Established and Emerging Passive and Hybrid Biological Sulfate Removal from Mining Effluents

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ABSTRACT

Changing regulations and water scarcity combined with increased fiscal pressure in the mining industry have increased the calls for new, lower cost methods for sulfate removal from mining effluents. In the last decade, membrane-based processes have been implemented on a large scale for advanced sulfate removal and have achieved a level of commercial acceptance in the mining industry. But membrane systems are complex and costly. On the other hand, many applications of sulfate removal in mining do not require a high removal efficiency, so simpler systems that are less costly may be more appropriate. Passive treatment offers the potential for reduced cost on sites where sufficient land area is available to construct treatment cells. Passive treatment has been demonstrated at a large number of sites, but has well-known drawbacks that encourage innovation. This paper will describe a recent project in passive biological sulfate removal for a mining effluent, and reports on the emerging concept of hybrid biological treatment. Hybrid treatment is intended to reduce the land area needed for passive treatment and thereby to make passive systems applicable for larger flow rates.

Keywords: Passive Treatment; Advanced Sulfate Removal; Hybrid Treatment

INTRODUCTION

Increasing pressure on water resources, changing regulations, and increasing awareness of the impacts of mining on water quality have led to increasing need for sulfate removal from mining effluents. Lime treatment has traditionally been used to reduce metals and acidity, but is able to remove sulfate only to the limit of gypsum solubility. The term "advanced sulfate removal" has been adopted by many to refer to sulfate removal below the level of gypsum solubility. Depending on the jurisdiction, and on the assimilative capacity of the receiving environment, some operations may be required to achieve an "end of pipe" sulfate limit of 300-500 mg/L, while others may be under even more strict limits.

In the last decade, a number of operators have successfully demonstrated advanced sulfate removal using membrane processes, at large flow rates, to achieve sulfate levels in product water of 100 mg/L or below (Hutton 2009). Examples include the eMalahleni water treatment plant (started 2005) and the Optimum Coal mine water treatment plant (2009) in South Africa, a facility at Kennecott Mine for treatment of impacted groundwater (2006) and the Northern West Virginia Water Treatment Plant (2013) in the USA. The product water from the eMalahleni and Kennecott plants is sent directly to local municipalities to provide drinking water.

On the other hand, alternatives to these large scale "active treatment" processes are sought which are less costly for applications where strict discharge limits are not required, for example, in cases where only 30-50% removal is desired. The cost of treatment to moderate sulfate levels should be significantly lower than the cost to meet strict levels. One option is to bypass part of the flow, allowing for a smaller capacity membrane plant, so the mixture of treated water and bypass water meets the objectives. Another option is to select membrane types which are semi-permeable to the target ions, thereby increasing the sulfate level in the effluent, and hopefully, decreasing costs. All the active treatment options, however, require a fully-staffed mechanical treatment plant with appropriate skills and training and attention to process control, to prevent costly problems such as scaling.

"Passive treatment" can offer sulfate removal with a greatly reduced level of complexity, greatly reduced staffing levels and skills, and as a result, potentially offers cost savings. Passive treatment research and development has been carried out over a period of decades. A large number of facilities have been constructed, but a relatively small subset of these projects involves designs specifically targeting sulfate removal. Passive treatment for advanced sulfate removal has met with mixed success, however the limitations of the process are beginning to be well understood and companies can now evaluate the passive treatment option with greater confidence. In general, passive treatment requires a much larger land area than active treatment, and as a result the process has not been frequently applied to large flow rates.

"Hybrid treatment", also known as semi-passive treatment, is an emerging concept that combines aspects of active treatment and aspects of passive treatment. In hybrid treatment, a biological sulfate reduction process takes place in a lined earthen vessel containing inert media and bacteria,

fed with a soluble electron donor and nutrients. The use of a soluble electron donor reduces the size of the vessel, and improves control, compared to passive treatment. The result is a process having low complexity, relatively low cost, and less operator input, but without necessarily requiring a large land area. The hybrid process has been successfully demonstrated on a small scale for selenium removal, however early attempts in sulfate removal have encountered problems.

