

Innovations in Ion-Exchange Technology for the Removal of Sulfate

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ABSTRACT:

In response to rising concerns about the effect of sulfate on water quality, human health, and agriculture, many jurisdictions around the world are imposing tighter regulations for sulfate discharge. This is driving the need for environmental compliance in industries like mining, metal processing, pulp and paper, sewage treatment, and chemical manufacturing. Technologies to treat sulfate include reverse osmosis, processes based on ettringite formation, biological sulfate reduction and precipitation with barium. Typically these technologies have one or more technical and economic limitations. BioteQ Environmental Technologies Inc. has developed a new ion-exchange technology which addresses these limitations and produces clean partially de-mineralized water that meets new sulfate regulation and a saleable gypsum product. This paper will profile this new ion-exchange technology, and provide two case study examples of commercial application.

BACKGROUND

SULFATE IN MINING EFFLUENTS The mining, mineral processing and metal production industry often generates wastewater streams with elevated concentrations of metals such as copper, zinc, cadmium, lead, manganese, nickel, iron, aluminum and magnesium. These metals can be present in process solutions, which may require treatment prior to disposal or recycle within a metallurgical process, or are present in site drainage due to natural reactions that take place within mining waste rock piles and tailings. The latter source of contaminated water is often termed acid mine drainage, or sometimes acid rock drainage, and is one of the most critical environmental issues that the industry faces today.

A feature of these wastewaters is that the metal cations are almost always balanced

by the sulfate anion (SO_4^{2-}). This is generally a result of metals extraction from ore bodies with minerals that contain sulfur atoms that oxidize to sulfate during the metal extraction process or due to natural oxidation processes in the waste rock and tailings. Furthermore, sulfur-containing reagents such as H_2SO_4 are often added to the metal extraction process. For example, the extraction of copper from oxide ore by leaching with sulfuric acid is widely practiced on very large scale in many countries. The winning of 1 pound of copper can result in the production of up to 3 pounds of sulfate or sometimes more. Consequently, large amounts of sulfate are typically present in mine, metal extraction and refining wastewaters.

THE NEED TO REMOVE SULFATE FROM WATER Historically, sulfate in water has not generally been subject to regulation. However, with the increasing realization that global water resources are limited and are declining as the

population grows and consumption increases, stricter regulations of water quality are being imposed to allow for its re-use or its safe disposal into the environment. For sulfate this has meant the introduction of water quality regulations in a number of jurisdictions worldwide to respond to the need to protect the health of humans, domestic animals, agriculture, and the fauna and flora in the environment.

For example, Chile has recently changed its regulations with respect to the discharge of waters containing sulfate, limiting sulfate to 250 mg/L for irrigation, 500 mg/L for discharges to groundwater, and 1,000 mg/L for discharges to bodies of surface water. Similar regulations are proposed or have already been enacted in other parts of the world, including Europe, Canada, the US and Australia.

Sulfate is not toxic to humans except at very high concentrations, however, it does increase total dissolved solids (TDS), or salinity, impart taste and odor to drinking water at lower concentrations and can cause digestive disorders at concentrations that are typically found downstream of mining and other industrial operations. For domestic and wild animals, drinking water containing sulfate can cause similar ailments and possible reproductive disorders. Moderate concentrations of sulfate in water used for irrigation can reduce agricultural crop yields due to the TDS by causing osmotic stress. On a broader scale, continual exposure to sulfate-bearing waters, causing increasing salinity, can have an adverse effect on chemical and biological processes essential to the health of soils, lakes, rivers, wetlands and estuaries. Sulfate, when present in the environment with organic material, can cause the growth of sulfate reducing bacteria and, in turn, the contamination of waters with sulfide, often leading to fish kill.

In addition to environmental concerns, sulfate, particularly as calcium sulfate, can cause problems in process waters due to scaling of boilers, heat exchangers, agitated tanks, pumps, pipelines and other process equipment. Failure to deal with the sulfate issue can increase costs significantly due to reduced volumetric capacity, reduced metallurgical performance, increased downtime for mechanical de-scaling and premature equipment failure.

