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Review

The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage[☆]

Margarete Kalin *, Andrew Fyson, William N. Wheeler

Boojum Research Ltd, 139 Amelia Street, Toronto, Ontario, Canada, M4X1E6

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Abstract

The oxidation of pyritic mining waste is a self-perpetuating corrosive process which generates acid mine drainage (AMD) effluent for centuries or longer. The chemical neutralization of these complex, buffered effluents result in unstable, metal-laden sludges, which require disposal to minimize long-term environmental consequences. A variety of passive treatment systems for AMD, developed in the past two decades, combine limestone and organic substrates in constructed wetlands. These systems work well initially but over the longer term fail due to clogging with and the depletion of available organic carbon. However, some ecologically engineered systems, which exploit the activities of acid reducing microbes in the sediment, rely on photosynthesis in the water column as a source of organic matter. The primary productivity in the water column, which also generates some alkalinity, provides electron donors for the microbial reduction processes in the sediment. In its consideration of 'passive' systems, the literature has placed undue emphasis on sulphate reduction; thermodynamical iron reduction is equally important as is the need to prevent iron oxidation. Secondary precipitates of iron play a significant role in sediment-driven biomineralization processes, which affect the anaerobic degradation of organic matter and the stability of the resulting metal sulfides. One such passive system, which utilized a floating root mass as a source of organic carbon, is described. An extensive review of the literature and the chemical and biogeochemical reactions of AMD treatment systems, lead to the conclusion, that sediment based ecological systems offer the greatest potential for the sustainable treatment of AMD.

Keywords: Acid mine drainage; Acid rock drainage; Passive treatment; Lime treatment; Ecological engineering; Microbial remediation

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Contents

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* Corresponding author. Tel.: +1 416 861 1086; fax: +1 416 861 0634.
E-mail address: margarete.kalin@utoronto.ca (M. Kalin).

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1. 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 $pH < 1$ and containing several g L^{-1} 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 1000 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 do such systems work? This paper will discuss the chemistry of both the conventional and alternative approach to the treatment of AMD.

2. The chemistry of conventional AMD treatment

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

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (3)$$

$$FeS_{2+} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

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 the presence of water (6).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (5)$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (6)$$

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

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (7)$$

Each metal in solution contributes a specific metal acidity to the AMD; additionally, specific metals precipitate at specific pH levels. For example, hydroxides of Fe^{3+} precipitate at about pH 3, and of Al^3 at pH 3.7 to 4.5. Divalent metal ions precipitate in the alkaline range, Ni^{2+} at about pH 8, Fe^{2+} at pH 8 to 9 and Zn^{2+} 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 neutralization 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 Fig. 1 which provides three-dimensional phase diagrams in the Fe–S–O–H system with log [Fe], log [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; Weast, 1971; Stumm and Morgan, 1996).

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, 2001; Meinrath and May, 2002). For inclusion of $FeCO_3$(s), the atmospheric CO_2 partial pressure has been assumed, but under anaerobic conditions higher partial pressures (typically up to 10% but sometimes higher) can be found. The drastic change in the relative stability fields of FeS_2(s) and $Fe(OH)_3$(s) between pH 2 (top) and pH 5 (middle) is evident. While in an acidic medium, $Fe(OH)_3$(s) is unstable. Its very low solubility product ($pKs=54$) causes a drastic stabilization at pH 5. At pH 7, Fe II phases, e.g. FeS and $FeCO_3$(s), may compete with Fe III and cause the observed decrease of the $FeCO_3$(s) 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.

It is possible to extrapolate the pH value required to induce precipitation from the data in Fig. 1. However, despite the general importance of pH in an AMD system, it is not the only important factor in metal removal; ionic strength, temperature, E_H, and concentrations of suitable complexing agents (e.g. humic substances) and interactions of the precipitated solids also play a role (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 first 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 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 Skouson et al. (1998) and Costello (2003) reviewed U.S. systems. All of the systems described remove metals as hydroxides, and produce neutralized water containing sulphates, mainly Mg and Ca sulphate or gypsum (Rose and Ghazi 1997). The resulting hardness of the water can be detrimental to the receiving environment (Moni and Dhas, 1989; Charles et al., 2002).

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.

2.1. Secondary waste characteristics

In a conventional treatment plant, hydrated lime is added to the AMD as slurry. The effluent is then aerated, and flocculants 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, 2003).

