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A REVIEW OF SULFATE REMOVAL OPTIONS FOR MINE WATERS

R.J.Bowell

SRK Consulting, Windsor Court, 1 Windsor Place, Cardiff CF10 3BX,
Wales

Abstract

Sulfide oxidation is a common phenomenon associated with many mined ore bodies and extracted or processed waste. Where the products of these chemical reactions can enter a water body the result is often a reduction in water quality through the increase of acidity, metals and dissolved salts. Due to an attributed lower environmental impact the release of sulfate has received little attention in many regulatory jurisdictions when compared to control of dissolved metals or acidity. Consequently the literature on sulfate removal from mine waters is comparatively small when compared to metal control despite the use and development of several technologies to reduce sulfate and total salt loadings. Sulfate control levels are based primarily on the secondary drinking water recommendations of approximately 500 mg/L, based on the laxative effect of high magnesium sulfate concentration.

Sulfate control in mine waters primarily follows one of two methodologies; (1) Removal through membrane separation of salts from water; (2) Removal of sulfate by salt precipitation through ion exchange, permeable reactive barrier, biological reduction or formation of insoluble mineral precipitate.

These approaches are reviewed within this paper and an economic and technical comparison made between the available technologies. Based on demonstrated technology and economic benefits the most promising technologies to date are biological sulfate reduction, SAVMIN, and GYPCIX. At sulfate concentrations less than 2000 mg/L the limestone/lime process is an effective low-cost or pre-treatment removal option for sulfate. As with any mine water treatment option site-specific conditions will control the most suitable option for a particular mining operation.

1. Introduction

Acid rock drainage mechanisms involve the oxidation of sulfide minerals and can lead to highly acidic, metal-rich waters with high sulfate content. However sulfate has a potential corrosive and purgative effect (AWWA, 1999). Waters rich in sulfate also have a high scaling potential. In South Africa, for example, it is estimated that 75% of gold mines have scaling processes essentially related to saturation of water with respect to $CaSO_4$ (Juby, 1989). Increasingly sulfate is being considered as one of the more significant long term water quality issues for mining operations and process plants, particularly in countries with problems of fresh water supply such as South Africa and Australia (Bosman, 1985; Maree et al., 1989; Adlem et al., 1991; Du Plessis and Swartz, 1992; Everett et al., 1994; Bowell, 2000; Geldenhuys et al., 2001; Younger et al., 2002).

This invited review will assess the options available for sulfate removal from mine waters and discuss an economic and technical comparison made between the available technologies

1.1 Sulfur hydrogeochemical cycle

Sulfur occurs in a number of oxidation states of which only three, the -2 (sulfide), 0 (native sulfur) and +6 (sulfate) are considered stable in nature, with sulfate the dominant aqueous sulfur species found in most aerobic geochemical systems (Chappelle, 1993). The dissolved concentration of sulfate in mine drainage appears largely to be controlled by the solubility of gypsum (~2.3 g/L $CaSO_4$ assuming no other interactions). This solubility generally equates to ~ 500 mg/L Ca and 1800 mg/L sulfate (Figure 1).

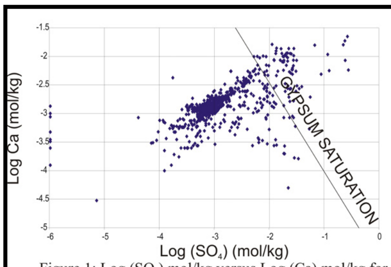

Figure 1: Log (SO_4) mol/kg versus Log (Ca) mol/kg for various ground and mine waters worldwide (from many sources)

The actual mechanisms involved in sulfide oxidation are complex and reviews have been published elsewhere (Nordstrom, 1982; Kleinnmann and Pacelli, 1991).The most common source of sulfate release is oxidation of FeS_2. Pyrite and/or marcasite generate the acidity of the mine waters and simultaneously supply large quantities of Fe and sulfate, for example, one tonne of ore with 1% pyritic sulfur can produce over 15 kg of ochre and 30 kg of sulfuric acid.

On weathering, sulfides can either release all sulfate or only a portion and form secondary salts, such as halotrichite. These minerals are highly soluble so can represent an instantaneous source of sulfate-rich water upon dissolution and hydrolysis. (Cravotta, 1994; Alpers et al., 2003).

Sulfate reduction has been identified to occur in sediments (Fillipek and Owen, 1980) natural wetlands and in mine waste (Kleinmann and Pacelli, 1991; Benner et al., 2002) and in natural gas reservoirs at low and high temperatures (Trudinger et al., 1985). Over time in these locations metal and sulfate concentrations have been observed to be lower and pH increases to pH 7-8. The activities of sulfur species may be directly or indirectly associated with the metabolism of microorganisms (Gould et al., 1994). Indirect activities include the dissolution of the minerals under acidic conditions that result from microbial metabolism, mineral precipitation in anaerobic environments, adsorption to microbes and the formation or disassociation of organometallic and arsine complexes. Direct metabolic activity requires minerals as either soluble trace element within the cell metabolic activity or to serve as specific oxidizing substrates, electron donors/acceptors in the oxidation reduction activities.

