International Network for Acid Prevention

Treatment of Sulphate in Mine Effluents

October 2003

LORAX ENVIRONMENTAL

EXECUTIVE SUMMARY

International Network for Acid Prevention

Executive Summary

In the treatment of Acid Rock Drainage (ARD) little attention has focused on the mitigation of dissolved sulphate; this may be attributed to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals. However, regulatory agencies are becoming increasingly concerned over elevated sulphate concentrations in effluents owing largely to its impact to the salinity of receiving waters. This concern will like result in more stringent regulatory standards for sulphate in effluent such that sulphate treatment becomes necessary. Although sulphate treatment is currently under investigation and in many cases in practice, comparatively little information has been documented. In light of this, the International Network for Acid Prevention (INAP) has decided to investigate the current state of the art of sulphate treatment.

The primary objective of this review is to present an overview of the current state of the art treatment processes to reduce sulphate (with or without dissolved metals) in mine effluents. The organization and sharing of knowledge on such processes will hopefully guide future developments in reducing dissolved sulphate in ARD.

The consumption of drinking water containing sulphate concentrations in excess of 600 mg/L commonly results in laxative effects. The taste threshold for the most prevalent sulphate salts ranges from 250 to 500 mg/L. While the World Health Organization (WHO) does not propose a health-based guideline for sulphate in drinking water, it does *recommend* that health authorities are notified if sulphate concentrations exceed 500 mg/L. Accordingly, most countries in the world *recommend* a drinking water standard for sulphate between 250 and 500 mg/L.

After a review of the available information, several treatment processes were selected for review. The selection criteria for each process were based on: (1) applicability to sulphate removal and (2) availability of data on sulphate removal and costs. The treatment processes meeting these criteria were organized into 4 categories:

(1) chemical treatment with mineral precipitation;
(2) membranes;
(3) ion-exchange; and,
(4) biological sulphate removal.

The selected sulphate treatment processes are well-documented and often tested in (pilot) plants or large field-trials. For many of the selected treatment processes at least some estimate of the capital and/or operational costs are available. Several other ARD treatment processes are not included in this review because they cannot be used for the removal of sulphate from ARD.

Treatment processes that represent chemical ammendments with mineral precipitation are: (1) lime or limestone addition, (2) addition of barium salts, (3) the SAVMIN process and (4) the cost-effective sulphate removal (CESR) process. Membrane technology include: (1) Reverse Osmosis (RO), (2) the SPARRO process and (3) Electrical Dialysis Reversal (EDR), while ion-exchange technologies include: (1) the GYP-CIX process and (2) Metal Precipitation and Ion-Exchange (GYP-CIX). The sulphate treatment processes that incorporate biological sulphate removal include: (1) Bioreactors, (2) Constructed Wetlands, (3) Alkalinity Producing Systems, and (4) Permeable Reactive Barriers.

The most important characteristics of the sulphate treatment processes used in the case studies are summarized in Table I to Table III for the different types of treatment technology.

When comparing costs of the different treatment processes it should be noted that: (1) estimated costs depend strongly on the specific process design, local market prices and local labour costs; (2) cost estimates are time-sensitive and have not been normalized to present day cost. Accordingly, the reported capital and operating costs should be used with caution.

Among the processes that use chemical treatment with mineral precipitation (Table I), the limestone/lime and SAVMIN processes appear to be the most suitable for sulphate removal from mine water. Although the limestone/lime process can only reduce sulphate concentrations to 1200 mg/L, it is inexpensive and therefore useful as a pretreatment process for other, more expensive treatment systems. The more expensive SAVMIN process, can reduce sulphate concentrations to very low levels. Both processes also remove (trace) metals from mine water. The BaS and CESR processes are probably the most expensive and the CESR process produces the largest amount of sludge. Compared to other types of treatment technology (Table II and Table III), chemical treatment processes with mineral precipitation produce the largest amount of sludge. Any development of new techniques which reduce or recycle these sludges would make the chemical treatment processes much more attractive.

Among the treatment processes that use membranes or ion-exchange (Table II), only the GYP-CIX process and possibly also the SPARRO process are really suitable for the treatment of scaling mine waters (high in SO_4 and Ca as opposed to high in Na and Cl). The major advantage of all treatment processes is that they can produce high quality water that can be used (sold) as drinking water. A major disadvantage of this class of treatment processes is the production of brine that requires disposal (and additional costs). Operating costs of the GYP-CIX process and possibly also the SPARRO process could be greatly reduced if the water pretreatment involved the limestone/lime treatment process.

The bioreactor and the permeable reactive barrier appear to be the most efficient among the treatment processes that use biological sulphate removal. Although the processes operate on different scales, both show the greatest potential for sulphate removal from mine water. Operating costs of the bioreactor could be further reduced by developing alternative, less-expensive carbon and energy sources. The latter could also contribute to the long-term performance of the permeable reactive barrier which is not known yet. Treatment processes that use biological sulphate removal also remove trace metals by precipitation of metal sulphides.

Constructed wetlands and alkalinity producing systems are the least efficient sulphate removal processes. It is doubtful that any substantial sulphate reduction occurs in alkalinity producing systems, and the contribution to the sulphate removal in constructed wetlands appears to be limited. The contribution of mineral precipitation (gypsum) to the removal of sulphate from mine water in wetlands, appears to be more important than the contribution of sulphate reduction. The limited extend of sulphate reduction in constructed wetlands may be related to their design, which were originally based on the removal of other dissolved elements (*e.g.* Fe, Mn). Hence, new designs may have to be developed if constructed wetlands are to be used specifically for sulphate removal by sulphate reduction. Despite the limited sulphate removal, trace metals are very effectively removed in constructed wetlands.

Based on an extensive review of available treatment technologies that can be used for sulphate removal from mine drainage, the following conclusions can be made:

- Existing treatment technologies for mine drainage are generally poorly documented and not readily available. A better organization (centralized) and exchange of information could greatly improve and guide future advances in the development of better and less expensive treatment technologies.
- Although stringent guidelines for sulphate concentrations in mine water do not yet exist, it is relatively easy to combine the removal of trace metals with the removal of sulphate using existing treatment processes (*e.g.* SAVMIN, GYP-CIX or Biological Sulphate Reduction).
- Chemical treatment processes with mineral precipitation are generally the least expensive but produce the largest amounts of waste (sludge). Improved methods to reduce or recycle the voluminous sludge need to be developed.
- With the possible exception of the SPARRO process, membrane treatment processes are not well suited for the treatment of mine waters because of the high concentrations of Ca and sulphate. Even with the production of high quality (drinking) water, operating costs are presently very high. Thus, unless high-purity water is required on site or can be sold to offset operational costs, membrane treatment processes will likely have less application for sulphate treatment.
- Treatment processes that use ion-exchange (GYP-CIX) are a good alternative for membrane treatment processes if scaling mine waters require treatment. The frequency of ion-resin regeneration can be reduced by pretreatment of the mine water (*e.g.* limestone/lime process). Similar to the water produced in membrane treatment processes, water produced by the GYP-CIX process can be sold as drinking water.
- Among the treatment processes that use biological sulphate reduction, the bioreactor and permeable reactive barrier are the most efficient. An added benefit of biological sulphate reduction is the removal of trace metals from the mine water. For an improvement of the efficiency of biological sulphate removal in constructed wetlands and alkalinity producing systems, additional research and development of their design is required.

- For the removal of sulphate from mine water, the limestone/lime process (as pretreatment), the SAVMIN process, the GYP-CIX process and biological sulphate reduction in a bioreactor or permeable reactive barrier appear to be the most suitable treatment processes. However, site-specific conditions will factor heavily into determining which approach is best suited to a particular mine site.

- Among the four most suitable treatment processes, sulphate removal by biological sulphate reduction has the greatest potential. The major advantages of biological sulphate reduction are: (1) both sulphate and trace metals can be reduced to very low levels; (2) the amount of waste produced is minimal; (3) capital cost are relatively low and operating costs can be drastically reduced by the development of inexpensive carbon and energy sources; (4) trace metals in mine drainage in certain circumstances can be selectively recovered and sold for additional savings

Table I:
Summary of case studies on chemical treatment processes with mineral precipitation

	Limstone/Lime	BaS	SAVMIN	CESR
	2001	1990	1999-2001	2001 ?
Pretreatment	no	no	no	no
Feed water	SO_4: 3,000 mg/L	SO_4: 27,500 mg/L	SO_4: 649 mg/L	SO_4: 29,100 mg/L
Product water	SO_4: 1,219 mg/L	SO_4: 190 mg/L	SO_4: 69 mg/L	SO_4: 190 mg/L
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[1]	unknown (low)	USD 0.48 M per 10^3 m^3/day (Δ SO_4: 2,000 mg/L)	USD 0.31 M per 10^3 m^3/day	unknown
Operating costs[1]	USD 0.10 / m^3	USD 0.36 / m^3 (Δ SO_4: 2,000 mg/L)	USD 0.17 / m^3	USD 0.79 / m^3 (Δ SO_4: 1,500 mg/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

[1] Assuming South African R 1 = USD 0.104 or R 9.62 = USD 1.00 (Nov. 2002)

Table II:
Summary of case studies on treatment processes using membranes and ion-exchange

	RO	**SPARRO**	**EDR**	**GYP-CIX**
	2001	1992-1994	2001	2001
Pretreatment	yes	yes	yes	no
Feed water	SO_4: 4,920 mg/L	SO_4: 6,639 mg/L	SO_4: 4,178 mg/L	SO_4: 4,472 mg/L
Product water	SO_4: 113 mg/L	SO_4: 152 mg/L	SO_4: 246 mg/L	SO_4: <240 mg/L
Brine production	yes	yes	yes	yes
Sludge production	low	low	low	low-moderate
Monitoring	low-moderate	low-moderate	low-moderate	low
Maintenance	high	high	high	moderate
Capital cost	USD 0.44-0.53 M[1] per 10^3 m^3/day	USD 0.52 M[2] per 10^3 m^3/day	USD 0.56-0.67 M[1] per 10^3 m^3/day	USD 0.33-0.37 M[1] per 10^3 m^3/day
Operating costs	USD 0.88 / m^3	USD 0.22[2] / m^3	USD 0.48 / m^3	USD 0.60 / m^3
Advantages	- drinking water quality	- drinking water quality - improved membrane life	- drinking water quality	- drinking water quality
Disadvantages	- scaling problems - short membrane life	- short membrane life	- scaling problems - short membrane life	- production of sludges
Improvements	- not suitable for scaling waters	- membrane life	- not suitable for scaling waters	- recycling of sludges

[1] Calculated from capital costs for plants with feed of 45-80 10^3 m^3/day (worst-case scenario Grootvlei mine water)
[2] Costs based on 1992 prices (S.A.), conversion used: South African R 1 = USD 0.104 or R 9.62 = USD 1.00 (Nov. 2002)

Table III:
Summary of case studies on treatment processes using biological sulphate removal

	Bioreactor	Constructed Wetland	Alk. Producing Systems	Permeable Reactive Barrier
	2001	1993/1999	1999	1999-2002
Pretreatment	yes	yes	yes	no
Feed water	SO_4: 8,342 mg/L	SO_4: 1,700 mg/L	SO_4: 3,034 mg/L	SO_4: 2,500-5,200 mg/L
Product water	SO_4: 198 mg/L	SO_4: 1540 mg/L	SO_4: 1,352 mg/L	SO_4: 840 mg/L
Sludge production	low-moderate	no	no	no
Monitoring	moderate-high	low	low	low
Maintenance	moderate	low	low	low
SO_4 reduction rate	12-30 g/L,day	0.3-197 mg/L,day	0 mg/L,day	max. 10.5-15.3 mg/L,day
Capital cost	USD 0.24 M[1] per 10^3 m^3/day (Δ SO_4: 2,000 mg/L)	unknown (low)	unknown (low)	USD 65,000
Operating costs	USD 0.27[1] / m^3 (Δ SO_4: 2,000 mg/L)	unknown (low)	unknown (low)	USD 30,000 / yr
Advantages	- also trace metal removal - recycling of H_2S and CO_2	- 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	- no sulphate reduction ?	- long-term performance ?
Improvements	- recycling of sludge - cheap C + energy source	- specific design requird	- specific design requird	- alternative reactive media

[1] Costs based on 1992 prices (S.A.), conversion used: South African R 1 = USD 0.104 or R 9.62 = USD 1.00 (Nov. 2002)

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1. INTRODUCTION

1. Introduction

1.1 Rationale

The primary effort in the treatment of Acid Rock Drainage (ARD) has dealt with acidity and dissolved metals due largely to their toxicity and the associated environmental liability. Considerably less attention has focused on the treatment of dissolved sulphate in ARD despite the high concentrations measured in some systems. This is in part attributed to the lower toxicity of sulphate when compared to those for acidity and trace metals in aquatic systems.

Increasingly, regulatory agencies are becoming concerned about elevated sulphate concentrations in effluents. This concern will result in more stringent standards for sulphate in effluents; inevitably, sulphate treatment will be required at many mine sites around the world. In response to such concerns, several sites in the United States, Australia, Canada and South Africa are currently investigating or using some form of sulphate treatment system. Much of this work has not been formally documented in research papers or technical reports, but contains valuable information on the operational practicality of treatment for this parameter. The increasing concern over sulphate, in concert with the disjointed nature of sulphate treatment options prompted INAP (the International Network for Acid Prevention) to investigate the current state of the art approaches to sulphate treatment.

