APPLICATIONS OF BIOLOGICAL H_2S PRODUCTION FROM ELEMENTAL SULFUR IN THE TREATMENT OF HEAVY METAL POLLUTION INCLUDING ACID ROCK DRAINAGE

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Abstract. BioteQ Environmental Technologies Inc. has developed and commercialized a high rate anaerobic biotechnology for on-site production of H_2S from elemental sulfur for low cost water treatment and sulfide reagent production. The process is demonstrated for mining and mineral process water treatment, including ARD treatment, with concurrent recovery of saleable metals and the reduction or elimination of toxic water treatment sludges. The production of H_2S takes place in a stand alone bioreactor, on demand, at ambient temperatures and pressures, minimizing on-site sulfide inventory, and thus improving the overall safety of the process. The main advantages of treating heavy metal pollution using biogenic H_2S are discussed and specific environmental and economic benefits are demonstrated using data from the existing commercial installations.

Additional Key Words: ARD, Sulfur Reduction, Metal Recovery, Water Treatment

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Introduction

The treatment of acid rock drainage, or ARD, has been successfully managed through the application of conventional lime based water treatment systems, producing effluent which usually meets the required environmental standards. The introduction of more stringent water quality regulations for effluents has, however, resulted in some difficulties in meeting standards for some elements using lime alone. Moreover, the sludges produced in the process, which are typically composed of heavy metal hydroxides, usually have no commercial value and must either be disposed of on-site or shipped to off-site disposal areas, where they require long term storage and management. In some cases, the sludges do not meet solid waste extraction procedure criteria for metals such as Cd, and therefore are categorized as hazardous waste and must be either be disposed of in secure solid waste disposal facilities, at high cost, or disposed of on-site in lined sludge ponds. On site sludge ponds are themselves undesirable due to aesthetic and political concerns, land costs and long term environmental liabilities.

BioteQ Environmental Technologies Inc. has developed and commercialized the BioSulphide® Process in which low cost biogenic sulfide, or in some cases chemical sulfide reagent, is used to selectively remove metals from contaminated water (Rowley et al, 1996). The process produces a high grade, marketable, metal sulfide product even from low grade feed solutions (Lawrence et. al 2005, Kratochvil et. al, 2005). The product, instead of needing disposal, is shipped off the site to conventional metal refineries. The revenues generated from the sale of products may allow for water treatment at a profit in some cases, offset treatment costs in others, and generally reduce sludge disposal and management costs. The effluent produced from the process will meet stringent environmental standards, can meet bioassay requirements, and be suitable for direct discharge to the environment. The BioSulphide process has been commercially applied at three sites in North America, and capital and operating costs have been established over a wide range of plant sizes.

This paper provides a brief overview of biogenic H_2S production and presents operating results from commercial plants with an emphasis on applications of the technology for the treatment of ARD.

Biogenic Sulfide for ARD Treatment

The key advantages of the BioSulphide® process over conventional ARD treatment technologies involving lime addition are as follows:

- Lower overall treatment costs together with superior environmental performance and better resource recovery have been demonstrated at the commercial scale at various sites.
- The process allows heavy metals to be selectively recovered from contaminated water producing high grade, high value marketable metal sulfide concentrates.
- The metal recovery is extremely efficient, due to the low solubility of metal sulfides, allowing for successful operation on even low grade solutions.
- Sales of recovered metals may allow for water treatment at a profit or at least offset treatment costs.

- The process can reduce or eliminate the costs associated with the disposal of conventional water treatment sludges and reduce or eliminate the long term liability of on-site disposal of those sludges.
- The effluent produced by the process will meet lower metal specifications compared to effluent from conventional processes.
- The effluent may be discharged directly to the environment and has been commercially demonstrated to be non-toxic as measured by bioassay methods, without dilution.
- The effluent will typically have lower total dissolved solids (TDS) than conventional processes.
- On-site, on-demand production of sulfide using the BioSulphide® process results in low sulfide inventories and consequently fewer safety concerns related to transport and storage than using chemical sulfide systems.
- Lower metal sulfide solubilities typically means faster reaction kinetics and smaller plant footprint compared to lime based systems.
- The elimination of water treatment sludges avoids the geotechnical costs of pond construction and the costs associated with devoting valuable land to sludge ponds

