Review of sulfate reduction based bioprocesses for acid mine drainage treatment and metals recovery

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Abstract

Biological sulfate reduction is attracting increasing interest in the mining industry. Sulfate reducing bacteria (SRB) can be used for treating acid mine drainage (AMD) and for recovering metals from mine waters. Biologically produced hydrogen sulfide precipitates metals as low solubility metal sulfides, while biogenic bicarbonate alkalinity neutralizes acidity. This paper reviews various passive and active SRB-based processes, bioreactor process configurations and alternative substrates for SRB. The cost of biological treatment depends on location, engineering design, the characteristics of the mine drainage, the substrate, profit obtained from metals recovered and the effluent discharge criteria.

Key words: acid mine drainage, bioprocess, bioreactors, metal recovery, passive treatment, sulfate reduction

Introduction

Acid mine drainage (AMD) can cause major environmental impacts in waterways (Gray 1997). Pollution control of AMD can be achieved by preventing AMD formation, migration and/or collection and treatment. Numerous physicochemical and biological techniques are available for the neutralization and removal of metals and sulfate from wastewaters. A widely used active treatment process for AMD is based on chemical neutralization and hydroxide precipitation of metals. Sulfide precipitation of metals has several benefits over hydroxide precipitation, such as lower effluent metal concentrations, better thickening characteristics of the metal sludge and the possibility to recover valuable metals (Kaksonen *et al*. 2006).

Several biological processes have also the potential to remove metals from wastewaters, including biosorption, intracellular uptake and accumulation, complexation, oxidation and reduction, and extracellular precipitation. Also, a number of biological processes can generate alkalinity which has potential use in neutralizing AMD. These include biological nutrient assimilation (Davison *et al*. 1995), denitrification, ammonification, methanogenesis, and reduction of iron and sulfate (Kaksonen and Puhakka 2007). Due to the potential for combined removal of acidity, metals and sulfate, biological sulfate-reduction appears to be the most promising of these for AMD treatment and metals recovery. The process is based on biological hydrogen sulfide and alkalinity production by sulfate-reducing bacteria (SRB):

$2\ CH_2O + SO_4^{2-} \Leftrightarrow H_2S + 2\ HCO_3^-$, where CH_2O is the electron donor.

The biogenic hydrogen sulfide precipitates dissolved metals as low solubility sulfides:

$H_2S + M^{2+} \Leftrightarrow MS(s) + 2H^+$, where M^{2+} denotes the metal, such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} or Fe^{2+}.

The metal precipitation reaction releases protons, thus adding to the acidity of the water. Therefore, excess sulfate needs to be reduced to compensate for the acidity. Bicarbonate alkalinity produced in the sulfidogenic oxidation of electron donors neutralizes the acidity of the water:

$HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O$

The potential utility of SRB in mining applications was proposed already in the late 1960s (Tuttle *et al* 1969). Since then, SRB-based treatment systems have been developed for AMD. More recently, the use of biogenic H_2S has been extended to the selective recovery of metals from various biohydrometallurgical process streams. This paper reviews various SRB-utilizing bioprocesses as well as some process design aspects.

Passive treatment

Passive SRB-based applications for the treatment of AMD contaminated groundwater include the enhancement of the microbial activity in groundwater aquifers through substrate injection (Figure 1 A) and permeable reactive barriers (Figure 1 B). Passive treatment applications for surface waters include infiltration beds (Figure 1C), anoxic ponds (Figure 1D) and wetland systems (Figure 1E) (Gazea *et al*. 1996; Kaksonen and Puhakka 2007).

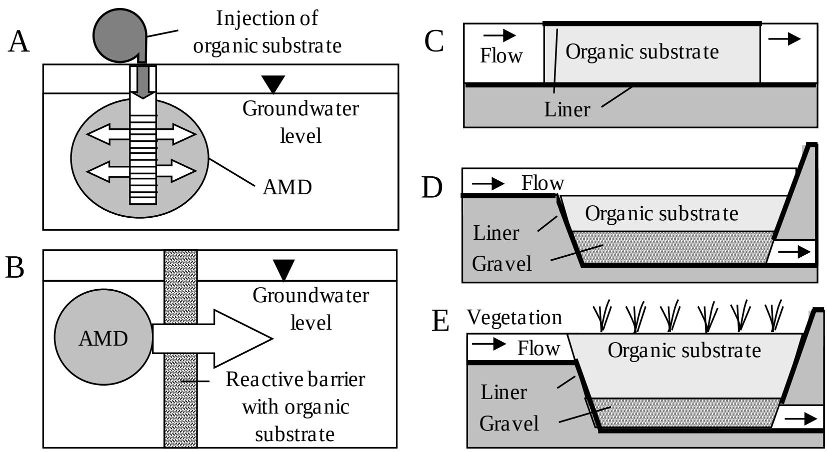

Figure 1 *Passive, sulfate reduction based applications for treatment of acid mine drainage (AMD): (A) injection of substrates into the subsurface, (B) permeable reactive barriers, (C) infiltration beds, (D) anoxic ponds, (E) anaerobic wetlands, adapted from (adapted from Kaksonen and Puhakka 2007).*

