

REDUCING WATER TREATMENT COSTS WHILE MEETING THE CHALLENGE OF ENVIRONMENTAL COMPLIANCE FOR THE MINING INDUSTRY

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ABSTRACT

BioteQ Environmental Technologies is working on design-finance-build-own-operate water treatment projects with mining companies worldwide. Under this business model, BioteQ designs, builds and operates treatment plants without requiring financial or technical assistance from its customers to develop the projects. This business model accelerates the introduction of new technologies by reducing the financial and technical risks to the industry. Significant reductions in the cost of water treatment, and in some cases a net profit from the treatment, are generated. The profit and/or savings are shared between BioteQ, who operates the treatment plant, and the mine owner, who can focus on the core business of metal extraction. The technologies developed by BioteQ provide new tools for mine owners and planners to reduce local environmental and social impacts. Firstly, the company has commercialized the BioSulphide® and ChemSulphide™ processes in which low cost biogenic sulphide or, in some cases, chemical sulphide reagent is used to remove metals selectively from contaminated water. Secondly, BioteQ is currently in the process of commercializing a suite of ion exchange processes collectively known as Sulf-IX™ which are designed to provide a robust, low cost method for sulphate and TDS removal from mining wastewater. This paper provides an overview of the BioSulphide, ChemSulphide™, and Sulf-IX™ processes and highlights operating results from existing sulphide-based commercial plants and the results from recent Sulf-IX™ pilot plant campaigns in Chile and elsewhere in which effluent sulphate concentrations below 250 mg/L were achieved.

RESUMEN

BioteQ Environmental Technologies está trabajando en el diseño-financiamiento-construcción-posesión-operación de proyectos de tratamiento de agua con compañías mineras alrededor del mundo. Bajo este modelo de negocio, BioteQ diseña, construye y opera plantas de tratamiento sin requerir asistencia técnica o financiera de sus clientes para desarrollar los proyectos. Este modelo de negocio acelera la introducción de nuevas tecnologías mediante la reducción de los riesgos técnicos y financieros para la industria. También se generan reducciones significativas en el costo de tratamiento de agua y, en algunos casos, una ganancia neta por el tratamiento. Las ganancias y/o ahorros son compartidos entre BioteQ, que opera la planta de tratamiento, y el dueño de la mina, quien se puede concentrar en el negocio principal de la extracción de metales. Las tecnologías diseñadas por BioteQ proveen a los dueños de mina y a los planificadores con nuevas herramientas para reducir los impactos ambientales y sociales. En primer lugar, la compañía ha comercializado

los procesos BioSulphide® y ChemSulphide™ en los cuales se utiliza sulfuro biogénico de bajo costo o, en algunos casos, sulfuro químico, como agentes para remover de manera selectiva metales de aguas contaminadas. En segundo lugar, BioteQ se encuentra actualmente en proceso de comercializar un paquete de procesos de intercambio iónico que de manera colectiva se conocen como Sulf-IX™ los cuales están diseñados para proveer un método robusto y de bajo costo para la remoción de sulfatos y de TDS de aguas de desecho minero. Este artículo provee un panorama general de los procesos BioSulphide, ChemSulphide™, y Sulf-IX™ y resalta los resultados operativos de plantas comerciales existentes y los resultados de campañas de pilotaje recientes del Sulf-IX™ en Chile y otros países en donde se han obtenido efluentes con concentraciones de sulfato menores que 250 mg/L.

DRIVERS FOR NEW TECHNOLOGY

BioteQ Environmental Technologies Inc. is an industrial process technology company specializing in water and waste treatment for the mining and mineral process industries. BioteQ has chosen to emphasize the development of technologies that recycle wastes into useful products. The company focuses on water-related environmental issues faced by the mining industry and on water management issues. As a consequence of the company's work on environmental technologies, some of BioteQ's major shareholders are 'green' or 'sustainable' investment funds as well as international water funds.

The company has benefited from a three way convergence of: 1) the global increase in demand for the commodities produced by the mining industry 2) the concomitant increase of pressure on, and awareness of, environmental issues, and 3) increasing global scarcity of fresh water supplies. For example, at the time of the kickoff of BioteQ's first copper recovery project in 2003, copper was priced at roughly \$US 2,000 per tonne, (\$US 0.90/lb). Five years later, recent copper prices have topped \$US 8,800 per tonne (\$US 4.00/lb). While consumable and labor prices as well as construction costs in key markets have increased, the higher copper price provides an incentive for copper recovery. Meanwhile, the industry has seen rising incentives and pressures for new mines and expansion projects to apply the latest sustainable technology to aspects of their operation such as water use and waste disposal. In arid mining areas such as Australia, China and Chile, a lack of fresh water supplies is a significant barrier to development.

