural oxidation ponds. Much has yet to be learned about the processes which control the anaerobic

degradation of organic matter and the stability of metal sulfides and other metal compounds in sediments.

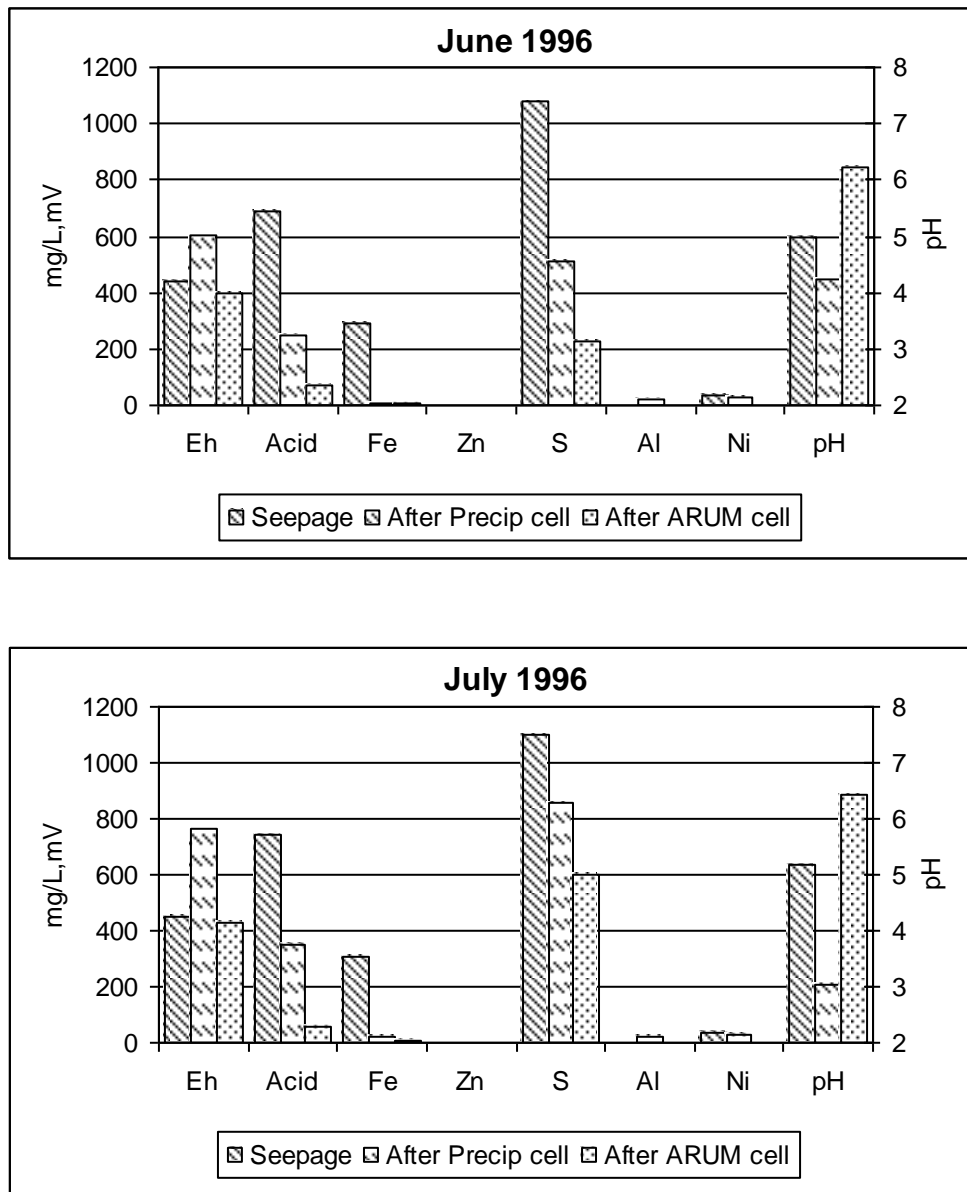


Figure 2a: Tailings seepage characteristics of the Copper Cliff ARUM system in 1996 (Kalin and Smith, 1997)