Passive SRB-based treatment approaches offer solutions with relatively low operating cost and minimal maintenance for treating AMD, and, thus, they are also suitable for remote mining areas (Table 1). However, the required treatment area may be large, metal recovery difficult, and control and predictability poor due to seasonal variations in rainfall and temperature. A prerequisite for successful *in situ* AMD treatment is a thorough hydrogeological characterization of the site. Higher water flow rates and oxygenated surface water may result in a pH decrease and resolubilization of the metal precipitates. Constructed wetland systems have been developed from an experimental concept to full-scale field application during the last three decades and used for the removal of nutrients, sulfate, metals and radionuclides from mine waters. Aerobic and anaerobic wetland units are often used consecutively and in combination with anoxic limestone drains. Vegetation growing on the submerged substrate can provide a continuous supply of carbon and energy for the underlying microbial community and protect against wind erosion at periods when the water level drops below that of the substrate. Unless accompanied by active maintenance of water levels, wetland treatment may not be effective in arid and semi-arid climates, as in large parts of Australia, and exposure of the metal-sulfide sediments to oxygen in the periods of drought can lead to the dissolution of the metals and the acidification of the system (Gazea *et al*. 1996; Kaksonen and Puhakka 2007).

Table 1 *Comparison of passive and active biological treatment methods for acid mine drainage treatment (adapted from Kaksonen and Puhakka 2007).*

Characteristics	Passive treatment	Active bioreactors
Operating costs	low	high
Need of labour	small	high
Treatment area	large	small
Metal recovery	difficult	easy
Control	poor	good
Predictability	poor	good

Active bioreactors

Compared to the passive biological treatment, active bioreactors are more compact, and offer more consistent performance and control (Table 1) (for a review, see Kaksonen and Puhakka 2007). On the other hand, bioreactor plants require significant start-up capital and continuous monitoring. Numerous reactor designs for biological sulfate reduction have been reported, such as continuously stirred tank reactor (CSTR), anaerobic contact process (ACP), anaerobic filter reactor (AFR), hybrid fermentation system (HFS), fluidized-bed reactor (FBR), up-flow anaerobic sludge blanket reactor (UASB), anaerobic hybrid reactor (AHR), gas lift reactor (GLR), anaerobic baffled reactor (ABR), and membrane bioreactor (MBR) (Speece 1983; Kaksonen and Puhakka 2007; Greben *et al.* 2009), but for many reactor types, consistent long-term performance has not been demonstrated. Several commercial scale sulfidogenic bioreactors are currently being used around the world for treating mine waters.

The reactor configuration has implications for the ratio of sludge retention time/hydraulic retention time (SRT/HRT). The achievable loading rates of a process are dictated by the biomass retention in the reactor. Minimal HRT minimizes the reactor volume and thus reduces capital costs. CSTRs are subjected to washout of active biomass. Biomass retention has been enhanced by employing sedimentation systems, like in ACPs, and cationic flocculants. Immobilized biomass reactors such as AFRs and FBRs allow the uncoupling of HRT from biomass retention time, and thus have potential for achieving high conversion rates. AMD treatment using AFRs has been developed from laboratory to full scale systems. The main shortcomings of AFRs are the channelling of the flow and clogging of the bed by precipitates. In the FBRs, channelling and clogging are avoided by fluidizing the inert biomass carrier with recycled water. FBRs have been reported to efficiently retain biomass and allow high mass transfer and reaction rates. Moreover, FBRs are well suited for the combined removal of metals, acidity and sulfate from wastewater, since the recycle flow in the FBRs dilutes high influent concentrations (Kaksonen *et al*. 2006). The down flow fluidized-bed reactor (DFBR), which is based on floatable carrier material, allows the recovery of solid products, such as metal sulfides, at the bottom of the reactor (Sahinkaya and Gungor 2010). High mass transfer and good mixing are also achieved in GLRs. In UASB reactors biomass retention is based on good settling characteristics of granular sludge. Due to the biomass granulation, no packing or carrier material is needed which reduces the start-up costs of the UASB compared to the AFR and the FBR. However, challenges in UASB reactors include poor or slow granulation and the rapid disintegration of the granular sludge under certain conditions. Sulfidogenic UASB reactors have been developed for metal recovery from bench to full scale applications (Scheeren *et al.* 1993). AHR is a combination of UASB and AFR, and by combining their advantages of high conversion rates and efficient biomass retention, AHR provides superior effluent quality. ABR is another recent modification of the UASB reactor in which the compartmentalized structure acts as a buffer against possible toxic effects of the AMD to SRB and facilitates the removal of metal precipitates from the bioreactor without adversely affecting the bioreactor performance (Bekmezci *et al.* 2011; Sahinkaya and Yucesoy 2011). MBRs offer enhanced biomass retainment compared to other suspension bioreactors. They may also prevent the SRB from having direct contact to toxic water, which is the case e.g. in extractive MBR. The drawbacks of MBRs are fouling of membranes due to microbes or metal precipitates and periodic backwashing is needed (Kaksonen and Puhakka 2007).