SULPHIDE TECHNOLOGY FOR WATER TREATMENT AND METAL RECOVERY

The BioSulphide® and ChemSulphide™ processes (Lawrence et al., 2005) are examples of successful commercialization of new technologies with existing full scale installations in the USA, Canada, Australia, and China. In the BioSulphide® Process, sulphide reagent in the form of H₂S is generated by the reduction of elemental sulphur in an anaerobic bioreactor and is used to precipitate heavy metals such as copper, zinc, nickel and cobalt selectively in a agitated contactor reactor. The precipitated metal sulphides are recovered using conventional clarification and filtration. The ChemSulphide™ Process is very similar but uses chemical sulphide reagent and is used primarily in smaller applications where the additional capital cost of providing a bioreactor is not justified. Advantages of both processes include:

- selective recovery of metal values as saleable sulphide concentrates

- elimination of the generation of heavy metal contaminated sludge along with the associated long term environmental liability
- production of effluents with very low metal levels to meet the most stringent environmental standards.
- can be operated at a lower overall operating cost than lime plants, when metal recovery is taken into account. In many cases, profitable water treatment is possible.

BioteQ currently has eight sulphide plants either operating or under construction ranging in sulphide capacity from 60 kg/d sulphide demand to over 3.7 T/d as S²⁻ and in hydraulic capacity from 35 m³/hr to 1000 m³/hr. Capital and operating costs have been established over a wide range of plant sizes.

Existing Mine Wastewater Treatment Practice – Lime Treatment

Lime treatment continues to be the most widely used process for wastewater treatment in mining but new challenges such as stricter effluent limits, concerns about the long term management of metal-laden lime sludges combined with the improved economic viability of metal recovery caused by rising metal prices has led to increasing attention to sulphide based water treatment.

Treatment of acidic metal-laden waste water from mining and metals processing industries has been practiced successfully for many years. While lime treatment has been the accepted convention, changing regulations highlight limitations of lime treatment:

- The treated water does not always meet new regulations with respect to dissolved metals and TDS (particularly with respect to sulphate), and
- The resultant lime sludge product represents a long term liability for the mine owner and can continue accumulating long after the mine ceases active operation.

An example of the impact of new regulation on conventional lime treatment is the Wellington Oro project in Colorado. Sulphide technology was selected instead of conventional lime treatment as the best technology for this site by the US EPA, primarily because there is no residual sludge produced and the ability to produce very low levels of metal in the treated water. While the plant is not yet commissioned, during piloting the process met the new effluent specifications with average effluent values of 0.6 ppb Cd and 52 ppb Zn during steady state operation, compared to the target effluent limits of 4 ppb Cd and 228 ppb Zn. Feed average values were 105 ppb Cd and 134,000 ppb Zn during the period. The plant is designed to produce a zinc rich concentrate for shipment off site and refining. The zinc-rich product from the pilot plant contained approximately 60% zinc on a dry weight basis. Samples of the zinc-cadmium sulphide product were tested under the toxicity characteristic leaching procedure (TCLP) to determine possible risks of storage and/or transport. The product passed the test with leachable cadmium levels below the detection limit. These data are taken from the pilot plant report prepared by BioteQ for the regulating authorities.

New Technology: BioSulphide® Process for Metal Recovery

Capital and operating costs of the BioSulphide® process are dependent on many site-specific factors but can be generically compared to alternative sources of sulphide used widely in the mineral processing and chemical industries such as:

- direct shipment of compressed H₂S gas;
- shipment of sulphide salts such as NaHS, Na₂S and Ca(HS)₂, and
- onsite production of H₂S from hydrogen and molten sulphur.