1.2 Regulatory Control, Sulfate Corrosion and Toxicity

The accumulation of salts such as calcium sulfate in waters limits the number of cycles of reuse of water on a mine site and creates environmental problems if discharged (Sayre, 1988; DWAF, 1989). This is particularly a problem where mining is active in semi-arid to arid environments such as western USA, southern Africa, the Middle East, Central Asia, parts of Australia and southern Europe. Demand on available water in some places is such that much of the water is recycled. For example in South Africa the average TDS of discharge water in the Rand Water Board Area has risen from approximately 130 mg/L in 1935 to in excess of 1000 mg/L in 1980 (Heynike and McCulloch, 1982). Although not toxic in itself elevated sulfate (concentrations above 600 mg/L) in drinking water has been observed to result in a purgation of the alimentary canal (WHO, 1996). Where high magnesium or sodium corresponds with high sulfate a laxative and/or dehydration effect has also been reported (WHO, 1996).

Increasing concern has led to the introduction of recommended guideline values, rather than standards, for sulfate and TDS in groundwater and effluent discharge (Table 1). These typically are based on USEPA or WHO guidelines as to the maximum concentration of a particular chemical constituent in drinking water or water utilized by livestock or for irrigation and generally recommend no more than 500 mg/L sulfate (WHO,1996; Sayre, 1988; DWAF, 1993; Flanagan, 1990; USEPA, 1999, 2002).

Table 1: Recommended maximum Sulfate levels, in mg/l

Country	Sulfate
USA effluent	500
Canada effluent	1500
EU guide limit	1000
DWAF effluent (South Africa)	600
Australia	1000
WHO guideline for drinking water	250

References: WHO, 1996; Sayre, 1988; DWAF, 1993; Flanagan, 1990; USEPA, 1999, 2002

2. Treatment options and selection

Information on the treatment options presented was obtained from published and unpublished sources from Europe, South Africa, Australia, and the USA. The various approaches are discussed under two broad caterogories; Membrane removal and Sulfur precipitation. A tabulated summary of each of the processes is presented in the appendix and are based on previous compilations by Bowell (2000) and Lorax (2003).

3. Membrane removal of sulfate

Membrane removal of sulfate utilizes three possible methods; reverse osmosis, electrical dialysis and filtration.

3.1 Reverse Osmosis

This process replies on a semi-permeable membrane which separates a strong solution and a dilute solution. 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.

In the case of 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 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) actively promotes precipitation of

$CaSO_4$ prior to membrane treatment, reducing the corrosion of the membrane walls and fouling by salt precipitation. 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 because of fouling. A number of disadvantages exist with SRO despite high salt and water recovery and reduced costs. Energy consumption is high; there is poor control of $CaSO_4$ seed and seed solution controls.

Redevelopment of the SRO process led to the patent of the Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process (Pulles et al., 1992). 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 5-6 for protection of the membrane process. A pilot plant for SRO has been operated in South Africa for 5000 hours and had a 96% water recovery reducing sulfate from approximately 6600 mg/L to 150 mg/L A water recovery of over 95% has been demonstrated by pilot studies. A problem observed during pilot operation of the process was difficulty in maintaining a flux rate of 550 $L/m^2/d$ due to fouling of the membrane, most likely due to suspended SiO_2 particles.

Laboratory testwork for a lower pressure RO circuit have been published (Everett et al., 1994). At pressures of ~ 600 Kpa, at least 80% recovery of water was achieved. Several pre-treatment steps have been proposed in order to extend membrane life. This includes chlorination to remove bacteria, water softening to buffer pH and ion exchange to reduce salt loading.

3.2 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 deleted 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 $CaSO_4$ 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 has high Fe, Mn, Na and Cl as well as sulfate (Juby and Pulles, 1990).

3.3 Filtration

Filtration is probably one of the more effective means by which suspended particles can be separated from fluids (Buchanan, 1987). Mine waters are characterized 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 requires pre-treatment where coarse particles dominate suspended load high fluid flow is present and consequently rapid rates of thickening and filtration.

Common techniques of filtration 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. 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.

Ultra-fine slurry particles can also be filtered using vacuum filtration and electrolysis (Bollinger, 1984). Electrofiltration is particularly suited to ultra-fine or colloidal particles (50% <2 μm). A well dispersed slurry is placed in an active electric field results in 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 (Ericksson, 1988). At the anode a densely packed precipitate or cake is formed with a low water content. Through electro-osmosis 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 ultra-fine particles. Electro-osmotic pressure operates in conjunction with the vacuum enabling the production of a clear filtrate at higher rates than conventional vacuum filters (Bollinger, 1984).

4. Sulfur precipitation approaches

The removal of sulfur from mine waters by precipitation may be approached in one of three ways:

1. Precipitation of gypsum or mirabilite, $Na_2SO_4.10H_2O$ through ion exchange removal, and saturation through converging of pure cation or anion streams.

2. Precipitation of an insoluble sulfate salt through chemical saturation and precipitation to produce gypsum, $CaSO_4.2H_2O$ (limestone/lime), barite, $BaSO_4$ (addition of barium salts) or ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ (addition of alum, gypsum and lime).

3. Precipitation of sulfur or sulfide through biologically mediated reduction. This has the benefit of potentially also removing metal sulfides that can be economically recovered as ore material (such as with the Biotech process installed at the Bisbee mining operation, Arizona).

4.1 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 solid 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 $CaSO_4$ sulfate, being an anion, would typically be exchanged for hydroxyl on a positively charged resin (an *anionic resin*) while calcium, a cation, would be exchanged for hydrogen and so be attached to a negatively charged resin (a *cationic resin*). As with 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-sulfate waters (GYPCIX).

