A REVIEW OF SULFATE REMOVAL OPTIONS FROM MINE WATERS

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ABSTRACT

Sulfide oxidation of pyritic material leads to high concentrations of sulfate in contact waters. Levels of sulfate can vary from a few hundred mg/l to several thousand mg/l. At very high concentration (> 1000 mg/l) sulfate has a purgative effect and is considered corrosive on concrete and cement. Current legislation worldwide places a limit around 400-500 mg/l on groundwater and 2000 mg/l on industrial effluent. Consequently some treatment is required.

Various treatment options are available for sulfates involving physical, chemical and biological processes. The selection of a treatment option is primarily dictated by sulfate and calcium concentrations. Conventional desalination techniques cannot be economically applied for treating most mine waters due to the problem of CaSO₄ scaling. Consequently options available include:

Membrane processes:
- Reverse Osmosis
- Dialysis
- Ultra- and nano-filtration techniques

Precipitation processes:
- Ion Exchange
- Sulfate coprecipitation (with Ca- and/or Ba-salts)
- Biological Sulfate Reduction, either in a bioreactor or in a constructed wetland

The adoption of a single or combined process will depend on economics and on the suitability of the method to remediate sulfate concentrations in the effluent at any particular site. This review will be illustrated through the use of case studies where sulfate treatment has been required and various options, proposed or implemented, assessed to achieve regulatory limits in mine or process water discharge.
INTRODUCTION

Acid rock drainage mechanisms involve the oxidation of sulfide minerals and can lead to highly acidic, metal-rich waters with a high sulfate content. Although sulfate is non-toxic, except at very high levels, it exerts a purgative effect. However, the corrosive effect of high sulfate waters, particularly towards concretes, is increasingly becoming the major water quality problem for mining operations and process plants (Maree et al., 1989; Adlem et al., 1991; Dill et al., 1994; Everett et al., 1994; Bowell and Bruce, 1995; Stuart et al., 1997; Van Gaans and Schuiling, 1997).

Current legislation worldwide places a limit around 400-500 mg/l on groundwater and 2000 mg/l on industrial effluent and consequently some level of treatment is often required. Options that will be reviewed in this paper include:

- **Reverse Osmosis:** Purification of water by forcing it under pressure through a membrane which is not permeable with respect to calcium and sulfate.
- **Dialysis:** Exchange of ion for more reactive or concentrated ion.
- **Filtration:** Fine filtration on micro- or nano-scale. At a fine nano-scale filtration process is more like pressure diffusion.
- **Ion Exchange:** Use of artificial resins or zeolites or treated coal to capture cations or anions from solution.
- **Sulfate coprecipitation:** Sulfate barriers may be constructed by using an inorganic source, which will precipitate, by chemical reaction a low solubility sulfate phase.
- **Biological Sulfate Reduction:** Under anoxic conditions sulfate may be reduced to sulfide through biologically assisted reactions. The reduction of sulfate to hydrogen sulfide is brought about by specialised strictly anaerobic bacteria. These organisms have a respiratory metabolism in which sulfates, sulfites and/or other reducible sulfur compounds serve as the final electron acceptors, with the resulting production of hydrogen sulfide.

The criteria by which one of these options are chosen typically depend on the ability of the process to adequately remove sufficient sulfate in a given time such that discharge of the treated water meets all regulatory requirements. A further criteria is that of economics. In any mining operation, the costs have to be balanced with the income. In a feasibility study, all the costs are assessed including the costs of environmental protection. The approach with the design of any aspect of the mine is generally BATNEEC (Best Available Technology Not Entailing Excessive Cost). The detail will be a function of the planning authority requirements and the philosophy of the mining company.

The approach taken for water treatment generally involves assessment of treatment alternatives and risk assessment for release of contaminants. However, a mine is developed on the basis of a return on investment. There is a limit as to the environmental costs beyond which the mine will not go ahead. Although risk assessments are done, the methods of assessment and monitoring cannot be considered...
as exhaustive and engineering decisions are made at some stage of investigation, which are commensurate with the level of investment in the mining project itself. This review will attempt to assess the advantages and limitations of the current options and criteria by which the most appropriate technology can be applied.

