Sulfidogenic Diffusive Exchange System for the Treatment of Acid Mine Drainage

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ABSTRACT

Sulfate-reducing bioreactors are good treatment options for acid mine drainage (AMD). In this technology, AMD flows through a bed containing reactive material, where sulfate, metals and acidity are removed by the metabolic activity of sulfate-reducing communities. The substrates should be affordable and provide organic matter that promotes the growth of microorganisms. We hypothesize that increasing organic substrate availability by utilizing finely ground organic material will increase sulfate reduction kinetics, although new reactor designs such as diffusive exchange systems (DES) will be needed to accommodate these finer substrates while keeping AMD throughput.

In this research, utilizing a fine organic substrate in a sulfidogenic DES bench scale reactor, we treated acidic AMD (pH down to 2.5) for a period of 14 months. Although the reactor was operated in a metal and acidity overloaded mode for the whole period, it achieved stable operation, reducing sulfate, removing metals and adding alkalinity. To our knowledge, this is the first time a biochemical reactor is operated passively, without external alkalinity source, at such low pH and high metal load. This stable operation indicates that a bioprotection mechanism based on chemical gradients protected the microbial community within the reactive layers of low permeability. In addition, the system did not show any permeability reduction. The metals precipitated along the interfaces between the reactive and conductive layers, where sulfide and metal gradients met, consistent with chemical-gradient-based bioprotection. Hence, the sulfidogenic DES holds promise for the passive treatment of highly acidic and toxic AMD. Higher reaction rates are possible within these reactors, and microbial consortia are protected from toxicity while no permeability reduction is observed.

Keywords: biochemical reactor, bioprotection, diffusive exchange, passive treatment, AMD.

INTRODUCTION

The mining waste rock and tailings represent a potential hazard for the environment, especially when the residues contain sulfide minerals that can be a source of acid mine drainage (AMD). The exposure of the metal sulfides to oxygen and water, accompanied by microbial activity, leads to the formation of drainage rich in sulfate, acidity and heavy metals (Dold, 2010). The AMD problem involves both active and abandoned mines dedicated to the extraction of metals or coal (Blowes et al., 2003).

In mines located in areas with intermittent precipitations, such as in Northern and Central Chile, and steep slopes where no flooding occurs, water, oxygen and sulfides strongly interact increasing the potential for AMD formation; additionally, the high evaporation rate causes the accumulation of sulfate salts that generate stronger AMD (Nordstrom, 2011). The potential AMD sources in Chile are significant: in 2002, 3,000,000 ton/day of waste rock were generated, and 650,000 ton/day of tailings (Ministerio de Minería & Consejo de Minería, 2002). On the other hand, Chile has a legacy of contamination of water resources due to past mining operations, which has to be addressed (Instituto de Ingenieros de Chile, 2011; Banco Mundial, 2011). Leaking tailing dams, acid mine drainage and small scale mining result in contamination of water resources that are often used for irrigation downstream. In Northern and Central Chile, many rivers present concentrations of metals and sulfate that exceed irrigation water quality standards. Since the 1980s, levels of arsenic, copper and sulfate have increased (Banco Mundial, 2011). These problems demand long-term passive solutions that are low cost and make use of local resources.

Several physicochemical and biological techniques have been developed to treat AMD. In conventional active treatment, acidity and metals are removed by continuous addition of alkaline substances (such as NaOH, $Ca(OH)_2$, CaO, Na_2CO_3 and NH_3), which can be expensive, specially when needed in high quantities; also, costs of operation and maintenance of active systems are high (Watzlaf et al., 2004). During the last decades, research has focused on the development of passive treatment systems for AMD, because passive systems have shown high metal removal at low pH values (pH 3-6), sludges that are chemically stable, low operational and maintenance costs, reduced chemical consumption and minimal consumption of energy. The passive treatment systems use addition of limestone to generate alkalinity and precipitate metals as oxides and/or use biological processes in which sulfate reduction takes place through which alkalinity is generated and metals precipitate as sulfides.