TECHNOLOGY DESCRIPTION

REQUIREMENTS FOR SULFATE REMOVAL TECHNOLOGIES APPLIED TO MINING EFFLUENTS

The fundamental requirement of any process to remove sulfate from water is that it has the capability to meet the regulatory limits imposed. Traditionally, dissolved metals and the associated acidity in wastewater have 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 sulfate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). However, the effluent from a lime plant will always contain soluble sulfate, usually in the range 1,600 – 1,800 mg/L, due to the solubility of gypsum. Consequently, lime plants cannot produce effluents with a sulfate concentration lower than approximately 1,600 mg/L, well in excess of the regulated values for sulfate.

For a sulfate removal technology to be successfully applied to mining effluents on a large scale, it must not only be capable of removing sulfate to the regulated concentrations, the technology must also meet the following criteria:

- Produce effluent water with sulfate below CaSO_4 saturation levels.
- Recover a high proportion of the feed water.
- Be able to remove sulfate from feed wastewater supersaturated with CaSO_4 hence have extremely high scaling potential. The technology must offer an effective management of scale formation.
- Deal effectively with solids that are either present in the feed (unreacted CaCO_3 , CaSO_4 or other suspended solids) or that are formed during the sulfate removal process.
- Produce by-products that do not require high cost disposal or could be recycled, which means that they should be non-hazardous/non-toxic and relatively low in volume.
- Should be a low-cost process, both with respect to capital and operating costs.
- Be broadly applicable to allow easy transfer from site to site, i.e. not be dependent on special local conditions.

- Be able to handle large hydraulic flows, common to mining applications.
- Employ simple and robust chemistry and physics of sulfate removal to minimize process upsets, reduce process monitoring and labor supervision costs.
- Provide partial removal of sulfate from approximately 1,800 to 1,000 mg/L or less as required.

TECHNOLOGIES FOR SULFATE REMOVAL

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

Lime Precipitation is the simplest and lowest cost alternative to remove sulfate from water, however, can only remove sulfate to the gypsum saturation level of approximately 1,800 mg/L as noted above. It can serve as a pre-treatment stage to treat sulfate-laden water prior to treatment by one of the following methods.

Membrane technologies, such as reverse osmosis are commercially the most common compared to other alternatives listed here. Membrane technology is an effective method for sulfate removal, however, there are technical and economic limitations including:

- Treated water recovery can be as low as 50% of the feed volume due to concerns about scaling the membranes, with the remainder reporting to a reject stream that requires disposal, which may be difficult to dispose of or require further high cost processing such as evaporation and crystallization for final treatment.
- High calcium and sulphate levels in membrane process feed lead to membrane fouling. Feed softening upstream of conventional membrane process is a pre-requisite. Sodium added during the softening stage to reduce scaling increases the TDS of membrane feed and accumulates in the reject.
- High capital costs, and poor economies of scale for large installations; membrane cost generally increases linearly with the filtration area.
- High operating cost due to high power consumption and cost of feed softening.

- Cannot operate in the presence of solids in the feed water, requiring pretreatment by filtration.

Processes based on "ettringite" formation – ettringite formation has limited commercial application due to:

- Difficulty with maintaining ettringite formation as the only sink for sulfate under the basic process conditions.
- Difficulty with responding to feed chemistry fluctuations.
- The processes have not been commercially demonstrated.
- The processes require the addition of a large amount of relatively costly reagents containing aluminum, which generate a large amount of aluminum-containing waste.
- The processes are generally not considered for cases where low levels of sulfate in the effluent are required.

Biological sulfate reduction (active and passive) – has been used in only a few commercial applications due to limitations such as:

- The process requires a large input of energy to raise the feed water temperature to a level that supports efficient growth of the sulfate reducing bacteria.
- The process requires a large input of a relatively costly organic reagent to act as an electron donor for the bacteria to reduce sulfate.
- The process generates a quantity of dissolved sulfide, a toxic substance equivalent to the sulfur removed from the water.
- The process encounters difficulties with separation of the slow growing sulfate reducers from the effluent and the requirement for very large vessels with many hours of retention time.
- The process is adversely affected by the presence of dissolved oxygen in the feed water, and thus must be pre-treated to remove oxygen.
- Wetland systems or the passive process is only suitable for very small flows, such as 20 Lpm.
- Many operators have struggled to achieve consistent steady state operation.