INAP is an industry based initiative that aims to globally coordinate research and development into management of sulfide mine wastes. The principal objectives of INAP are to promote significant improvements in the management of sulphidic mine materials and the reduction of liability associated with ARD through knowledge sharing, research, and development of technology. An assessment of state of the art treatment technologies for sulphate is consistent with this mandate and is the subject of this report.

The main objective of this review is to present an outline and summary of the current state of the art in sulphate treatment processes (with or without dissolved metals) in ARD and effluents. The organization and sharing of knowledge on sulphate treatment will hopefully guide future developments in reducing dissolved sulphate in ARD and mine effluent.

The report is divided into five chapters. The remainder of Chapter 1 is dedicated to a brief assessment of toxicity and health effects associated with sulphate in concert with water quality guidelines. Chapter 2 outlines the approach to selection of appropriate sulphate treatment processes while Chapter 3 presents the details of each of the selected technologies. Chapter 4 offers select case studies to illustrate the strengths, weaknesses, costs and potential improvements on the selected technologies and Chapter 5 compares and contrasts the various processes, and thus provides a framework for decision-making in selecting an appropriate technology.

1.2 Toxicity, Health Effects and Guidelines

Sulphate is one of the least toxic anions with a lethal dose for humans of 45 g as potassium or zinc salt (WHO, 1996); in such cases, it is questionable as to whether the toxicity is associated with the sulphate or the counter ion. The reported minimum lethal dose of magnesium sulphate in mammals is 200 mg/kg.

People consuming drinking water containing sulphate in concentrations exceeding 600 mg/L commonly experience cathartic effects, resulting in purgation of the alimentary canal (WHO, 1996). However, with time humans appear to be able to adapt to higher sulphate concentrations. Dehydration has also been reported as a common side effect following the ingestion of large amounts of magnesium or sodium sulphate. The taste threshold concentrations for the most prevalent sulphate salts are 250 to 500 mg/L.

Accordingly, the World Health Organization (WHO) does not propose a health-based guideline value for sulphate in drinking water. However, because of laxative effects associated with high sulphate levels in drinking water, WHO *recommends* that health authorities are notified of sulphate concentrations in drinking-water that exceed 500 mg/L. Based on the same information, the United States Environmental Protection Agency (USEPA) uses a “secondary standard” (NSDWR) of 250 mg/L for sulphate in drinking water (USEPA, 2002), which is based on the observed taste threshold. Secondary standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (*e.g.* tooth discoloration) or aesthetic effects (*e.g.* taste or odor) in drinking water. Most countries in the world *recommend* a drinking water standard for sulphate between 250 and 500 mg/L.

Guidelines for water quality and (mining) effluents differ considerably among countries, states or provinces; those of the USEPA are reasonably representative and are discussed as an example.

The USEPA does not list a specific value for the sulphate concentration in the “National Recommended Water Quality Criteria” (USEPA, 1999). However, it recommends a Total Dissolved Solids (TDS) concentration of 250 mg/L. This implies that the maximum allowed sulphate concentration in water is less than this value 250 mg/L. Although the USEPA only *recommends* water quality criteria, most states adopt these guidelines. For fresh water used for drinking and food processing the TDS may not exceed 500 mg/L. By inference, sulphate concentrations in this case may not exceed approximately 250 mg/L. The TDS of fresh water used for agriculture may not exceed 1,000 mg/L whereas fresh water used for aquaculture has a TDS limit of 1,500 mg/L. Apart from these general guidelines Alaska and other states also regulate the water quality of specific rivers and lakes (USEPA, 2000).

The Clean Water Act (CWA, 1972) gives the USEPA the authority to set effluent limits on an industry-wide (technology-based) and on a water quality basis that ensure protection of the receiving water. The CWA allowed the USEPA to authorize the National Pollutant Discharge Elimination System (NPDES) permit program to state governments. Anyone who wants to discharge pollutants has to obtain first an NPDES permit. Effluent guidelines and standards for the (ore) mining industry are organized under different subcategories (ores) in the Ore Mining and Dressing Point Source Category. Guidelines are developed based on the degree of pollutant reduction attainable by an industrial category through the application of pollutant control processes. These guidelines include effluent limitations representing the degree of effluent reduction by the application of the best practicable control technology currently available (NPT) and by the application of the best available technology economically achievable (BAT). For the Copper, Lead, Zinc, Gold Silver and Molybdenum Ores subcategory effluent limitations are set for pH and dissolved metals but not for sulphate or TDS concentrations. The absence of rigorous guidelines is ultimately why treatment of dissolved sulphate in ARD and effluent has received less attention than the treatment of acidity and dissolved metals.

2. APPROACH

2. Approach

2.1 Selection of Treatment Processes

Information on existing sulphate treatment processes was obtained from available literature and knowledge provided by mining associations in Canada, US, Australia, and South Africa. After a review of the available information, different treatment processes were selected for review. The selection of treatment processes was based on (1) applicability to sulphate removal and (2) availability of data on sulphate removal and costs. The selected treatment processes were organized into 4 categories: (1) chemical treatment with mineral precipitation, (2) membranes, (3) ion-exchange, and (4) biological sulphate removal (Table 2-1).

Table 2-1:
Sulphate Treatment Processes Described in Report

Chemical Treatment	Membranes	Ion Exchange	Biological Sulphate Removal
Limestone/Lime	Reverse Osmosis	GYP-CIX	Bioreactors
Barium Salts	SPARRO	GYP-CIX hybrid	Constructed Wetland
SAVMIN	Electrical Dialysis Reversal		Alkalinity Producing Systems
CESR			Permeable Reactive Barriers

The sulphate treatment processes presented in Table 2-1 are well-documented and in most cases tested in pilot plants or large field trials, very few full-scale plants exist. For many of the selected treatment processes at least some estimate of the costs involved is available. Several other ARD treatment processes are not included in this review because they cannot be used for the removal of sulphate from ARD or effluent.

2.2 Characteristics of Treatment Processes

Characteristics of the different sulphate treatment processes are described in terms of the key properties and processes involved, the impact on water quality. In addition, the monitoring and maintenance required to sustain the performance of the sulfate treatment processes are discussed. If relevant, design modifications of the treatment processes are also included in their description.

2.3 Evaluation of Treatment Processes

The various sulphate treatments presented in Table 2-1 are evaluated using selected case studies. The case studies are meant to demonstrate the operational use of each process, including advantages, disadvantages and future needs. If available, specific data on capital and operating costs, including monitoring and maintenance, are reported. However, it is very important to note that the case studies are from different sites with markedly differing conditions, issues and costs. Accordingly, caution must be exercised in making direct comparisons between treatment techniques based on the case studies alone. Rather, the case studies are better used to provide information on the magnitude and variability of the loadings experienced at different sites and the efficacy of a particular treatment to a specific problem. Overall the case studies are used to assess the performance of the sulphate treatment systems under different effluent scenarios.

3. SULPHATE TREATMENT PROCESSES

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3. Sulphate Treatment Processes

This chapter describes the details of the various sulphate treatment processes. Processes are broadly categorized as those utilizing: chemical treatment, semi-permeable membranes, ion exchange and biological mechanisms. Discussions in this chapter are limited to process details; examples and case studies are presented in Chapter 4.

3.1 Chemical Treatment with Mineral Precipitation

3.1.1 Lime and Limestone

Lime ($Ca(OH)_2$) and limestone ($CaCO_3$) are traditionally used for the neutralization of ARD but can also be used for the removal of sulphate from ARD through precipitation of gypsum ($CaSO_4$ $2H_2O$):

$$Ca(OH)_2 \text{ (s)} + H_2SO_4 = CaSO_4 \cdot 2H_2O \text{ (s)}$$

$$CaCO_3 \text{ (s)} + H_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O \text{ (s)} + CO_2 \text{ (g)}$$

The levels to which sulphate concentrations are reduced are controlled by the solubility of gypsum, which, depending on the composition and ionic strength of the solution, range from 1500 to 2000 mg/L. Considering the relatively high sulphate levels remaining in the treated water after reaction with lime or limestone, the process may be better suited as a pre-treatment step for ARD waters high in dissolved sulphate concentrations.

More recently, an integrated limestone/lime process was developed that is capable of reducing the sulphate concentration in ARD to less than 1200 mg/L (Geldenhuys, 2001). The schematic of this process is shown in Figure 3-1 and consists of the following three steps:

1. Limestone neutralization to raise the pH to circum-neutrality, resulting in CO_2 production and gypsum precipitation
2. Lime treatment to raise the pH to 12 for $Mg(OH)_2$ precipitation and enhanced gypsum precipitation ('crystallization'); and,
3. pH adjustment with CO_2 (recovered from phase 1) with concurrent $CaCO_3$ precipitation.

Key processes responsible for the improved sulphate removal are: the precipitation of $Mg(OH)_2$ and the presence of gypsum seed crystals in the second phase. Both greatly enhance the precipitation of gypsum.

Using ARD water with a sulphate concentration of 3000 mg/L as feed water, the sulphate concentration in the treated water (undersaturated with respect to gypsum) was reduced to less than 1200 mg/L. The sulphate treatment process produces gypsum and limestone sludges. The limestone sludge produced in the third step is relatively pure and can be recycled in the first step of the treatment process. The liming step can have the added benefit of removing other problematic cations and trace metals. Depending on the degree of automation the treatment process requires a low to moderate amount of monitoring and maintenance particularly in comparison to other sulphate treatment strategies.

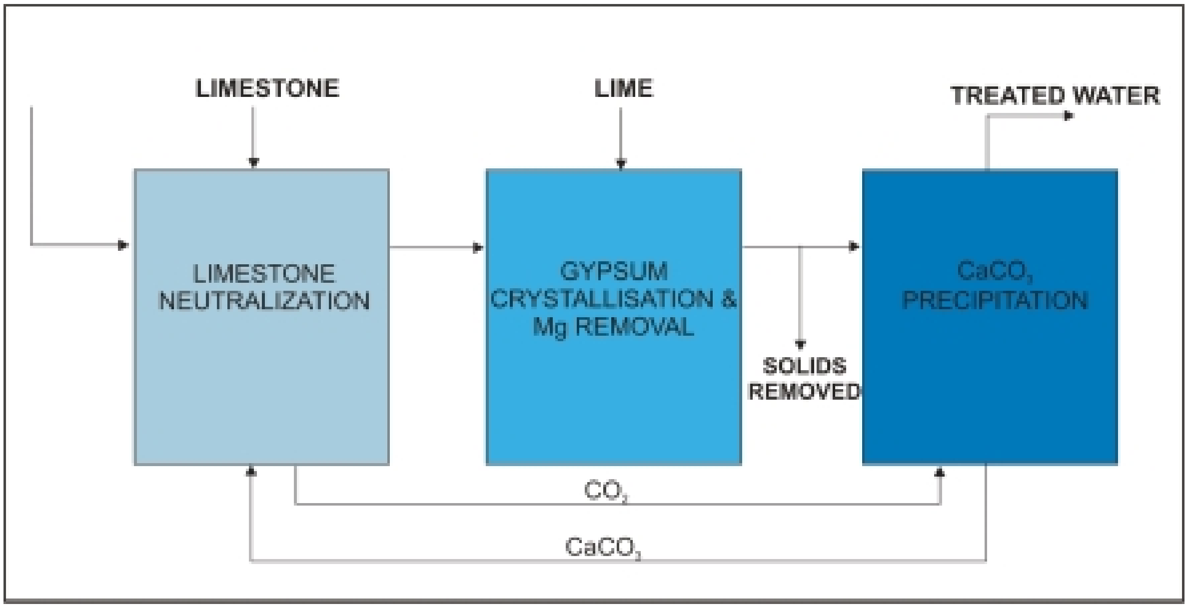


Figure 3-1: Schematic Illustration of Integrated Limestone/Lime Treatment Process

3.1.2 Barium Salts

Barite ($BaSO_4$) is highly insoluble making it an excellent candidate as a removal phase for sulphate treatment. The barium salts commonly used for sulphate removal by precipitation include $Ba(OH)_2$, $BaCO_3$ and BaS after the following reactions:

$$BaCO_3 (s) + H_2SO_4 = BaSO_4 (s) + H_2CO_3$$

$$Ba(OH)_2 (s) + H_2SO_4 = BaSO_4 (s) + 2H_2O$$

$$BaS (s) + H_2SO_4 = BaSO_4 (s) + H_2S (g)$$

Both barium hydroxide and barium sulphide are highly effective in removing dissolved sulphate over the entire pH range. Barium carbonate is less effective under neutral to strongly alkaline conditions and under very acidic conditions, sulphate removal by barium carbonate is strongly reduced. This sulphate treatment process can also be modified to include the removal of dissolved metals from ARD water (Figure 3-2).

However, barium salts are expensive, thus the barium sulphate sludge is often recycled to reduce costs and to provide additional income through the production of elemental sulphur.