In biological treatment systems such as anaerobic wetlands, remediation of dissolved metals is mainly caused by sulfate reduction, which simultaneously removes sulfate, metals and acidity. Metals are also precipitated as a result of some abiotic reactions that result from the reducing ambient that is generated (Kosolapov et al., 2004) such as precipitation of metal oxides or carbonates driven by a pH increase (Gadd, 2000). The precipitation of metals by sulfate reduction occurs when the produced H_2S reacts with the metals to produce insoluble precipitates (Zagury et al., 2006). For sulfate reduction to be successful a pH range of 5 to 8 is required; outside this range, reduction diminishes and the capacity of metal removal is reduced. At low pH (< 5), sulfate reduction is normally inhibited and the solubility of metal sulfides increases (Neculita et al., 2007). However, sulfate-reducing bacteria (SRB) surviving at pH of 2.5 have been found, although with only slight alkalinity generation (Tsukamoto et al., 2004). Also, a reduced anaerobic medium is required for sulfate reduction with redox potential (Eh) of less than -100 mV (Rabus et al., 2006). The substrate usually used to drive sulfate reduction is principally made of organic residues such as animal feces, compost and agricultural residues (Neculita et al., 2008). Adequate proportions of different organic sources are required for long-term operation of the biological treatment system (Sheoran et al., 2010). The efficacy of these systems will be affected by pH variations, metal concentrations, and concentrations of sulfide produced in-situ, which may be also toxic.

The development of biological treatment systems must be focused on the adequate proportions of different organic sources, avoiding AMD toxicity to microorganisms, and studying the key bacterial populations involved in treatment. Research results suggest that a good organic energy source for sulfate reducing communities must contain several carbon sources (Waybrand et al., 1998; Zagury et al., 2006). Substrates with cellulose have been confirmed to be more efficient than lignocellulosic substrates (Waybrand et al., 1998). An optimum mixture must contain equal proportions of cellulosic and non-cellulosic organic residues (Neculita et al., 2008). The non-cellulosic organic residues (compost and manure) accelerate the activity of sulfate reducers at the start of the system (Wildeman (2006), cited by McCauley et al., 2009). The cellulose delivers the long-term organic matter and must be hydrolyzed and fermented by a microbial consortium that provides the simple carbon sources to SRB.

Our research addresses protection from toxicity. We take advantage of chemical gradient-based bioprotection, a mechanism by which some bacteria in a community induce pore-water metal gradients (Schwarz & Rittmann 2007a; 2007b). Bioprotecting gradients can occur over a broad range of scales: μm - mm in biofilms, mm - cm in freshwater and marine sediments, and cm - m in groundwater aquifers. An excellent example of this community-based bioprotection mechanism involves SRB, which produce sulfide that can coordinate toxic free metals to form solids. Results of previous analytical and numerical modeling (Schwarz & Rittmann, 2007a; 2007b) provide evidence that gradient resistance ought to work much better in diffusion-dominated systems, compared to advection-dominated systems. This insight led us to develop the diffusive exchange system (DES) approach to be used in permeable reactive barriers or constructed wetlands. In DES reactors, layers of low conductivity (low-K) containing reactive organic materials are intercalated between layers of high conductivity (high-K) that transport the AMD across the reactor. Because diffusion dominates transport in the reactive layers, microbial communities can take advantage there of the chemical-gradient mechanism for protection from toxicants. Specifically, we experimented with a porous layered system where the reactive sulfate reducing layers with low hydraulic conductivity were intercalated between sand layers with higher hydraulic conductivity. The sulfide produced in the reactive layers diffused to the sand layers where the metals precipitated. This system avoided the direct contact between microorganisms and the flowing AMD.

METHODOLOGY

The DES reactor, with horizontal gravitational flow, had dimensions of 120 cm x 60 cm x 10 cm (L x H x W) (Fig. 1). It was filled with horizontal layers of 10 cm thickness of reactive material and sand (3 each). The flow was controlled by means of a peristaltic pump feeding the upgradient well (Masterflex, 0.02–100 rpm). Both upgradient and downgradient, a 10 cm zone was included to facilitate distribution of influent flow over the reactor height and retain the reactive material, respectively. The reactor had a glass wall on one side, to allow observation of materials, and positions where precipitates deposited.

The geometric design of the reactor fulfilled the analytical criteria of Schwarz & Rittmann (2007a) for chemical-based bioprotection. In this case, the criteria were used to define the minimum thickness of reactive layers and maximum flow velocity.