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 over time the alkalinity of the sludges decreased while the calcite and gypsum content increased, that freeze–thaw cycles and natural dewatering increased density, and that HDS sludges had a higher metal content and improved crystallinity, with a reduced potential for metal leaching. 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 Pedersen (1996) conclude, lime effectively removes metals and hydrogen ions from AMD, but it also creates abundant and unstable secondary wastes. It is no

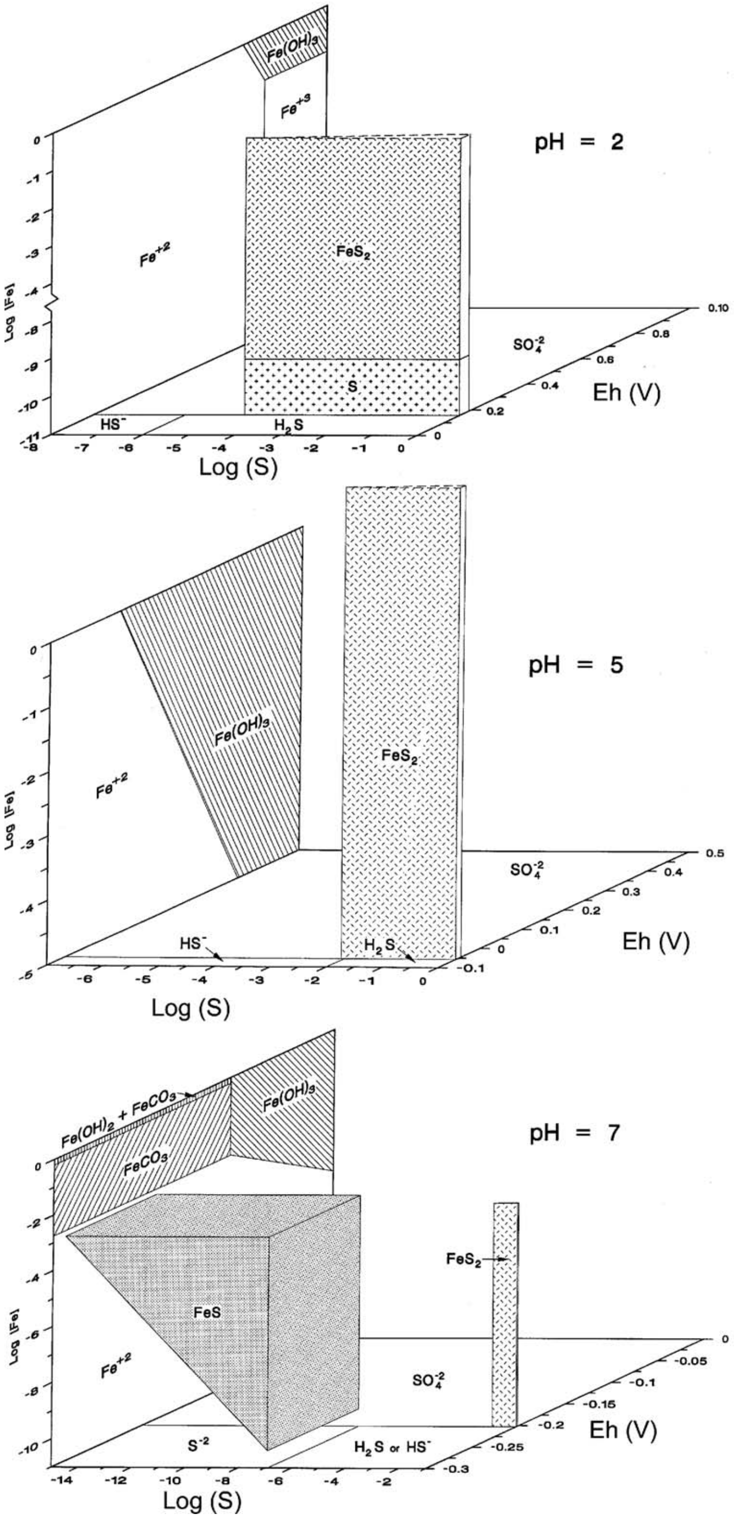

Fig. 1. Three-dimensional phase diagrams in the Fe–S–O–H system with log [Fe], log [S] and E_H as coordinates at the pH 2, pH 5 and pH 7. Note the log scale and the [range].

panacea and cannot be considered environmentally sustainable.