TREATMENT OPTIONS

Water is often a major if not the major issue facing a mine or milling operation. It is becoming increasingly essential to recycle as much water as possible on a mine site and to close the water circuit. Desalination techniques for recovering drinking water from seawater have a limited direct application in the mining industry. However, if applied, some degree of modification is required because of the effects of scaling and corrosion. Waters rich in sulfate have a high scaling potential. In South Africa it is estimated 75% of gold mines have scaling processes essentially related to saturation of water with respect to CaSO₄ (Juby, 1989). The processes for treating sulfate rich waters can be deemed as involving either a membrane or precipitation route.

MEMBRANE PROCESSES

Reverse Osmosis

This process relies on a semi-permeable membrane, which separates a strong solution and a dilute solution. Under natural conditions pure water will permeate through a membrane to dilute the concentrated solution with the membrane preventing the passage of salts. The greater the concentration differential across the membrane, the higher the tendency for water to permeate to the concentrated solution. This hydraulic force is the osmotic pressure of the system.

In reverse osmosis an external hydraulic pressure is applied to the saline brine thus forcing water through the membrane against osmotic pressure. Thus hydraulic pressure needs to exceed osmotic pressure. In the case of a brine concentration of ~ 30 g/l osmotic pressure is around 25 bars. Where water is low in calcium (<100 mg/l) and sulfate (<700 mg/l), conventional reverse osmosis can be used, although at higher concentrations of both scaling will occur. Modified processes have been proposed including seeded reverse osmosis (SRO, Harries, 1985) and special reverse osmosis has been developed to treat mine waters (SPARRO) in South Africa (Chamber of Mines Organization, 1988).

Seeded Reverse Osmosis (SRO)

By actively promoting precipitation of CaSO₄ prior to membrane treatment corrosion of the membrane
walls and fouling by salt precipitation can be avoided. This pre-treatment method involves a suspension of seed crystals introduced into the effluent via recycling of waste slurry. This crystal slurry is approximately 10% solids and a tubular reverse osmosis (TRO) system is required because hollow fibre systems are unsuitable due to problems caused by fouling. A pilot plant for SRO has been operated in South Africa for 5000 hours and had a 96% water recovery. A number of disadvantages exist with SRO despite high salt and water recovery and reduced costs. Energy consumption is high and there is poor control of CaSO₄ seed and seed solution controls.

**Slurry Precipitation and Recycle Reverse Osmosis (SPARRO)**

Redevelopment of the SRO process led to the patent of the SPARRO process. The process requires pre-treatment by cooling, filtration and readjustment of pH 5-6 for protection of the membrane process. A water recovery of over 95% has been demonstrated by pilot studies. A fatal problem of the process is to maintain the required flux rate of 550 l/m²/d due to fouling of the membrane.

**Electrodialysis and Electrodialysis Reversal (EDR)**

This process uses direct electrical current across a stack of alternating cation and anion selective membranes. In the effluent, anions are attracted to the anode but cannot pass through anion-impermeable membranes and are thus concentrated. Cations move in the opposite direction and are impeded by cation-impermeable/anion-permeable barriers. The initial container has thus been depleted of salts and the cleaned water can be extracted. By the use of current reversal the process is greatly improved. The anode and cathode can be periodically changed as can the effluent and clean water channels. This reduces potential for membrane fouling and facilitates regeneration of the membrane by self-cleaning. A major advantage of EDR over other RO techniques is that the system is not sensitive to effluent temperature or pH. Capital costs are reduced as are working costs due to lower working pressures. However CaSO₄ scaling can occur due to inadequate pre-treatment. A pilot plant study at Beatrix gold mine in South Africa achieved a recovery of 80% salt ad recycled 84% water. The water had high Fe, Mn, Na and Cl concentrations as well as high sulfate concentrations (Juby and Pulles, 1990).