BIOLOGICAL SULFATE REMOVAL

Biological treatment removal utilizes an organic carbon source, or hydrogen, as an electron donor to and sulfate as a terminal electron acceptor, thereby achieving reduction to sulfide through cellular metabolism. In a broader context, a variety of organisms use a variety of terminal electron acceptors in cellular metabolism, depending on the environment. A conceptual model of electron transfer in cellular metabolism is provided in Figure 1.
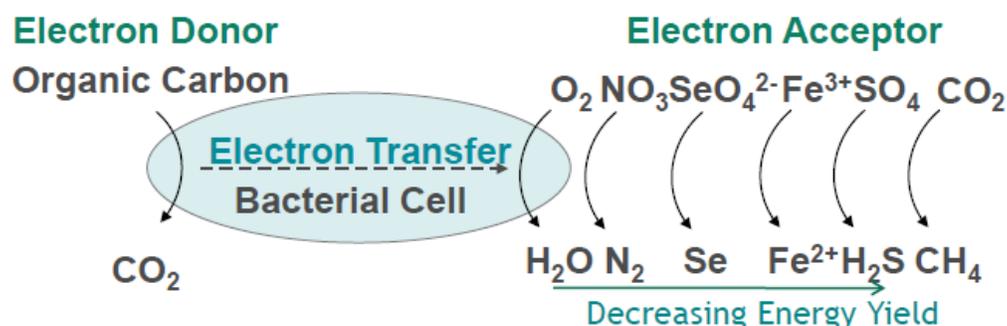

Figure 1 Electron donors and acceptors

There is a decreasing energy yield for successive electron acceptors illustrated by the figure, and, for example, oxygen and nitrate must be depleted prior to sulfate being reduced. The oxidation of organic carbon and the reduction of sulfate produces carbon dioxide (present at neutral pH as bicarbonate), water, and sulfide (present at neutral pH as a mixture of dissolved hydrogen sulfide and bisulfide).

A range of organic carbon sources have been employed for sulfate reduction, including but not limited to: methanol, ethanol, sugarcane waste, agricultural waste, sawmill waste, abattoir waste, sewage sludge, compost biosolids, cleared vegetation, and garden waste (Kumar 2011, Liamlean 2007). Selection of the lowest cost electron donor depends on the availability of materials close to the mine, and on the pre-processing costs that are required to deliver the material to the system.

Sulfide Sequestration

For biological treatment to be successful, it is essential that, once sulfate reduction is achieved, the resulting sulfide be removed from the system. The reasons are, firstly, sulfide is toxic and generally must be removed from effluents to low levels prior to release to natural water bodies. Secondly,

sulfide can off-gas from a treatment system as hydrogen sulfide, which is a health and safety or aesthetic concern and can add complexity to operation and maintenance. Thirdly, if not removed from the bioreactor effluent, sulfide can be oxidized back to sulfate through exposure to oxygen, in a process called reversion, which defeats the purpose of the process.

Some of the failures or difficulties of biological sulfate removal in the past have been associated with sulfide sequestration rather than sulfate reduction. Sulfide sequestration can be achieved in a variety of ways. In water sources that contain significant quantities of metals, the sulfide will act as a ligand and many base metals will precipitate. Alternatively, some of the sulfide may be removed using air-stripping, however this option produces a sulfide off-gas, and, practically, cannot achieve low levels of dissolved sulfide in the effluent. Air stripping may be combined with oxidation of sulfide to elemental sulfur, which is a solid and can be normally be separated from the liquids. The sulfur oxidation process can be biologically catalysed and is pH dependent. However, the process of oxidizing sulfide to sulfur can be difficult to control in passive systems, increasing the chance of reversion to sulfate, and creating polysulfides.

If the metals in the feed are not sufficient to sequester all of the sulfide, then a supplemental source of metals may be provided, and this usually consists of an abundant, low-cost iron carbonate, oxide or hydroxide material. Iron sulfate or chloride salts are not appropriate, since the resulting release of the sulfate or chloride ion to the effluent is counter to the overall objectives. Other base metal hydroxides can sequester sulfide, and their use depends on local availability. Also, the material should not contribute undesirable impurities, such as lead or arsenic, to the effluent. A reduced or partially reduced iron source is preferred, such as ferrous hydroxide, or magnetite to prevent redox reactions that contribute to reversion. Ferrous hydroxide sequesters sulfide as follows in equation 1.