The GYPCIX process (Gussmann and Nagy, 1993; Robertson et al., 1993) is a novel process based on ion exchange resins which uses low cost reagents such as lime and sulfuric acid for resin regeneration (Figure 2). The resins used have been designed so as to target calcium and sulfate so as to reduce gypsum levels in effluent thereby reducing TDS and corrosion potential. Additionally a pure gypsum product is the result of both cationic and anionic exchange and can be sold commercially thus offsetting treatment costs. The reactions occur by mechanisms such as:

Cation Regeneration

$R{=}Ca^{2+} + H_2SO_4 = 2\ R{=}H^+ + CaSO_4$

Anion Regeneration

$R{=}SO_4^{2-} + Ca(OH)_2 + CaSO_4$

Pilot plant results in South Africa suggest that fouling caused by gypsum precipitation in conventional ion exchange circuits can be avoided using the GYPCIX process (Robertson et al., 1993). As the waste streams can be combined the gypsum in the slurry can be settled and the supernatant water recycled so improving water recovery.

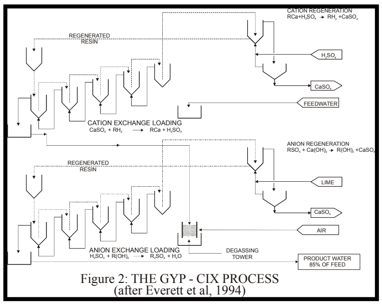

Figure 2: THE GYP - CIX PROCESS
(after Everett et al, 1994)

In a pilot plant the effluent of Berkeley Pit, Butte, Montana was treated by the GYPCIX process and the results are given in Table 2. 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.

A variant of the GYP CIX process was developed by Feng et al. (2000) to co-remove metals and sulfate. In this approach mine water was completely oxidized with hydrogen peroxide as a pre-treatment and this was followed by magnetite-seed precipitation to create Fe-Mn hydroxide precipitate. This was accomplished at pH > 5 to prevent formation of H_2S gas. Sodium sulfide addition followed this to form metal sulfides, which were precipitated at pH > 8 through lime addition. The Fe-Mn hydroxide-oxide fraction can be magnetically separated from the base metal sulfide fraction.

Table 2: Results of GYPCIX treatment on Berkeley Pit effluent (Robertson et al., 1993)

	UNLIMED	**LIMED**	**GYPCIX**
TDS, mg/l	10000	3000	350
pH	2.7	8.5	8.0
Ca, mg/l	490	600	50
Mg, mg/l	420	350	20
Na, mg/l	70	70	50
Fe, mg/l	1100	0.1	<0.1
Mn, mg/l	182	3.6	<0.1
Cu, mg/l	186	<0.1	<0.1
Zn, mg/l	550	<0.1	<0.1
Sulfate, mg/l	8000	1980	200

4.2 Chemical Saturation and Sulfate Salt 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. 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 fine sulfate particles.

4.2.1 Formation of Gypsum

The removal of sulfate by addition of lime or limestone occurs through saturation of $CaSO_4$. The precipitation of insoluble gypsum ($K_{sp} \sim 10^{-2.3}$) 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). The impact of lime treatment on Berkeley pit effluent can be observed to have a pronounced influence on water quality but is nowhere as significant as Ba-salts (Table 3). Similar methods have been proposed for neutralizing acidic drainage with both limestone and dolomite (Maree and DuPleiss, 1994). Recent schemes proposed have demonstrated the ability of semi-passive limestone/lime process to reduce sulfate in mine waters to < 1000 mg/L (Gelddenhuys et al., 2001).

Table 3: Treatment of Sulfate-rich effluents by Ba- and Ca-salt precipitation
Shown as % removal

pH	Lime	$BaCO_3$	BaS	$Ba(OH)_2$
2.9	62.3	24.2	95.6	107.7
7.9	80.5	101.6	110.8	137
12	51	90.1	90.1	134

4.2.2 Formation of Barite

The removal of sulfate by barium carbonate was demonstrated to be effective over 30 years ago (Kun, 1972) by a process such as:

$BaCO_3\ (s) + SO_4^{2-} = BaSO_4\ (s) + CO_3^{2-}$

Kun (1972) recognized three main problems with the method on an industrial scale, the requirements for more soluble Ba in solution than is required stoichiometrically, 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 reform $BaCO_3$ (Wilsenach, 1986). Further consideration of $BaCO_3$ to remove sulfate has come from two research programs in South Africa in the late eighties (Trusler et al., 1988; Maree, 1989; Maree et al., 1989; Adlem, 1997). The processes proposed by these workers are summarized in Figure 3.

Barium carbonate and lime would be added to the effluent to soften the water and produce a precipitate. From experimental work 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. The slurry from the reactor is then sent to a thickener where clean water can be decanted and recycled in the mine or process operation. The thickened slurry is then filtered, dried and treated to recycle barium and collect sulfur. In a modification of this process a two-stage fluidized bed reactor system has been proposed although this process has difficultly with high metal concentrations and separation of fine $CaCO_3$ and $BaSO_4$ (Maree et al., 1989).

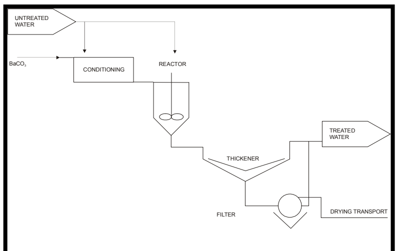

Figure 3: PROCESS FLOW SHEET FOR BARIUM CARBONATE PROCESS (modified from WRC 203/1/90)

As an alternative to $BaCO_3$, BaS has been proposed (Maree et al., 1989; Bosman et al., 1991) as a greater quantity of sulfate is recovered but not as much gypsum is produced; acid waters can be treated directed, eliminating the need for a pre-neutralization step; and sludge disposal (essentially gypsum) is greatly reduced.

