

Reduction of Sulfate Concentrations in Neutral Mine Effluent

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September 27, 2005

Purpose and Overview

Elevated concentrations of sulfate (500-4000 mg/L) exist in certain neutral drainages that contain reactive rock, but sufficient carbonate to neutralize the sulfuric acid produced. Due to concerns that sulfate may degrade surface water, cost-effective methods are required for reducing the contaminant load into these streams. This review examines methods primarily for sulfate removal, although selenium is very often simultaneously removed. The chemistry of selenium, particularly the redox chemistry, has distinctive similarities to sulfur, and reductive processes are known to reduce selenium to the insoluble elemental form. We have conducted limited column studies and noted that selenium removal can be very efficient under sulfate reducing conditions. However, site specific conditions may affect the efficiency of selenium removal, and additional testing will be necessary to establish success.

The comments below provide a broad overview of methods for sulfate removal, and a suggestion for treatment using a biological process. However, a detailed engineering analysis and pilot scale process tests are required to fully assess which method will be both robust and cost effective at a particular location.

Sulfate Removal

While several methods for sulfate removal from drainage water are available, few are available that meet the criteria of reducing sulfate concentration to less than 500 mg/L at a reasonable cost (\$1 to \$5/1000 gallons). Sulfate is a soluble ionic material that has only recently received substantial attention for treatment methods. *Bowell (R.J. Bowell, "Sulfate and salt minerals: the problem of treating mine waste", Mining Environmental Management, May 2000)* has provided a useful review of sulfate removal methods with an estimate of costs. However, the ultimate treatment cost will depend on site specific characteristics that very likely will affect selection of the appropriate treatment method.

Sulfate removal methods from drainage water have focused primarily on mine sites where oxidation of sulfide minerals has released high concentrations of sulfate (100- >10,000 mg/L). Many of these sites are releasing water that is acidic, and the methods usually combine neutralization and sulfate removal simultaneously. For neutral drainages, the solubility product of gypsum, generally will keep sulfate to less than 4,000 mg/L, although exceptions have been observed where equilibrium conditions have not

been established for the drainage. The following methods have been employed for sulfate removal:

1. Chemical precipitation and/or ion exchange: (a) The most common method for sulfate removal uses addition of lime, particularly when acidic water is being treated. This is an inexpensive process, but is not specifically applicable to the neutral drainage because it is not effective for removal of sulfate below about 1500 mg/L. (b) A second process that should be examined further is the Bioteq GYP-CIX method (www.bioteq.ca/GypCIX_Rev_Aug_21.pdf). This is effectively an ion-exchange treatment that utilizes sequential ion-exchange columns to first remove calcium followed by a second ion-exchange column to remove sulfate. It has been tested at a 50gal/min rate in a pilot scale operation and company supplied data on the web site suggest that operation costs are on the order of \$2-5/1,000 gallons for reduction of sulfate concentrations from 1,500 mg/L to 250mg/L. No information was provided on the capital costs or management cost. (c) Additional sulfate removal methods that should be considered are the SAVMIN(<http://www.mintek.co.za>) and CESR processes that utilize lime and aluminum hydroxide to precipitate sulfate as ettringite. Costs are not specified, although the process appears cost-effective and reportedly can reduce sulfate to below 250 mg/L. (d) An additional chemical treatment process uses barium sulfate precipitation for sulfate removal, followed by recovery and reuse of barium using a thermal reduction treatment.

All of the above treatments are active processes and probably will require continuous monitoring and management. Each also produces a sludge that will need to be managed. All are relatively new (< 5-10 years) and further consideration is required to assess which, if any, would be applicable to neutral drainages from waste rock dumps. The actual capital and operating costs are difficult to estimate at present, but would probably be in the range of \$600,000 to \$3,000,000 for capital costs and \$2-\$5/1000 gallons for operating costs for a 50 gal/min treatment rate.

2. Reverse Osmosis and membrane methods. Unlike the methods above, reverse osmosis methods are well tested and robust. The costs of these treatments, however, are generally higher than either the chemical precipitation methods or biological processes. This is balanced by the greater confidence that these methods are well-established. Extensive information is available on RO treatments.

3. Biological sulfate reduction: Sulfate reducing bacteria (SRB) are increasingly used for treatment of acidic drainage from mines, both in coal regions as well as hard rock sites. The process is relatively simple in that a carbon/electron source is provided to sulfate reducing bacteria that use it to convert sulfate to sulfide. The sulfide is then removed as a metal precipitate, as elemental sulfur, or purged from a slightly acidic water using carbon dioxide. The advantage of this process is that it can be operated with a minimum amount of management on site in a semi-passive manner, and thus can provide significant cost advantages.