3. 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; Skouson et al., 1998; Costello 2003). Aerobic wetlands, anaerobic or compost wetlands, vertical flow wetlands, AMD treatment ponds, bioreactors 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 (Skouson 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 stable coatings reduce limestone dissolution and 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 biomineralization 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 (Jones and Gusek, 2004; Tsukamoto and Miller, 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, over a longer term, can supply organic substrates for sulphate reduction as well as such other nutrients as phosphate and nitrate. Moreover, suitable organic wastes are often available locally at little or even no cost (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.

The longevity of passive AMD treatment systems has been recently reviewed (Eger and Wagner, 2003; Sjöblom 2003). Ziemkiewicz et al. (2003) assessed the projected long-term performance and cost-effectiveness of 137 passive systems in the eastern United States and predicted that most would fail or at best perform 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 although most systems evaluated had been operated for less than five years. Eger and Wagner (2003) observed that the effective life span of such systems was determined by the availability of degradable organic carbon. Bioreactors utilize inoculants of sulphate-reducing bacteria (SRB) to treat effluents both in situ (Jones and 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 metals. 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 where the metal content and flow of the effluent are sufficiently high, uses hydrogen sulphide generated by SRB to remove metals for economic gain (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 et al., 2001; Totsche 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. Willscher (2003) 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 primary production of photosynthetic organisms and concluded that they provided no economically practical solution to treat the problems afflicting the Tagebauseen. Their conclusion was based on alkalinity generation within the water column, which is insufficient and not sustainable without microbially active sediments. We believe that systems incorporating flourishing populations of primary producers such as algae in the water column, can be considered truly sustainable in conjunction with sediments, which they supply with carbon.

3.1. Photosynthesis in the water column or controlled eutrophication

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

$$106CO_2 + 138H_2O + 16NO_3^- \rightarrow [C_{106}H_{260}O_{106}N_{16}] + 138O_2 + 16OH \quad (8)$$

$$106CO_2 + 106H_2O + 16NH_4^+ \rightarrow [C_{106}H_{260}O_{106}N_{16}] + 106O_2 + 16H^+ \quad (9)$$

biomass

Microcosm studies of the Tagebauseen suggest that the addition of nitrate or ammonium stimulates phytoplankton growth and induces 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 because primary productivity in the open water column in ponds or lakes below pH 4.5 is limited by very low inorganic carbon or CO_2, which becomes insoluble and hence unavailable to photosynthesis. In such waters, alkalinity generation through photosynthesis occurs only on the surface of the sediment in the algal mats that draw upon the inorganic carbon generated by decomposition within the sediment, or transported in from the water surface. Another key component of biological AMD treatment processes is the availability of phosphate which is required by primary producers and all other organisms for growth. Phosphate, however, is scarce in AMD due to its adsorption to iron hydroxide particles and, in fact, its availability was found to be the limiting factor in the biological productivity of the Tagebauseen (Krumbeck et al., 1998). Phosphate added to an English lake acidified by acid rain stimulated biological alkalinity generation (Davison et al., 1995). In these lakes, iron is not abundant, but in anoxic sediments, phosphate is released with the reductive dissolution of iron hydroxides and becomes available as a nutrient for organisms. Thus, the availability of phosphate is critical to the biologically mediated treatment of AMD.

In microcosm experiments with waters of the Tagebauseen, nutrients and organic substrates were added to induce eutrophication of 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 produced from the controlled eutrophication of the water column sustained biogeochemical cycling processes in the sediment. Clearly, eutrophication in the water column enriches the sediment — the key driver of neutralization.

3.2. Microbial reduction reactions in sediments

Most sediments are anoxic with the redox potential decreasing with depth. Following the reduction of oxygen by aerobic respiration, Eqs. 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 and 25 °C) is most negative for de-nitrification and least negative for sulphate reduction, indicating that nitrate reduction is the prevailing process.