The reactive material was a mixture of *Pinus radiata* bark compost, digested sludge from a local wastewater treatment plant, sand, and calcium sulfate to promote initial sulfate reduction. To inoculate the mixture, it was wetted with anaerobic digester content of the same wastewater treatment plant.

The reactor was fed with local spring water modified to obtain a pH of 2.5–3.5 and concentrations of 450 mg/L Fe (II), 100 mg/L Zn, 20 mg/L Mn, 5 mg/L Cu and 3,100 mg/L SO_4^{2-}. During 14 months, the flow was controlled at 1.5 ml/min. Concentrations of SO_4^{2-} (Method 4500E (APHA, 2005)), H_2S-HS^- (Method 4500-S2-D (APHA, 2005)), Zn^{2+} (Method 3500-Zn-B (APHA, 2005)), Fe (Method 3500-Fe (APHA, 2005)), Cu (Method 3500-Cu (APHA, 2005)), Ni (Method PAN (HACH)), pH, and Eh, were determined in the influent and effluent weekly. Influent pH was initially 3.5, but then changed to 2.5 to chemically stabilize the reactor feed, since at pH of 3.5, precipitates were observed in the feed tank, probably due to Fe oxidation and precipitation.

During the last 5 months, the effluent was also fed to a 10-L bucket (the "settler"), to test the effect of oxidizing conditions on treatment performance and effluent quality.

Finally, after 3 months, the possibility of rejuvenating spent organic layers was tested. A solution of 20 g/L of microcrystalline cellulose (MCC) (Sigmacell, 20 μm) was injected into reactive layers at 5–cm intervals (27 g of MCC in total).

Figure 1 Experimental system

RESULTS AND DISCUSSION

Although the reactor was operated under metal and acidity overload for the entire period of 14 months, it consistently reduced sulfate and metal concentrations, and added alkalinity. This is the first time a biochemical reactor has been operated passively, without an external source of alkalinity, such as calcite, at very low pH and high metal load.

This stable operation is indicative of a bioprotection mechanism based on chemical gradients protecting the microbial community within the reactive layers of low permeability (Schwarz & Rittmann, 2007a; 2007b; 2010). Additionally, the system did not show any permeability reduction. Metals precipitated along the interfaces between the conductive and reactive layers, where sulfide and metal gradients meet, consistent with the bioprotection mechanism based on chemical gradients.

Fig. 2 shows measured concentrations of chemical parameters at the inlet and outlet of the reactor for the 14-months operation period. For the last 5 months, values at the outflow of the settler are also shown. Influent concentrations were measured at the feeding well, located immediately upgradient of the porous materials. Similarly, effluent concentrations were measured at the downgradient well. These wells were separated from the porous materials by a fine mesh. In the entry well, pH and metal concentrations already differed from nominal values in the feeding tank. This difference was significant during the first 3 months due to iron oxidation and precipitation in the feeding tank and well. Hence metal concentrations are shown from month 4 on. Chemical instability of Fe was finally avoided by reducing the pH in the feed to 2.5. Even then, feeding well values fluctuated around nominal values probably because feeding well composition is already affected by biochemical reactions in the reactor.

The sulfide peak occurred after the MCC injection. This peak was coincident with a decrease in effluent sulfate. Although, the stimulating effect lasted less than 2 months, higher MCC concentrations could be used to make it last longer.