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 oxidize sulfides, possibly catalyzed by bacteria. Economically valuable metals can then be recovered (Maree et al., 1989; Bosman et al., 1991). Alternatively the gas H_2S can be formed and vented through a wet scrubbing circuit to recover sulfur. A possible flow sheet for this process is given in Figure 4.

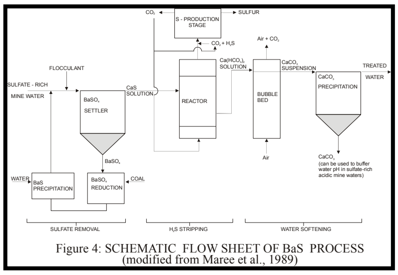

Figure 4: SCHEMATIC FLOW SHEET OF BaS PROCESS (modified from Maree et al., 1989)

The use of $Ba(OH)_2$ has also 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 for complex water treatment associated with the

$BaCO_3$ and BaS processes, does not require long retention times for reactions (such as in the $BaCO_3$ process), and does not require stripping of H_2S as in the BaS process.

As a consequence of all of these reactions direct buffering of protons can occur or, alternatively alkalinity is generated for neutralizing free protons. Because of the cost of barium and its environmental toxicity it is advantageous to have a barium recovery plant to recycle barium 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 metal hydroxide precipitation on the surface of the barium salt. The process additionally removes transition metals, Mg, NH_3 and, to a limited extent, Na. Thus the overall TDS is lowered as well as the concentration of deleterious elements. The $Ba(OH)_2$ causes significant $CaSO_4$ precipitation improving sulfate removal by 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 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 mine waters.

4.2.3 Precipitation of Ettringite

Sulfate removal through the precipitation of Ettringite has been proposed by Smit (1999) as the SAVMIN process. The three stages of the process successively remove metals as hydroxides through lime addition (to pH 12) as a pre-treatment step (Figure 5).

This is followed by removal of gypsum through seed crystallization and in the third step aluminum hydroxide addition to form insoluble ettringite. Finally, prior to discharge, CO_2 is added to reduce pH and precipitate pure $CaCO_3$. The ettringite can either then be disposed of or dissolved in sulfuric acid to recycle $Al(OH)_3$. The resulting effluent can then be seeded with gypsum to produce more gypsum precipitate. Trials at the Stillfontein plant in South Africa successfully treated 500 m^3 of water with a sulfate concentration of 800 mg/L to < 200 mg/L. A variant on the SAVMIN process is the *Cost Effective Sulfate Removal* (CESR) process. In addition to sulfate, metals can also be removed by this process more effectively. Other contaminants, such as nitrate, are removed during the ettringite precipitation step.

4.3 Biological Sulfate Reduction

Under anoxic conditions sulfate may be removed from mine waters as

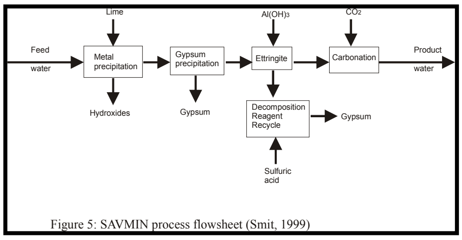

Figure 5: SAVMIN process flowsheet (Smit, 1999)

stable sulfide precipitates. Under these conditions sulfide minerals remain stable and have low solubility (Arenesen et al., 1991). Flooded underground mine workings and open pits can be anoxic, and as such provide a suitable environment for the implementation of a sulfate reduction system. Alternatively a dedicated reactor can be used or anaerobic conditions created in a passive system, such as a constructed wetland. The presence of sulfides (H_2S odor) in many mine water discharges indicates that sulfate reduction is already occurring in mine workings (Huang and Tahija, 1990). The reduction of sulfate to hydrogen sulfide 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 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).

Due to the natural occurrence of the sulfate reducing bacteria, sulfate reduction can be utilized *in situ* for the treatment of acid rock drainage provided the correct conditions can be maintained to sustain bacterial activity. Anaerobic conditions may be enhanced by sealing shafts, adits and air vents. For conditions to be sufficiently anaerobic however, it is likely that a significant depth of water will be required. A wide variety of organic substrates have been investigated for this purpose including molasses, sewage sludge, straw, newspaper, sawdust and manure. Other possibilities are wastes from the chemicals industry such as short chain organic acids. Sulfide precipitation, like hydroxide precipitation, is not just dependent on availability of constituent ions but also on environmental parameters. At low pH copper and iron sulfides can be readily precipitated over a wide pH range but zinc, which forms sulfides in a similar way, has a much slower rate of formation than copper or iron sulfides. Neutral or mildly alkaline conditions tend to be the most favorable for sulfide formation.

4.3.1 In-situ reactor

Because sulfate reducing bacteria occur naturally there is a possibility of treating high sulfate waters using an *in situ* process So far fixed bed reactors and in-pit reactors have been utilized (Arnesen et al., 1991; Huang and

Tahija, 1990; Robins et al., 1997) but stirred reactors with a suspended solid medium have also been proposed, with the aim of achieving higher reduction rates through improved operating conditions and reactor utilization.