An example of a sulphate treatment process using barium sulphide is shown in Figure 3-2. Barium sulphide and ARD water are added to a reactor/clarifier. The mixture is maintained at a constant pH by addition of CO_2. The precipitated barium sulphate, accumulating at the bottom of the clarifier, is collected for thermal reduction at 1,200°C:

$$BaSO_4\,(s) + C\,(s) = BaS\,(s) + 2CO_2\,(g)$$

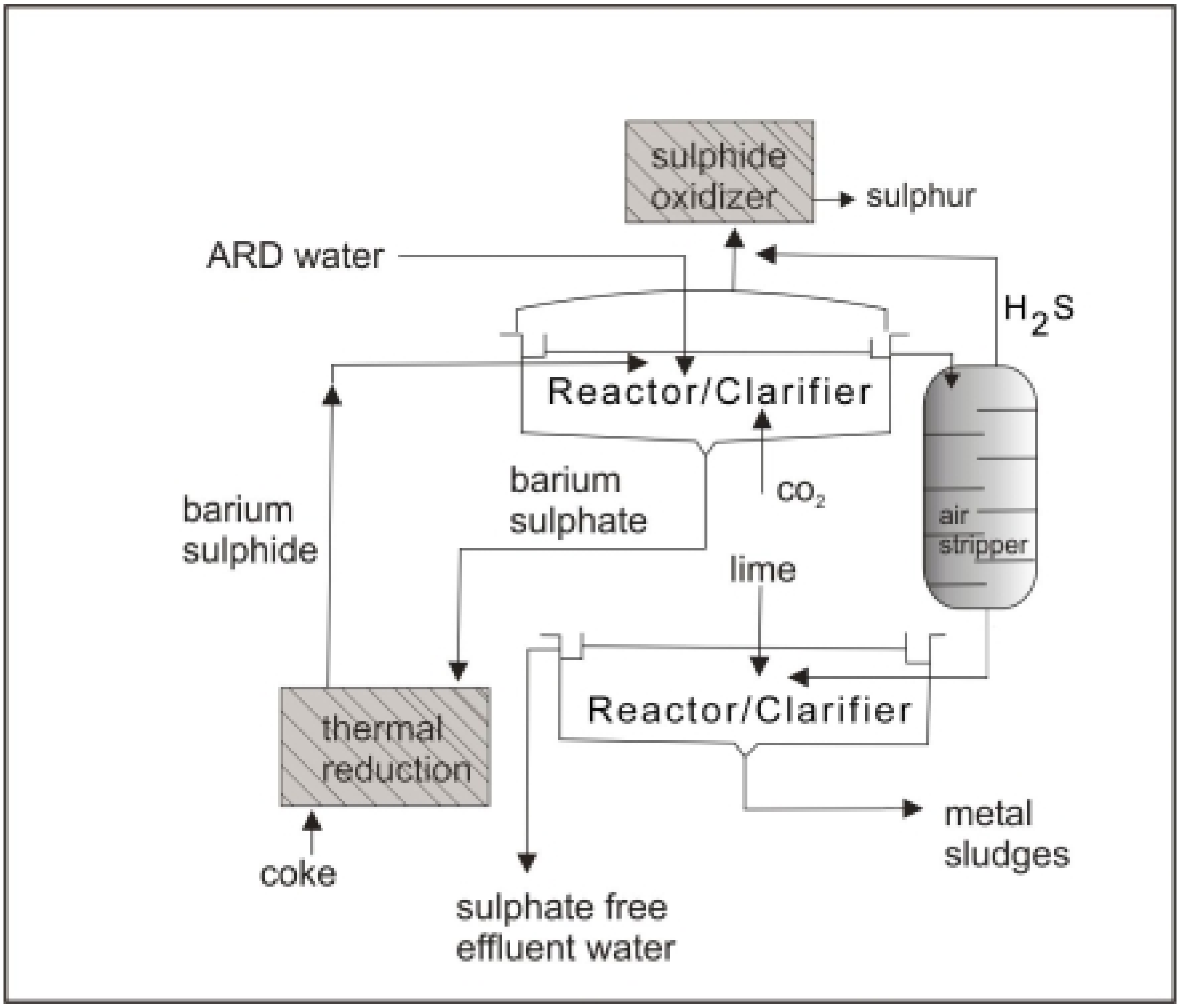


Figure 3-2: Schematic Representation of the BaS Treatment Process

The BaS recovered through thermal reduction is used again in the sulphate precipitation stage. The H_2S (g) produced in the process of barium sulphate precipitation is collected by an air stripper and is converted to elemental sulphur in a sulphide oxidizer. Sulphide-free water from the first reactor/clarifier is then transferred to a second reactor/clarifier where lime is added to precipitate and remove dissolved metals.

3.1.3 SAVMIN

The SAVMIN process uses precipitation reactions during successive stages to remove dissolved sulphate from ARD water (Smit, 1999). The different stages of the treatment process are illustrated in Figure 3-3.

In the first stage lime is added to the feed water to raise the pH to approximately 12. Dissolved metals and magnesium are precipitated as hydroxides:

$$Me^{2+} + Ca(OH)_2\ (s) = Me(OH)_2\ (s) + Ca^{2+}$$

After removal of the metals and magnesium the water is seeded with gypsum crystals to catalyze the precipitation of gypsum from the supersaturated solution. A portion of the precipitated gypsum is returned as seed crystals to the feed water while the rest is removed.

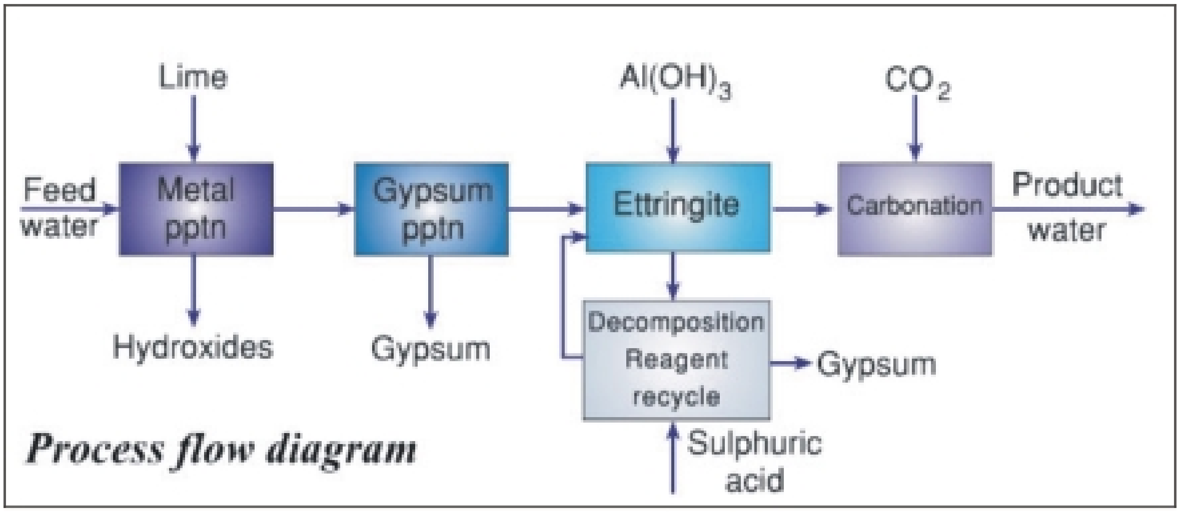


Figure 3-3: SAVMIN Process Flow Diagram

In the third stage, aluminum hydroxide is added to the water, which is still supersaturated with respect to gypsum. The addition of aluminum hydroxide results in the precipitation of *ettringite* ($3CaO\cdot 3CaSO_4\cdot Al_2O_3\cdot 31H_2O$).

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3\ (s) + 37H_2O = 3CaO\cdot 3CaSO_4\cdot Al_2O_3\cdot 31H_2O\ (s) + 6H_3O^+$$

Precipitation of ettringite occurs between pH 11.6 and 12.0, removing both calcium and sulphate; elevated pH is maintained through addition of lime. The ettringite slurry is removed from the feed water by filtration and thickening.

In the fourth stage the waste water stream (pH 11.7, dissolved SO_4^{2-} <200 mg/L) is treated with CO_2 to lower the pH. Relatively pure $CaCO_3$ is precipitated and removed by filtration. Alternatively the pH can be adjusted to precipitate $Ca(HCO_3)_2$.

The ettringite slurry is decomposed with sulphuric acid to regenerate aluminum hydroxide for reuse in the third stage of the treatment process:

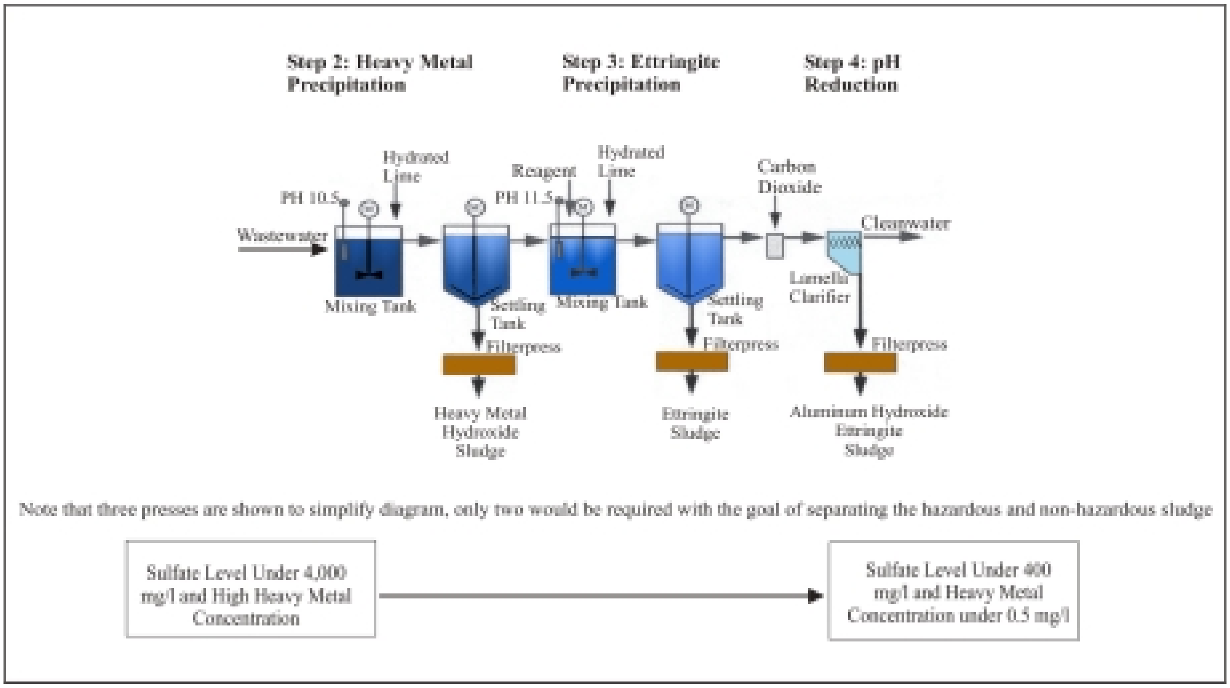
$$3CaO\cdot 3CaSO_4\cdot Al_2O_3\cdot 31H_2O\ (s) + 6H_3O^+ = 6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3\ (s) + 37H_2O$$

The aluminum hydroxide is recovered by thickening and filtration, and reused in the third stage of the treatment process. The remaining solution is seeded with gypsum crystals to precipitate gypsum. After removing the precipitated gypsum by filtration and thickening, the gypsum-saturated solution is returned to the ettringite decomposition stage.

In a demonstration plant at the Stillfontein gold mine in South Africa, 500 m^3 of contaminated water (600-800 mg/L SO_4) were treated with the SAVMIN process at throughputs up to 1100 L/hr. Dissolved sulphate concentrations in the treated water were below 200 mg/L and dissolved metals were removed to very low levels.

3.1.4 CESR

The 'Cost Effective Sulphate Removal' (CESR) process, also known as the 'Walhalla' process, is similar to the SAVMIN process in that it relies on the precipitation of ettringite to remove sulphate from water. A flow diagram with the successive process steps is shown in Figure 3-4. In addition to sulphate, the treatment process is also effective in removal of dissolved metals.



Note that three presses are shown to simplify diagram, only two would be required with the goal of separating the hazardous and non-hazardous sludge

Figure 3-4: CESR Process Flow Diagram

In the first process step (not shown in Figure 3-4), hydrated lime is added to the feed water to precipitate gypsum. The pH is maintained at a level that prevents precipitation of metals and minimizes the volume of metal-laden sludge. The non-hazardous gypsum sludge is removed from the feed water by dewatering and filtration.

In the second process step, additional liming raises the pH of the feed water to 10.5 and results in the precipitation of dissolved metals as metal hydroxides. Raising the pH also causes additional gypsum precipitation. The metal-bearing sludge is removed from the settling tank by dewatering and filtration.

The removal of dissolved sulphate is completed in the third process step. After raising the pH to 11.5 with lime, a proprietary reagent (derived from the cement industry) is added to precipitate ettringite ($3CaO \cdot 3CaSO_4 \cdot Al_2O_3 \cdot 31H_2O$). The primary distinction between the SAVMIN and CESR process is the proprietary reagent used CESR in place of the aluminum hydroxide used in the SAVMIN process.