1) $Fe(OH)_2 + H_2S = FeS(s) + 2H_2O$

In the case of an oxidized iron source, such as ferric hydroxide or ferrihyrite, the ferric ion will be preferentially be reduced to ferrous ion, resulting in the oxidation of sulfide and the production of elemental sulfur, as described in equation 2. Depending on the pH, some of the elemental sulfur will be soluble as polysulfide, as shown in equation 3. The polysulfide, if present, is undesirable since it is likely to report to the effluent and eventually revert to sulfate. Therefore, the success of sequestration processes using oxidized iron involves the control of the formation of polysulfide, and the separation of the elemental sulfur.

2) $2Fe^{3+} + S^{-2} = 2Fe^{2+} + S^o(s)$

3) $S^{2-} + n\ S^o = S^o_n S^{2-}$
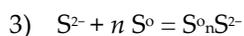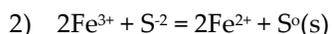
If ferric hydroxide ($Fe(OH)_3$) is used as the iron source, then one third of the sulfide mass could follow this pathway, while two thirds would deport at FeS. Magnetite, ($Fe^{2+}Fe^{3+}_2O_4$) has been successfully used as a sequestering agent, and is discussed in the passive treatment case study below. Magnetite is an insoluble, black mineral that is widely available. It may be finely ground and added to the mixture of media as part of a sulfide sequestration system. The makeup of the media, the predicted longevity, and testing of such, are the subjects of recent and ongoing work (Blumenstein 2012, Van Niekerk 2015). A final stage of aeration is typically required to polish the

effluent to remove excess nutrients from the biological treatment system, and to oxidize a trace amount of residual sulfide downstream of the sulfide sequestration system. The final aeration also serves to increase the dissolved oxygen concentration of the effluent prior to discharge.

PASSIVE TREATMENT EXPERIENCE

Passive treatment systems commonly consist of biochemical reactors (BCRs), sulfide sequestration, and final polishing/aeration. A BCR is typically a gravity-flow bioreactor with a limestone-buffered organic treatment medium that is intended to require minimal operation and maintenance (Gusek, 2002). Passive BCRs consist of a series of geomembrane-lined cells or ponds filled with organic media, located outdoors. The organic media in the BCRs typically consists of woodchips and/or hay and limestone. A considerable amount of innovation has been seen in the development of the media for the BCR, to facilitate biological processes and to promote hydraulic conductivity. This organic matter provides a surface for the growth of microbial colonies and is gradually degraded to generate the organic carbon required for sulfate reduction. The typical construction of a BCR is shown in Figure 2.
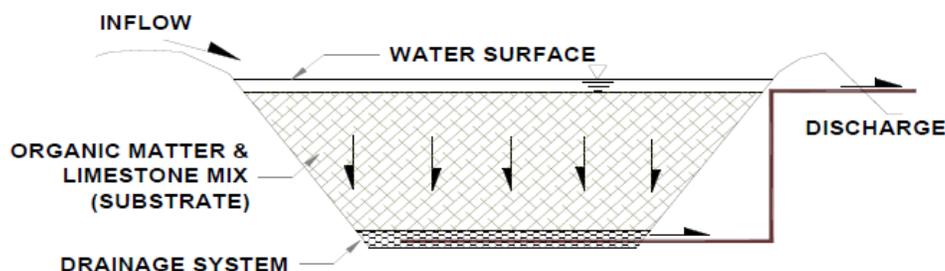

Figure 2 Profile of a BCR

A range of treatment mechanisms may be working in a BCR, depending on the particular feed conditions and the design as summarized below (Reisman 2009):

- biological reduction of sulfate to sulfide and subsequent precipitation of metal sulfides,
- alkalinity increase due to biological sulfate reduction and dissolution of limestone contained within the substrate,
- precipitation of metal hydroxides, and
- sorption of trace metals (e.g., Cd, Cu, Pb, Zn) to metal hydroxides and the organic medium.