Based on limnological-microbiological-geochemical studies a series of three zones have been described for the Summer Camp Pit lake in Nevada (Bowell, 2002) . The upper oxic zone is characterized by high levels of total epifluorescent algae and heterotrophic aerobic bacteria and has high dissolved oxygen content and consequently total sulfur is dominated by sulfate. This zone extends to a depth of 6 m, after which a transitional zone develops, which is characterized by an increase in the presence of heterotrophic anaerobic bacteria and decreasing levels of total epifluorescent algae and heterotrophic aerobic bacteria. Within this zone sulfates (and thiosulfate) are being gradually reduced to sulfide. This zone grades into a zone with little or no available dissolved oxygen and is dominated by heterotrophic anaerobic bacteria. In this zone sulfate is being actively reduced to sulfide and the potential exists for the precipitation of metal sulfides. The addition of raw potato and steer manure amended systems increased sulfate reduction (Gannon et al., 1996). It was found that raw potato-stimulated sulfate reduction was effective at low levels whereas steer manure stimulated sulfate reduction by bacteria at mid-high levels. Using 2500 mg C/l raw potato, 80% sulfate reduction was achieved and additionally soluble arsenic, after an initial increase, decreased to less than 1% of initial values in some cells, presumably due to formation of arsenic sulfide.

4.3.2 Constructed Bioreactors

Anaerobic bioreactors use bacterial reduction of sulfate and iron to accomplish precipitation of metal sulfides (Figure 6).

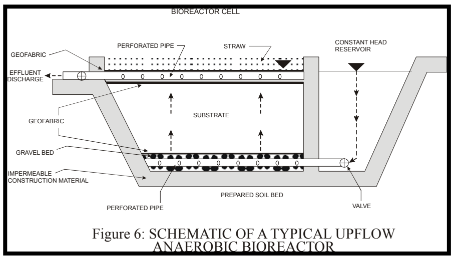

Figure 6: SCHEMATIC OF A TYPICAL UPFLOW ANAEROBIC BIOREACTOR

These reactions can only occur in an anaerobic reactor as the bacteria cannot tolerate oxygen. Effluent treatment therefore requires a uniform rate and flow through the substrate to be effective. 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 produced a sulfate reduction rate of 1.7-2.2 g/l/d over 70 hours reducing effluent drainage sulfate from over 3000 mg/l to less than 250 mg/l.

4.3.3 Constructed wetlands

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 effluent (Machemer et al., 1993; Younger et al., 2002). In the Pelenna valley a pilot scheme was assessed for the effectiveness of wetlands in removing sulfate (Rees and Bowell, 1999). The design discharge flow rate is 3 l/s at an average pH 5.6 with an average total iron content of 21.7 mg/l and sulfate content of 459 mg/l. Over the ten year period of monitoring on the pilot scheme sulfate has been observed to decrease. Sulfur isotope analysis of pore waters from the scheme indicated that whilst sulfate reduction was occurring in the beds, subsequent metal sulfide oxidation offset the treatment with the net effect that in the long term sulfate attenuation would not occur (Rees and Bowell, 1999).

4.3.4 Permeable Reactive Barriers

Permeable Reactive Barriers are a reactive zone in an aquifer created for removal of contaminants by reaction with an introduced material. Although no specific PRB has been developed for sulfate treatment, the reduction in high levels of sulfate in groundwater at an Ontario mine site has been reported (Benner et al., 1999). In this system a mixture of gravel and compost was used to create a biological sulfate reduction zone that precipitated iron sulfide at a rate of sulfate removal of 14 mg/L/day over a 3-year period. A major limitation on the application of such a system is the requirement for stoichiometrically equivalent amounts of reduced metals to sulfide ions in order to limit sulfur dispersion.

5. Evaluation of treatment options for sulfate removal

The criteria by which one of these options is 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 (as important) criterion 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.

Whilst a direct evaluation of the differing merits of the different sulfate removal options outlined in this review is difficult to compare, due to the importance of site-specific requirements, some general comments can be made. Membrane and ion-exchange type processes tend to have high capital and operating costs associated with them (Appendix). Many of the processes also are susceptible to fouling of the membrane or column and virtually all require some form of pre-treatment. In terms of mine water treatment GYPCIX and SPARRO appear to be the most suitable for treatment of high sulfate waters. However, in an economic evaluation of requirements for the treatment of water at the Grootelvei mine in South Africa (Schoeman and Steyn, 2001) operating costs and associated savings were such that EDR and GYPCIX processes were more favourable than RO methods (Table 4).

Table 4: Calculated costs for the treatment of Grootvlei mine water (from data published by Schoeman & Steyn, 2001)

	Reverse Osmosis	**EDR**	**GYPCIX**
Unit cost, US$/m^3	0.88	0.48	0.60
Annual operating costs, $ M	21.9	9	9.6
Brine disposal, US$0.19/m^3	0.82	1.9	2.5
Annual saving (drinking water)	5.5	4.2	3.5
Total annual operating costs, US$M[1]	17.2	6.7	8.6

[1] Calculated costs for a 80,000 m^3/day plant

Chemical precipitation processes, although not widely demonstrated, show some potential for application. However they all require high quantities of relatively pure chemicals for successful operation and produce high volumes of waste. Of the processes reviewed the limestone/lime and SAVMIN processes are the most applicable to mine waters. Where cheap sources of Ba-salts can be procured the Ba-precipitation processes could also be highly effective in reducing sulfate in mine effluents.

In recent years the majority of research related to sulfate removal has focused on biological sulfate reduction and currently these are the most widely applied methods (after addition of lime/limestone) for sulfate removal. The advantage of processes such as the Biotech method in producing a commercially value by-product (metal sulfide concentrate), the low volume of resulting solid waste, and the relative inexpensive approach, make bioreactors the most favourable approach currently in sulfate removal from mine waters.