Other contaminants including metals, nitrate, chloride, fluoride and boron may coprecipitate with ettringite. As gypsum interferes with the precipitation reaction of ettringite, it is important that all gypsum is removed from the feed water during the preceding process steps. The sludge is removed from the settling tank, a portion of which may be reused as seed crystals in the third process step.

In the final process step, the pH of the feed water is adjusted with CO_2 (g) to meet local discharge criteria and prevent scaling. After lowering the pH, the water is clarified and discharged. The small amount of sludge produced in the clarifier consists predominantly of aluminium hydroxide, calcium carbonate and ettringite. Unlike SAVMIN, CESR does not recycle the ettringite.

The CESR process is used in treatment plants at flow rates up to 350 gallons per minute. It can reduce sulphate concentrations in most industrial wastewaters to less than 100 mg/L.

3.2 Membranes

Membranes are used in two commercially important water treatment processes: Electrodialysis (ED) and Reverse Osmosis (RO). However, membranes are used differently in each application (Figure 3-5). In ED, an electric potential is used to move dissolved ions selectively through a membrane, leaving behind the pure water. In contrast, RO uses high-pressure pumps to force water through a semi-permeable membrane which excludes all but pure water.

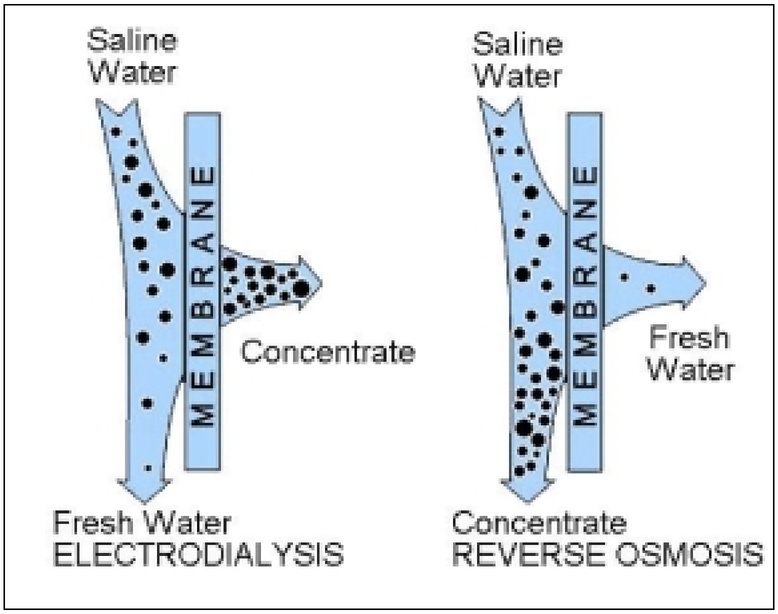


Figure 3-5: Function of Membrane in Electrodialysis and Reverse Osmosis

3.2.1 Reverse Osmosis

In RO the feed water is pumped into a closed vessel where it is forced under pressure to pass through a semi-permeable membrane. As only pure water passes through the membrane, the concentration of dissolved salts in the remaining feed water increases. To avoid complications due to precipitation and elevated osmotic pressure, a portion of the feed water is discharged without passing through the membrane ('controlled discharge'). This discharge water (or brine) is the primary waste product from the RO process itself and must be managed accordingly. Depending on the chemical composition of the feed water, the applied pressure and the type of membrane used, the controlled discharge varies from 20% to 70% of the feed water flow (AWWA, 1999).

An RO system (Figure 3-6) consists of four basic components: (1) pretreatment, (2) high-pressure pump, (3) membrane assembly and (4) post-treatment (Buros, 1998).

To prevent membrane fouling by suspended solids, mineral precipitation or microbial growth, the feed water must be pretreated. Pretreatment generally involves filtration and chemical treatment to minimize mineral precipitation (scaling) and microbial growth.

A high-pressure pump is required to supply pressures ranging from 17 to 27 bar for brackish feed water and pressures ranging from 54 to 80 bar for saline feed water. Most of the energy required in RO is used for the pressure supply.

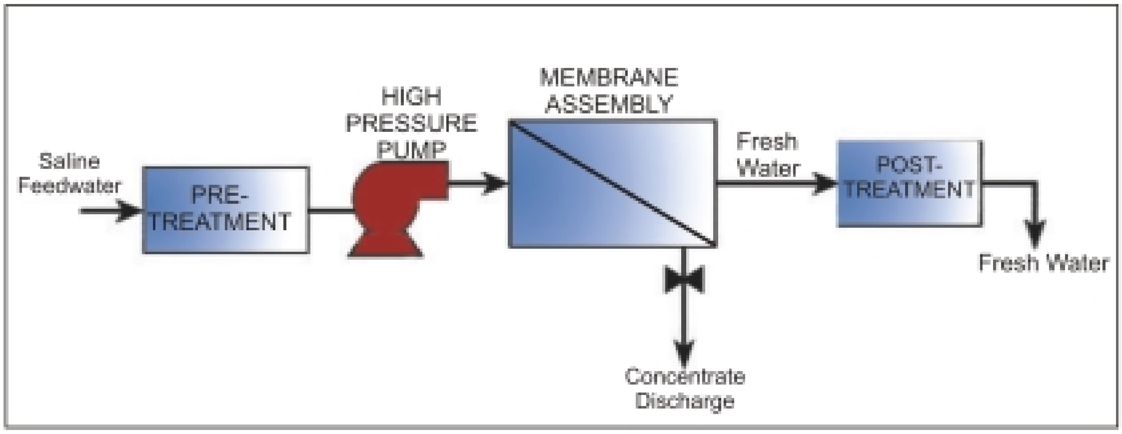


Figure 3-6: Basic Components of a Reverse Osmosis Plant

The membrane assembly consists of a pressure vessel and a membrane capable of withstanding a high pressure gradient. The membranes used vary in their performance and thus, very small quantities of contaminant do end up in the treated water. Membrane assemblies exist in a variety of configurations depending on the manufacturer and the expected quality of the feed water. The two most commonly used membrane assemblies are the spiral and the hollow fiber (Figure 3-7). Both are used for brackish and saline feed water.

Post-treatment involves 'conditioning' of the treated water (adjusting of pH, alkalinity and hardness; removal of H_2S (g)) and preparation for distribution.

The two most important factors that determine the operating costs of the RO treatment system are: (1) the efficiency of the membrane, and (2) the energy use. Improvements in these two areas in recent years have reduced the operating costs of the RO treatment system (AWWA, 1999).

Mechanical failure and fouling greatly affect membrane life, particularly in wastewater applications. The development of low-pressure membranes, the application of nanofiltration and improved methods of water pretreatment have improved the efficiency of the membranes and reduced the operational costs of the RO treatment system (Durham et al., 2001).

The energy costs of the RO treatment system are also reduced by recovery of energy from the RO process. Treated water leaves the vessel under high pressure that can be converted into mechanical or other types of energy by 'energy recovery devices' (turbines, pumps etc.).

The RO treatment system can produce high quality water (*e.g*. drinking water), even from seawater. However, operating costs and water recovery may vary considerably depending on the quality of the feed water used. Using a tubular RO system in a pilot plant, the sulphate concentration in drainage water can be reduced from in excess of 2000 mg/L to 15 mg/L at a water recovery of 70% and a feed water flow rate of 1.7 m^3/h. Full scale RO systems can accommodate considerably larger flows.

All of the membrane approaches to sulphate treatment produce brine as a waste product. The composition of the brine will vary depending on the composition of the feed water and thus the manner in which brine is disposed will vary accordingly.

In arid climates, the brine can be evaporated, leaving a comparatively small quantity of mixed evaporite. In cool or wet climates, heating may be required to promote evaporation or alternate disposal options must be considered. Brine disposal strategies are highly site-specific but may include other forms of treatment (*i.e.*, lime addition) if metals or sulphate are sufficiently elevated.

3.2.2 SPARRO

Waters with high levels of calcium and sulphate severely limit the water recovery (<80%) in RO treatment. Other dissolved substances such as aluminum and iron may also cause membrane fouling and limit the application of an RO treatment system without an extensive pretreatment system. Such a pretreatment system can become too complex and make the RO system uneconomical.

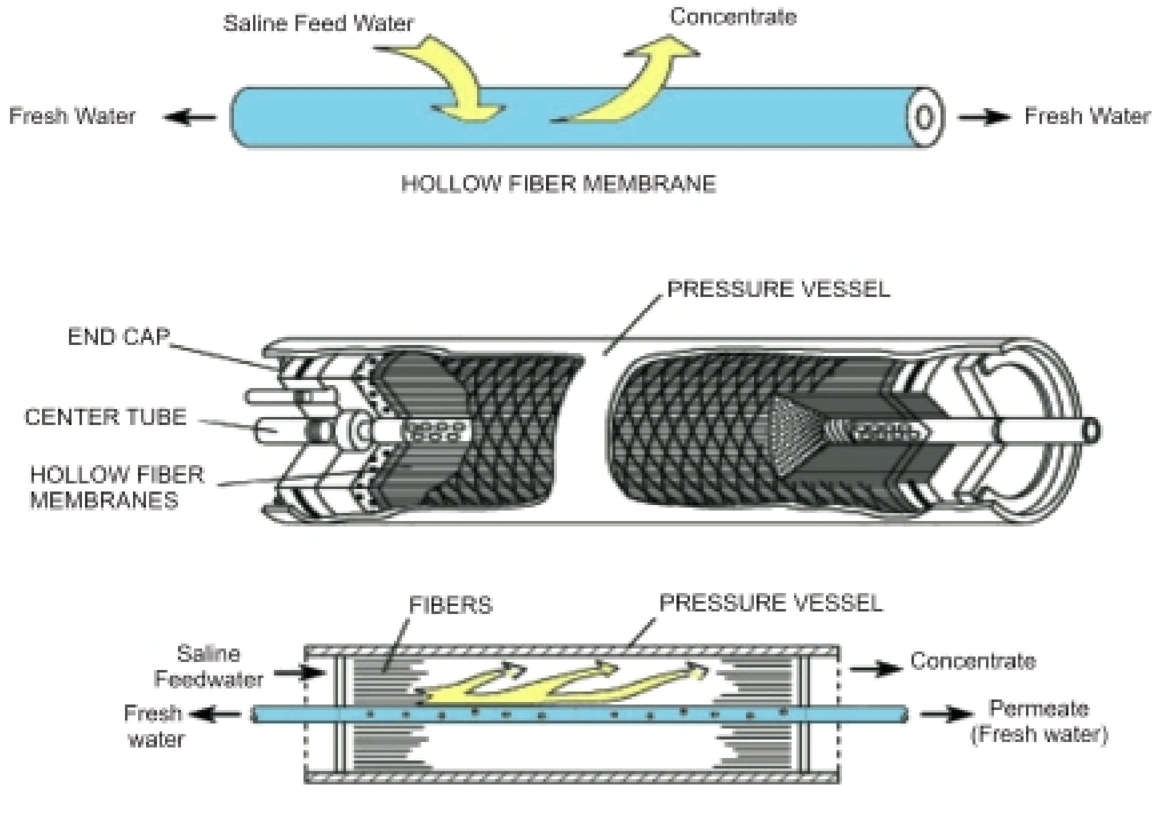


Figure 3-7: Hollow Fiber Membrane Assembly

Seeded RO is particularly attractive for waters high in dissolved calcium and sulphate. The seeding process is illustrated in Figure 3-7. Gypsum seed crystals (3-10 % slurry) are added to the feed water of a tubular RO system and serve as nucleation sites for the precipitation and crystalization of gypsum and other minerals. This prevents mineral precipitation on the membranes (scaling). The seed crystals are recycled from the concentrate to the feed water.

Research on seeded RO resulted in the development of the ‘Slurry Precipitation and Recycle Reverse Osmosis’ (SPARRO) process (Pulles *et al.*, 1992; Juby *et al.*, 1996). Compared to existing seeded RO systems, the design of the SPARRO process incorporates three major improvements: (1) lower power consumption, (2) independent control of gypsum seed and concentrate blowdown, and (3) utilization of a novel pumping system. Other design modifications involve the size of the reaction vessel and the membrane configuration (Pulles *et al.*, 1992; Juby *et al.*, 1996).

Schematic representations of a SPARRO plant are shown in Figures 3-8 and 3-9. After a pretreatment stage involving pH adjustment, removal of suspended solids through coagulation, settling and filtration, the feed water is pumped into a storage tank. From the storage tank, water is pumped under high pressure to the RO membrane module bank. Before reaching the module bank the feed water is mixed with the recycled gypsum slurry from the reactor. The treated water is stored while the flow concentrate ('controlled discharge') is split into two portions. One portion is sent to the hydrocyclone and another portion is returned to the reaction vessel. Both the overflow and underflow of the hydrocyclone are subdivided; using a programmable controller, one part of the flow is discharged into the reactor and another part of the flow is blowndown as brine (overflow) and seeds (underflow). The residence time of the concentrate in the reactor is approximately one hour, sufficient to allow crystal growth.

The long-term effects of the seed slurry on the tubular RO membranes were tested in a separate plant, 'the membrane lifetime test plant' (MLT, Pulles *et al.*, 1992). The plant was operated in parallel with the SPARRO plant using the same feed water. A schematic representation of the MLT plant is shown in Figure 3-9.