The target metals are typically: arsenic, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, and Zn. Although the process can be operated as a stand-alone facility, it can be integrated with a conventional lime based treatment system for upstream metal recovery as sulfides followed by the removal of Fe and Al as hydroxides in the lime plant. Removal of the toxic heavy metals as saleable products improves the water quality of the lime plant effluent, can reduce reagent consumption, and reduces the liabilities associated with long term sludge management since the sludge would be assured of meeting solid waste disposal criteria. Since all the toxic heavy metals are absent, the lime sludge may be marketable as a cement admixture or an ingredient for brick making.

Biological Production of Hydrogen Sulfide and Metal Removal

In the BioSulphide® Process, hydrogen sulfide is produced by reacting elemental sulfur with an electron donor, such as acetic acid, in the presence of sulfur-reducing bacteria under anaerobic conditions according to reaction (1).

$$4\ S + CH_3COOH + 2\ H_2O \rightarrow\ 4\ H_2S + 2\ CO_2 \qquad (1)$$

The sulfur reducing bacteria act as a catalyst enabling reaction (1) to proceed kinetically forward at 25° C and the system pressure of +30 cm WC. A continuous production of H_2S is achieved by removing the gaseous products of reaction (1) from the bioreactor. The bioreactor is designed as a conventional stirred tank with the hydraulic retention time of several months. Since elemental sulfur and not sulfate is used as the sulfur source for generating H_2S, no process water other than that contained in the reagents enters the bioreactor. Thus the bioreactor becomes a true stand-alone H_2S generator. The main advantages of using the biological H_2S generation include:

- Low cost compared to the cost of Na_2S, NaHS, or compressed H_2S;
- Minimal hazards and increased safety mainly due to the low system pressure and low inventory of H_2S. At any point in time the amount of H_2S stored in the bioreactor(s) is a small fraction of the daily H_2S production. This often allows the avoidance of special permitting;
- Low capital cost mainly due to the ambient temperature and pressure in bioreactors that are designed as conventional stirred tanks compared to pressure vessels with expensive agitator seals; and
- Easy to scale-up and down over a wide range of H_2S production capacities;

The hydrogen sulfide produced is passed to an agitated, anaerobic contactor where metals are precipitated as sulfides which are then dewatered in a conventional clarifier – filtration circuit. Fig. 1 provides a simplified BioSulphide® process flowsheet in which a single metal product is produced. Metals can be precipitated selectively so that additional contactor – dewatering circuits can be provided to produce separate high-grade metal sulfide products that are shipped to a smelter for metal winning and refining.