Biological sulfate reduction and metal precipitation using biogenic H_2S can be applied in single or separated unit processes (Figure 2). Single-stage treatment processes (see Fig. 2A) offer lower-cost approach for AMD treatment as compared to processes with two or more unit processes, but they may not be viable if the water is very acidic or contains high concentrations of heavy metals. Therefore, alkaline materials have been used in many single stage treatment systems to generate additional alkalinity. A single-stage approach with AFRs for sulfate reduction and metal precipitation was used in the Palmerton pilot plant installed to treat metal-contaminated drainage from a smelting residues dump at the former New Jersey Zinc Company plant in Palmerton, Pennsylvania (Dvorak *et al.* 1992). Another example is the full-scale UASB reactor at the Budelco zinc refinery in Budel-Dorplein, Netherlands, that remediates metal-containing groundwater (Scheeren *et al.* 1993). In single-stage systems, presence of SRB and metal precipitates within the reactor may make it difficult to remove precipitates from the bioreactor.

In some cases, several bioreactors have been used in series to enhance sulfate reduction and metal precipitation. Another approach is to recycle part of the treated water to dilute the influent (Figure 2B). Metals can also be pre-precipitated prior to the biological step by recycling either sulfide-containing water (Figure 2C) or H_2S-containing gas (Figure 2D). The separation of the biological sulfate or sulfur reduction and metal sulfide precipitation with the biogenic sulfide into separate unit processes alleviates toxicity of metals and low pH on the SRB. It also allows selective metal precipitation by the control of pH and H_2S dosing, and reduces the amount of biomass and organic substrates in the metal sulfide sludge. As various metal sulfides have different solubility products, a stepwise increase of solution pH facilitates the selective recovery of metals (see Figure 3). A drawback of having multiple reactor units is increasing investment and operational costs due to increased and more complex instrumentation. Separation of the chemical sulfide precipitation and biological H_2S production is the basis of the process demonstrated at the Britannia Copper Mine, in British Columbia, Canada (Rowley *et al*. 1997). Copper and zinc were selectively precipitated in consecutive steps of the chemical circuit by using sulfide– and alkalinity-containing effluent from two bioreactors. Recycling of H_2S-containing gas (see Fig. 2D) may assist the selective precipitation of valuable metals, since no alkalinity is introduced to the precipitation step. However, the metal sulfide precipitation produces protons adding up to the acidity being fed to the bioreactor. Therefore, gas recycling has often been used in combination with chemical neutralization or water recycling.

If the metals and sulfate to be removed are in different water fractions, a treatment approach depicted in Figure 2E can be used. Treatment of multiple water streams was demonstrated at Kennecott's open pit copper mine in Bingham Canyon, Utah, USA (Hammack and Dijkman 1999). Gaseous biogenic H_2S was used to selectively recover copper from a leach water stream and bioreactor liquid effluent was used to precipitate metals from sulfate-containing water, and to produce elemental sulfur. The sulfate-containing effluent from the metal precipitator was fed to the bioreactor to maintain biological sulfate reduction. Some sulfate reducers are able to reduce elemental sulfur as an alternative electron acceptor. If no sulfate-containing stream is available for the treatment of metal-containing waters, elemental sulfur can be supplied to an offline bioreactor to produce H_2S gas that is fed to the metal precipitation units (Figure 2F) (Kaksonen and Puhakka 2007). Sulfur reduction as an alternative to sulfate reduction has been utilized, for example, in the treatment plant at Caribou Mine, Canada. In this plant, lime was used to neutralize the acidic solution after the metal recovery (Dijkman *et al*. 2002).

Substrates for sulfate reduction

The optimization of SRB-based processes includes the consideration of several factors, such as microbial community composition, influent composition and load, and operational conditions. The cost-effectiveness of the processes largely depends on the external electron donor and carbon source.

