Sulphate and salt minerals: the problem of treating mine waste

Whilst issues such as cyanide, toxic metals, arsenic and acidity are generally given the highest priority in connection with the treatment of mine waste or effluent, they are not generally the most persistent. Volumetrically dissolved salt constituents such as sulphate, sodium and calcium are generally more conservative and as such much more difficult to mitigate. The question of scale is illustrated when one considers the products of pyrite oxidation. From one tonne of ore containing 1% pyritic sulphur over 15 kg of ochre and 30 kg of sulphuric acid can be produced.

Table 2: Treatment of Sulfate-rich effluents by Ba- and Ca-salt precipitation, shown as % removal.

pH	Lime addition	$BaCO_3$	BaS	$Ba(OH)_2$
2.9	62.3	24.2	95.6	98.1
7.9	80.5	81.6	98.8	97.7
12	51	90.1	98.1	98.1

Although sulphate is non-toxic, except at very high levels, it exerts a purgative effect. The corrosive effect of high sulphate waters, particularly towards concretes, is increasingly becoming a major water quality problem for mining operations and process plants as regulatory set limits on water quality become increasingly tighter. Additionally, in many countries, such as parts of Southern Africa, a significant quantity of surface water resource has already been impacted not just by industry but by agriculture, urbanisation and in places aridisation. In these areas, the aquatic ecosystem is already stressed and could not tolerate further impact.

Sulphate is often the dominant contaminant from mine water and can form a wide range of salts. In many arid environments it can become the dominant contributor to salinity in the vicinity of the discharge. Where salts are accumulated, such as dams or mine pit lakes, (figure 1) and are infrequently flushed significant levels of sulphate can accumulate. Current legislation world-wide places a limit around 400-500 mg/litre on groundwater and 2,000 mg/litre on industrial effluent and, consequently, some treatment is often required.

Table 1: Results of using GYPCIX process on Berkeley Pit mine water (from Robertson et al., 1993)

	UNTREATED	LIMED	GYPCIX
TDS, mg/litre	10,000	3,000	350
pH, su	2.7	8.5	8.0
Ca, mg/litre	490	600	50
Mg, mg/litre	420	350	20
Na, mg/litre	70	70	50
Fe, mg/litre	1,100	0.1	<0.1
Mn, mg/litre	182	3.6	<0.1
Cu, mg/litre	186	<0.1	<0.1
Zn, mg/litre	550	<0.1	<0.1
Sulphate mg/litre	8,000	1,980	200

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. Both active and passive technologies exist to mitigate the problems of salt accumulation in mine water effluent

Various treatment options are available for sulphates involving physical, chemical and biological processes. Essentially, these processes work either through separation of salts through a membrane or through precipitation of sulphate as an insoluble salt, a reduced sulphide solid or through water evaporation and brine saturation. The selection of a treatment option is dictated by sulphate and calcium concentrations, due to the problem of $CaSO_4$ scaling.

MEMBRANE PROCESSES

Reverse Osmosis: Purification of water, by forcing it under pressure through a membrane which is not permeable with respect to certain solutes, such as calcium and sulphate. This technology can be applied almost universally, although in iron-rich or very acidic waters a pre-treatment step is required.

Waters rich in sulphate have a high scaling potential; in South Africa it is estimated that 75% of gold mines have scaling processess essentially related to saturation of water with respect to $CaSO_4$.

Typically, only water in which calcium (<100mg/litre) and sulphate (<700mg/litre) are low can use conventional reverse osmosis. Modified processes have been proposed including seeded reverse osmosis that uses a suspension of salt crystals to promote precipitation. Due to fouling a tubular reverse osmosis system is required. A pilot plant for seeded reverse osmosis has been operated in South Africa, for a period of 5,000 hours, and had a 96% water recovery rate. Redevelopment of the seeded reverse osmosis process led to the patent of the special reverse osmosis process (SPARRO). Extensive pilot plant test work has been undertaken and included the precipitation of metals by increasing effluent pH to 10 as a pre-treatment step. This is followed by cooling, filtration and readjustment of pH to 5-6 for protection of membrane process. A water recovery of over 95% has been demonstrated by pilot studies. A major problem of the process is to maintain a daily flux rate of 550 litres/m^2 due to fouling of the membrane, most likely due to suspended SiO_2 particles.

A major disadvantage with all reverse osmosis processes is that pre-treatment, such as chlorination to remove bacteria, and water softening to buffer pH and iron (and trace metal) precipitation is generally required.