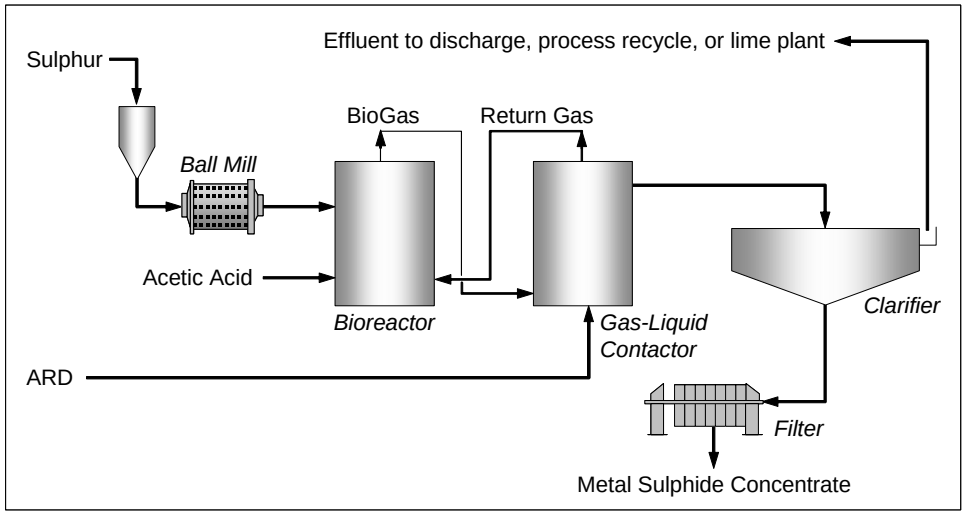

Figure 1. Simplified Flowsheet of the BioSulphide® Process

The BioSulphide® Process using sulfur differs significantly from conventional biogenic sulfide processes using sulfate as the electron acceptor for bacterial metabolism. Sulfate reduction is described variously elsewhere (Hammack et. al, 1994) but there are few examples of the process being commercialized (Tabak et. al, 2003) and no examples of profitable metal recovery from low grade leach solutions. There are two major advantages of the BioSulphide® process over the sulfate reduction process which have contributed to its commercialization: 1) sulfur requires one quarter of the quantity of electron donor compared to sulfate in the production of sulfide., resulting in a proportional decrease in equipment sizing and operation costs, and 2) the bioreactor is isolated from the metal bearing feed, which eliminates the need to heat the feed water to the bioreactor temperature, eliminates the inhibition of the bacterial culture by dissolved metals, and allows the operation of the bioreactor under optimum conditions at all times.

Commercial Examples

Three commercial plants have been built, commissioned, and operated by BioteQ, and a fourth plant is currently under construction. Three additional plants are in the engineering stage. The BioteQ plants are:

- Caribou, New Brunswick, Canada (220 gpm, 60 kg/d H_2S);
- Raglan, Quebec, Canada (880 gpm, 150 kg/d H2S); and
- Bisbee, Arizona, USA (2000 gpm, 3.7 tonnes/day H2S)
- Blackwell, Oklahoma, USA (300 gpm, 90 kg/d) – under construction
- Wellington-Oro, Colorado, USA (150 gpm 60 kg/d) – engineering and procurement in progress
- Britannia Mine, British Columbia, Canada – pilot testing and feasibility

Selected examples of commercial plants are described below.

Water Treatment at Raglan Mine, Quebec

The Raglan Ni mine is located on the Ungava peninsula in the Canadian arctic and is owned by Falconbridge Ltd. The wastewater treatment campaign lasts only 5 months of the year due to the extreme northern climate. Prior to the application of the BioSulphide® Process in 2004, the mine wastewater was treated using a Low-Density Sludge (LDS) lime treatment process. Initially, the sulfide-based treatment plant was operated alongside the original lime plant. Due to the low water temperature (close to 0ºC) and Ni being the only contaminant in the water at concentrations ranging from 10 to 40 mg/L, the lime treatment operated with an overdose of chemicals including lime, H_2SO_4, and a Fe^{+3} iron based coagulant in order to meet the Ni discharge limit of 0.5 mg/L. This resulted in a significant increase in the dissolved solids (TDS) of the water during treatment. The low density amorphous lime sludge was deposited in an open pit where difficulties with solids settling were often experienced. In 2005, the BioSulphide® plant has operated on its own and the plan is to phase out operation of the lime plant.

The engineering and construction of the BioteQ treatment plant was completed in less than 7 months in 2003 and the operation of the plant commenced in June 2004 following the spring thaw. Figures 2 and 3 show exterior and interior views of the plant. The discharge water quality objectives, including a) the Ni discharge limit and b) the toxicity tests, were met within 2 weeks of the plant start-up. Nickel was assayed both by standard methods employed by the Raglan Mine, and using independent laboratories, required for verifying environmental compliance. Similarly, toxicity assays employed rainbow trout, and were conducted by independent laboratories with results sent directly to the Quebec Ministry of the Environment. The Ni sulfide produced in the process is up to 40% Ni on a dry weight basis and has been successfully incorporated with the conventional Ni flotation concentrate produced at the Raglan mine and filtered using conventional filter presses. The product from the Raglan plant is shipped for refining along with the mine concentrate to the Falconbridge smelter in Sudbury, Canada. In the case of Raglan, the gross revenues from the Ni recovery represent roughly 25% of the water treatment costs, while the overall water treatment costs have been approximately halved compared to lime treatment.