**Filtration**

Filtration is probably one of the more effective means by which suspended particles can be separated from fluids. Different purification schemes are broadly defined on particle size and flow (Buchanan, 1987).

Any filtration process requires pre-treatment where coarse particles dominate suspended load, high fluid flow is present and consequently rapid rates of thickening and filtration. However with an open
structure such suspensions are poorly packed and therefore solid/fluid ratios are low. Conversely fine particles will have good packing but low rates of thickening and filtration. Pre-treatment can create a material which is a mix of these two extremes improving efficiency of packing (thereby reducing disposed sludge volume) whilst still maintaining a good filtration and thickening rate. More common techniques involve the use of polyelectrolytes or metal salts to act as a precipitating agent or target for flocculation (Purchas, 1968). More physical rather than chemical techniques are also available including screening, freezing or thawing, elutriation and irradiation.

A number of filtration options are available from deep bed filters which can be used to clarify fluids to high purity, slow or continuous (or rapid) sand filters can be used to reduce turbidity and TDS. Pulsed bed filters utilise a shallow bed of fine sand to capture non-flocculated solids with the system periodically regenerated by a pulsed system. Gravity-fed filters can be used with low or rapid rates of filtration. Many of these techniques are discontinuous but continuous filtration methods have also been proposed and range from Cartridge filters, usually applied to the removal of low concentrations of TDS from low-flow streams to Cross flow Microfiltration which filter continuously at a near-steady rate. The technique utilises a tangential constant flow to minimise fouling and is used in other membrane separation techniques such as RO, ultrafiltration and nanofiltration (Eriksson, 1988).

Ultrafine slurry particles can also be filtered using vacuum filtration and electrolysis (Bollinger, 1984). Electrofiltration is particularly suited to ultrafine or colloidal particles (50% <2 μm). A well dispersed slurry is placed in an active adc field leading to migration of particles towards the anode since they have a net negative charge. As most slurries are at high pH the net negative charge is due to surface pH exceeding pH_{pzc} imparting a negative charge on mineral surfaces (Parfitt, 1978; Bowell et al., 1996). At the anode a densely packed precipitate or cake is formed with a low water content. Through electroosmosis the cake can be further dewatered, increasing water recovery. The cathode essentially acts as a mechanical filter in which a vacuum is created on the filtrate side forming a thin precipitate or cake on the filter cloth. This acts as a trap for ultrafine particles. Electrosomotic pressure operates in conjunction with the vacuum enabling the production of a clear filtrate at higher rates than conventional vacuum filters (Bollinger, 1984).

**PRECIPITATION PROCESSES**

**Ion Exchange**

Ion exchange resins are materials which contain large polar exchange groups held together by a three dimensional network (Helffrich, 1962). The process is an exchange of ions or molecules between solid and liquid with no substantial change to the solids structure. One of the targeted ions is essentially...
removed from the liquid phase and attached to the solid structure in exchange for another ion (typically hydrogen or hydroxyl) thus rendering the target ion immobile.

In the case of CaSO₄ sulfate, being an anion would be typically exchanged for hydroxyl on a positively charged resin (a anionic resin) while calcium as a cation would be exchanged for hydrogen and so be attached to a negatively charged resin (a cationic resin). When exhausted the resin can be regenerated by the reverse reaction by washing in an acid solution for a cationic resin and sodium hydroxide for an anionic resin.

Similar to reverse osmosis scaling of CaSO₄ is common in conventional circuits. To overcome these problems a modified form of ion exchange has been developed to treat Ca-sulfate waters. The GYPCIX process (Gussmann and Nagy, 1993) is based on ion exchange resins which uses low cost reagents such as lime and sulfuric acid for resin regeneration. The GYPCIX process can be used to treat solutions with sulfate up to 2000 mg/l and calcium up to 1000 mg/l. Thereafter membrane filtration is required to remove salts.