The rate of degradation of organic material varies with media age and temperature and is likely the limiting factor in sulfate reduction in a BCR. Sulfide sequestration is achieved using an anaerobic sulfide polishing cell (SPC) that contains iron media. Effluent from the BCRs that contains high levels of sulfide flows through the SPC where sulfide is precipitated as an iron sulfide solid. Flow through a passive system is achieved through gravity flow and chemical addition is generally not required. Maintenance is performed at periodic intervals, for example, with SPCs media renovation every 3-5 years and BCRs media replacement every 10-20 years.

Advantages and disadvantages of passive biological sulfate removal

Passive treatment is well-researched and the benefits and limitations of the process are well understood:

- Passive treatment is not well suited to meeting strict effluent limits, due to a lack of process feedback signals and lack of process control mechanisms.

- Passive sulfate removal is founded on a biological process which is sensitive to low temperatures, and therefore may be sensitive to cold climates. However, as a mitigating measure, the BCR may be covered by an insulating layer of water, soils or even foam, to prevent freezing. Nevertheless, BCRs generally need to be sized for ambient feed water temperatures; lower temperatures require larger reactors.

- The breakdown of organic matter to produce volatile fatty acids (VFA) is believed to be the rate limiting step, and it is not directly linked to the subsequent consumption of VFAs for sulfate reduction. Under normal operation, most passive systems suffer from some degree of nutrient leakage. Nutrient leakage can result in failure to meet water quality objectives in terms of nitrogen, phosphorous or biological oxygen demand. An aerobic polishing cell, trickling filter, and/or lagoon may be installed downstream to help address the problem.

- Passive systems require large land areas, particularly for large flow rates. The availability of land near mining operations may be the limiting factor for passive systems.

- Passive systems benefit from a low degree of complexity. Often, little or no concrete, mechanical, electrical and structural work is required, drastically reducing capital costs compared to conventional active treatment systems, and simplifying maintenance operations.

- Passive systems cannot treat for chloride and generally do not result in a reduction in total dissolved solids (TDS) where chloride, magnesium, or other common anions are present.

- Passive systems benefit from low power consumption and are suitable for remote sites without access to line power. Depending on the site, water generally flows by gravity through the treatment system.

- Passive systems benefit from lower labour inputs, due to inherent differences including lower complexity, compared to active systems.

- Passive system can take advantage of low grade, lower cost carbon sources, which make the operating cost competitive compared to active biological sulfate removal systems.

Passive sulfate removal treatment case study

Golder Associates has been actively developing passive systems for various applications over the past 10 years both in the Americas and in Africa. In spite of a large number of published case studies involving passive treatment, there are few that have been designed specifically for sulfate removal. One such case is an operating coal mine located in a rainy and temperate part of Canada, shown in Figure 3. The feed sulfate level, typically 400-700 mg/L and the target for treatment is 300 mg/L, so the treatment effciency need not be high. This is considered an excellent application for passive treatment.

The feed is predominantly calcium sulfate, with a limited amount of metals available to sequester sulfide. The system contains a biochemical reactor (BCR) for sulfate reduction, an anaerobic sulfide

polishing cell (SPC), and aerobic lagoon and a settling pond. The SPC consists of a mixture of woodchips and a locally available magnetite. The pilot demonstration work commenced in 2009 (Blumenstein 2012) and a demonstration system at a quarter of the full scale (planned to be approximately 65 m3/hr) was constructed summer of 2012. The land area required from the demonstration scale was 0.8 ha. The feed and effluent sulfate data is shown in Figure 4, below. Data collection and compilation are ongoing.

The preliminary results from the case study are promising, and the system will continue to be adjusted through operations. The anaerobic sulfide polishing cell was commissioned in early 2013. The effluent from the SPC consistently is below 1 mg/L sulfide, and this residual is oxidized in the aerobic cells.