Figure 2. Exterior of Raglan plant

Figure 3. Interior of Raglan plant

At Raglan, the improved environmental sustainability of Ni recovery when compared with on-site disposal of the Ni sludges from the conventional lime process has produced significant environmental and operational benefits. The elimination of the sludge formerly produced from water treatment is an integral part of the future mine development in that the open pit could be used for waste rock storage once the LDS lime treatment is eliminated.

Engineering, procurement, and construction of the new water treatment plant at the remote Raglan site were entirely managed by BioteQ, which is 100% owner of the plant. Falconbridge pays BioteQ a monthly plant lease fee, and a treatment fee of CAD$1.06/m3 of water treated. Therefore the reduction in water treatment costs and the environmental benefits were achieved with zero investment of capital and a minimum investment of staff time by the mine owner. Training, human resources and data management are handled by BioteQ, while Falconbridge have the responsibility for the procurement of plant consumables including process reagents and fuel for the remote power plant.

The schematic of the original lime plant and the new BioteQ water treatment is shown in Fig. 4. H_2SO_4 was added to the lime plant effluent to lower the discharge pH to compliance levels. A summary of the plant operating data is presented in Table 1. The plant feed flow and Ni concentration varies over the course of the 5 month treatment campaign, depending on the ice thickness and water temperature in the wastewater impoundment. The plant has demonstrated excellent reliability and availability in the 2005 treatment season, with plant effluent quality typically maintained around 0.15 mg/L Ni and mechanical availability of 88%, even when the feed water temperature fell below 1^{o}C. The majority of the plant down time has been due to maintenance of the plant's power plant.

Contaminated Groundwater Treatment at Blackwell, Oklahoma, U.S.

A new BioSulphide® treatment plant is currently being constructed in the city of Blackwell, Oklahoma, as part of a pump-and-treat system for contaminated groundwater. The plant is designed to treat up to 300 US gallons per minute of groundwater contaminated with 10 mg/L Cd and 100 mg/L Zn, originating from an old Zn smelter site, and will be required to meet the discharge limits of 0.4 mg/L Zn and 0.007 mg/L for Cd. The toxic metals will be removed in a single stage precipitation process yielding a Zn/Cd concentrate that will be shipped off site to a smelter. The chemical reactions taking place in the precipitation circuit can be written as follows:

$$CdSO_4(aq) + H_2S\ (g) + Na_2CO_3(aq) \rightarrow CdS(s) + Na_2SO4(aq) + H_2CO_3(g) \qquad 2$$

$$ZnSO_4\,(aq) + H_2S\,(g) + Na_2CO_3(aq) \rightarrow ZnS(s) + Na_2SO_4(aq) + H_2CO_3(g) \qquad 3$$