In nature, the kinetics of these processes is slow. All four reactions are mediated by indigenous microorganisms in anoxic environments where appropriate electron acceptors (NO_3-, Mn^{4+}, Fe^{3+}, SO_4^{2-}) 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)

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O \Delta G^\circ -113 kJeq^{-1} \quad (10)$$

Manganese reduction

$$2MnO_2 + CH_2O + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O \Delta G^\circ -97 kJeq^{-1} \quad (11)$$

Iron reduction

$$4\mathrm{Fe(OH)_3} + \mathrm{CH_2O} + 8\mathrm{H^+} \rightarrow \mathrm{CO_2} + 4\mathrm{Fe^{2+}} + 11\mathrm{H_2O}\Delta G^\circ{-47}\mathrm{kJeq}^{-1} \qquad (12)$$

Sulphate reduction

$$\mathrm{SO_4^{2-}} + 2\mathrm{CH_2O} + 2\mathrm{H^+} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2S} + 2\mathrm{H_2O}\Delta G^\circ{-25}\mathrm{kJeq}^{-} \qquad (13)$$

The generated sulfide (Eq. (13)) can react with Fe^{2+} (or other metal ions) to form metal monosulphides according to Eq. (14) , thus re-generating a metal-containing solid, biogenic or framboidal pyrite as FeS_2.

$$\mathrm{Fe2} + \mathrm{H2S} \rightarrow \mathrm{FeS} + 2\mathrm{H^+} \qquad (14)$$

Precipitation of FeS generates hydrogen ions but removes iron from the system which decreases metal acidity, thus completing the remediation cycle. Pyrite precipitation overall neither generates nor consumes hydrogen ions.

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 sulphur 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 sulphate.

A detailed investigation of Lake 239 in the Experimental Lakes Area of northwest Ontario found alkalinity generation to be 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 came from the biological reduction of SO_4^{2-} (35%) and NO_3^- (26%) with the ion exchange between H^+ and Ca $^{2+}$ 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; Widdel and Hansen, 1992; 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 the combination of the hydrogen sulphide produced by SRB with the Fe^{2+} 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 follows that iron is also a relevant component in alkalinity production — provided the oxidation of Fe^{2+} and Fe^{3+} can be prevented.

The work on passive systems places undue emphasis on sulphate reduction at the expense of iron reduction, which is at least as important. Typically, when both dissolved iron and sulphate are abundant in AMD, bacteria that reduce Fe^{3+} 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 Fe^{3+} is fully reduced will sulphate reduction come into play. But, in natural sediments, both processes can occur simultaneously (Blodau and Peiffer, 2003). The reduced iron produced through Fe^{3+} reduction combines with sulphides from sulphate reduction to produce the desired stable precipitates. A better understanding of the relationship between iron and sulphate reduction is essential for the effective employment of these processes for AMD treatment.

3.3. Natural iron precipitate formation

Base metal waste rock piles release Fe^{3+} which forms iron hydroxides and oxyhydroxides when it contacts near neutral rain water, generating hydrogen ions. Waste rock seepages hence emerge at pH values >3. Seepages emerging from tailings dams generally release Fe^{2+}. Therefore, depending on the waste material or the origin of the AMD/ARD, the characteristics of iron vary. Consequently, tailing seepages have a high chemical oxygen demand, similar to plumes of contaminated groundwater when they emerge as surface waters. Fe^{2+} may precipitate as iron oxide and hydroxysulphate when values of pH are above 5. These processes are elementary chemical reactions which cannot be influenced significantly by microbes.

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, oxyhydroxysulphate or amorphous to crystalline oxyhydroxides with Schwertmannite ($Fe_8O_8(OH)_6SO_4$) and Goethite ($Fe(OH)_3$) 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 (Blodau and Peiffer, 2003; Regenspurg et al., 2004). The relationship of iron precipitate transformation to biological alkalinity generation needs to be investigated in more detail.

In Goethite-dominated sediments, the reduction of iron and sulphate coexists at the sediment surface. Under these conditions, pH values are in the neutral range and sulphides are abundant throughout the sediment core. Neutralization rates in the Tagebauseen vary by orders of magnitude (Peine and Peiffer, 1996, 1998). The fermentation of organics and the sum and balance of iron- and sulphate-reduction rates and the re-oxidation of H2S are controlled by their respective Gibbs free energies. The thermodynamics of such systems are described in detail in Blodau and Peiffer (2003). These authors concluded that there is little accumulation of sulphides in AMD affected lakes where Fe3+ precipitates as Schwertmannite, 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 sulphides and other metal compounds in sediments.