The SPARRO treatment process (Figure 3-8) was capable of reducing the sulphate concentration in the feed water from 6,639 mg/L to 152 mg/L at a water recovery of 95% and with a treated water flow rate of 0.85 L/s. However, problems encountered with failing and fouling of membranes resulted in salt rejection rates and membrane lives that were below the design criteria. Improvements in membrane performance will increase the economic viability of the SPARRO treatment process.

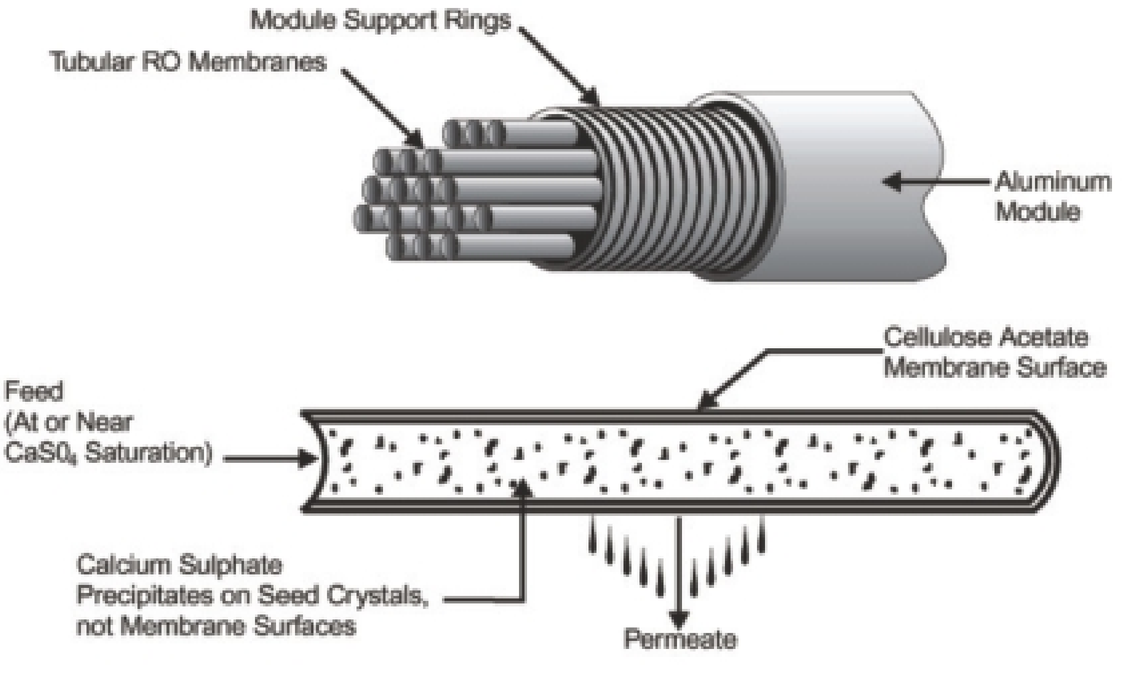


Figure 3-8: Conceptual Illustration of Seeded Reverse Osmosis

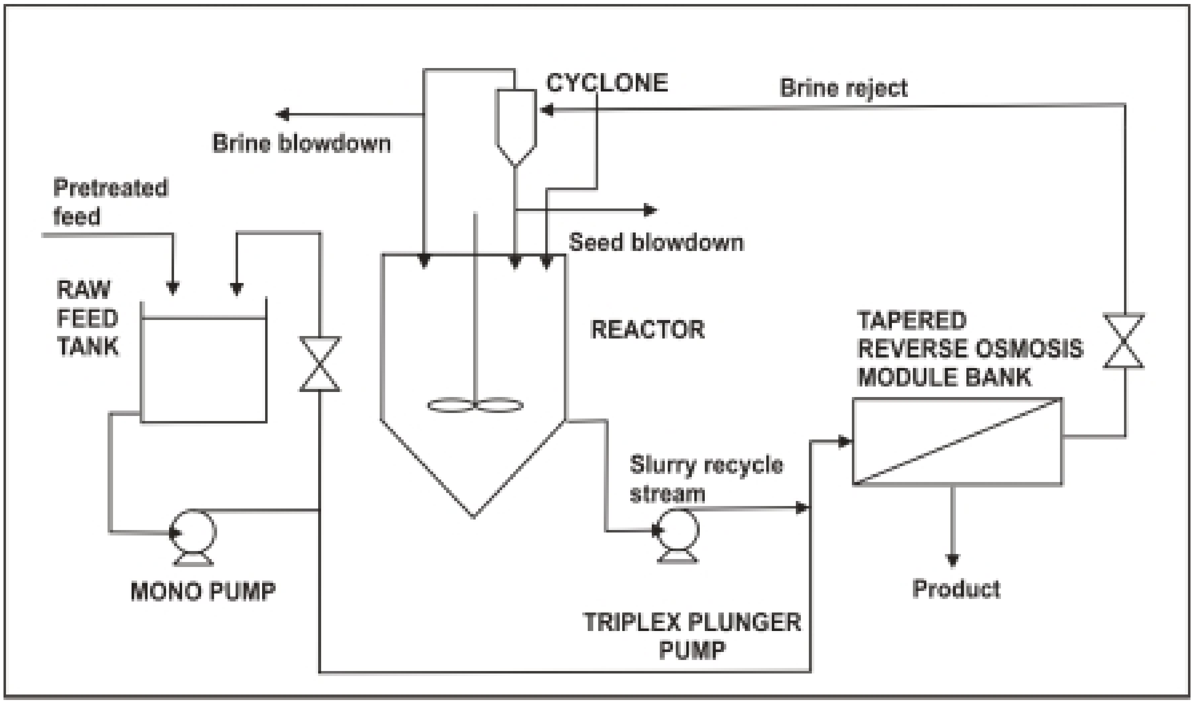


Figure 3-9: Schematic Representation of MLT Plant

3.2.3 Electrical Dialysis Reversal

Electrodialysis (ED) is a membrane separation process that is based on the migration of ions through ion-selective membranes as a result of an electrical force. In ED only the dissolved salts (*i.e.* charged ions) move through the membranes, not the uncharged water molecules. The principle of ED is illustrated in Figures 3-10 and 3-11 (Valerdi-Perez *et al.*, 2001). Starting with feed water, two different stream flows develop in parallel in each membrane unit. One is progressively depleted in dissolved solids (‘product stream’) while the other is enriched in dissolved substances (‘concentrate stream’).

Anions in the feed water are attracted to the positive electrode and can only pass through the anion-selective membrane but not through the cation-selective membrane. The reverse applies to cations. Through the arrangement of the ion-selective membranes relative to the electrodes, cations and anions become ‘trapped’ in the concentrate stream flow while water molecules are ‘left behind’ in the product stream flow. Each pair of membranes is called a cell. The basic ED unit consists of several hundred cell pairs connected with electrodes and is called a membrane stack.

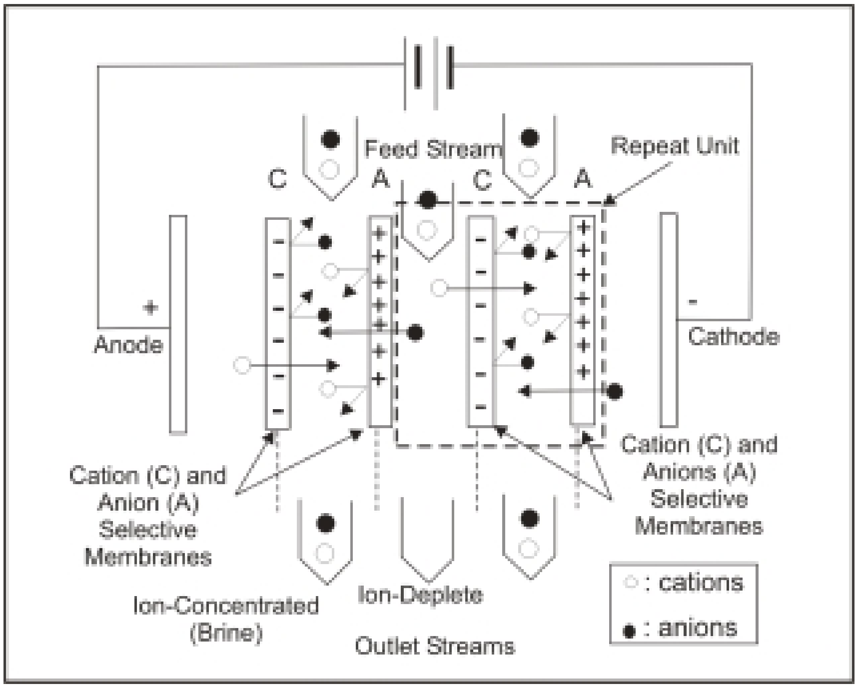


Figure 3-10: Principle of Electrodialysis. Scheme of an Electrodyalizer with Two Cell Pairs: Migration of Ions is Caused by the Action of an Electric Field

The electrical dialysis reversal process (EDR) operates on the same principle as ED. However, at regular intervals (several times per hour), the polarity of the electrodes is reversed and the product and concentrate stream flows switch position. Immediately after each polarity reversal the product water is discharged (1-2 minutes) until the stack is flushed and the water quality is restored. The major advantage of the polarity reversal (EDR) is that the cells are periodically cleaned and deposits on the membranes are minimized. EDR requires less chemical pretreatment than ED to prevent membrane fouling and is also able to treat feed water with a higher concentration of suspended solids than RO.

An EDR unit (Figure 3-12) consists of five basic components (Buros, 1998): (1) pretreatment, (2) membrane stack, (3) low-pressure pump, (4) power supply for direct current, and (5) post-treatment. Pretreatment is necessary to prevent entry of materials that damage the membranes or clog the narrow channels in the cells. A low-pressure pump is necessary to circulate the water through the membrane stack, which is in turn powered by direct current provided by a rectifier. Post-treatment involves water 'conditioning' (*e.g.* adjustment of pH, alkalinity, hardness) and preparation for distribution.

Although EDR was developed at the same time as RO, ED existed long before RO was introduced. It is mainly used for desalination of brackish water and the production of potable water. A 5.8 m^3/hr EDR pilot plant is able to reduce the TDS concentration in mine water from 3,200 mg/L (SO_4^{2-} 74 mg/L) to 640 mg/L (SO_4^{2-} 5 mg/L) at a water recovery up to 84%.