Dialysis: 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

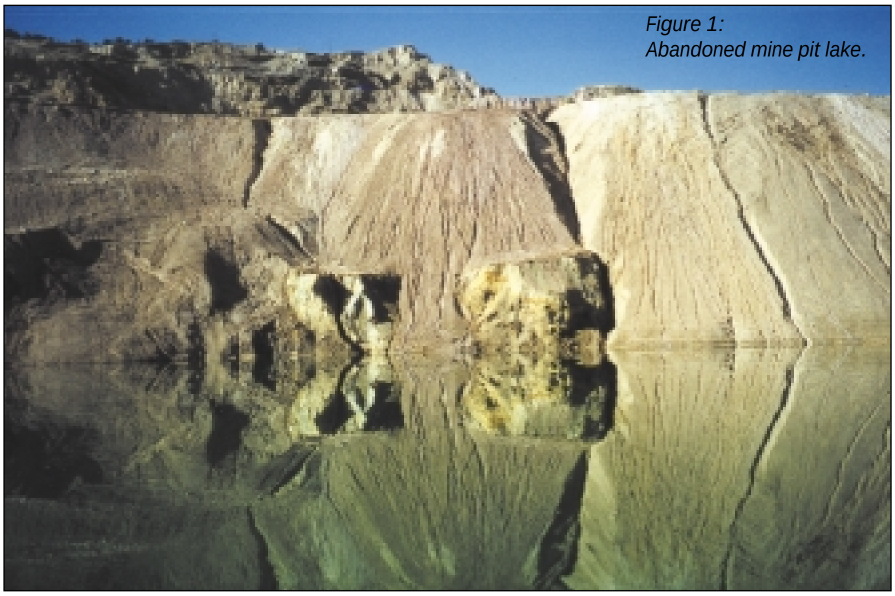


Figure 1: Abandoned mine pit lake.

pass through anion-impermeable membranes and are thus concentrated. 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 Electrical Dialysis Reversal (EDR) over other reverse osmosis techniques is that the system is not sensitive to effluent temperature or pH. In a pilot plant study at Beatrix gold mine in South Africa, a recovery of 80% salt was achieved whilst 84% of water (which has high Fe, Mn, Na and Cl as well as sulphate) was recycled.

Filtration Techniques: 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. Mine waters are characterised by high suspended solid loadings which can be efficiently removed by settlement of coarse material and filtration of the majority of particles, most of which are less than 30 μm.

Any filtration process treatment where coarse particles dominate the suspended load requires pre-treatment. Common techniques involve the use of polyelectrolytes or metal salts to act as a precipitating agent or target for flocculation. Physical, rather than chemical, techniques are also available including screening, freezing or thawing, elutriation and irradiation.

Table 3: Mechanism of BaS process (taken from Maree et al., 1989).

BaS stage

$BaS (s) + SO_4^{2-} = BaSO_4 (s) + S^{2-}$

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

$Me^{2+} + S^{2-} = MeS$

Alternatively the gas H_2S can be formed and vented through a wet scrubbing circuit to recover sulfur.

CO^2 sparging stage for H_2S stripping

$S^{2-} + CO_2 + 2H_2O = H_2S + HCO_3- + OH^-$

$Ca^{2+} + 2 HCO_3- = Ca(HCO_3)_2$

Water softening by lime addition

$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$

or

Water softening through CO_2 stripping:

$Air + Ca(HCO_3)_2 = Air + CaCO_3 + CO_2 + H_2O$

Thermic reduction (recycle stage as discussed above)