The direct shipment of H₂S gas may not be practical depending on local safety and permitting constraints unless a source is located very close to the point of use. A liquefied H₂S tank, for example, capable of storing 25T of sulphide or a one week supply for a typical project could render a 160m x 160m x 10m plant area lethal within minutes of a rupture, cause serious health and safety concerns over a much larger area and cause noxious odors over more than one square kilometer. Presumably, the siting of such a storage tank near a populated area would not be permitted. In the case of BioteQ's BioSulphide® plant in Bisbee, Arizona (Lawrence et al., 2007), the bioreactor generates up to 3.7 tonnes per day of sulphide but only retains 3.6 kg of H₂S inventory at any one time, making it a vastly safer plant than the compressed liquid alternative.

Sulphide salts are widely used but may be constrained by operating costs due to fluctuating commodity prices of the salt or of the contained alkali such as NaOH or lime. The cost of sulphide salt shipment may be constrained by transport costs for users located far from tide water or a rail link, particularly when the reagent is delivered as an aqueous solution. If the sulphide salt is shipped in flake form, then the energy cost of drying the chemical raises the unit cost and the stability of the product may be an additional concern. Finally, the use of sulphide salts may be constrained by processing concerns, such as their use in copper precipitation circuits where the presence of sodium, or the incremental increase in the pH of the process at the point of use are not desirable. In the case of the SART process (used in gold-copper ore processing), the savings in acid cost may also be significant through the replacement of a basic sulphide salt with acidic biogenic sulphide gas. These factors all tend to favour biogenic H₂S over the three alternative sulphide sources cited above.

When compared to other onsite production methods, such as a molten sulphur – hydrogen reactor, the BioSulphide® process would be more favourable in terms of capital cost due to the following factors:

1. The materials of construction used in a bioreactor for sulphide production may be carbon steel or FRP, whereas more expensive materials such as stainless steel or other corrosion-resistant alloys are used for the molten sulphur – hydrogen process.
2. The bioreactor operates at near atmospheric pressure, compared to the molten sulphur process, which takes place in pressure vessels, resulting in lower reaction vessel costs for biogenic H₂S production.
3. The bioreactor operates at near ambient temperature (~30°C) whereas the molten sulphur process takes place at elevated temperature; hence, biogenic H₂S production is at a lower energy cost and, again, uses simpler materials of construction.
4. The bioreactor may be a single large stirred tank with relatively simple low-cost controls, whereas the molten sulphur process is complex in comparison consisting of a hydrogen-generating plant, a steam plant, and a reactor vessel.
5. In cases where the point of use is not accessible by a natural gas line, then the cost of generating hydrogen for the molten sulphur process either by electrolysis or using liquid fuels may make the process cost prohibitive. The bioreactor, in contrast, uses inexpensive and readily transportable feeds including: granular sulphur, a waste product from sour-gas

processing, a carbonaceous nutrient source used by the microorganisms as an electron donor, and simple agricultural fertilizers.

Case Study: Raglan Water Treatment Plant

The most significant benefit of the ChemSulphide® Process, when compared to lime treatment for acid drainage, is the elimination of sludge production with concurrent recovery of valuable metals in a saleable form. The BioteQ plant, built in 2004 at Xstrata Nickel's Raglan Mine located in the Canadian Arctic, removes nickel from the mine drainage as NiS product which is shipped with the Raglan nickel concentrate off site for refining (Bratty et al., 2006). The process produces water with discharge quality which passed trout and daphnia bioassay testing on undiluted effluent. The process saves expenses that would otherwise be incurred for sludge handling and disposal while also generating income from the nickel recovered, which aligns the process with sustainable development principles. Overall, the cost of water treatment has been estimated to be half that of the lime and ferric chloride system that the BioteQ plant replaced based on data from the first year of operations and the last year of operations of the lime plant that was replaced.

The process reliability of the Raglan plant has been very high due to the joint BioteQ and Xstrata implementation of ISO14001 environmental management systems in 2006. The nickel concentration in the effluent is consistently reduced well below the nickel discharge criterion of 0.5 mg/L, regardless of the feed concentration.

Results

The plant operation has been continuously improved since commissioning in 2004. In 2007, the average nickel in the treated water was 0.136 mg/L in 2007 for a feed concentration range of 1.8 to 44 mg/L nickel. The water treatment capacity of the plant has almost tripled from the design capacity of 350,000 m³/year to over 900 000 m³/year while keeping the same environmental performance. The plant reliability, which is the amount of volume discharged compared to the amount of volume treated, has been increased from 86% in 2006 to 94% in 2007.