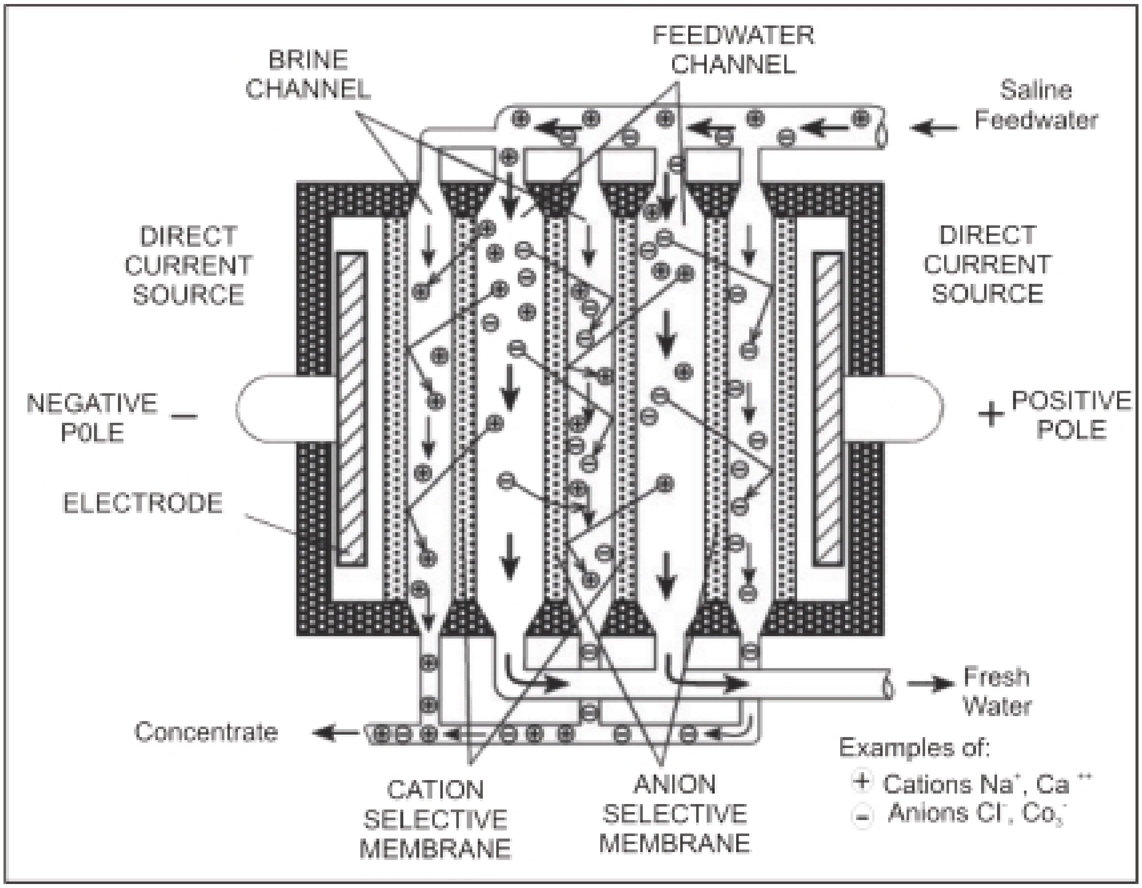


Figure 3-11: Movement of Ions in the Electrodialysis Process

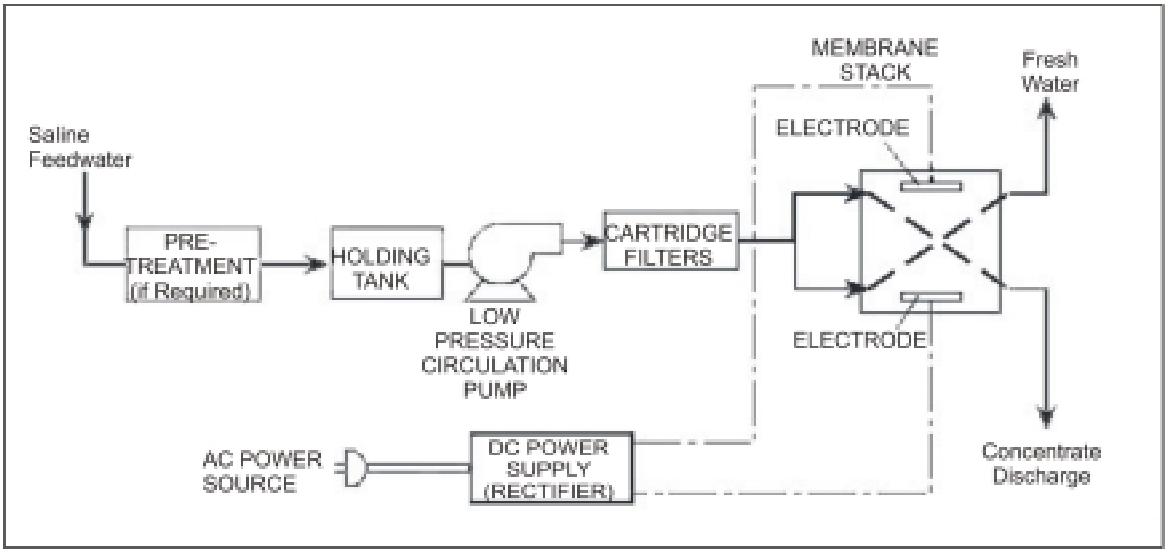


Figure 3-12: Components of an Electrodialysis Plant

3.3 Ion-Exchange

3.3.1 GYP-CIX

GYP-CIX is an ion-exchange technology that is used to remove major ions from water. It is particularly well-suited to the removal of dissolved sulphate from water that is close to saturation with gypsum. A schematic process flow diagram for the treatment of mine water with GYP-CIX is shown in Figure 3-13 (Schoeman and Steyn, 2001).

The untreated feed water is pumped to the cation loading section where it passes multiple fluidized contact stages. Cations like Ca^{2+} are removed from the feed water through cation exchange with the strong acid cation resin (**R**-H):

$$2\mathbf{R}\text{-H} + Ca^{2+} (+ SO_4^{2-}) = \mathbf{R_2}\text{-Ca} + 2H^+ (+ SO_4^{2-})$$

After passing the cation resin the water is pumped to a degassing tower where carbonate alkalinity is removed. After removal of dissolved carbonates the water is pumped to the anion loading section where it passes multiple fluidized contact stages. Anions like SO_4^{2-} are removed from the feed water through anion-exchange with the weak base anion resin (**R**-OH):

$$2\mathbf{R}\text{-OH} + SO_4^{2-} (+ Ca^{2+}) = \mathbf{R_2}\text{-}SO_4 + 2OH^- (+ Ca^{2+})$$

The treated water has a neutral pH and is low in dissolved calcium, sulphate and other dissolved substances including metals. The number of contact stages used depends on the quality of the feed water used and the required quality of the treated water.

The novelty of the GYP-CIX process is that it uses a low-cost resin regeneration technique that produces gypsum as a solid waste product. Unlike conventional ion-exchange resin regeneration with NaOH and HCl, GYP-CIX uses $Ca(OH)_2$ and H_2SO_4 for the regeneration of the ion-exchange resins:

$$\mathbf{R_2}\text{-Ca} + 2H^+ + SO_4^{2-} = 2\mathbf{R}\text{-H} + Ca^{2+} + SO_4^{2-}$$

$$\mathbf{R_2}\text{-}SO_4 + 2OH^- + Ca^{2+} = 2\mathbf{R}\text{-OH} + SO_4^{2-} + Ca^{2+}$$

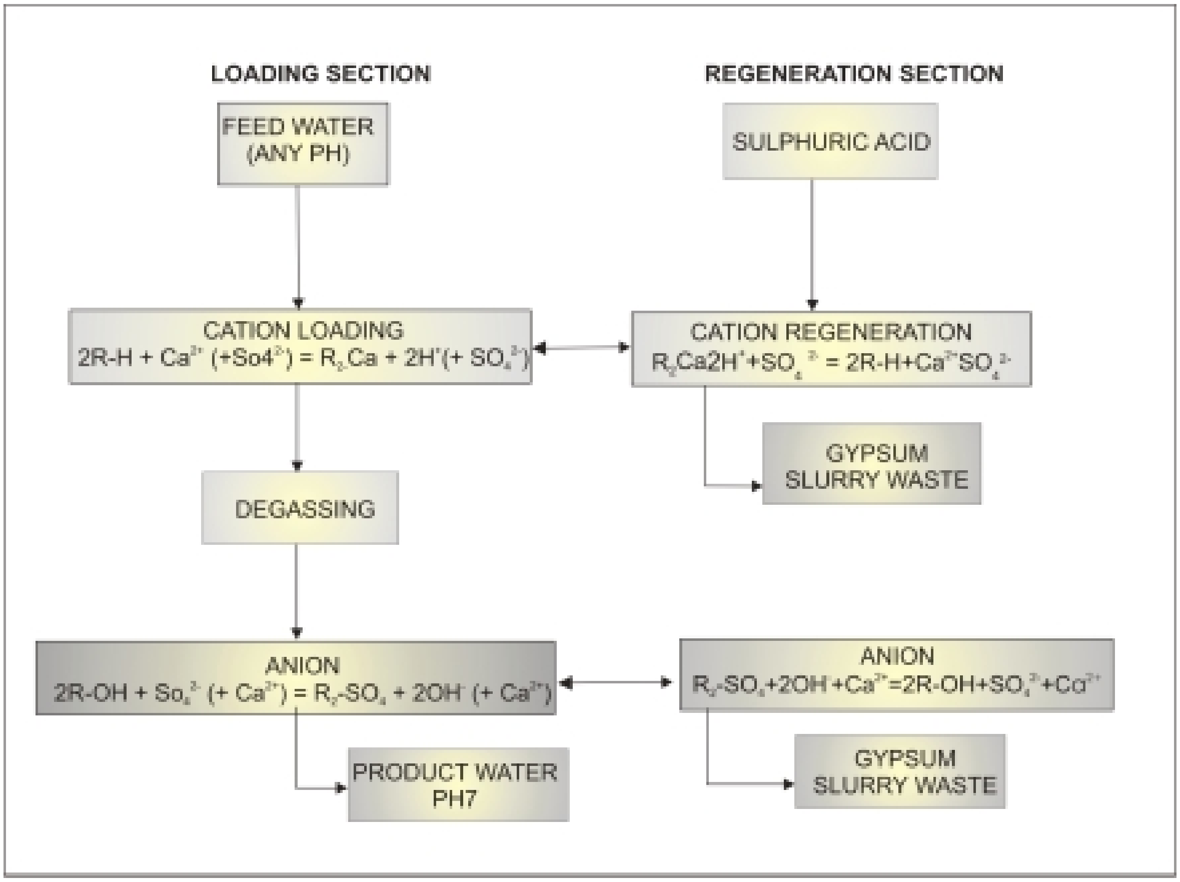


Figure 3-13: Simplified Process Flow Diagram of the GYP-CIX Process for Treatment of Mine Water

The cation resin is regenerated using a 10% sulphuric acid solution seeded with gypsum crystals recirculated from a reservoir. The solution hosts high concentrations of dissolved calcium and sulphate such that in the presence of seed crystals, gypsum is readily precipitated while the formation of a supersaturated contact solution is avoided. After regeneration of the cation resin, the gypsum is washed out and allowed to settle in a clarifier. The washed resin is thoroughly rinsed with treated water and returned to the cation loading section.

Similar to the cation resin, the anion resin to be regenerated is contacted with a 2% lime solution, seeded with gypsum crystals. The anion regeneration also produces gypsum, which is treated in a similar fashion to the gypsum in the cation section. Before being returned to the anion loading section, the anion resin is rinsed with treated water.

Continuous precipitation of gypsum in both cation and anion regeneration allows the reuse of the regeneration solution, which minimizes reagent use. If high water recoveries are required, the gypsum sludges from the cation and anion regeneration can be combined to generate additional gypsum.

In the GYP-CIX process the flows of feed water and treated water are continuous and uninterrupted; flow rates of 50 gallons per minute have been used in pilot plants. The GYP-CIX treatment process can reduce the TDS concentration in feed water from 2,000-4,500 mg/L (SO_4 1,200-2,800 mg/L) to less than 240 mg/L (SO_4 <50 mg/L) at water recoveries ranging from 50% and 90%.

3.3.2 Metal Precipitation and Ion-Exchange (GYP-CIX)

Using laboratory-scale experiments with acid mine water from a gold mine, a treatment process that involves metal precipitation followed by ion-exchange was tested (Feng *et al.*, 2000). The ion-exchange process used is very similar to the GYP-CIX process. Schematic representations of the two process stages are shown in Figure 3-14 (metal precipitation) and Figure 3-15 (ion-exchange).

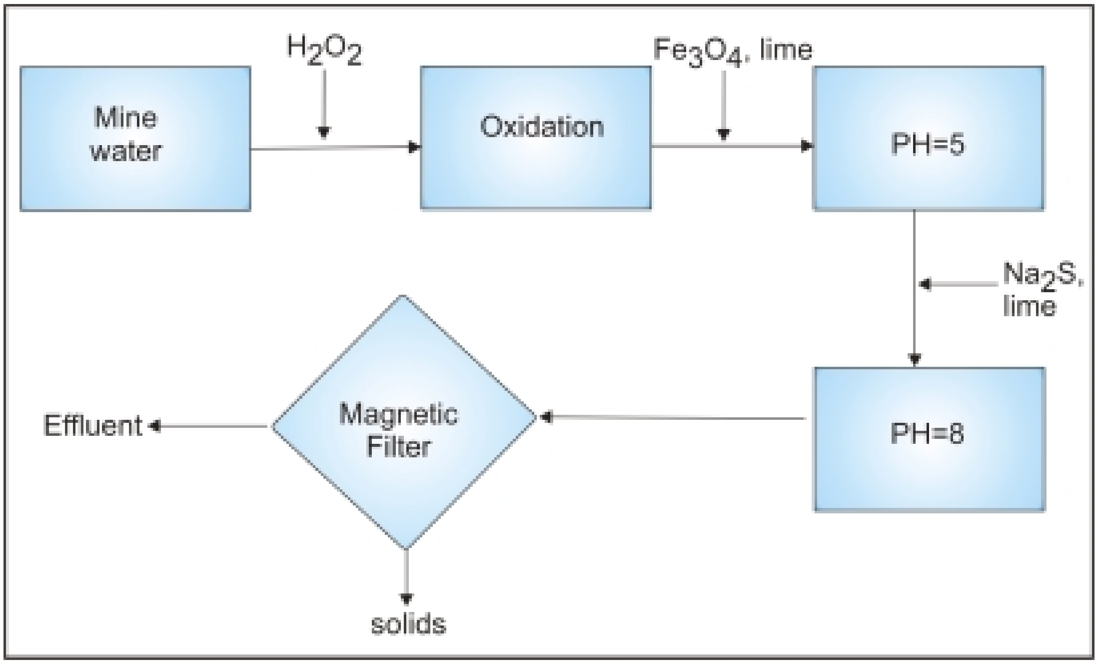


Figure 3-14: Flowsheet of the Proposed Precipitation Process

In the precipitation process (Figure 3-14) the mine water is first oxidized with hydrogen peroxide, to ensure iron and manganese are in their fully oxidized states. After oxidation, magnetite (Fe_3O_4) seeds are added (0.5 g/L) and the pH is raised to pH 5 using lime. The main objective of adjusting the pH to 5 is to prevent the development of H_2S (g) after addition of sodium sulphide (Na_2S) in the next process step. After addition of sodium sulphide, the pH of the slurry is increased to pH 8 with lime and metal sulphides and hydroxides are precipitated. The precipitates are subsequently filtered magnetically to yield separated solids and partially treated mine water.