**Sulfate co-precipitation**

Sulfate barriers may be constructed by using an inorganic source, which will produce a low solubility sulfate phase. Both lime and barium salts have been proposed (Maree et al., 1989; Tahija et al., 1990; Everett et al., 1994; Maree and du Plessis, 1994). With all the precipitation mechanisms the addition of a chemically inert large particle material, such as carbon, to the reactor feed will facilitate better settling of the sulfate precipitate. This is because the ultra fine precipitates will attach to the larger particles and will thus settle quicker than isolated small sulfate molecules.

**Lime treatment**

The precipitation of insoluble gypsum (Kₛ ≈ 10⁻²³) usually occurs as a by-product of lime addition in response to buffering of drainage pH rather than designed remediation of sulfate concentrations (Tahija et al., 1990). Similar methods for neutralising acidic drainage with limestone (Maree et al., 1995) and dolomite (Maree and du Plessis, 1994) have also been proposed.

**Barium Carbonate**

The removal of sulfate by barium carbonate was demonstrated to be effective over 25 years ago (Kun, 1972) by a process such as:

\[ \text{BaCO}_3 (s) + \text{SO}_4^{2-} = \text{BaSO}_4 (s) + \text{CO}_3^{2-} \]

Kun recognised three main problems with the method on an industrial scale. Dissolved Ba in excess of
stoichiometric requirements was needed in the process (in our work we have found it required 2-4 times more Ba depending on the chemistry of competing anions such as phosphate and arsenate), long retention times and high cost of Ba. The cost problem can be overcome by recycling Ba through roasting of barite to form BaS and then purging with CO$_2$ to form BaCO$_3$ (Velman, 1984; Wilsenach, 1986).

Further consideration of BaCO$_3$ to remove sulfate has come from two research programs in South Africa in the late eighties (Trusler, 1988; Trusler et al., 1988; Edwards and Buckley, 1989; Maree, 1989; Maree et al., 1989). Barium carbonate and lime would be added to the effluent to soften the water and produce a precipitate. From experimental work (WRC, 1990) it was found that CaCO$_3$ was necessary to act as a seed to encourage BaSO$_4$ formation from BaCO$_3$ due to the insolubility of the latter ($K_{sp} \sim 10^{-8}$). Calcium salts were found to achieve a better removal than Na or Mg salts as the products (CaCO$_3$/CaSO$_4$) were much less soluble.

In a modification of this process a two-stage fluidised bed reactor system has been proposed (Maree et al., 1989). However this work demonstrated that where some transition metal levels were high (Fe, Mn, Ni) metal hydroxides can coat the BaCO$_3$ thus limiting the reaction with sulfate. A further problem is the difficulty in separating fine CaCO$_3$ and BaSO$_4$.

**Barium Sulfide**

As an alternative to BaCO$_3$, BaS has been proposed (Maree et al., 1989; Bosman et al., 1990). The benefits of the BaS process over BaCO$_3$ are:

- A greater quantity of sulfate is recovered as not as much gypsum is produced;
- Acid waters can be treated directly eliminating the need for a pre-neutralisation step;
- Sludge disposal (essentially gypsum) is greatly reduced.

The various reactions in the process can be summarised (Maree et al., 1989) as:

**BaS stage**

\[
\text{BaS (s)} + \text{SO}_4^{2-} = \text{BaSO}_4 (s) + S^{2-}
\]

The $S^{2-}$ gas may be used to precipitate metals by a reaction such as:

\[
\text{Me}^{2+} + S^{2-} = \text{MeS}
\]

The presence of metals in solution and production of metal sulfides can significantly reduce the recovery of Ba from the process. This can be avoided by sulfuric acid leaching which will oxidise sulfides possibly catalysed by bacteria. Economically valuable metals can then be recovered (Maree et al., 1989; Bosman et al., 1991). Alternatively, the gas H$_2$S can be formed and vented through a wet
scrubbing circuit to recover elemental sulfur.

With the addition of BaS at 6 g/l (ratio of Ba: SO₄ ~ 1.5:1) sulfate was reduced from 4 g/l to less than 100 mg/l in 30 minutes. The excess CO₂ was stripped off with air and water was softened by this process.