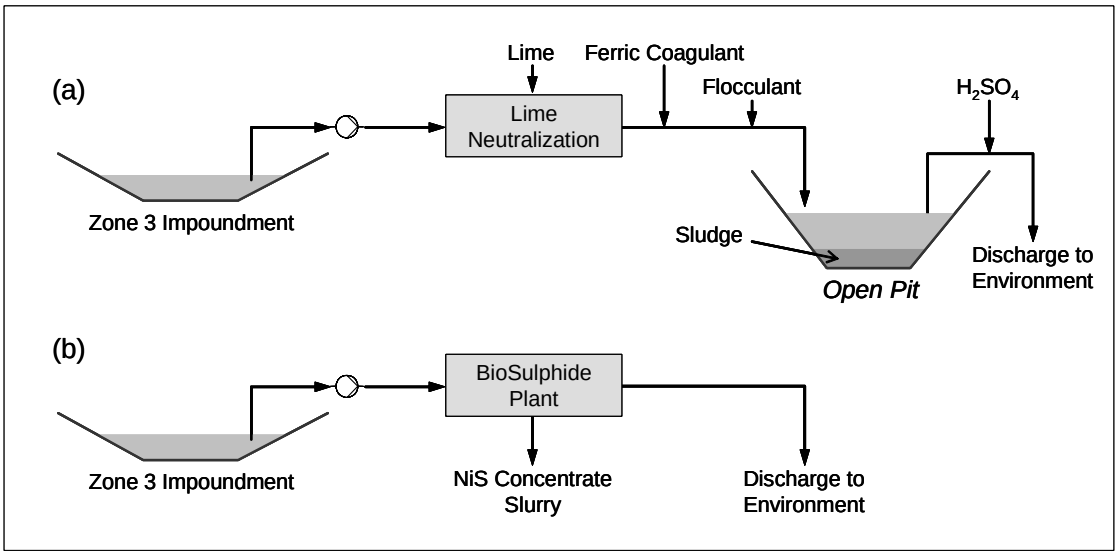

Figure 4. (a) Lime and (b) BioteQ minewater treatment at the Raglan Mine

Table 1. Summary of Raglan Operating Performance Data

Sulfide capacity	150 kg/d
Feed flow	140 to 180 m^3/hr
Feed pH	5.2 to 6.8
Ni concentration	10 to 40 mg/L
Average Effluent Quality	
Ni	0.15 mg/L
pH	8.2
Toxicity	non-toxic
Power Consumption	Genset capacity of 250 kW including building heat and heat tracing
Plant Capital Cost	CAD$ 1.8 Million (including building)
Capital Pay-back	3 years

Various sources of alkalinity may be used for neutralizing the free acidity released from H_2S but soda ash was selected in order to maximize the grade of the Zn product. Since the metal product will be saleable, no sludge will be generated that requires expensive disposal, and the revenues from the metal recovery will pay for concentrate handling and shipping. The contaminated site and the new BioSulphide® treatment plant are located within the city limits and the treatment plant will be installed inside a building equipped with a dual gas scrubbing system for protection against sulfide gas emissions.

The main advantages of applying the BioSulphide® process in Blackwell include:

- zero sludge production thus eliminating high sludge disposal costs,

- process performance guarantee to meet the Zn and Cd discharge limits,
- low on-site H_2S inventory that will not exceed 10 kg thus facilitating permitting and mitigating sulfide safety concerns.

Wellington Oro, Colorado, U.S.

The Wellington Oro Mine operated as a Zn-silver mine and has been closed since the 1970's. The Town of Breckenridge in Colorado, and the Summit County Open Space and Trails Department has selected BioteQ to treat water from the Wellington Oro Mine, which is located near Breckenridge. The selection of the BioteQ sulfide precipitation technology was approved by the US Environmental Protection Agency as the preferred technology for the site. Surface drainage from the mining area produces an acidic wastewater that requires treatment before discharge to the French Gulch tributary of the Blue River. The plant will be designed to treat acidic wastewater and recover Zn, Pb and Cd into a Zn-rich concentrate product for shipment off site for final refining. BioteQ is responsible for the design, construction and commissioning of the treatment plant and ongoing process maintenance. Lyntek, a Denver based engineering and construction company, will be BioteQ's partner on the project. It is anticipated that the plant will be constructed and commissioned in 2006.

The new water treatment plant will have a capacity of 150 US gallons per minute with a sulfide demand of approximately 60 kg/d. The treatment plant will remove Zn and Cd to discharge limits of 300 and 4 ppb, respectively. Zinc and Cd leaching from the Wellington Oro mine are recognized to be major contributors of metal loading to downstream tributaries and an objective of implementing water treatment will be to establish a new trout fishery in the Blue River. The Wellington Oro plant chemistry is very similar to that of the Blackwell plant, so the technical risks of the project are low.

The chief advantages of the BioSulphide process for Wellington Oro are as follows:

- Production of high quality water for discharge directly to the environment
- No waste sludge production which eliminates the need for long term storage requirements in an area of intensive recreational use and high land values
- Production of a saleable Zn product to partially off-set long term treatment costs

Britannia Mine Water Treatment

The Britannia mine, located on the coast 50 km north of Vancouver near Squamish, British Columbia, operated as a Cu mine from 1905 to 1974. Groundwater flow through the abandoned mine tunnels results in acidic effluent containing Cu, Zn, Cd and Pb along with Fe and Al that discharges into the ocean. Currently under construction to treat the ARD is a HDS lime treatment plant, designed, financed, built and to be operated by EPCOR Water Services Inc. in partnership with the B.C. Ministry of Sustainable Resource Management. BioteQ has acted in a senior review capacity during the design stage of the lime plant and is taking part in a pilot plant for a second phase involving the BioSulphide® process. The HDS plant was commissioned during the fourth quarter of 2005. The plant will produce clean water for discharge to the environment but will also produce a metal-laden sludge product that will be deposited on the site.