$BaSO_4 + 2C = BaS + 2CO_2$

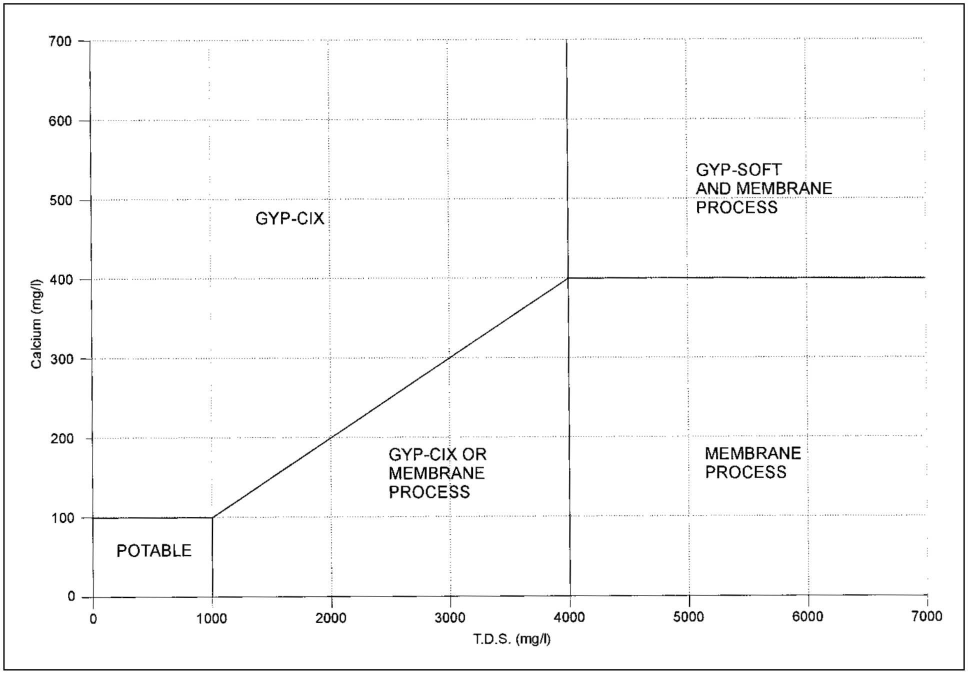
A number of filtration options are available from deep bed filters, which can be used to clarify fluids, to high purity, slow or continuous (or rapid) sand filters, which can be used to reduce turbidity and dissolved load. Pulsed bed filters utilise a shallow bed of fine sand to capture non-flocculated 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 total dissolved solid from low-flow streams, to cross flow microfiltration, which filters 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 reverse osmosis, ultrafiltration and nanofiltration. Ultra-fine slurry particles can also be filtered using vacuum filtration and electrolysis. Electrofiltration is particularly suited to ultra-fine or colloidal particles (50% <2 μm).

Ion Exchange: Similar to reverse osmosis, an exchange of ions occurs between solid and liquid but 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 $CaSO_4$ sulphate, being an anion it would be typically exchanged for hydroxyl on a positively charged resin (an *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 $CaSO_4$ is common in conventional circuits. To overcome these problems a modified form of ion exchange has been developed to treat Ca-sulphate waters, for example the GYPCIX (Gypsum Ion Exchange) process offered through Chemeffco of South Africa.

The GYPCIX process is based on ion exchange resins which uses low cost reagents such as lime and sulphuric acid for resin regeneration. The resins used have been designed so as to target calcium and sulphate so as to reduce gypsum levels in effluent, thereby reducing total dissolved solid and corrosion potential.

Pilot plant results in South Africa have shown that fouling caused by gypsum precipitation in conventional ion exchange circuits can be avoided by the GYPCIX process, although the application is limited to waters of a certain chemistry (figure 2). As the waste streams can be combined, the gypsum in the slurry can be settled and the supernatant water recycled so improving water recovery. In a pilot plant, the effluent of the Berkeley Pit, in Butte, Montana was treated by the GYPCIX process and the results are given in Table 1.

Figure 2: Criteria for GYPCIX application (as proposed by Robertson et al., 1993).



The GYPCIX process can be used to treat solutions with sulphate up to 2,000 mg/litre and calcium up to 1,000 mg/litre. Thereafter, membrane filtration is also required to remove some of the salt components.

PRECIPITATION MECHANISMS

Sulphate barriers may be constructed by using an inorganic source, which will produce a low solubility sulphate phase. Both lime and barium salts have been proposed. 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 sulphate precipitate. This is because the ultra-fine precipitates will attach to the larger particles and will thus settle quicker than isolated fine sulphate particles.

The precipitation of insoluble gypsum usually occurs as a by-product of lime addition, in response to buffering of drainage pH rather than designed remediation of sulphate concentrations. For an effluent of low quality, both lime and barium-salts have been

Technique	Salt removed %	Water recovery %	Cost† Operating
Electro Dialysis	80	80	0.81
Tubular RO	80	85	1.01
SPARRO	80	95	1.05
GYPCIX (TDS>2 g/litre)	90	90	1
(TDS 2-6.5g/litre)	80	80	1.1
$BaCO_3$	60	50	0.85
BaS	75	85	0.8
$Ba(OH)_2$	95	75	1.1
Lime	50	40	0.75
SRB reactor	68	65	0.4
Wetland	40	0*	0.2

† Cost in US$/Ml

* Wetland discharges treated water and does not usually recycle water which is often used to dilute untreated overflow effluent

Table 4: Cost comparison and process performance of treatment options.

assessed in laboratory studies, the results of which are given in table 2.