Precipitation with barium – has been used at a number of small sites, but has several limitations:

- a The process uses a relatively costly reagent containing barium.
- b The process in turn produces a large amount of barium-containing waste which can be difficult to dispose of.
- c Barium is not commonly available at mine sites.

Ion Exchange – a new ion exchange process developed in-house is the only process that potentially fulfills all of the requirements for sulfate removal in mining effluents, as follows:

- a The only waste stream produced is solid gypsum which forms under ambient temperature and pressure, is non-toxic, non-hazardous, low volume, and in fact could be reused in manufacturing of low cost construction material such as drywall, and/or certain type of precast concrete based products, and as a fertilizer additive.
- b The process has robust chemistry based on low cost, commercially available resins (water softening type) over a relatively wide range of temperatures.
- c The process can cope with the presence of solids due to the unique reactor design of the ion exchange contactors developed in-house.
- d Low operating cost, mainly due to the use of lime and sulfuric acid as the two primary reagents consumed in the process, compared to soda ash and electron donor reagents required for membrane and biological sulfate removal processes, respectively.
- e Operating costs are also low due to low power consumption compared to membrane processes and biological sulfate reduction.
- f Low capital cost compared to membrane processes and biological sulfate reduction.
- g A more efficient means of dealing with scaling compared to membrane processes.
- h Ion-exchange is ideally suited to the partial removal of sulfate as the mass transfer is fast and the equilibrium/driving force is high at

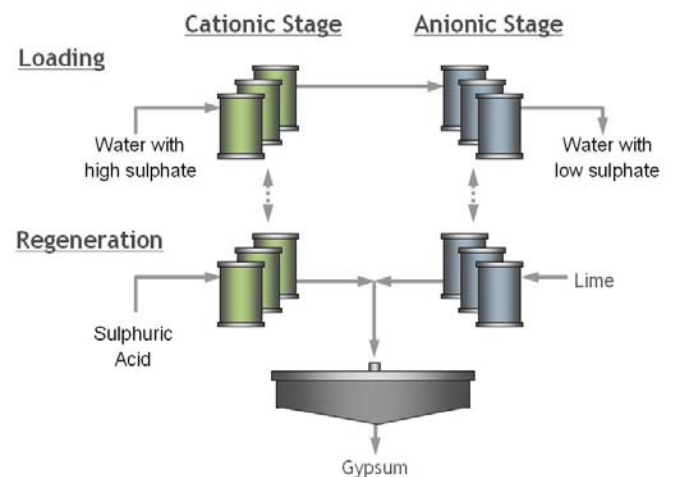
sulfate concentrations over 100 mg/L. The “leakage” of ions that is typically perceived as a negative aspect of ion exchange in most water treatment applications, is acceptable and translates into cost reduction.

- i Water recovery in the ion exchange process is high since the waste product is solid, unlike membrane technologies in which a significant volume of brine, containing high concentrations of sulfate and other ions, is produced.
- j The product water is partially demineralized. The ion exchange process can achieve a significant reduction in the TDS level from the wastewater.

PROCESS DESCRIPTION

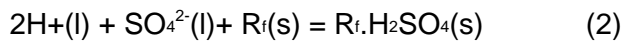
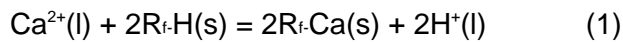
The new ion exchange process described is a two stage process employing two different resins to achieve demineralization of the feed by removing calcium and sulfate ions (Ca^{2+} and SO_4^{2-}) from water. The resins are regenerated using low-cost reagents, sulfuric acid and lime, so that the only products of the process are reusable/dischargeable water and a solid gypsum product that might also have value, depending on local market potential. Figure 1 shows a simple schematic of the process.

Figure 1: Sulf-IX™ Ion Exchange Process for Sulfate Reduction



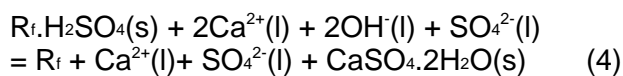
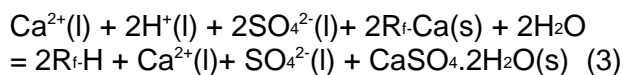
The process is particularly suited for the removal of sulfate from lime plant effluent but is applicable for the treatment of any process

stream 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 sulfate (equations 1 and 2).



where, (s) and (l) stand for 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), sulfuric 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. Gypsum forms during regeneration, however, does not interfere with the calcium removal process. Commercially available technical grade lime and sulfuric acid are used in regeneration.