Piloting now under way will determine the feasibility, economic benefit and environmental improvement of incorporating the BioSulphide® process upstream of the lime plant. The

BioSulphide® process would remove toxic metals including Cu, Pb, Zn, and Cd from the mine drainage at relatively low pH. The BioSulphide® concentrate would be sent offsite for refining. The lime plant would then produce a sludge consisting mainly of Fe, Al and gypsum, reducing the disposal costs and/or long term liability which can be associated with toxic solid waste sludges. The pilot plant will also test the feasibility of using the non toxic lime plant sludge as a cement admixture and in brick making, which would eliminate the production of all solid water treatment plant waste at the site. Additional pilot work will test the effectiveness of the use of a hydrogen-rich gas as an electron donor for the bioreactor. The gas will be produced by BioteQ's Partial Oxidation System (POS) burning diesel or natural gas and the waste heat would be used in the brick making process. The pilot work is supported by EPCOR and the Industrial Research Assistance Program of the National Research Council of Canada.

Installation of a BioteQ plant upstream of the EPCOR water treatment plant, utilizing partial oxidation burner technology in combination with established sulphur reduction technology, could have the following environmental and financial advantages:

- reduced overall operating costs by reducing the lime consumption in the HDS plant
- recovery of a saleable metal concentrate, containing Cu, Zn, Cd and Pb, to off-set treatment costs as well as recycle the otherwise wasted metals to productive use
- production of a "clean" hydroxide sludge which could be used to form saleable construction materials that could eliminate sludge storage requirements in perpetuity as well as provide additional income to off-set treatment costs
- create a sustainable treatment solution for the Britannia site

Other Applications of the BioSulphide® Process

BioteQ has successfully engineered, constructed, commissioned, and operated a 2000 US gallons per minute and 3.7 tonnes sulfide/day biogenic system for Cu recovery from leaching of a low grade stockpile in Bisbee Arizona. The project is a joint venture with the property owner, Phelps Dodge, and is operated by the joint venture company, Copreco LLC. The stockpile leach formerly employed a cementation process for Cu recovery but it was decommissioned due to falling Cu tenor in the pregnant solution. The BioSulphide® plant was commissioned in 2004 and was designed to recover 3 million pounds of Cu per year with a payback on capital of less than 3 years.

Biogenic sulfide may be produced on-site and on-demand at low cost for a variety of other mining and mineral processing applications including:

- Separation of Mo from Cu in mineral flotation;
- Separation / purification of Ni and Co from laterite leach solution produced using Pressure Acid Leach (PAL); and
- Cyanide recovery using the Sulphidisation, Acidification, Recycling and Thickening (SART) process

Figure 5. BioSulphide® Plant for copper recovery at Bisbee, Arizona

Conclusions

The BioSulphide® technology developed and commercialized by BioteQ is proving to be an effective process both for environmental control and/or metal recovery either in standalone facilities or in combination with conventional lime treatment. Some key features of the technology are as follows:

- The BioSulphide process selectively removes metals from ARD and other acidic meta-laden effluents at low cost
- Economic metal recovery enables the reduction, and in certain cases the elimination, of water treatment plant sludges otherwise requiring expensive disposal.
- The BioSulphide Process has been successfully commercialized by BioteQ Environmental Technologies Inc who have engineered, built and operated three commercial plants ranging in size from 60 kg/d to 3.7 tonnes/day of H2S;
- The commercial plants have demonstrated that the BioSulphide Process permits a profitable recovery of metals such as Cu, Ni and Co from low grade solutions that cannot be processed economically by conventional technologies such as cementation or SX-EW;
- Relatively low capital cost of the BioSulphide plants have demonstrated to yield fast pay-backs hence permitting profitable metal recovery in projects with relatively short duration;
- The operating results from the existing plants show that the BioSulphide Process can meet strict environmental regulations regarding discharge of metals into the environment;
- The discharge from a BioSulphide treatment plant is non-toxic and passes bioassay guidelines

- The sulfide based system is more applicable to low water temperatures than the lime based system.

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