Figure 3 Passive BCR in Canada (2012)
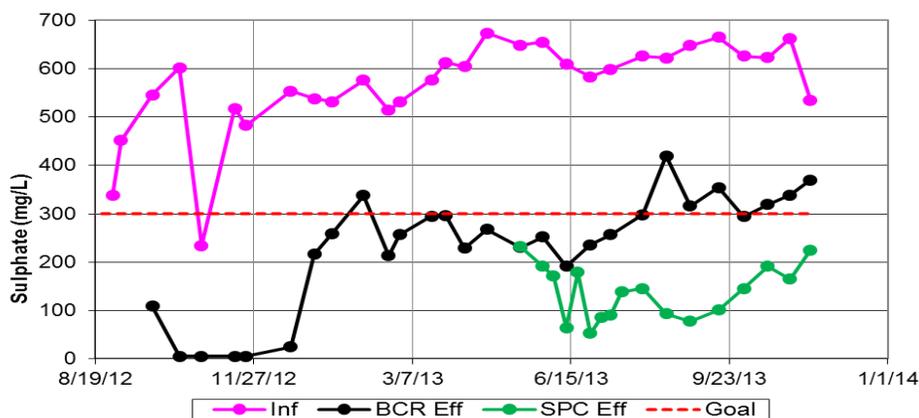
Figure 4 Preliminary Results from a Passive BCR in Canada
Notes: Inf – Influent to the BCR; BCR Eff – BCR Effluent; SPC Eff – SPC Effluent

7

HYBRID TREATMENT

The hybrid biological reactor concept has been developed to address some of the limitations of passive treatment systems, and to make passive treatment more applicable to large flow rates. Hybrid reactors operate on the principles of biological sulfate reduction, except the reactors are constructed using inert media in lined, covered, earthen basins, and are fed a soluble nutrient source by means of a metering pump. Although the biological sulfate reduction process can be engineered in an "active" mechanical treatment plant, but this process has all the disadvantages of cost and complexity of the membrane plants mentioned above. As a result, there are very few commercial examples of the active biological sulfate reduction process. Hybrid reactors, in contrast, are designed to contain few moving parts, draw very little electrical power, and to require a minimum of operator intervention. Hybrid systems are intended for cases where only partial sulfate reduction is required and where strict process control is not necessary, including cases with a relatively constant flow rate. The hybrid system takes advantage of the benefits of both active and passive systems, with lower costs than active systems and using less land area than conventional passive systems. While hybrid biological sulfate systems are in the early stage of development, they are anticipated to offer the following benefits:

- A variety of soluble electron donors can be utilized, including low cost or dilute options that are not recommended for conventional active treatment systems, such as compost leachate, silage or waste biological sludge.

- Hybrid systems eliminate most of the concrete, steel, mechanical equipment, electrical equipment, and much of the ancillary infrastructure, along with the engineering and construction costs associated therewith.

- Hybrids decouple sulfate reduction from the rate-limiting carbon metabolism of a BCR, reducing the size of the sulfate reducing bioreactor.

- Hybrids, like passive reactors, may be buried to protect from freezing in cold climates.

- Bioreactors may be constructed using a variety of on-site materials, such as coal beneficiation rejects, taconite wastes, or gravels.

- Hybrids are unique compared to passive systems in that they may be back-flushed, reducing problems with hydraulic conductivity, greatly extending their life span and allowing for higher loading. Early problems with passive treatment have commonly been associated with the mundane problem of flow distribution and distribution piping.

- Hybrids are intended to eliminate heating of water needed for typical active biological processes, by increasing the size of the bioreactor bed but at a reasonable cost.

- Hybrids require a small amount of electrical power, but unlike active biological or membrane systems, do not necessarily require access to line power.

- Hybrids, like passive systems, eliminate continuous operator attention and reduce labour costs compared to active systems.

- Hybrids improve control of nutrient leakage.

- The largest operating cost of a hybrid system is the electron donor. For a case study employing ethanol, the cost is estimated to be less than $0.10 per m^3 of feed to reduce

sulfate from 600 mg/L to 300 mg/L, assuming the current market price for ethanol of $830/t. Lower cost alternatives, using waste products, are also possible.