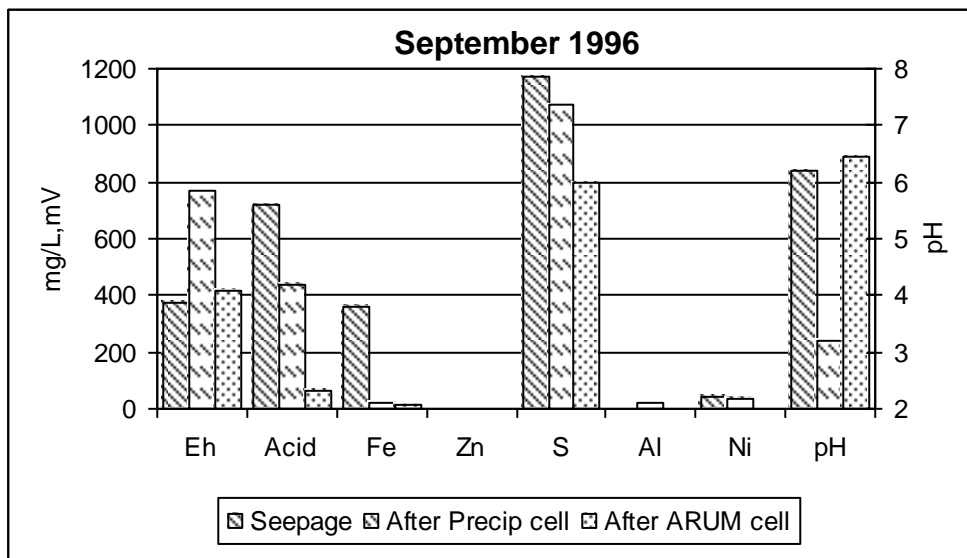
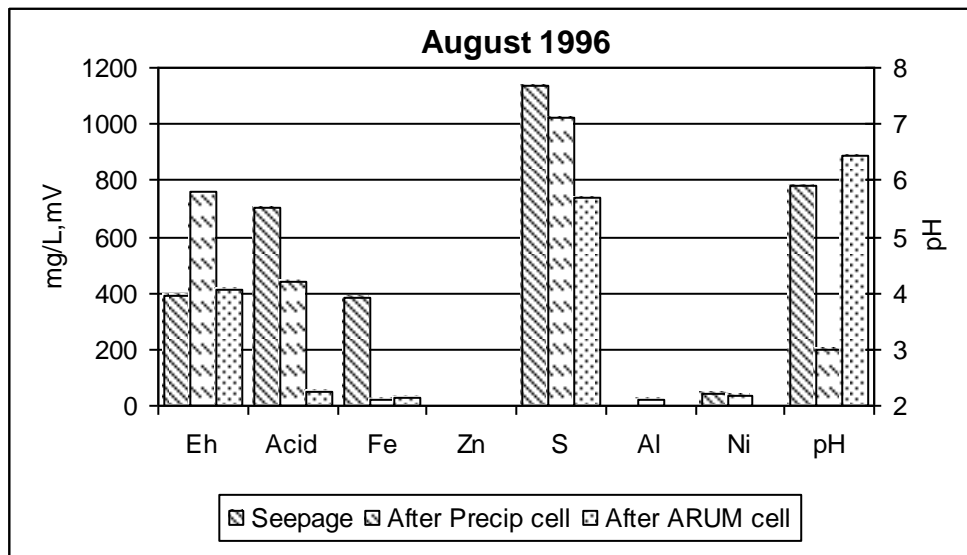


Figure 2b: Tailings seepage characteristics of the Copper Cliff ARUM system in 1996 (Kalin and Smith, 1997).

Constructing a sediment for ARUM

In the pilot test system constructed at Copper Cliff, the outflow of the two oxidation-precipitation cells entered reducing ponds, in which sediments had been built up with organic materials. The ARUM process was enhanced by the addition of floating cattail/vegetation rafts which minimized wind-induced turbulence and doing so reduced oxygen in the water, provided a further microbial habitat in their root mass, and contributed a continual supply of organic litter to the sediment below into the water (Kalin, 1993). The performance of the ARUM cells, when the system had reached a final configuration, receiving the acid input from the oxidation cells are reproduced from Kalin and Smith (1997) in Fig. 2a and b.

Passage through the ARUM cells resulted in the removal of nearly all the remaining nickel and zinc, most of the acidity and much of the sulfur. The high rates of sulfur removal are indicative of sulfate reduction. To confirm that bio-mineralization processes would take place in the constructed sediment, three 170 dm³ plastics drums were filled with organic flax, hay, straw and rusty iron in the form of reinforcing bars and nails to create reducing conditions in a simulated iron-enriched sediment. Fig. 3a and 3b illustrated these so-called ARUMators, which contained sampling ports at different depths within the drums.



Figure 3a: Arumator under construction.