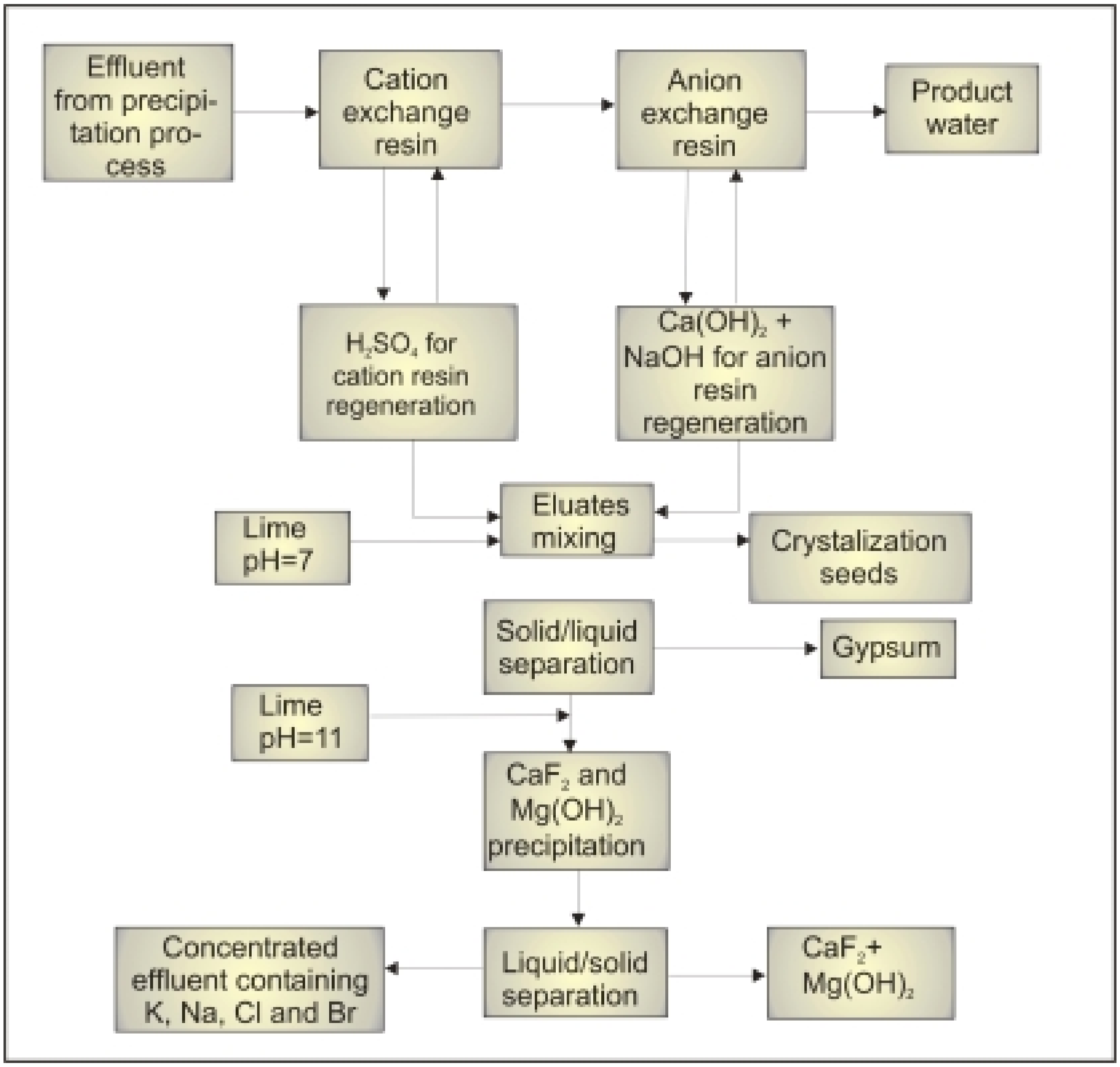


Figure 3-15: Proposed Process for Desalination of the Effluent Form Precipitation Process

In laboratory-scale experiments, all dissolved metals could be precipitated by addition of lime and sodium sulphide. The dissolved sulphate concentration was reduced from 6,305 mg/L to 3,353 mg/L in the precipitation process stage. The partly treated mine water was still high in alkaline and earth-alkaline metals as well as in chloride, sulphate and fluoride. The turbidity (1.8 NTU) of the partly treated mine water was still within the limits (< 4 NTU) for subsequent use in the ion-exchange process stage.

The ion-exchange process used in the next treatment stage is very similar to the GYP-CIX process described earlier with only slight differences in the regeneration of resin. After the ion-exchange process stage the concentrations of major ions in the treated water complied with drinking water standards; the dissolved sulphate concentration in the partially treated mine water was further reduced from 3,353 mg/L to less than 50 mg/L.

3.4 Biological Sulphate Removal

Biological sulphate removal can be a cost-effective alternative to the treatment processes discussed earlier as it relies on the biochemistry associated with a suite of microbial communities. Accordingly, a brief discussion of salient background information is presented as a foundation upon which the various biological sulphate treatment processes are described.

3.4.1 Introduction

In order to generate energy for metabolic activity, microbes facilitate the transfer of electrons from electron-rich (reduced) substrates (*i.e.*, organic matter, H_2, CO, etc.) to electron-deficient (oxidized) species (*i.e.*, oxidants such as oxygen or sulphate).

Biological sulphate removal systems rely on the microbial use of sulphate as an oxidant and its subsequent reduction to hydrogen sulphide (HS^-). In reality, biological sulphate removal occurs in two steps. The first step involves dissimilatory sulphate reduction by sulphate reducing bacteria (SRB):

$$4CH_3OH + 3SO_4^{2-} = 4HCO_3^- + 3HS^- + H^+ + 4H_2O$$

The sulphide produced in the first step is then oxidized to elemental sulphur (S) by chemotrophs (colorless sulphur bacteria) or by phototrophs (purple and green sulphur bacteria), (Hanselmann, 1994):

$$2HS^- + O_2\ (g) + 2H^+ = 2S\ (s) + 2H_2O$$

or

$$2HS^- + CO_2(g) + 2H^+ = 1/6C_6H_{12}O_6 + 2S(s) + H_2O$$

Under oxygen-limited conditions ($O_2(g)$ <0.1 mg/L), S (s) is the main product of sulphide oxidation while sulphate is formed under sulphide-limiting conditions (Hulshoff Pol *et al*, 1998). Sulphide removal after the first step can also be accomplished by precipitation as metal sulphides (MeS) and by H_2S (g) stripping (*e.g.* wetlands or bioreactors).

Unlike aerobic bacteria, anaerobic bacteria depend much more on each other for the (stepwise) mineralization of organic substrates. This is illustrated in Figure 3-16, which shows the functional relationship between the various types of anaerobic bacteria (Fenchel *et al.*, 1998).

Fermenting bacteria are the only anaerobic organisms that can hydrolyze complex organic polymers into fatty acids, alcohols, acetate and H_2(g):

$$C_6H_{12}O_6\ \textit{(glucose)} = 2CH_3CHOHCOOH\ \textit{(lactate)} \qquad (A1)$$

$$C_6H_{12}O_6 = 2CH_3COOH\ \textit{(acetate)} \qquad (A2)$$

$$CH_3COCOOH\ \textit{(pyruvate)} + H_2O = CH_3COOH + CO_2(g) + H_2(g) \qquad (A3)$$

Obligate acetogens ferment low molecular weight fatty acids and alcohols into acetate and hydrogen gas:

$$CH_3(CH_2)_3OH\ \textit{(butanol)} + 3H_2O = 2CH_3COOH + 4H_2(g) \qquad (B1)$$

In the absence of suitable organic substrates, homoacetogens reduce $CO_2(g)$ with $H_2(g)$:

$$2CO_2(g) + 4H_2(g) = CH_3COOH + 2H_2O \qquad (B2)$$

Sulphate reducing bacteria use only a limited range of organic substrates including low molecular weight fatty acids, alcohols and $H_2(g)$. These substrates are supplied by fermenting bacteria. One group of SRB uses mainly $H_2(g)$ or lactate (with incomplete oxidation to acetate) as substrates:

$$4H_2(g) + SO_4^{2-} + 2H^+ = H_2S(g) + 4H_2O \qquad (C1)$$

$$2CH_3CHOHCOOH\ \textit{(lactate)} + SO_4^{2-} = 2CH_3COOH + 2HCO_3^- + H_2S(g) \qquad (C2)$$

Another group of SRB uses acetate as a substrate with complete oxidation:

$$CH_3COOH + SO_4^{2-} = 2HCO_3^- + H_2S(g) \qquad (C3)$$

Finally, there is evidence of anaerobic oxidation of methane (CH_4) by SRB:

$$CH_4(g) + SO_4^{2-} + H^+ = H_2S(g) + HCO_3^- + H_2O \qquad (C4)$$

Among the methanogens, two main groups are distinguished. One group (acetoclastic methanogens) uses acetate as a substrate:

$$CH_3COOH = CO_2(g) + CH_4(g) \qquad (D1)$$

The other group (hydrogenotrophic methanogens) uses $H_2(g)$ as an electron donor for the reduction of $CO_2(g)$, $CO(g)$ or formate:

$$CO_2(g) + 4H_2(g) = CH_4(g) + 2H_2O \qquad (D2)$$

Biological sulphate removal is used in a number of wastewater treatment technologies. The technologies discussed in this review include: (1) bioreactor, (2) constructed wetland, (3) alkalinity producing system and (4) permeable reactive barrier (PRB). The technologies that use biological sulphate removal (except bioreactor) are considered to be passive treatments.

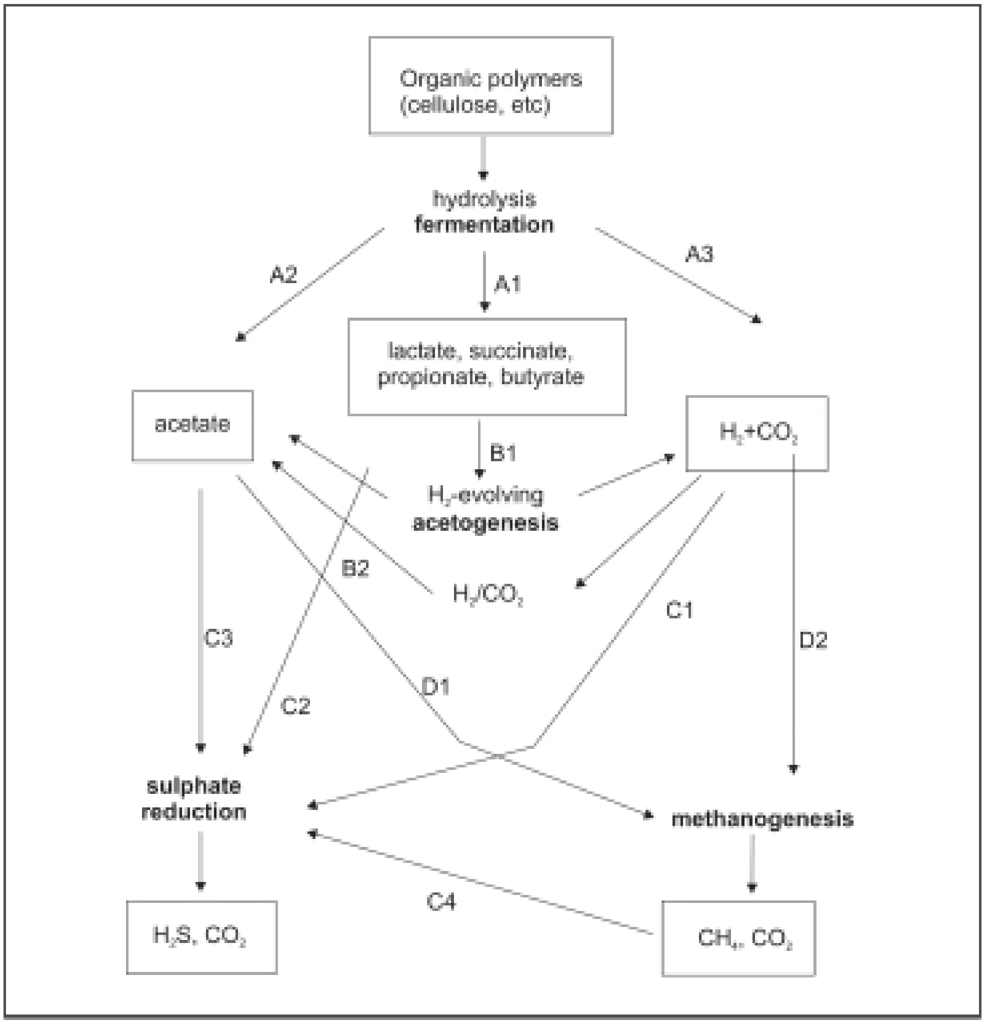


Figure 3-16: Anaerobic Pathways

Biological sulphate removal is limited by (1) substrate utilization in the presence of other anaerobic bacteria and (2) toxicity induced by H_2S and dissolved metals.

In the presence of sulphate, acetogens and methanogens compete with SRB for the available substrates. SRB compete very effectively with methanogens for common substrates (H_2(g) and acetate). In the absence of sulphate, acetogens are necessary for the conversion of fatty acids and alcohols into acetate and H_2(g). Under acidic conditions, homoacetogens outcompete (hydrogenotrophic) methanogens for H_2(g) and the produced acetate is degraded by the (acetoclastic) methanogens. Under more neutral conditions, (hydrogenotrophic) methanogens dominate H_2(g) consumption (Fenchel *et al.*, 1998).