Where sulfate levels are very low there is no requirement for sulfate treatment. Below sulfate levels of approximately 500-1500 mg/l, passive measures can be utilized, while at higher levels (1500-10000 mg/l) a wide range of options are available including Reverse Osmosis, SAVMIN, GYPCIX, filtration, desalination, bioreactors and salt precipitation. At very high levels of sulfate (> 10000 mg/l) co-precipitation is probably most suitable, options for which include SAVMIN, CESR and possibly bioreactors.

6. Conclusions

Sulfate removal from mine waters is still considered to be of secondary importance compared to removal of metals and acidity. As such it is comparatively less understood and few case studies exist for evaluation.

Future trends in regulatory practice may promote more research and application of sulfate removal technologies as desalination of mine water effluent becomes more important.

Various options exist for sulfate removal. Chemical precipitation is generally the least costly, but produces high volumes of waste by-products. The SAVMIN process, although expensive in terms of proposed operating and capital costs, offers the most efficient treatment of high sulfate waters by precipitation methods.

Membrane and ion exchange processes, with the exception of SPARRO and GYPCIX, are not suitable for mine water treatment unless extensive pre-treatment is applied.

Biological Sulfate Reduction offers perhaps the most versatile and widely applicable approach to sulfate removal from mine waters and has the benefit of being able to couple sulfate and metal removal.

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References

AWWA, 1999 Water Quality and Treatment. 5th Edition, American Water Works Association. McGraw Hill Inc., New York.

Adlem, C.J.L., Maree, J.P., and Pleiss, P.Du. 1991 Treatment of sulfate-rich mining effluents with the Barium Hydroxide process and recovery of valuable by-products. In: 4th International Mine Water association Congress, Ljubljana (Slovenia)-Portschach (Austria), September 1991, 211-221.

Adlem, C.J.L. 1997 Treatment of sulfate-rich effluents with the barium sulfide process. MSc thesis. University of Pretoria, South Africa.

Alpers, C.A., Nordstrom, D.K. ad Spitzley, J. 2003 Extreme acid mine drainage from a pyritic massive sulfide deposit: The Iron Mountain end-member. In: Environmental Aspects of Mine Wastes, editors: J.L. Jambor, D.W. Blowes and A.I.M Ritchie. Mineralogical Association of Canada Short Course Series No. 31, 407-430.

Arnesen, R.T. et al. (1991) Monitoring water quality during filling of the Løkken mine: Role of sulfate reducing bacteria in metals removal. 2nd Int. Conf. Abatement Acid Drainage, Montréal, Canada, 16-18/9/91.

Benner, S.G., Blowes, D.W., Gould, W.D., Herbert, R.B., and Placek, C.J. 1999 Geochemistry of a permeable reactive barrier for metals and acid mine drainage. Environmental Science and Technology, 33, 2793-2799.

Bollinger, J.M. 1984 New filtration concepts using Electrodeposition. Chem.Eng., May 1984: 327-374.

Bosman, D.J. 1985 Productive use of water in mining. SA Water bulletin. February 1985.

Bosman, D.J., Clayton,J.A., Maree, J.P. and Adlem, C.J.L. 1991 Removal of sulfate from mine water. In: Proceedings of the ARD in Pyrite Environments, Lisbon, Portugal, 16-19 September 1990. 211-221

Bowell, R.J. 2000 Sulfate and salt minerals: the problem of treating mine waste. Mining and Environmental Management, 11-14.

Bowell, R.J. 2002 Hydrogeochemical dynamics of Pit Lakes. In: Younger, P.L. and Robins, N. (eds) Mine Water Hydrogeology and Geochemistry. Geological Society of London Special Publication, No.198, 159-186.

Buchanan, J. 1987 Basics of filtration. Water Sewage & Effluent. September 1987; 35-36.

Chamber of Mines Research Organization 1988 New desalination program on stream. R&D News CM. October 1988.

Chappelle, F.M. 1993 Groundwater Microbiology and Geochemistry. Prentice-Hall.

Cravotta, C.A. III 1994 Secondary iron-sulfate minerals as sources of sulfate and acidity. In: Environmental Geochemistry of Sulfide Oxidation (eds: C.N. Alpers and D.W. Blowes). Am.Chem. Soc. Sym. Series, 550. 1994. 345-364.

Department of Water Affairs and Forestry, South Africa 1993 South African Water Quality Guidelines 4 vols. DWAF, SA.

Dill, S., Du Preez, L., Graff, M. and Maree, J. 1994 Biological sulfate removal from acid mine drainage utilizing producer gas as carbon and energy source. 5th International Mine Water Congress, September 1994: 631-641.

Du Pleiss, G.H. and Swartz, J.A. 1992 Tubular Reverse Osmosis treatment of Secunda mine water: a pilot plant investigation. Water Science Technology, 25, 193-201.

Du Preez, L.A., Maree, J.P., and Jackson-Moss, C.A. 1992 Biological sulfate removal from industrial effluents. Environ. Tech., 13: 875-882.

Eckenfelder, W W 1989 Industrial Water Pollution Control. McGraw Hill, 400pp

Eriksson, P. 1988 Nanofiltration extends the range of membrane filtration. Environmental Progress, 7: 58-62.

Everrtt, D.J., Du Plessis, J. and Gussman, H.W. (1994) The removal of salt from underground mine waters. Mining Env. Management, March 1994: 12-14.

Feng, D., Aldrich, C., and Tan, H. 2000. Treatment of acid mine water by use of metal precipitation and ion exchange. Minerals Engineering, 13(6), 623-642.

Fillipek, L.H. and Owen, R.M. 1980 Early Digenesis of organic carbon and sulfur in outer shelf sediments from the Gulf of Mexico. Am. J.Sci., 280: 1097-1112.