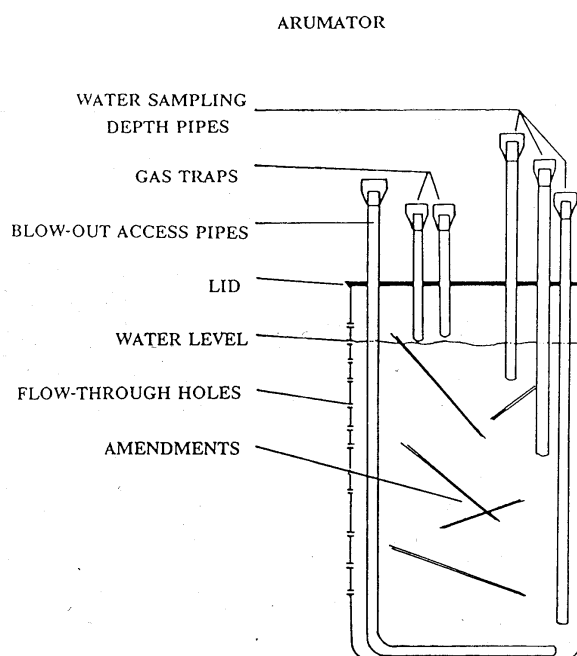


Figure 3a: Arumator schematic.

Fig. 4 gives an E_H -pH diagram of iron, specifying the Fe^{2+}/Fe^{3+} boundary under consideration, of aqueous hydroxo species. The lines ' O_2/H_2O ' and ' H_2O/H_2 ' indicate the stability limits of the water. The boomerang-shaped field in the center indicates the E_H -pH limits of natural environments as specified by the studies of Baas-Becking et al. (1960).

The range of E_H -pH conditions observed in the three ARUMators after one year are indicated by three square fields, all located inside the stability field of Fe^{2+} and at the low pH boundary of the limits given for natural environments. Clearly, microbial reduction would establish reductive conditions in the sediment and ameliorate seepage pH. These conditions were maintained without addition of chemicals and persisted.

Geochemical simulations using the program PHREEQE by Parkhurst et al (1980) were carried out on the seep water and from the ARUMators to determine the degree of saturation for metal sulfides, sulfates, carbonates and hydroxides in the created sediment of the ARUMators. Data were reported by Kalin (1991) and are summarized here. All samples, both seepage and ARUMators showed supersaturation, i.e., they indicate the potential to precipitate for alunite, barite, cristobalite, gypsum, hematite, quartz and cuprous-ferrite. In addition, seepage samples were saturated with ferrihydroxide, goethite, jarosite maghemite, magnetite and cupric-ferrite. The higher pH values in two out of three ARUMators gave rise to some supersaturation with respect to $Al(OH)_3$, $Al_4(OH)_{10}$, boehmite, calcite, dolomite, gibbsite, magnesite, siderite and rhodochrosite. Low pE values were accompanied in some or all samples at different depths by supersaturation with pyrite, cuprite, chalcocite (djurleite/anilite/blaublei), covellite, chalcopyrite, spalerite, otavite, greenokite and galena. Clearly, conditions existed within the ARUMators, and the larger ARUM test systems to promote the biomineralisation of metals from AMD effluent.

After the ARUMators had been immersed for a year in the pilot cells, the straw and flax in them was subjected to sequential extraction analysis (according to a modification of the protocol of Goering and van Soest (1970) for forage fiber) to determine the rate of decomposition. The acetone fraction showed a 4-5 % loss, representing lipids and resins. The HCl reflux produced a 33 % loss of soluble sugars, (starch, amino acids, hemicellulose) and, after sulphuric acid digestion, a 3-4 % loss in cellulose (Kalin, 1991). This was 40 to 42 % of the material that was potentially degradable in sediment conditions, with the remainder being mainly lignin and lignocellulose. Equivalent of alkalinity generated by the decomposing organic matter were estimated based on Davison and Woof (1990) and Lerman and Stumm (1989). The degradable carbon content (12 g) of the amendment added to the ARUMators vastly exceeded the requirements needed by microbes to generate the measured alkalinity regardless of the microbial process involved.

In an open system, such as the ponds in the Copper Cliff system, some carbon will diffuse to surface waters and be lost to the atmosphere as CO_2 . However, if degradable carbon sources are delivered to the sediment or anoxic water immediately above the sediment, it is likely that most of their carbon will be captured by anaerobic alkalinity generating processes.

In summary, the ARUMators showed that the decomposition of organic matter can occur in AMD seepage and that it can account for alkalinity changes, which in turn lead to the geochemical changes which support the treatment of the AMD without need for neutralizing chemicals.