The technology was initially based on an ion exchange technology developed in South Africa, which also uses sulfuric acid and lime for resin regeneration. The new ion exchange process, however, eliminates the need for resin

movement in the process, maximizes resin capacity, improves the separation of gypsum from resin, and allows efficient sulfate removal from wastewater rich in magnesium. These and other process developments have resulted in a significant reduction in the estimated costs of constructing and operating a commercial plant. Pilot results to date show that the resin loss/fouling cost is less than 5% of the operating cost of the process. There is little change in the leakage pattern from run to run.

The composition of the feed water must be considered when setting the treatment targets for sulfate removal, especially if there is not a lime plant upstream of the ion exchange plant. One of the main limitations of ion exchange for sulfate removal is that it removes primarily Ca^{2+} and SO_4^{2-} while letting all other ions, including K^+ , Na^+ , and Cl^- , and most of the Mg^{2+} , pass through to the effluent. Unique to this new process where the only product produced is solid gypsum, there is very little K^+ and Na^+ removed while some Cl^- is removed but not preferentially to sulfate. The extent of the magnesium removal is controlled by a small continuous bleed of regenerant from the cation circuit which enhances the uptake of Mg by the cation resin. The amount of Mg loaded equals the amount bled under complete regenerant solution recycle. Where sodium is the cause of elevated sulfate in the effluent a “polishing” stage can be added using short bed contactors charged with Strong Base Anion (SBA) resin, using NaOH for resin regeneration, producing a concentrated solution of Na_2SO_4 that would require disposal.

Conventional up-flow fluidized bed contactors are employed in both the cation and anion stages and materials of construction that can be considered include HDPE, FRP or SS316L for the cation circuit and HDPE or FRP for the anion circuit (due to the potential buildup of chloride in the anion circuit regenerant solution SS316L is not recommended for the anion circuit).

COMMERCIAL CASE STUDIES

The company has piloted the new ion exchange process in the United States, Canada and Chile, and is currently constructing two commercial demonstration plants. The first commercial scale demonstration plant (>100

usgpm) is being built in the US to treat a contaminated ground water source directly by ion exchange, to produce a treated water containing less than 500 mg/L sulfate. The second commercial demonstration plant under construction is designed to treat 350 usgpm of a refinery bleed stream, following heavy metal removal and sulfate reduction to saturation by conventional lime precipitation, and replace an existing reverse osmosis plant and associated evaporation and crystallization circuits. The treatment objective of the second plant is to provide a high recovery of treated water to meet agricultural quality requirements of 250 mg/L sulfate content.

CASE STUDY 1 – GROUNDWATER The first commercial demonstration plant, currently under construction, has been designed from pilot data to treat a groundwater stream located at a mine site in the US. The feed water to the ion exchange plant is expected to have the following composition:

<u>Parameter</u>	<u>Maximum</u>	<u>Average</u>
Flow (usgpm)	125	125
pH	7.9	7.1
Ca (mg/L)	600	450
Cl (mg/L)	200	120
Mg (mg/L)	150	100
Na (mg/L)	250	140
SO4 (mg/L)	2,100	1,500

The treatment target for this plant, for the average feed water composition, is 400 mg/L sulfate, with average concentrations of 85 mg/L calcium, based on the pilot results. The sulfate target is determined by the feed water composition – in this case, only 70% of the feed sulfate is balanced by calcium, with the remainder as sodium sulfate. To remove sulfate to <250 mg/L (which is the regulated target in some jurisdictions) a polishing stage using SBA resin can be employed, as described above.

A process flowsheet and simple mass balance for Case Study 1 is shown in Appendix A. Resin losses are expected to be low based on pilot testing to date as well as full scale testing of the contactors that will be used in this plant. The resin inventory is 1 m³ in the cation stage and 1.7 m³ in the anion stage. Direct operating costs are expected to be \$US 9.70 per 1,000 US gallons treated (or about \$US

0.80 per pound of sulfate removed). The plant is being constructed by the mine owner and therefore the capital cost estimate is not available for publication. The ion exchange plant will be provided on a fee basis.