4. Constructing a sediment for Acid Reduction Using Microbiology (ARUM)

A pilot test system to derive design criteria for the construction of microbially active sediments, was constructed in 1990–1993 in Sudbury, Ontario. The system consisted of oxidation/precipitation cells and two reducing cells with a combined area of 2000 m^{-2} into which seepage flowed at the rate of 1 to 5 L min^{-1} (Kalin, 1993). It was hoped that similar systems, constructed in seepage collection ditches or within remnant tailings ponds on tailings beaches, could effectively treat AMD or, at least, provide a pre-treatment stage or conventional water treatment. In fact, Acid Reduction Using Microbiology (ARUM) has since been successfully applied at sites in Canada (Fyson et al., 1995; Kalin et al., 1995b, 1999, and in Brazil for the effluent from abandoned mine workings Kalin and Caetono Chaves, 2003).

The two oxidation/precipitation cells exploited the substantial amounts of Fe^{2+} present in the seepages at the site to generate iron oxyhydroxides that co-precipitated and adsorbed other metals. Metal removal for the period from June to September 1996, in the fifth year when the system reached its optimal configuration, is evident. Seepage flow was low, at about 1 L min^{-1}. The pH of the inflow to the oxidation/precipitation cells ranged from 5 to 6 but leaving it, to enter the ARUM treatment cells, the pH was 3 to 4. A considerable reduction in iron and metals had occurred.

The ARUM treatment cells contained sediments constructed from organic materials and floating cattail/vegetation rafts. Those floating vegetation covers minimized wind-induced turbulence which reduces oxygen in the water, provided a further microbial habitat in their root mass, and contributed an on-going supply of organic litter to the sediment (Kalin, 1993). The performance of the ARUM cells, at their optimum, is provided in Fig. 2, which was previously published in Kalin and Smith (1997).

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 sulphur. The high rates of sulphur removal are indicative of sulphate reduction. To confirm that bio-mineralization processes would take place in the constructed sediment, three 170 dm^{-3} plastic 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 b illustrates these so-called ARUMators, which contained sampling ports at different depths within the drums.

Fig. 4 shows an E_H–pH diagram of iron including aqueous hydroxo species, specifying the Fe^{2+}/Fe^{3+} boundary under consideration. The lines 'O_2/H_2O' and 'H_2O/H_2' indicate the stability limits of the water. The boomerang-shaped field in the centre 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