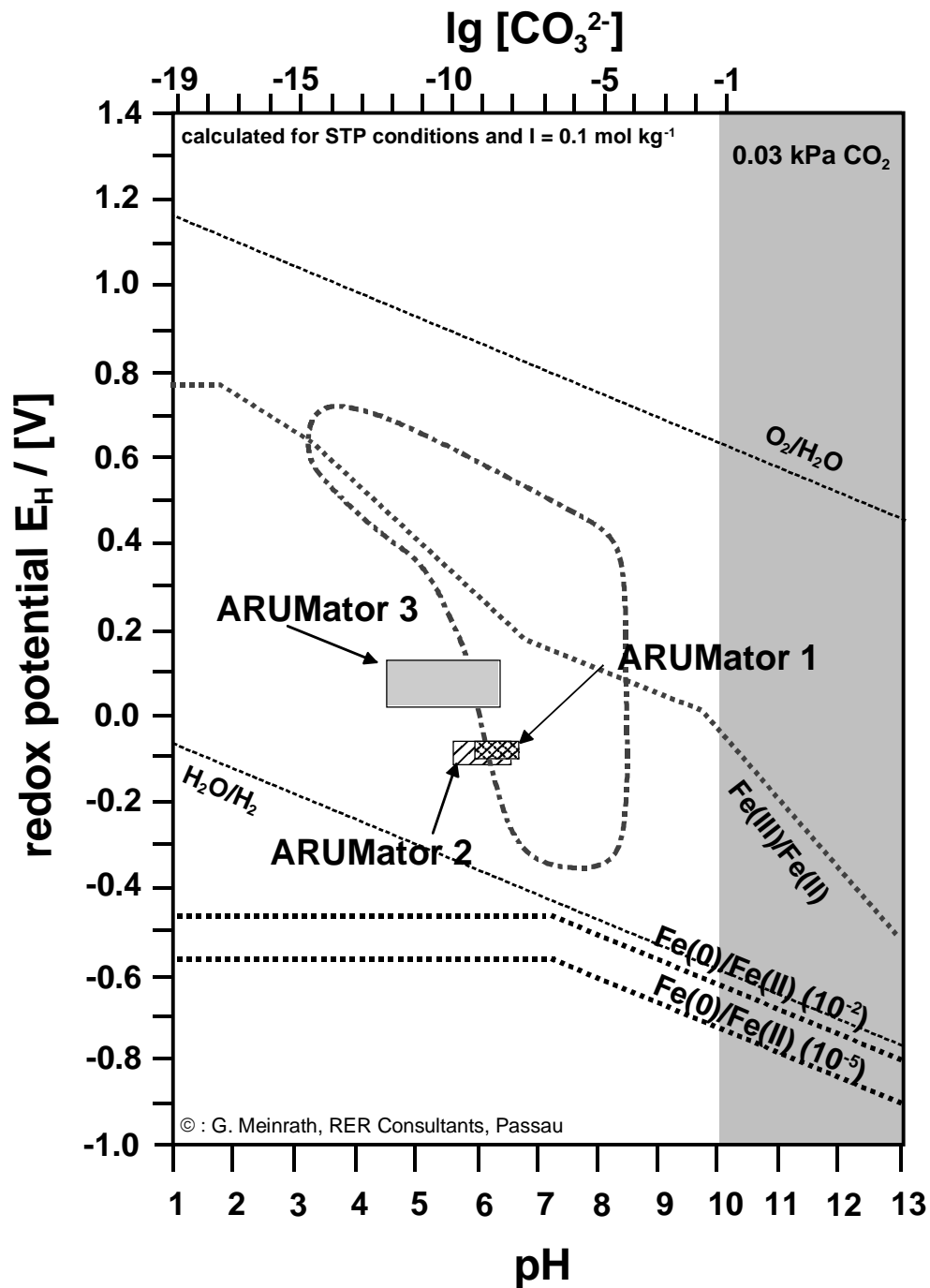


Figure 4. E_H -pH diagram of iron of Arumator samples from Kalin, 1991

Conclusion

A half century has passed since microbial role in AMD was identified, but we have yet to find a solution. This paper has reviewed the chemical reactions that drive conventional and alternative strategies employed against AMD and found neither to be fully effective or sustainable. Conventional liming achieves neutralisation through pH reduction and the stoichiometric consumption of sulphur, but leads to the creation of unstable secondary wastes. Alternative, passive approaches integrate chemical, biological and microbiological processes but

are plagued by hydraulic problems, particularly the clogging due to precipitation of metals which interferes with the biological and microbiological activity.

Extensive research into the German Tageauseen has confirmed that sediments are the key to biogenic acid consumption. Can we engineer a self-contained, self-sustaining treatment system that will economically and effectively treat AMD. Perhaps not yet, but it is the view of the authors that ecologically sound strategies for treating AMD offer the greatest promise. The ARUM project in Copper Cliff demonstrated that it is relatively simple matter to create environments for microbial consortia within reconstructed sediments sustainably enriched by the water column above them. In particular, further research is required into the bio-mineralization in sediments, exchange processes between sediment and the water column, the generation of biodegradable carbon sources within treatment systems and the interactions of microbial consortia with iron in iron-rich sediments.

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