Flanagan, P.J. 1990 Parameters of water quality: Interpretation and standards. Environmental Resources Unit. 160pp.

Gannon, J., Wielinga, B., Moore, J.M., Policastro, P., McAdoo, D and Meikle T. 1996 Field Investigations of the Sulfate reducing potential in the

Summer Camp Pit lake. Bitterroot consultants. 1996. 12pp.

Geldenhuys, A.J., Maree, J.P., de Beer, M. and Hlabela, P. 2001 An integrated limestone/lime process for partial sulfate removal. Proceedings of Environmentally Responsible Mining in South Africa, September 2001. CSIR, Pretoria, South Africa.

Gould, W.D., Bechard, G. and Lortie, L. 1994 The nature and role of microorganisms in mine drainage. In: Environmental Geochemistry of Mine Waste*,* (eds: J.L.Jambor and D.W. Blowes). 185-199, MAC.

Gussman, H.W. and Nagy, P. 1993 The development and operation of the GYPCIX pilot plant, JCI MPRL, Johannesburg, SA, July 1993.

Harries, R.C. 1985 A field trial of Seeded Reverse Osmosis for desalination of a scaling type mine water. Desalination, 56: 227-236.

Haynike, J.J.C. and McCullough, S.F. 1982 The impact on an Urban and Industrial complex of mineral pollution in the water supply. Wat. Sci. Tech., 14: 381-395

Helfferich, F. 1962 Ion Exchange. McGraw-Hill, San Francisco: 624 pp.

Huang, H-H. and Tahija, D., 1990 On the nature of Berkeley Pit Water. Proceedings Mineral and Hazardous Waste Processing Symposium. Butte Montana 10/01/90.

Juby, G.J.G. 1989 Membrane desalination of mine water. WISA Conference. March 1989.

Juby, G.J.G. and Pulles, W. 1990 Evaluation of Electrodialysis reversal for desalination of brackish mine water. WRC Report 179/1/90.

Kleinmann, R.L.P. and Pacelli, R.R. 1991 Biogeochemistry of acid mine drainage. Mining. Eng.*,* 33, 300-6.

Kun, L.E. 1972 A report on the reduction of the sulfate content of acid mine drainage by precipitation with barium carbonate. Anglo American Research Laboratories. D/3/W/1.

Lorax 2003 A review of sulfate treatment. Report to INAP by Lorax consultants. Electronic document, INAP website.

Machember, S.D., Reynolds, J.S., Laudon, L.S., and Wildeman, T.R. 1993 Balance of sulfur in a constructed wetland built to treat acid mine drainage, Idaho Springs, Colorado. Appl. Geochem., 8: 587-603.

Marree, J.P. 1989 Sulfate removal from Industrial effluents. PhD thesis. Univ. Orange Free State.

Maree, J.P., Bosman, D.J. and Jenkins, G.R. 1989 Chemical removal of sulfate, calcium and metals from mining and power station effluents. Water Sewage and Effluent, 9: 10-25.

Marree, J.P. and Du Plessis, P. 1994 Neutralization of acid mine water with calcium carbonate. Wat.Sci.Tech.*,* 29: 285-296.

Maree, J.P., Hulse, G., Dods, D. and Schutte, C.E. 1991 Pilot plant studies on biological sulfate removal. Water Pollution Research and Control, part 3. CSIR.

Nordstrom D.K. 1982 Aqueous pyrite oxidation and the consequent formation of secondary minerals. In: Acid Sulfate Weathering, 37-56. Soil Sci. Soc. Am.

Pulles, W., Juby, G.J.G., and Busby, R.W. 1992 Development of the Slurry Precipitation and Recycle Reverse Osmosis Technology for desalinating mine waters. Water, Sci. Tech., 25. 25pp.

Rees, S.B. and Bowell, R.J. 1999 Stable Isotopic Modeling of the Longevity of Treatment Processes Operating in a Constructed Wetland for the Amelioration of Acid Mine Drainage. In: IMWA 20th Mine Water Conference, Seville, September 1999, 585-590

Robins, R.G. et al.1997 Chemical, physical and biological interaction at the Berkerley Pit, Butte, Montana. Tailings and Mine Waste `97. 529-541. Balkema, Rotterdam.

Robertson, A.M., Everett, D., Du Plessis, P. 1993 Sulfate removal by GYPCIX process following lime treatment. In: SUPERFUND XIV Conference, 30/11-2/12/93, Washington USA.

Sayre, I.M. 1988 International Drinking Water Standards. Journal of AWWA, January 1988.

Schoeman J.J. and Steyn, A. 2001 Investigations into alternative water treatment technologies for the treatment of underground mine water discharged by Grootelvei Proprietary Ltd into the Blesbokspruit, South Africa. Desalination, 133, 13-30.

Smit, J.P. 1999 The purification of polluted mine water. Proceedings of the International Symposium on Mine Water & Environment for the 21st Century, Seville, Spain.

Tahija ,D., Huang, H-H., Flores, C., and Shi, Y. 1990 On the treatment of Berkerley Pit Water. Proceedings Mineral and Hazardous Waste Processing Symposium. Butte Montana 10/01/90.

Trudinger, A., Chambers, L.A., and Smith, J.W. 1985 Low temperature sulfate reduction: biological versus abiological. Can.J.Earth Sci., 22, 1910-1918.

Trusler, G.E., Edwards, R.I., Brouckaert, C.J., and Buckley, C.A. 1988 The chemical removal of sulfates. Proceedings of the 5th National Meeting of the South African Institute of Chemical Engineers, Pretoria, W3-0-W3-11.