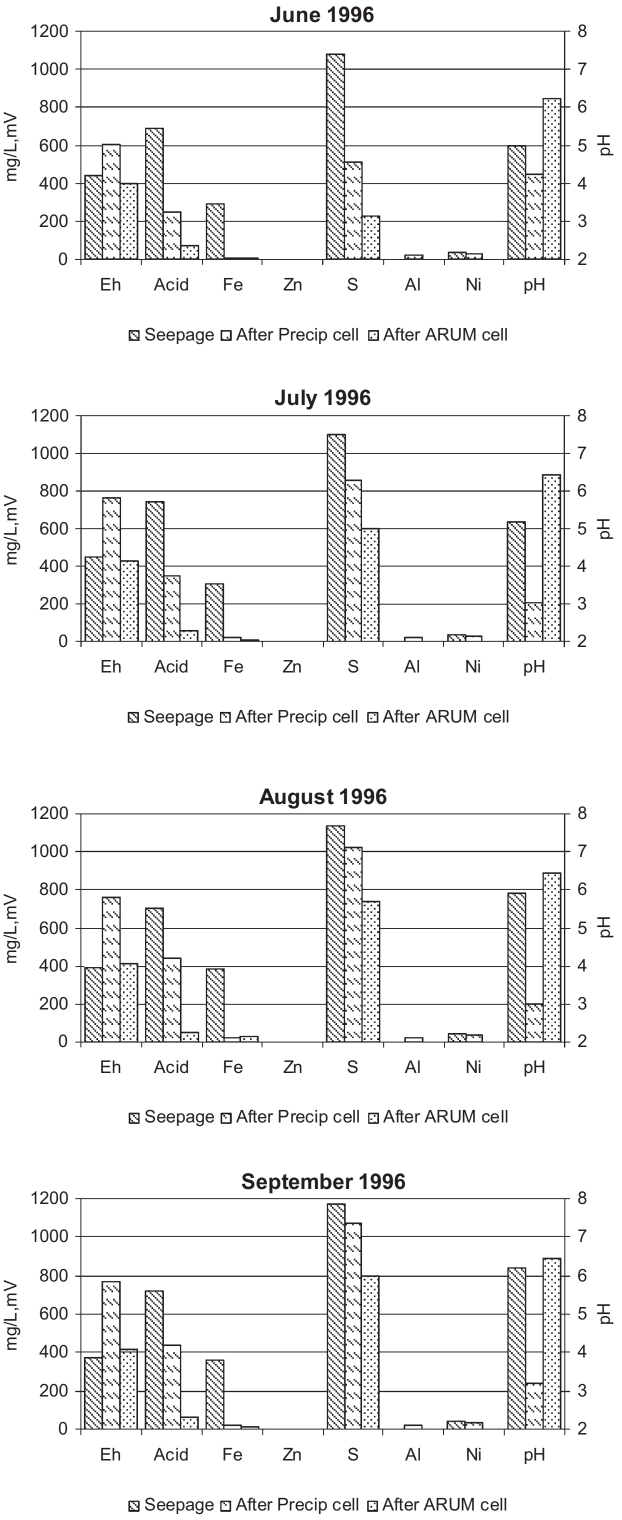

Fig. 2. Tailings seepage characteristics of the Copper Cliff ARUM system in 1996 (Kalin and Smith, 1997).