We have used a sulfate reducing bioreactor effectively to treat an acidic seep at the Leviathan Mine in Alpine county for approximately 4 years. While sulfate removal has not been the primary objective, we have observed sulfate removal rates of over 1000 mg/L when the system was operated under appropriate conditions and with bioreactor residence times that allowed efficient sulfate removal. We have examined the use of several carbon sources for sulfate reduction, and have found that ethanol is the best of those tested. It has a low toxicity and is efficiently utilized by SRB systems. We are now examining the use of biodiesel waste (primarily glycerol) as a carbon source. This carbon source is very inexpensive (free to \$0.50/gallon) and could further reduce the cost of treatment, assuming the present preliminary studies are confirmed.

Sulfate removal using a SRB bioreactor is a potentially attractive method to examine for the neutral drainages also. As discussed below, the reagent costs for treatment (ethanol) are comparatively low, and SRB systems are efficient for removal of selenium and arsenic, as well as other divalent metals. However, because the drainages being considered are neutral to slightly alkaline, pilot scale testing is required to determine if water quality criteria can be met with respect to sulfide. Sulfide that is discharged back into the stream will simply reoxidize to sulfate.

Based on both laboratory column studies and field studies by us and others (particularly J.S. Maree at CSIR in South Africa; www.csir.co.za) sulfate removal using ethanol as a carbon source is effective. For acidic influent waters containing metals, the sulfide produced precipitates as metal sulfides, and release of sulfide is less of a concern. However, for the neutral mine drainage which contains only low levels of metals, and has a slightly alkaline pH, sulfide removal would probably require an additional treatment step, for which we do not have experience at Leviathan. We have conferred previously with Dr. Maree, and he proposes two options. The first is a second biological process (using either chemotrophic bacteria or phototrophic bacteria) that oxidizes sulfide to elemental (and insoluble) sulfur. The second utilizes carbon dioxide to reduce the pH to approximately 6.0 and purges the unionized hydrogen sulfide out of the water, which can then be recaptured in a basic solution.

The residue of this process is calcium carbonate, sulfur and the precipitated metal sulfides (e.g. arsenic, nickel, copper) that form in the anaerobic bioreactor. The sludge generated, however, is generally substantially less than with the chemical precipitation methods above. However, a flushing mechanism, similar to that at the Leviathan bioreactor will be required to routinely (1-2 times per year) flush out and capture the sludge. Because the sludge from each of the processes will contain arsenic, it will need to be characterized to determine how it can be managed. The costs for this management can vary substantially, depending on whether it needs to be treated as a hazardous waste.

An initial design of a sulfate reducing bioreactor for treatment of 100 L/min would consist of a bioreactor tank/pond of approximately 400 m³ containing a solid support (e.g. wood chips or rocks) with a void volume of 50%. The dimensions would be approximately 10 m x 20 m x 3 m deep and a 1:1 slope on all sides. A retention time of 12 hours is necessary for consumption of ethanol, and a 200 m³ bioreactor gives a

retention time of slightly over 24 hours. The system would be an upflow design and also contain a flushing system to periodically remove precipitated substances. Ethanol would be added at a rate of 0.4 mL/L of influent water, and is sufficient to remove 100 % of the sulfate, based on the stoichiometry of sulfate reduction. The amount may need to be adjusted up or down after the system has been acclimated. At \$2.00/gal of ethanol (current price at Leviathan), the cost for ethanol is approximately \$0.80/1000 gal. Additional costs for sulfide removal and pumping will bring the estimated operating costs to \$1.50-\$3.00/1000 gal. In his review of sulfate removal processes and costs, Bowell (see above) suggests that bioreactor costs for sulfate removal are less than the other methods by a factor of 1.5-3. Again, any estimate of treatment costs will need to be evaluated on a site specific basis. .

The sulfide in the effluent of the SRB bioreactor would be removed by one of the processes suggested by Dr. Maree (see above) but would require pilot scale testing to determine which method would be most cost-effective for the specific requirements of the site and discharge limitations.

The cost for construction of an SRB bioreactor treatment system will depend on the particular design selected. However, the bioreactor construction is very simple and consists of a lined pond, a series of pipes to deliver and release water and a system for flushing the precipitates. The cost is likely to be less than \$400,000. A sulfide removal system would be an additional capital expense.

Several factors will need to be evaluated prior to selection of any of these alternatives. These include:

1. Where will the treatment facility be located? Is there sufficient room or should the drainage from each of the waste rock dumps be piped to a central location?
2. What is the flow rate that must be treated? Efficiencies of scale are likely different for each treatment option.
3. Which method will provide the greatest reliability for meeting the water quality requirements? How will each treatment system affect other constituent (particularly selenium) concentrations?
4. How are each of the treatment options affected by temperature?

Conclusion

Methods for sulfate removal from mine water have evolved substantially over the previous decade, primarily due to the need for sulfate removal at South African sites. Operating costs have been reduced substantially, and removal of sulfate from 1500 mg/L to less than 250 mg/L has been observed at pilot scale and operational tests at costs estimated to be less than \$5/1000 gallons. Because of the uncertainty in operating requirements, a numerical comparison of the costs for each of the methods proposed above is not presently available for the drainages being considered. Additionally, the cost estimates provided by Bowell are based, in part, on costs in South Africa, and may well be different under a different economic and regulatory environment in the U.S.