SULPHATE REMOVAL TECHNOLOGY

BioteQ has developed the Sulf-IX™ Process to remove sulphate from wastewaters and industrial process effluents to meet new sulphate regulations using ion-exchange technology. The process uses cationic and anionic resins to remove calcium and sulphate, respectively, and employs low cost reagents, namely sulphuric acid and lime, for resin regeneration. The products of the process are clean water, below 250 mg/L sulphate, and clean gypsum solids. The process offers significant technical advantages compared with all other available technologies, and promises to be the most cost effective method for sulphate removal.

A feature of sulphate contaminated waste water in mining is that the metal cations are nearly always balanced by the sulphate anion (SO₄²⁻). This is due to the fact that most metals are won from ore bodies containing minerals that contain sulphur atoms that oxidize to sulphate during the metal extraction process or due to natural oxidation processes in the waste rock and tailings. Furthermore, sulphur-containing reagents such as H₂SO₄ are often added to the metal extraction process. For example, the extraction of copper by leaching with sulphuric acid is widely practiced on very large

scale in many countries. The winning of 1 kg of copper can result in the addition of up to 3 kg of sulphate or more, depending on the degree of additional sulphate-producing reactions taking place in mining wastes due to oxidation of residual sulphide minerals.

The fundamental requirement of any process to remove sulphate from water is that it has the capability to meet the regulatory limits imposed. Traditionally, metals and the associated acidity in wastewater have typically been removed by precipitation and neutralization by adding lime, normally as calcium hydroxide. Reaction with lime removes metals by precipitation as hydroxides and also causes the removal of sulphate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). However, the effluent from a lime plant will always contain soluble sulphate, usually in the range 1,600 – 1,800 mg/L, due to the solubility of gypsum. Consequently, lime plants cannot produce effluents with a sulphate concentration lower than 1,600 mg/L, well in excess of current regulated values for sulphate in many jurisdictions.

Several technologies are either commercially available or are promoted as being able to remove sulphate. These include:

- Membrane technologies, such as reverse osmosis
- Processes based on “ettringite” formation (SAVMIN and CESR)
- Biological sulphate reduction (active and passive)
- Precipitation with barium

Figure 1 shows a simple schematic of the Sulf-IX™ process.

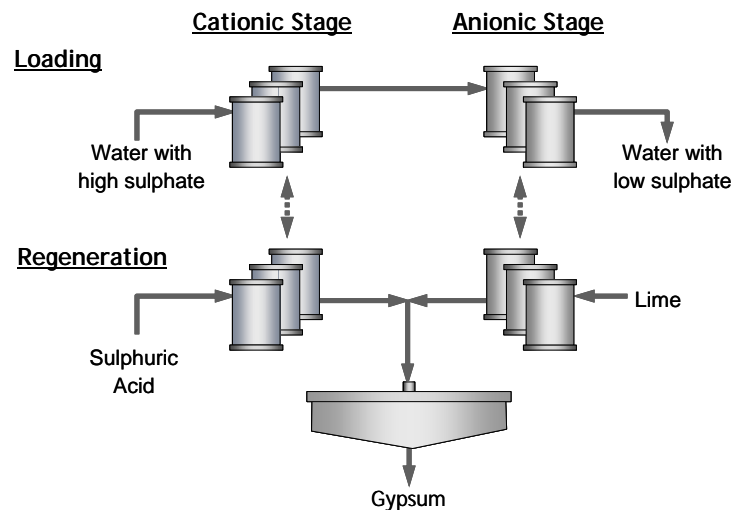


Figure 1. Simple schematic of the Sulf-IX™ Process

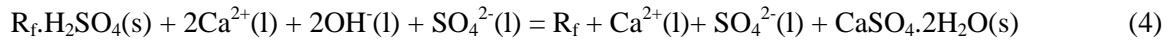
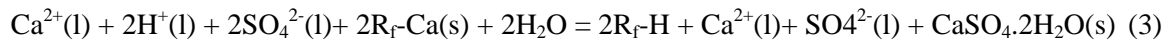
The process is particularly suited for the removal of sulphate from lime plant effluent but is applicable for the treatment of any process stream, groundwater or wastewater high in Total Dissolved Solids (TDS) and Ca/Mg hardness. The complete process cycle includes resin loading, regeneration and rinsing. Feed water is first passed through a series of contactors containing cation exchange resin to remove primarily calcium and magnesium by loading the cations onto the resin,

and then through contactors containing anion exchange resin to remove sulphate (equations 1 and 2).



where, (s) and (l) represent solid and liquid phases, respectively, and R_f depicts the resin functional groups.