USEPA, 1999 National Recommended Water Quality Criteria Correction. EPA 822-Z-99-001, Washington DC.

USEPA, 2002 Edition of Drinking Water Standards and Health Advisories. EPA 822-R-02-038, Washington DC.

WHO 1996 Guidelines for drinking water quality. Geneva (2 vols.), 2nd edition.

Wilsenbach, I., 1986 Cost estimate for barium sulfate reduction. Internal report of the Division of Water Technology, CSIR, 620/2616/6.

Younger, P.L., Banwart, S.A., and Hedin, R.S. 2002 Mine water: Hydrology, Pollution, Remediation. Kluwer Oordecht.

Table A.1

Summary of case studies on treatment processes using membranes and ion-exchange (after Bowell, 2000; Lorax, 2003)

	RO	SPARRO	EDR	GYP-CIX	Filtration
Pretreatment	yes	yes	yes	no	Yes
Feed water sulfate limits	SO_4: any	SO_4: any	SO_4: any	SO_4: any	SO_4: any
Sulfate removal	SO_4:>99%	SO_4:>99%	SO_4:>95%	SO_4:>95%	SO_4:>95%
Brine production	yes	yes	yes	yes	yes
Sludge production	low	low	low	low-moderate	moderate-high
Monitoring	low-moderate	low-moderate	low-moderate	low	moderate-high
Maintenance	high	high	high	moderate	high
Capital cost	£0.46 M[1] per 10^3 m^3 / day	£0.48 M[1] per 10^3 m^3 / day	£0.39 M[1] per 10^3 m^3 / day	£0.22 M[1] per 10^3 m^3 / day	£ 0.28 M[1] per 10^3 m^3 / day
Operating costs	£ 0.49 / m^3	£ 0.17 / m^3	£ 0.27 / m^3	£ 0.33 / m^3	£ 0.15 / m^3
Advantages	- drinking water quality	- drinking water quality - improved membrane life	- drinking water quality	- drinking water quality	- drinking water quality
Disadvantages	- scaling problems - short membrane life	- short membrane life	- scaling problems - short membrane life	- sludge production	- scaling problems - short membrane life
Improvements	- not suitable for scaling waters	- membrane life	- not suitable for scaling waters	- sludge recycling - metal recovery	

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[1] Conversion used: South African R 15 = £1 = USD1.78)

Table A.2

Summary of case studies on treatment processes with mineral precipitation

	Limestone / Lime	**BaS**	**SAVMIN**	**CESR**
Pretreatment	no	no	no	no
Feed water sulfate limits	SO_4: any	SO_4: any	SO_4: any	SO_4: any / L
Sulfate removal	50 %	>98%	>90%	>95%
Brine production	no	no	no	no
Sludge production	low-moderate	low-moderate	moderate-high	high-very high
Monitoring	moderate-high	high	high	high
Maintenance	low	low	low	low
Capital cost[2]	£ 0.13 M per 10^3 m^3 / day	£ 0.25 M per 10^3 m^3 / day (ΔSO_4: 2,000mg / L)	£ 0.18 M per 10^3 m^3 / day	£0.22 M per 10^3 m^3 / day
Operating costs[1]	£ 0.34 / m^3	£ 0.22 / m^3 (SO_4: 2,000mg / L)	£ 0.12 / m^3	£ 0.44 / m^3 (SO_4: 1,500mg / L)
Advantages	- also trace metal removal - very cheap	- low levels of sulphate - recycling of expensive BaS	- low levels of sulphate - recycling of ettringite - also trace metal removal	- low levels of sulphate - also trace metal removal
Disadvantages	- limited sulphate removal - production of sludges	- little trace metal removal - production of sludges	- production of sludges	- production of sludges
Improvements	- recycling of sludges	- recycling of sludges	- recycling of sludges	- recycling of sludges

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Table A.3
Summary of case studies on treatment processes using biological sulphate removal

	Bioreactor	**Constructed Wetland**	**Alk. Producing systems**	**Permeable barrier**
Pre-treatment	yes	yes	yes	no
Feed water sulfate limits	SO_4: any	SO_4: <2000mg / L	SO_4: <2000mg / L	SO_4: <2000mg / L
Sulfate removal	>90 %	>50%	>50%	>80%
Sludge production	low-moderate	moderate-high	moderate-high	moderate
Monitoring	moderate-high	low	low	low
Maintenance	moderate	low	low	low
SO_4 reduction rate	5-30g / L, day	0.03-0.2mg / L, day	0-0.05mg / L,day (low)	<1-20mg / L,day
Capital cost	£ 0.18 M per 10^3 m^3 / day (ΔSO_4: 2,500mg / L)	£0.06 M per 10^3 m^3 / day	£0.08 M per 10^3 m^3 / day	£45,000
Operating costs	£0.17 / m^3 (ΔSO_4: 2,500mg / L)	£0.05 / m^3	£0.06 / m^3	£16,850 / yr
Advantages	- also trace metal recovery - recycling of H_2S and CO_2 - low maintenance	- also trace metal removal - passive treatment	- gypsum precipitation - also (trace) metal removal	- passive treatment - also trace metal removal
Disadvantages	- cost of C + energy source - production of sludge	- little sulphate reduction - sludge disposal - limited time life	- sludge disposal - limited time life	- long-term performance unknown - prone to scaling
Improvements	- recycling of sludge - cheap C + energy source	- specific design required	- specific design required	- alternative reactive media