Golder Associates has successfully applied the hybrid concept to selenium reducing bioreactors at a demonstration site. Biological selenium removal operates on similar principles as sulfate removal. The hybrid concept was applied at the Leviathan Mine, and this case study offers insight on early variations on the concept applied to base metal removal, at relatively low flows of 2-7 m3/hr (Mayer 2006, Tsukamoto 2002). A pilot scale hybrid system fed with ethanol and molasses was tested on scrubber blowdown in the Minnesota Iron Range (Eger, 2004). Like passive treatment, hybrid treatment requires a system to sequester sulfide, usually based on contact of the water with iron compounds (ideally ferrous oxides or hydroxides). An example process flow diagram is shown in Figure 5, below.
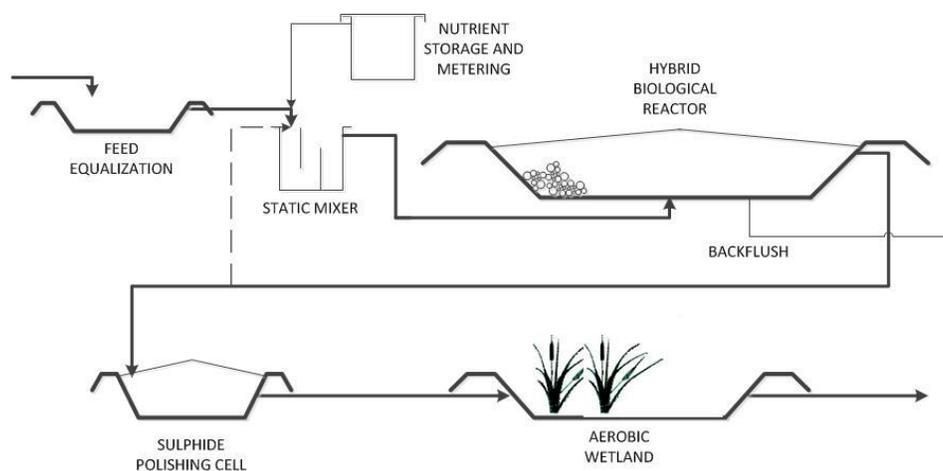

Figure 5 Example Hybrid System Process Flow Diagram

Sludge from the bioreactor back-flush is an organic material, mixed with feed suspended solids, and precipitated metal sulfides, depending on the application. The media in the sulfide polishing cell may be drawn from a range of locally available materials, ideally magnetite or other iron oxides. Depending on the specific feed water, part of the hybrid reactor overflow may be recycled to provide a ligand for specific influent metals. Lessons from the design of passive bioreactors inform the detailed design of hybrid reactors, such as: sizing, hydraulics, packing, flow distribution, and prevention of clogging and short-circuiting.

CONCLUSION

Active treatment, using membrane separations, has been demonstrated at a number of sites around the world, and has achieved commercial acceptance at large flow rates for advanced sulfate removal. Active treatment in general suffers from a high degree of complexity and as a result, a high cost. Furthermore, many operators require only partial removal of sulfate, for example, 50% removal, therefore less capital and operator intensive processes are more suitable.

Passive treatment has recently been successfully demonstrated for advanced sulfate removal. The process suffers from certain drawbacks, including the requirement for large land areas to treat large flow rates, and the risk of nutrient loss to the effluent. A key element of the most recent passive treatment case studies is the successful sequestration of sulfide using magnetite containing media, reducing the problems of sulfide gas release, or of reversion of sulfide to sulfate which in the past have hampered the success of certain passive biological sulfate removal case studies.

Hybrid biological treatment seeks to combine the best features of both active and passive treatment to offer cost savings for large scale sulfate removal projects without requiring a large land area. Hybrid treatment is an emerging concept, but is already commercially proven at least two sites for selenium reduction and has been demonstrated for base metal removal. Hybrid treatment seeks to decouple the processes that break down complex organic carbon sources from the sulfate reduction process. Such systems are designed to make use of readily available inert mine wastes as media to achieve a low unit cost for the bioreactor. Hybrid systems are unique compared to passive systems in that they may be back-flushed and thus offer longer reactor life spans.

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