Ion exchange resins have finite capacities to remove ions from feed water hence must periodically undergo regeneration (equations 3 and 4).



As can be seen from reaction (3), sulphuric acid is used for cationic resin regeneration. Solid gypsum dihydrate formed during regeneration is separated from the spent regenerant solution in a clarifier and, following the addition of H_2SO_4 , the “refreshed” regenerant solution is 100% recycled to resin regeneration in subsequent resin cycles. Similarly, reaction (4) shows that lime is used for anionic resin regeneration, with gypsum formed and separated in a clarifier. Following the addition of $\text{Ca}(\text{OH})_2$, the “refreshed” regenerant solution is 100% recycled to resin regeneration in subsequent resin cycles.

The technology was initially based on the GYP-CIX technology developed in South Africa, which also uses sulphuric acid and lime for resin regeneration. The Sulf-IX™ process, however, overcomes difficulties of the GYP-CIX process associated with limited process flexibility for varying feed chemistry, mechanical entrainment of gypsum in the regeneration stage, and limitations on sulphate removal when magnesium is present in significant concentration in the feed water. These and other process developments have resulted in a significant reduction in the estimated costs of constructing and operating a commercial plant. Estimates carried out on a number of potential applications indicate that the operating cost to reduce sulphate from the concentration of a typical lime plant effluent to less than 500 mg/L will be in the range US\$0.60 to \$6.00 per m^3 depending on several site specific factors, including the scale of the plant flow and the concentration of magnesium in the feed. Magnesium can also load on the cationic resin but its removal is much lower than calcium due to the high solubility of magnesium sulphate relative to calcium sulphate and can therefore build up in the cation resin regeneration circuit. If this is the case, treatment of a bleed from the cation regeneration circuit is required to remove magnesium from the circuit, and is part of the Sulf-IX™ technology.

Pilot Results of the Sulf-IX™ Process

Pilot programs have been conducted on simulated and actual effluents from three different locations. In all cases the feeds had a pH of >8 and were saturated in gypsum and therefore represented the water quality which might be expected following lime treatment of mining wastewater.

In theory, the solubility of gypsum at saturation is 2.37 g/L as dihydrate, equivalent to 551 mg/L as calcium or 1322 mg/L as sulphate. In practice, feeds to the pilot plant cation stages varied from 570 to 730 mg/L as Ca, even though no appreciable levels of solids were present in the feed. Effluents from the cation stage were easily reduced to 30 mg/L as Ca in over 100 cycles. The sulphate concentration in feed to the anion stages varied between 1400 and 2100 mg/L. Effluents containing down to 230 mg/L sulphate over 100 cycles were achieved. Lower effluent values for Ca and SO₄ are possible but at increased unit costs so meeting lower values depends on the owner's economic and environmental constraints. The variability of the feeds demonstrates that a system to treat water discharging from the lime treatment system must be robust enough to handle this variability in the solubility of gypsum.

In a particular run of over twenty cycles in the cation stage, the average feed and effluent Ca concentrations were 620 mg/L and 52 mg/L respectively, with an average resin capacity of 0.37 meq/L achieved. In contrast, in a different set of 23 cycles, the average feed and effluent concentrations were 730 mg/L and 77 mg/L respectively, and the average resin capacity was 0.89 meq/L. These data indicate that if higher effluent Ca levels can be tolerated, then the columns loading cycles can be extended and the resin capacity increased.

In the anion stage testing, the sulphate removal from 1,600 mg/L to 230 mg/L was achieved in a particular set of fifteen cycles, giving an average resin capacity of 0.8 meq/L. These data provide a basis for the sizing and costing of a particular application of the Sulf-IXTM technology.

The main conclusion of piloting efforts has been that the process is capable of meeting low effluent targets, while the formation of solid gypsum during the regeneration step can be controlled, blinding of the resin beads can be avoided, resulting in long resin life. This has been demonstrated in three extensive programs having a total of nearly one thousand regeneration cycles.