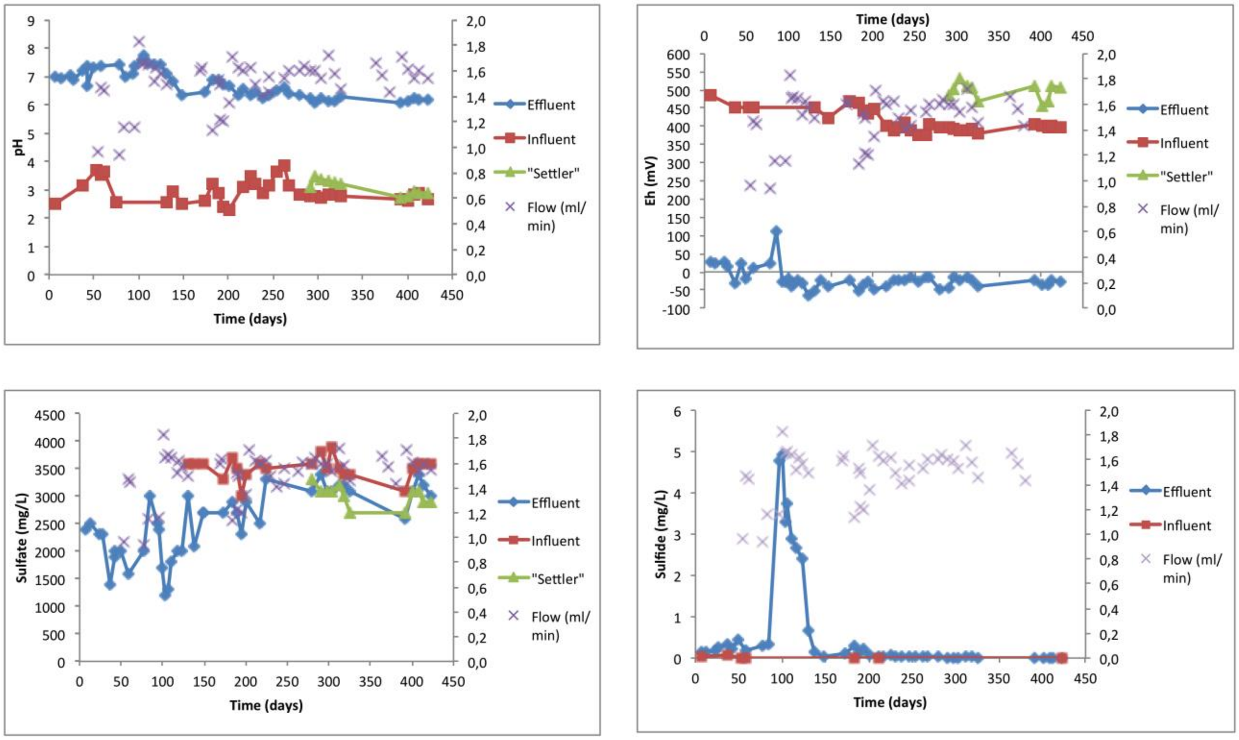

Figure 2 Measured values of pH, Eh, and concentrations of sulfate and sulfide

The effluent pH was near neutral all the time, and hence the reactor neutralized proton acidity, generating an adequate environment for the microbial community. On the other hand, the acidity coming from Fe (II) was only partially neutralized. Under oxidizing conditions in the settler, Fe (II) oxidation and Fe (III) precipitation occurred, and the pH dropped to influent values at which Fe (II) oxidation slowed down significantly. As the Fe graph shows (Fig. 3), the reactor itself removed little Fe, but a significant fraction was removed in the settler as hydroxides, thanks to the alkalinity added by the reactor, that also neutralized part of Fe acidity. Additionally, the reactor showed negative redox potentials, allowing successful establishment of sulfate reducing communities.

Zn removal (Fig. 3) occurred within the reactor, probably as sulfides, as evidenced by white precipitates along interfaces between reactive and conductive layers. Also, sulfide solubility products are lower for zinc than for iron, hence sulfide generated in the reactive layers, reacted preferentially with zinc. Similarly, nickel was only removed in the reactor.