**Barium Hydroxide**

The use of Ba(OH)₂ has been proposed to treat more neutral waters where metals have been largely precipitated already as metal hydroxide salts (Adlem et al., 1991). The process eliminates the necessity of complex water treatment associated with the BaCO₃ and BaS processes, does not require long retention times for reactions (such as in the BaCO₃ process) or the need to strip H₂S as in the BaS process.

**Comparison between the Ba-salts**

All three processes can remove sulfate from solution from very high levels to within regulatory standards. In the case of BaS and Ba(OH)₂ acidic solutions can be treated directly, although in practice some lime treatment is required for very acidic solutions to prevent hydroxide mantling if Ba(OH)₂ is used. The process additionally removes transition metals, Mg and NH₃ and to a limited extent removes Na as well. Thus the overall TDS is lowered as well as the concentration of deleterious elements. The Ba(OH)₂ causes significant CaSO₄ precipitation improving sulfate removal, up to 30%, but increasing the volume of sludge requiring disposal. A major benefit of the process is that valuable by-products are created, the sale of which can be used to offset treatment costs. In the BaCO₃ and BaS processes sulfur, metals and Ba-salts can be commercially produced while NaHS is produced in the Ba(OH)₂ process. Overall the BaS process is perhaps the most attractive for treating AMD as:

- The reaction is rapid, not requiring the long retention times of the BaCO₃ process;
- No neutralisation step is required prior to treatment;
- No pre-treatment is required to metals as in the Ba(OH)₂ process;
- The only precipitate by BaS is BaSO₄ and not CaSO₄ as in the hydroxide process or CaCO₃ as in the carbonate process;
- Enables recovery of high quality BaSO₄ and by a further stage high quality CaCO₃.

BaS has to be formed in the thermic reduction of BaSO₄ as part of the recycling stage in all three processes.
2.4.1 Biological Sulfate Reduction

Under anoxic conditions sulfate may be removed from the mine waters as stable sulfide precipitates with the conversion of sulfate to sulfide being the result of microbial activity. Under anaerobic conditions sulfide minerals remain stable and have extremely low solubilities (Arenesen et al., 1991; Barta et al., 1997). Flooded underground mine workings and open pits can be anoxic, and as such provide a suitable environment for the implementation of a biological sulfate reduction system. Alternatively a dedicated bioreactor can be used or anaerobic conditions may be created in the form of passive treatment systems, such as a constructed wetland. The presence of sulfides (H₂S odour) in many mine water discharges indicates that sulfate reduction is already occurring in mine workings (Tasse et al., 1994). The reduction of sulfate to hydrogen sulfide is brought about by specialised strictly anaerobic bacteria. These organisms have a respiratory metabolism in which sulfates, sulfites and/or other reducible sulfur compounds serve as the final electron acceptors, with the resulting production of hydrogen sulfide (Chappelle, 1993). The organic substrates for these bacteria are generally short chain acids such as lactic and pyruvic acid. In nature these substrates are provided through fermentative activities of other anaerobic bacteria on more complex organic substrates (Gould et al., 1994). A wide variety of organic substrates have been investigated for the purpose of biological sulfate removal including molasses, sewage sludge, straw, newspaper, sawdust and manure. Other possible carbon sources are wastes from the chemicals and food industry such as short chain organic acids and organic rich wastes or effluent streams in general.

**In-situ treatment of mine water**

The natural occurrence of sulfate reducing bacteria lends itself to being a possible *in-situ* process for the treatment of high sulfate mine water. So far the injection of waste sewage sludge underground into the flow path of the mine water as *in situ* treatment (Dill and Graff, 1997) has been suggested. A problem with sulfate reduction, the generation of bisulfide and formation of mineral sulfides that might occur is the slow reaction kinetics of mineral precipitation versus sulfate reduction rates. Resulting excess bisulfide might decrease the *in situ* sulfate reduction rates. The appropriate design of the in situ treatment system, which has to consider the geological and geohydrological aspects of the respective area can overcome these problems. Detailed knowledge of these factors will form the design basis for the dosage schedule for the organic waste to be injected underground into the mine water flow path.