CASE STUDY 2 – LIME PLANT EFFLUENT

The second commercial demonstration plant currently under construction has been designed to treat a lime plant effluent stream located at a refinery. The ion exchange plant is designed to replace an existing reverse osmosis (RO) plant that was commissioned in 2006. The RO plant and related evaporation and crystallization plants perform well to remove sulfate, however, the operating costs have been unacceptably high for the owner. The feed water to the ion exchange plant is expected to have the following composition:

<u>Parameter</u>	<u>Maximum</u>	<u>Average</u>
Flow (usgpm)	350	350
pH	9.8	9.2
Ca (mg/L)	550	430
Mg (mg/L)	200	80
NH4 (mg/L)	6,490	5,440
SO4 (mg/L)	19,700	14,600

The treatment target for this plant, for the average feed water composition, is <250 mg/L sulfate to meet agricultural water regulations, again based on pilot plant results. To meet this target the refinery plant will be minimizing the use of sodium based reagents to avoid the use of a polishing stage for sodium removal. It is important to note the ammonia content of the feed water to the ion exchange plant. In this particular case an ammonia regeneration stage will be added to the plant to allow treatment of the contained sulfate as well as generate a revenue stream to off-set plant operating costs.

Based on pilot testing the operating costs are estimated to be \$US 18 per 1,000 US gallons treated (or about \$US 1.50 per pound of sulfate removed). The capital cost of the ion exchange plant, including all construction directs, indirects, and commissioning costs is expected to be \$US 7.3 million, including the ammonia regeneration circuit. This circuit will result in a net benefit from sale of recovered ammonia sulfate of about \$US 13 per 1,000 US gallons. For comparison the capital cost of the RO plant was about \$US 20 million and the

operating cost is about \$US 80 per 1,000 US gallons treated, including evaporation / crystallization of brines and disposal of contaminated ammonia salts.

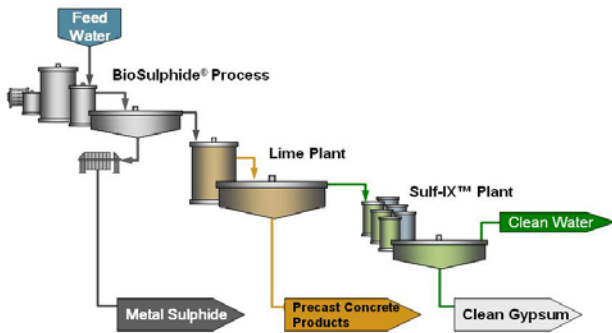
TOTAL WATER TREATMENT SOLUTION

The ion exchange technology can also be integrated with commercially proven sulfide treatment technologies, as well as lime neutralization, in what the Company calls the Total Water Treatment concept. At many mining and other industrial sites, wastewater and process streams contain metals and sulfate which must be removed to allow discharge of a final effluent which meets both metal and sulfate regulations. Total water treatment is illustrated by the schematic flowsheet shown in Figure 2. By integrating these three technologies, mining effluents can be treated to remove all regulated components of the contaminated water with the potential of producing no solid or liquid waste products requiring further treatment or long term storage.

metals such as iron and aluminum, and sulfate down to a concentration of 1,600 – 1,800 mg/L. Since the heavy metals can be removed in the upstream sulfide process, the sludge produced in the lime plant could be essentially free of toxic metals and could, therefore, be considered for use as a filler material for precast concrete construction materials.

Finally, the new ion exchange process described above would be used to remove sulfate from the lime plant effluent down to the regulated concentration (usually 250 mg/L). Since essentially all other components have already been removed from the water, the products from ion exchange would be clean gypsum, which could be used as an agricultural supplement or used in construction materials, and clean water, which could provide a revenue stream for residential, industrial or agricultural use.

Figure 2: Total Water Treatment



The contaminated water would be first treated using patented sulfide technology to selectively remove and recover valuable metals such as copper, nickel, cobalt and zinc into saleable, high-grade metal sulfide products. As has been proven several commercial plants built to date, if the metal concentrations are sufficiently high in the feed, this initial stage of treatment can provide a rapid payback of capital and ongoing profitable operation, and could significantly offset the costs of the subsequent two stages of treatment.

The sulfide plant effluent would pass to a conventional lime plant to remove remaining

APPENDIX A – PROCESS MODEL, CASE 1

Process Model - Case 1