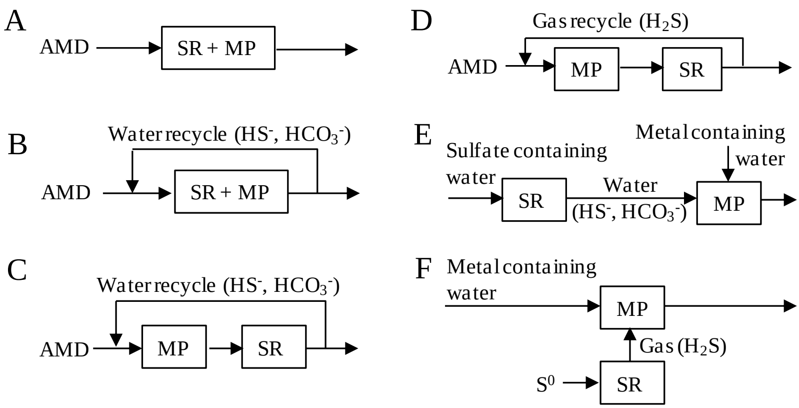

Figure 2 *Possible configurations of bioreactor processes for acid mine drainage (AMD) treatment and metal recovery. SR = sulfate or sulfur reduction, MP = metal precipitation (adapted from Hao 2000; Kaksonen and Puhakka 2007).*

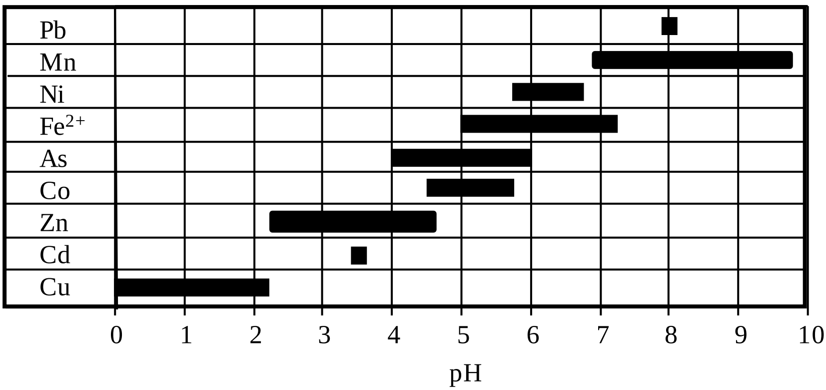

Figure 3 *Used and/or recommended pH values for the selective precipitation of metals as sulfides (adapted from Hammack et al. 1994; Govind et al. 1997; Tabak et al. 2003; Kaksonen and Puhakka 2007)*

Many sulfate- and metal-containing waters are low in organic matter, and hence supplementation of organic carbon substrate (or $H_2 + CO_2$) is often necessary to promote sulfate reduction. Depending on the application, solid, liquid, or gaseous substrates may be preferred. For passive treatment applications, solid plant or waste materials are often required to allow passive operation without pumping. However, solid substrates have a limited lifetime and have to be replaced or supplemented with liquid or gaseous substrates once the original substrate has been depleted. In active bioreactors, liquid or gaseous substrates allow continuous operation. The choice of the substrate is based on several criteria: *(i)* the ability of SRB to utilize the substrate, (*ii)* the suitability of the substrate for the particular application, (*iii)* the sulfate load to be reduced and the cost of the substrate per unit H_2S produced, *(iv)* the availability in sufficient quantities, and *(v)* the possible remaining pollution load from the incompletely degraded substrate. SRB can oxidize various intermediate products originating from the anaerobic degradation of complex organic compounds including H_2, carboxylic acids, alcohols, some sugars and aromatic compounds, but direct utilization of biopolymers by SRB is very rare. Various waste materials such as sewage sludge and glycerol-methanol waste remaining after the production of biodiesel fuel may be a low-cost alternative for defined substrates. However, their availability may be restricted to certain areas. The use of complex plant materials and waste products may result in higher chemical oxygen demand (COD) in the effluent due to the more recalcitrant compounds. For some complex materials, pre-treatment such as hydrolysis or post-treatment may be necessary to achieve more complete biodegradation. Synthesis gas (mixture of H_2, CO_2 and CO) produced by steam reforming natural gas has been proposed as an inexpensive alternative for H_2 + CO_2. However, the CO of the synthesis gas can inhibit some SRB (Kaksonen and Puhakka 2007). Research is currently undertaken on the possibilities of using methane as substrate for SRB. Moreover, recent research indicates that SRB may be able to reduce sulfate with electrons directly derived from electrodes in bioelectrochemical systems (Su *et al*. 2012).

Conclusions

Biological sulfate reduction offers various alternative passive and active approaches for AMD treatment and metal recovery. The overall treatment cost depends on the engineering design and location of the plant, the characteristics of the wastewater stream, the selection of the substrate for the SRB and the effluent discharge criteria. Profits obtained from metals recovered in bioreactor processes may offset a part of the treatment costs. Low-cost substrate alternatives such as waste glycerol from biodiesel production, methanol, wastewaters, and bioelectrochemical systems may further increase the uses of SRB-processes.

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