**Constructed bioreactors**

Anaerobic bioreactors can be used for the bacterial reduction of sulfate and metal rich water leading to precipitation of metal sulfides. These reactions have to occur in strictly anaerobic reactors as the...
sulfate reducing bacteria do not tolerate oxygen. Effluent treatment in constructed reactors benefits
from a uniform rate and flow through the substrate. In an experimental reactor the removal of sulfate
was found to be dependent on energy source, flow and time (Dill et al., 1994). The biological
reduction of sulfate from industrial effluents has been shown to be an effective method with producer
gas being a reliable energy source (Maree et al., 1991; Du Preez et al., 1992). From studies by Dill et
al. (1994) a pilot plant (packed bed biofilm reactor) produced a sulfate reduction rate of 1.7-2.2 g/l/d
over a period of 70 days reducing effluent drainage sulfate from over 3000 mg/l to less than 250 mg/l.
A fluidised bed reactor with dispersed biomass which was compared to the packed bed biofilm reactor
proved to reduce the required hydraulic retention time by 20% while increasing the sulfate removal
efficiency from 70 to 90% (Dill and Maree, 1996).

**Constructed wetland**

Perhaps an extreme end of the bioreactors is the use of constructed wetlands to reduce sulfate levels.
In recent years constructed wetlands have become increasingly popular in dealing with closed mines
where little or no records are preserved and it is not possible, in general, to prevent or contain the toxic
waste. In this case the best available practice is to treat the mine drainage (Kalin et al., 1991; Wood,
1995; Cambridge, 1996). This was the case at Wheal Jane where discharged acidic metal-rich mine
water is currently being treated by conventional metal precipitation processes at a current annual cost
of £750,000 pa.

**ECONOMIC COMPARISON**

In a feasibility study, all the costs are assessed including the costs of environmental protection. The
approach with the design of any aspect of the mine is generally BATNEEC (Best Available
Technology Not Entailing Excessive Cost). The detail will be a function of the planning authority
requirements and the philosophy of the mining company.

The approach taken for water treatment nowadays, generally involves assessment of treatment
alternatives and risk assessment for release of contaminants. However, a mine is developed on the
basis of a return on investment for the funders. There is therefore a limit as to the environmental costs
beyond which the mine will not go ahead. Although risk assessments are done, the methods of
assessment and monitoring cannot be considered as exhaustive and engineering decisions are made at
some stage of investigation, which are commensurate with the level of investment in the mining project
itself.

Costs vary widely from simple filtration and constructed wetland systems, which are characterised by
lower salt and water recoveries to the capital-intensive membrane filtration systems, which have
exceptionally high salt and water recoveries. The recovery of valuable products, such as clean water, sulfur, metal salts, gypsum, lime, and Ba-salts are also important considerations. The economic recovery of these commodities can be used to offset capital and working costs consequently making a more expensive treatment plant the most economic option. However, this has to be balanced with future strategy for the site including ownership, social and economic reuse of the site post-closure and long term liabilities and waste disposal.

CONCLUSIONS

The demanding regulatory requirement to reduce Total Dissolved Solids and sulfate levels in many mine and process waters coupled with the need for more effective recovery of water demands that more operations are required to desalinate and recycle process and mine water. Conventional desalination techniques are unsuitable due to scaling, fouling and corrosion. Methods to cope with these problems have been developed, many up to pilot plant scale although few have actually gone as far as the commissioning of a full scale plant. As existing resources become scarcer and as demand on fresh water in mining areas increase by other users this situation is likely to change.

Various treatment options are available for sulfates involving physical, chemical and biological processes. The options available can be divided into Membrane filtration processes such as Reverse Osmosis, Dialysis and Ultra- and nano-filtration techniques on the one hand and Precipitation processes such as Ion Exchange, Sulfate co-precipitation (with Ca- and/or Ba- salts) and Biological Sulfate Reduction, either in situ or ex situ on the other hand.

The adoption of a single or combined process will depend on economics and on the suitability of the method to remediate sulfate concentrations in the effluent at any particular site.

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