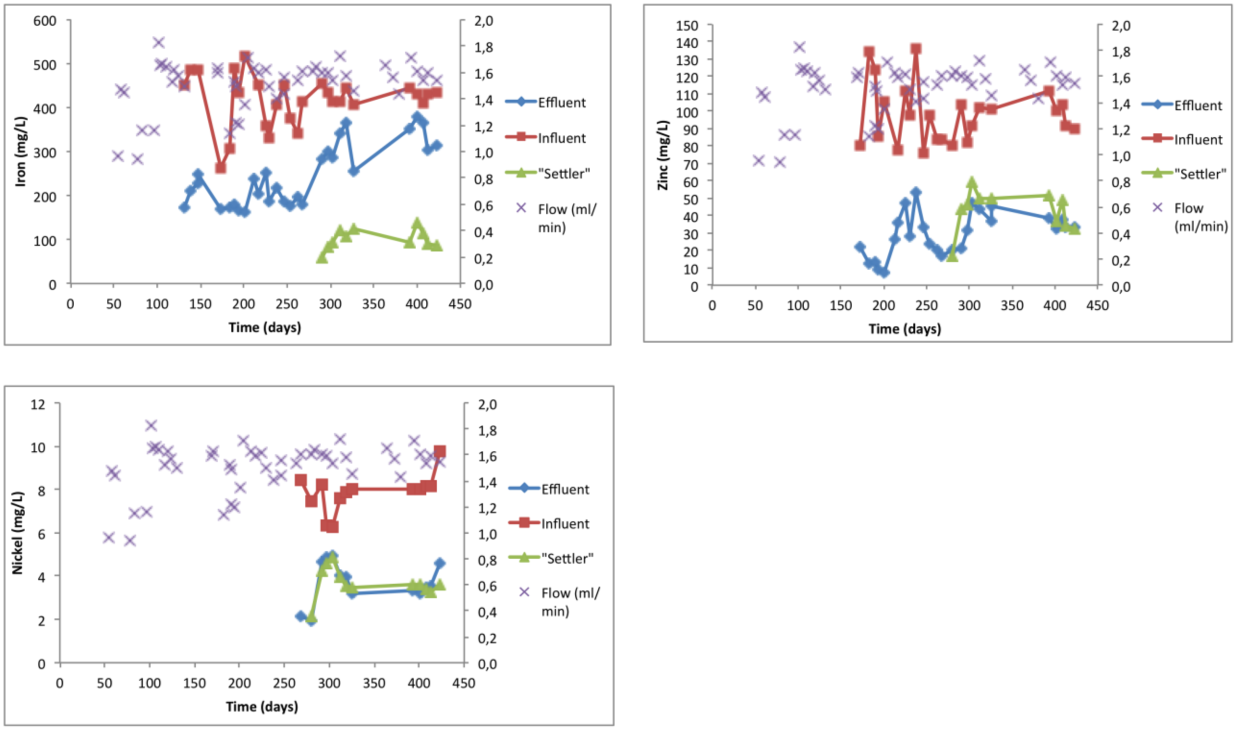

Figure 3 Measured concentrations of metals Fe, Zn, and Ni

Figure 4 shows white precipitates along the boundaries between layers, consistent with gradient-based resistance.

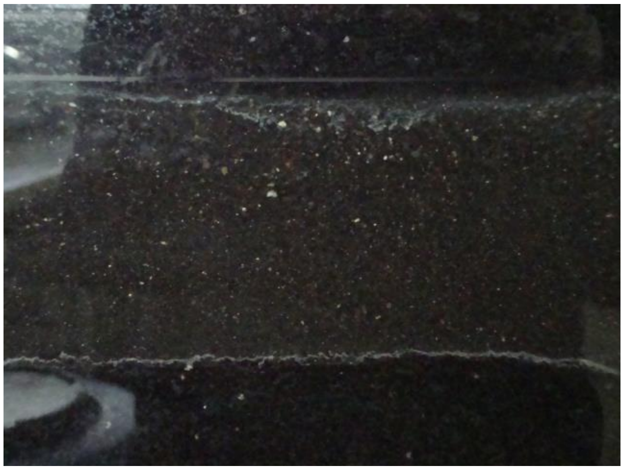

Figure 4 Location of precipitates along layer boundaries. The darker is the organic layer

CONCLUSIONS

DES reactors hold promise for passive treatment of highly acidic and toxic AMD, like the one generated by the copper mining industry in Chile. Within these reactors higher reaction rates are feasible, microbial consortia are protected from toxicity, and no permeability reduction due to precipitate formation is observed.

The key characteristic of DES systems is that reactive zones are separated from the zones of advective transport of contaminated water. An advantage of this zonation is that reactive and conductive zones can be optimized independently. The advection zone can be optimized to maintain an adequate hydraulic conductivity in the long term by using highly permeable materials. Similarly, higher sulfate–reducing rates in reactive zones of DES systems by using finely ground organic materials are possible.

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REFERENCES

APHA (2005) *Standard methods for the examination of water and wastewater*, 20th edn, American Public Health Association, Washington, D.C.