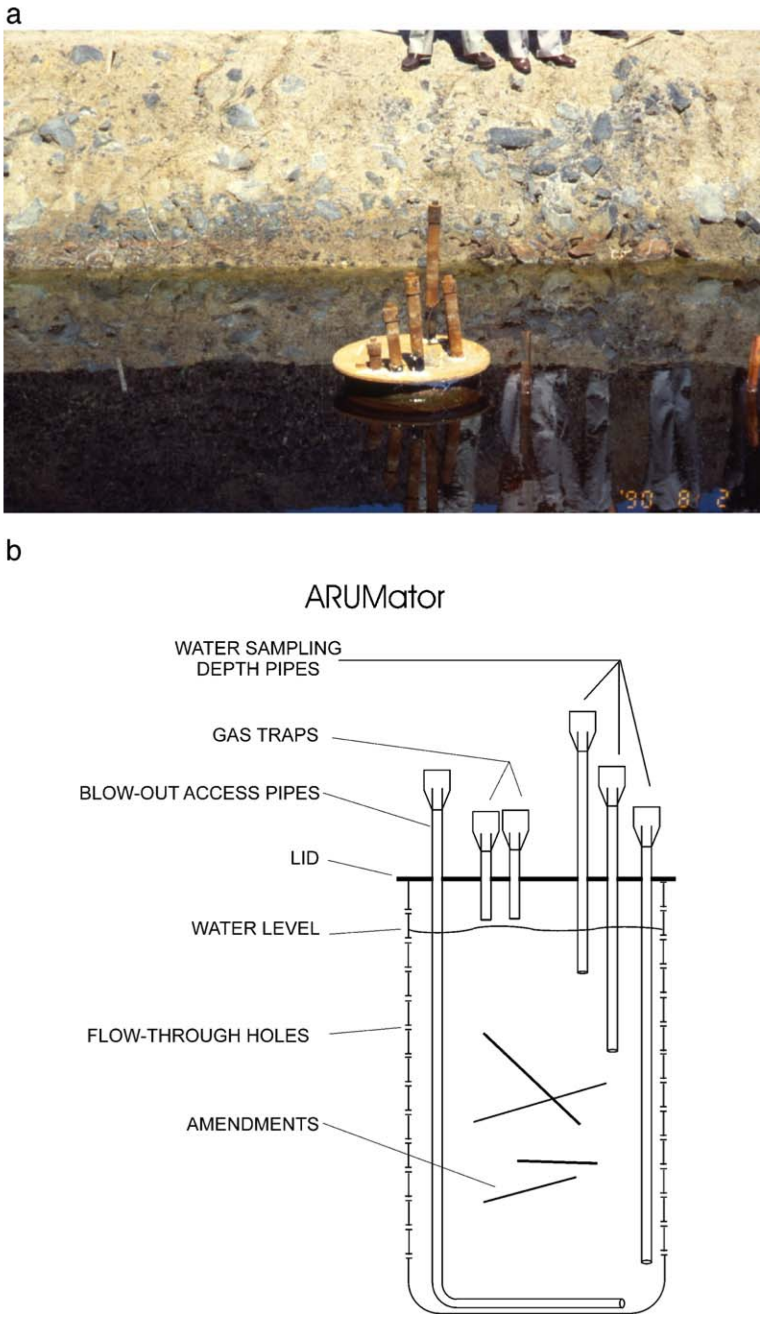

Fig. 3. (a) ARUMator under construction. (b) ARUMator schematic.

ameliorate seepage pH. These conditions persisted without addition of chemicals.

Geochemical simulations using the program PHREEQE (Parkhurst et al., 1990) were carried out on the seep water and from the ARUMators to determine the degree of metal sulphide saturation, sulphates, carbonates and hydroxides in the created sediment of the ARUMators. Data were reported by Kalin (1991) and are summarized here. All samples from the ARUMators showed supersaturation, i.e., they indicate the potential to precipitate alunite, barite, cristobalite, gypsum, hematite, quarts 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

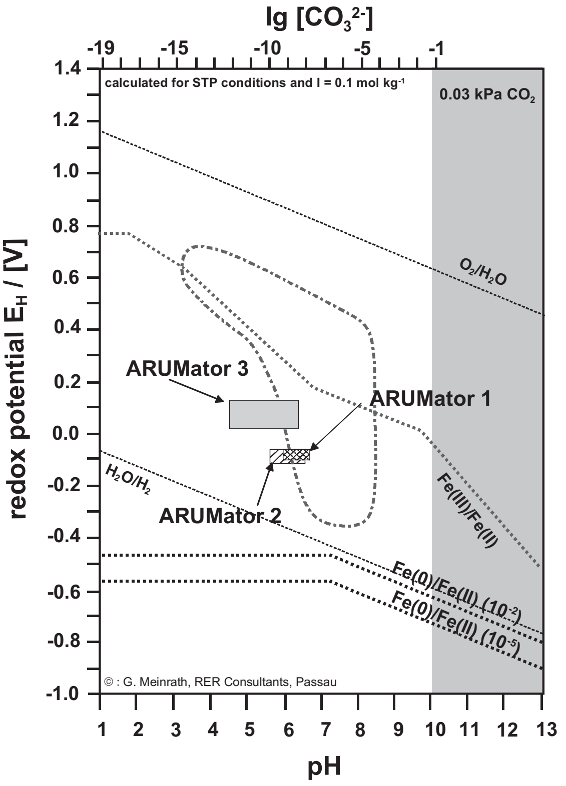

Fig. 4. E_H–pH diagram of iron and the ARUMator samples from Kalin, 1991.

with respect to $Al(OH)_3$, $Al_4(OH)_{10}$, boehmite, calcite, dolomite, gibbsite, magnesite, siderite and rhodochrosite. Low p*E* values were accompanied in some or all samples at different depths by supersaturation with pyrite, cuprite, chalcosite (djurleite/anilite/blaublei), covellite, chalcopyrite, sphalerite, otavite, greenokite and galena. Clearly, conditions existed within the ARUMators, and the larger ARUM test systems to promote the biomineralization of metals from AMD effluent.

After the ARUMators had been immersed for a year in the pilot cells, the straw and flax in them were subjected to sequential extraction analysis (according to a modification of the protocol for forage fibers of Goering and van Soest (1970) 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 under sediment conditions, with the remainder being mainly lignin and lignocellulose. 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.

Equivalents of alkalinity generated by the decomposing organic matter were estimated based on Davison and Woof (1990) and Lerman and Stumm (1989). 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 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.

5. Conclusion

A half century has passed since the microbial role in AMD was identified, but we have yet to find a sustainable means of reversing its effects. This paper has reviewed the chemical reactions that drive conventional and alternative treatment scenarios and found neither type to be fully effective or sustainable. Conventional liming achieves neutralization 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 Tagebauseen 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 (Acid Reduction Using Microbiology) project in Copper Cliff demonstrated that it is relatively a simple matter to create environments for microbial consortia within constructed sediments, sustainably enriched by the water column. In particular, further research is required into 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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