Commercial Status of the Sulf-IXTM Process

BioteQ has piloted the Sulf-IXTM process in the United States, Canada and Chile, and is currently working with a number of companies around the world on sulphate reduction projects. It is anticipated that a (>100 m³/h) commercial demonstration plant for the Sulf-IXTM technology will be operated in 2008 or early 2009 in the United States. In addition, BioteQ has a construction and operating agreement with Molybet (Molybdeno y Metales, S.A.) of Chile to provide the technology for final water treatment to remove calcium and sulphate from solution on a finance-build-own-operate basis. Application of the Sulf-IXTM technology at Molybet would replace the existing soda ash softening and reverse osmosis plant and associated evaporation and crystallization plants, to provide a high recovery of treated water to meet a water quality discharge requirement of 250 mg/L sulphate.

INTEGRATED PROCESSING CONCEPT

BioteQ has introduced the concept of total mine waste water treatment that combines three technologies to produce clean water and eliminate the generation of solid waste products that require long term environmental management as shown in Figure 2.

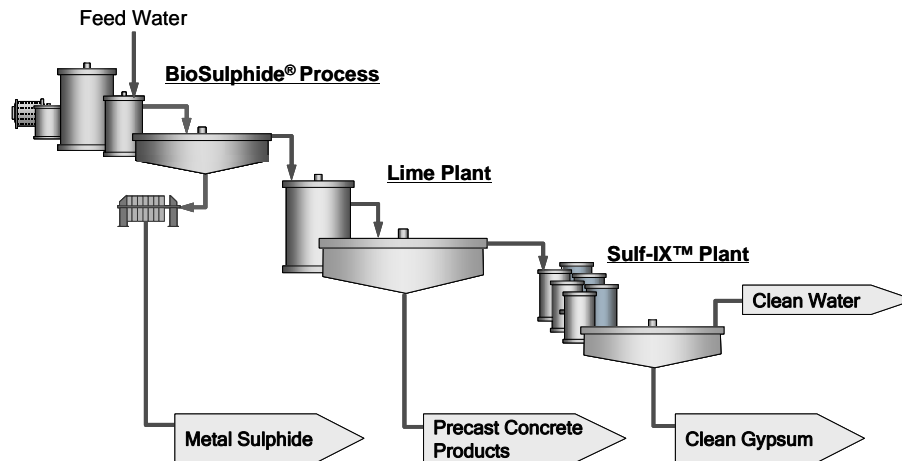


Figure 2. Integrated processing for total water treatment

In the first stage, heavy metals are recovered selectively and the concentrate(s) are sold to a refinery to generate a revenue base to off-set treatment costs using sulphide technology. Next, iron and aluminum are removed using lime and the heavy metal free sludge maybe used in the production of pre-cast concrete construction materials, again as a revenue base to off-set treatment costs. Finally, sulphate is lowered to meet stringent water quality standards for irrigation, disposal or process recycle using ion exchange technology described above, which provides the potential to produce saleable quality water in certain locations.

The sulphide technologies required for the first stage are now fully commercialized. BioteQ has operated a pilot facility at the Britannia Mine site in British Columbia, Canada to identify the critical factors for commercial scale up of the lime sludge processing stage, and the first two commercial plants for the Sulf-IX™ technology are scheduled for construction in 2008.

CONCLUSION

As demands on the mining industry intensify, and commodity prices remain high, industry leaders will continue to seek to apply new technology and will be rewarded in doing so. BioteQ provides a business model for such companies to introduce new technology to their operations with the minimum of risk. BioteQ has developed two significant water treatment technology platforms, namely: 1) the BioSulphide Process® and ChemSulphide™ Process for water treatment and concurrent base metal recovery and 2) the Sulf-IX™ group of technologies for sulphate removal from mining wastewaters for water discharge or for recycle. These technologies can be integrated with existing technologies to provide additional treatment benefits.

The sulphide-based processes have been demonstrated at four operating commercial plants with flow rates up to 1000 m³/hr and sulphide demand up to 3.7 T H₂S per day. The sulphate removal processes have been demonstrated under extensive pilot testing over several years, meanwhile the first commercial scale plant is expected to be built in 2008. The sulphide and sulphate technology platforms may be integrated with conventional lime treatment, to provide a sustainable water treatment alternative to conventional practice. BioteQ is an example of an industry service

provider that has specialized in the field of water treatment and metal recovery. As such, the company benefits from trends of increased metal values, higher costs for fresh water and increased awareness of more sustainable mining practices. BioteQ's focus on a narrow area of business creates synergies in human resources, training, operations management and technical support, while reducing technical and economic risk for its client and partners.

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