Banco Mundial (2011) *Diagnóstico de la gestión de los recursos hídricos en Chile*, B. M., Santiago.

Blowes, D.W., Ptacek, C.J., Jambor, J.L. & Weisener, C.G. (2003) 'The geochemistry of acid mine drainage', in *Treatise on Geochemistry*, Elsevier, vol. 9, pp. 149–204.

Dold, B. (2010) 'Basic concepts in environmental geochemistry of sulfide mine-waste management', in *Waste Management*, INTECH, pp. 173–198.

Gadd, M. (2000) 'Bioremedial potential of microbial mechanisms of metal mobilization and immobilization', *Current Opinion in Biotechnology*, vol. 11, pp. 271–279.

Instituto de Ingenieros de Chile (2011) *Temas prioritarios para una política nacional de recursos hídricos,* I. I. CH., Santiago.

Kosolapov, D., Kuschk, P., Vainshtein, M., Vatsourina, A., Wiebner, A., Kastner, M. & Muller, R. (2004) 'Microbial processes of heavy metal removal from carbon-deficient effluents in constructed wetlands', *Eng. Life Sci.*, vol. 4, pp. 403–411.

McCauley, C.A., O'Sullivan, A.D., Milke, M.W., Weber, P.A. & Trumm, D.A. (2009) 'Sulfate and metal removal in bioreactors treating acid mine drainage dominated with iron and aluminum', *Water Research*, vol. 43, pp. 961–970.

Ministerio de Minería & Consejo Minero (2002) *Guía metodológica sobre el drenaje ácido en la industria minera*, M. M & C. M., Santiago.

Neculita, C., Zagury, G. & Bussiere, B. (2007) 'Passive treatment of acid mine drainage using sulfate-reducing bacteria: critical review and research needs', *Journal of Environmental Quality*, vol. 36, pp. 1–16.

Neculita, C.M. & Zagury, G.J. (2008) 'Biological treatment of highly contaminated acid mine drainage in batch reactors: long-term treatment and reactive mixture characterization', *Journal of Hazardous Materials*, vol. 157, pp. 358–366.

Nordstrom, D.K. (2011) 'Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters', *Applied Geochemistry*, vol. 26, pp. 1777–1791.

Rabus, R., Hansen, T. & Widdel, F. (2006) 'Dissimilatory sulfate– and sulfur–reducing prokaryotes', in *The Prokaryotes*, vol. 2., pp. 659 –768.

Schwarz, A.O. & Rittman, B.E. (2007a) 'Analytical–modeling analysis of how pore–water gradients of toxic metals confer community resistance', *Advances in Water Resources*, vol. 30, pp. 1562–1570.

Schwarz, A.O. & Rittmann, B.E. (2007b) 'Modeling bio–protection and the gradient–resistance mechanism', *Biodegradation*, vol. 18, pp. 693–701.

Schwarz, A.O. & Rittmann, B.E. (2010) 'The diffusion–active permeable reactive barrier', *Journal of Contaminant Hydrology*, vol. 112, pp. 155–162.

Sheoran, A.S., Sheoran, V. & Choudhary, R.P. (2010) 'Bioremediation of acid–rock drainage by sulfate–reducing prokaryotes: a review', *Minerals Engineering*, vol. 23, pp. 1073-1100.

Tsukamoto, T.K., Killion, H.A. & Miller, G.C. (2004) 'Column experiments for microbial treatment of acid mine drainage: low-temperature, low-pH and matrix investigations', *Water Research*, vol. 38, pp. 1405–1418.

Watzlaf, G.R., Schroeder, K.T., Kleinmann, R.L.P., Kairies, C.L. & Nairn, R.W. (2004) *The passive treatment of coal mine drainage*, DOE/NETL–2004–1202.

Waybrant, K., Blowes, D. & Ptacek, C. (1998) 'Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage', *Environmental Science and Technology*, vol. 32, pp. 1972–1979.

Zagury, G., Kulnieks, V. & Neculita, C. (2006) 'Characterization and reactivity assessment of organic substrates for sulfate–reducing bacteria in acid mine drainage treatment', *Chemosphere*, vol. 64, pp. 944–954.