As can be observed under the range of conditions used, $Ba(OH)_2$ and BaS gave the best results and were almost double that of lime in the reduction of sulphate from the effluent. The mechanism by which barium sulphide reduces effluent sulphate is shown in table 3. All three processes can remove sulphate 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, magnesium and ammonia and to a limited extent removes sodium as well. Thus the overall dissolved solids content is lowered as well as the concentration of deleterious elements. The benefits of the BaS process over $BaCO_3$/ $Ba(OH)_2$ are:

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

The $Ba(OH)_2$ process causes significant $CaSO_4$ precipitation improving sulphate 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 $BaCO_3$ and BaS processes sulphur, metals and Ba-salts can be commercially produced, whilst NaHS is produced in the $Ba(OH)_2$ process. Overall the BaS process is perhaps the most attractive for treating acid rock drainage (ARD) as;

- the reaction is rapid, not requiring the long retention times of the $BaCO_3$ 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 $BaSO_4$ and not $CaSO_4$, as in the hydroxide process, or $CaCO_3$, as in the carbonate process;
- it enables recovery of high quality $BaSO_4$ and by a further stage high quality $CaCO_3$; and
- BaS has to be formed in the thermic reduction of $BaSO_4$ as part of the recy--cling stage in all three processes.

Biological Sulphate Reduction: Under anoxic conditions sulphate may be reduced to sulphide through biologically assisted reactions. The reduction of sulphate to hydrogen sulphide is brought about by specialised strictly anaerobic bacteria and is accomplished primarily by two genera: *Desulfovibrio* (five species) and *Desulfotomaculum* (three species). These organisms have a respiratory metabolism in which sulphates, sulphites and/or other reducible sulphur compounds serve as the final electron acceptors, with the resulting production of hydrogen sulphide. Limitations on this process are the ability of the bacteria to accept high concentrations of toxic metals or high acidity.

Biologically mitigated sulphate reduction can be undertaken actively in a dedicated reactor or can be achieved passively in an anaerobic cell as part of a constructed wetland. The major difference being that the passive treatment is designed to be more 'self-sufficient', although in practice still requires maintenance and renewal of carbon source.

ECONOMIC COMPARISON

Table 4 gives a comparison of the capital and operating costs for several of the processes described. As can be observed 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, sulphur, 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.

ASSESSMENT OF OPTIONS

Despite the comprehensive range of processes available it is possible to provide a crude simple assessment tree for assessing sulphate options (figure 3). Essentially this is based on the criteria of salt levels present and economics of the mining operation. This kind of technical assessment based on geochemistry and geochemical engineering has to also include economic, environmental and social considerations. Consequently, where sulphate levels are very low there is no requirement for sulphate treatment. Above sulphate levels of approximately 500 mg/litre, passive measures can be utilised while at higher levels (500-10,000 mg/litre) a wide range of options are available including reverse osmosis, GYPCIX, filtration, desalination and salt precipitation. At very high levels of sulphate (> 10,000 mg/litre) co-precipitation is the most suitable option.

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A full list of references can be obtained from the author on request

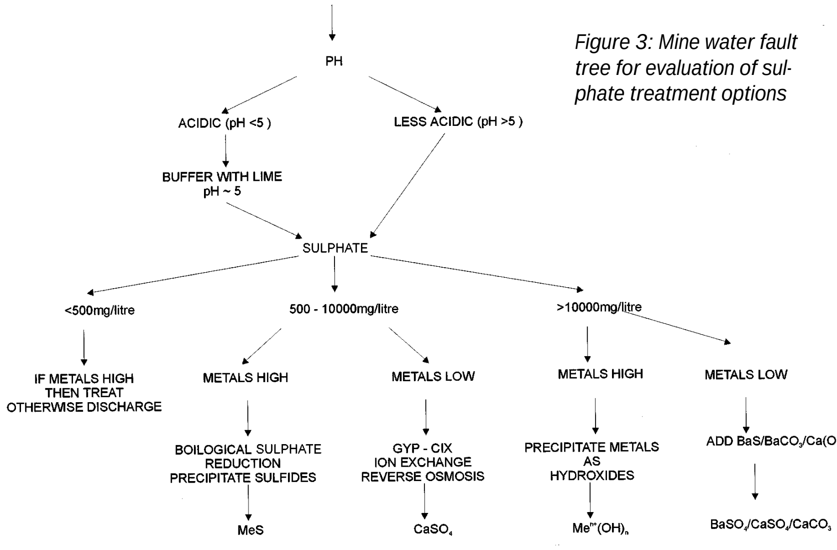

Figure 3: Mine water fault tree for evaluation of sulphate treatment options