Hydrogen sulphide (H_2S) can be toxic for many bacteria (Smith, 1993; McCartney and Oleszkiewicz, 1993). SRB are generally less sensitive to H_2S(g) than other anaerobic bacteria. The toxic effect may be attributed to the non-ionized state of H_2S(g), which allows it to cross the cell membrane more readily. In the cell it may interfere with the sulphur metabolism or affect the intracellular pH (Oude Elferink *et al.*, 1994). Also dissolved (trace) metal concentrations appear to inhibit sulphate reduction. The metal sulphides formed appear to act as barriers that prevent the access of reactants to the necessary enzymes (Utgikar *et al.,* 2001; Utgikar *et al.,* 2002).

3.4.2 Bioreactor

In the development and use of bioreactors for biological sulphate removal, several issues have received particular attention. These issues involve the substrate used, the toxicity of the waste stream to SRB and the type or design of bioreactor used.

SRB prefer relatively simple organic compounds as a carbon and energy source and rely on other anaerobic bacteria (*e.g.* fermenters) to oxidize more complex organic compounds (*e.g.* molasses) to products such as lactate and pyruvate. The competition of SRB with other anaerobic bacteria (*e.g.* methanogens, acetogens) for the available substrate will depend on the ratio of the chemical oxidation demand (COD) and the sulphate concentration of the wastewater (Hulshoff Pol *et al.,* 1998). At a COD/sulphate ratio > 0.67 there will be sufficient organic matter to completely reduce the available sulphate. At lower ratios the amount of organic matter is insufficient for a complete sulphate reduction and additional substrate is required.

If insufficient electron donors and carbon sources are available for sulphate reduction, appropriate electron donors can be added. The selection of an appropriate electron donor will depend on: (1) costs, and (2) potential residual or 'rest-pollution' by the added electron donor (*i.e.,* unconsumed substrate). In studies on biological sulphate removal in bioreactors a wide variety of substrates have been used, including spent mushroom compost (Dvorak *et al*., 1992), decomposable plant material (Harris and Ragusa, 2001), straw (Kosschorreck *et al*., 2002), ethylene glycol (Miller and Tsukamoto, 2002), methanol (Glombitza, 2001) and ethanol (de Smul *et al*, 1997 and Greben *et al.,* 2000). The choice of substrate is obviously determined by availability and costs. However, based on the 'rest-pollution' effect, simple organic compounds (*e.g.* ethanol or methanol) or synthesized gas (mixture of H_2, CO_2 and CO) are preferred over complex (organic) wastes or pure H_2(g) (too expensive). High sulphate loading rates (30 g/L,day) can be achieved with a (80:20) mixture of H_2(g) (energy source) and CO_2(g) (carbon source) in gas-lift reactors (van Houten *et al.,* 1994). Considering the costs of H_2(g), synthesis gas is an economic alternative for larger applications whereas methanol and ethanol are preferred for smaller applications.

When sulphate is in excess and H_2(g) is limiting, SRB compete with acetogens and methanogens for the available H_2(g). Based on growth kinetics, the competition at low H_2(g) concentration would follow the order SRB>methanogens>acetogens. However, in studies with gas-lift reactors acetogens appear to outcompete methanogens for the H_2/CO_2

substrate when sulphate is available in excess (Weijma *et al.*, 1999). Under sulphate limiting conditions the reverse applies.

A problem associated with having the microbial biomass in the waste stream (one reactor) is the potential toxic effect of the wastewater on the microbial population. SRB and other anaerobic bacteria can be exposed to highly acidic conditions, high $H_2S(g)$ concentrations and toxic dissolved metal concentrations. In highly acidic mine waters (*e.g.* pH 3) acidophilic SRB are more efficient in oxidizing various substrates than neutrophilic SRB (Kolmert and Johnson, 2001). High $H_2S(g)$ concentrations (50-130 mg/L) have a toxic effect on anaerobic bacteria and inhibit sulphate reduction (McCartney and Oleszkiewicz, 1993). In practice, anaerobic treatment is never inhibited for wastewaters with a COD to sulphate concentration ratio larger than 10, due to the stripping effect of the biogas that is produced (McCartney and Oleszkiewicz, 1991; Rinzema and Lettinga, 1988). The potential toxic effect of dissolved metals and metal sulphides (Utgikar *et al.*, 2001; Utgikar *et al.*, 2002) has been addressed earlier.

A large variety of bioreactors have been developed and are currently used, including mixed, packed bed, fluidized bed, sludge blanket (UASB) and gas-lift reactors. However, the most significant progress in reactor design for ARD treatment probably occurred in a study reported in 1988 (Nakamura, 1988). Using a continuous flow, fluidized bed reactor the generated H_2S (g) was stripped with an inert gas and used in a separate reactor to precipitate metals from ARD water. This was the first time in the treatment of ARD that sulphate reduction and precipitation of metal sulphides were performed in separate reactors.

The new approach has major advantages over the old approach in which sulphate reduction and precipitation of metal sulphides occur in the same reactor:

- SRB and other anaerobic bacteria are no longer exposed to potential toxic conditions associated with the wastewater to be treated;
- the loading of the waste stream occurs in a separate reactor and is no longer dependent on the biomass retention (separate reactor);
- a smaller reactor and a greater variety of substrates can be used;
- the precipitation of metal sulphides can be controlled in an environment that does not affect SRB. Moreover, it is possible to control the successive precipitation of different metal sulphides in separate reactors allowing a relatively pure recovery of individual metals from ARD water.

The THIOPAQ technology uses biological sulphate removal in a bioreactor. The system consists of two biological process stages: (1) sulphate reduction to sulphide (anaerobic stage), and (2) sulphide oxidation to elemental sulphur (aerobic stage).

For the reduction of sulphate to sulphide a reductant (electron donor) needs to be added. Suitable electron donors for small-scale THIOPAQ systems are ethanol or various fatty acids. Ethanol is first converted into acetate and hydrogen gas by anaerobic bacteria (acetogens):

$$CH_3CH_2OH + H_2O = CH_3COOH + 2H_2\ (g)$$

The hydrogen gas and acetate formed are then consumed in the sulphate reduction reaction. For large-scale applications (> 2 t/day H_2S), hydrogen gas is a preferred electron donor (reductant). Hydrogen gas (with carbon dioxide) can be produced on-site by cracking methanol or by steam reforming natural gas or LPG. The hydrogen gas and carbon dioxide are then consumed in the sulphate reduction reaction. The operating costs are higher with ethanol than with hydrogen gas but the latter requires additional capital for a reformer.

Excess hydrogen sulphide is biologically converted into elemental sulphur in the aerobic reactor:

$$H_2S\ (g) + \tfrac{1}{2}\ O_2\ (g) = S\ (s) + H_2O$$

The overall equation for the conversion of sulphate to elemental sulphur in the THIOPAQ process is:

$$SO_4^{2-} + 5H_2\ (g) + O_2\ (g) + 2CO_2\ (g) = S\ (s) + 2HCO_3^- + 4H_2O$$

The equation demonstrates that the sulphate reduction process generates alkalinity that can be used to neutralize acidic ARD water.

In practice many process variants of the THIOPAQ technology are being used and tailored to a host of applications. In this review the THIOPAQ technology will be demonstrated by two applications in the mining industry (Boonstra *et al*, 1999): the Budel Zink (Budelco) refinery (Netherlands) and the Kennecott mine (U.S.).

Various wastewater streams are produced in the Budel Zink refinery process, mainly containing dissolved zinc and sulphate. Since 1992, a sulphate reducing bacteria (SRB) plant has been operated to treat wastewater streams with a low level of dissolved sulphate (< 1 g/L). In the SRB plant, sulphate is reduced to sulphide, which is then precipitated as zinc sulphide. The precipitated zinc sulphide is recycled to the main zinc refinery process.

Due to changes in the environmental legislation, two highly concentrated sulphate waste streams could no longer be treated by conventional liming that produced gypsum. The two wastewater streams are: (1) wash tower acid containing 10 g/L sulphuric acid, 0.5 g/L fluoridic acid (HF) and 0.5 g/L dissolved zinc, discharged at 25 m^3/h, and (2) magnesium bleed (to prevent accumulation of magnesium in the electrolyte) containing 300 g/L sulphate, discharged at 0.5 m^3/h. The wastewater streams could not be treated in the existing SRB plant because the maximum sulphate loading capacity would be exceeded and fluoride would not be sufficiently removed.

A schematic representation of the processes used to treat the wastewater streams is shown in Figure 3-17 and includes the following steps:

1. Neutralization of wash tower acid with calcine (ZnO);
2. Fluoride removal by precipitation as CaF_2 in a 'Crystallactor' (patented pellet reactor);
3. Mixing with magnesium bleed;
4. Biological conversion of sulphate to sulphide (THIOPAQ) using H_2 (g) as the electron donor and CO_2 (g) as the carbon source. The latter are produced on-site with a reformer that converts natural gas and steam into H_2 (g) and CO_2 (g);
5. Precipitation and separation of zinc sulphide (ZnS);
6. Dewatering of the produced ZnS slurry and recycling in the refinery; and,
7. Treatment of the bioreactor effluent in the existing SRB plant (conversion of the excess sulphide into elemental sulphur).

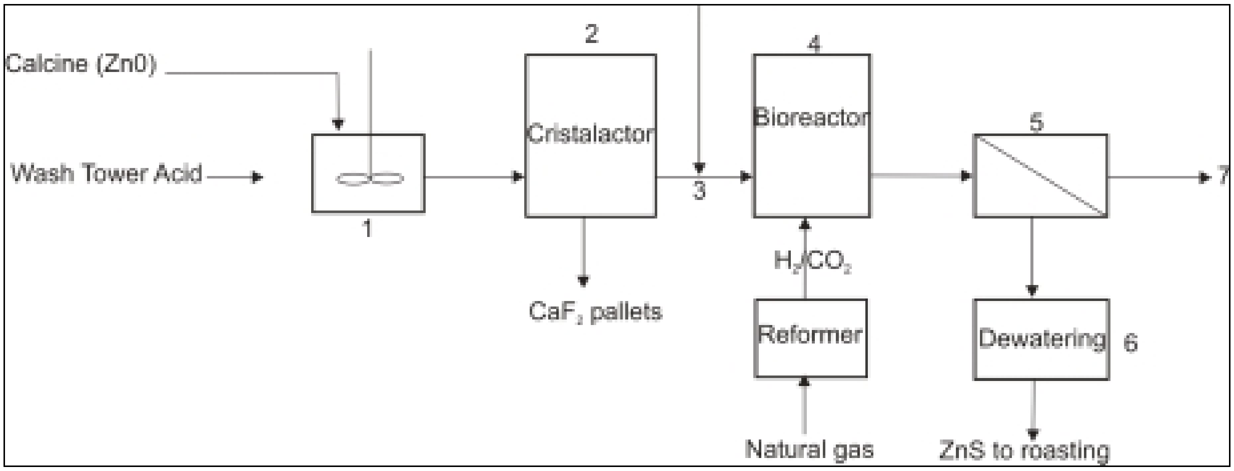


Figure 3-17: Schematic Flow Diagram for the Biological Process at Budelco

The various treatment steps resulted in strongly reduced (dissolved) concentrations of sulphate (<300 mg/L), fluoride (<50 mg/L) and zinc (<0.2 mg/L).

At the Kennecott mine THIOPAQ is used in a demonstration plant equipped with a 5 m^3 bioreactor to treat contaminated groundwater (high concentrations of dissolved sulphate and metals) and a dilute waste rock leachate (very high in dissolved copper). A schematic representation of the THIOPAQ demonstration plant at Kennecott is shown in Figure 3-18. The plant can be divided into two sections:

1. Biological H_2S production.

   Using hydrogen gas as the electron donor, sulphate in the feed water (groundwater) is converted to hydrogen sulphide in the anaerobic reactor. Part of the hydrogen sulphide is recirculated and mixed with the feed water to remove dissolved metals by precipitation as metal sulphides. The excess hydrogen sulphide produced in the anaerobic reactor is transferred to the aerobic reactor and oxidized to elemental sulphur. The alkalinity generated in the conversion of sulphate into elemental sulphur is used to precipitate dissolved aluminum and iron as hydroxysulphates and dissolved calcium and magnesium as carbonates.

2. Copper recovery from waste rock leachate.

   Part of the hydrogen sulfide gas from the anaerobic reactor is transferred to a gas-liquid contactor to react with the dissolved copper in the waste rock leachate and form copper sulphide. The precipitated copper sulphide is removed in a clarifier and returned to the smelter. The excess hydrogen sulphide gas is recycled to the anaerobic reactor.

   Using a feed water flow rate of 0.2 m^3/h for the groundwater treatment, the pH was increased from 2.5 to 8.5. Dissolved sulphate was reduced from 30 g/L to 0.5 g/L while dissolved copper decreased from 60 mg/L to less than 0.1 mg/L.

   For the waste rock leachate treatment a feed water flow rate of 4 m^3/h was used. The dissolved copper in the leachate was reduced from 180 mg/L to less than 0.3 mg/L. The copper was almost quantitatively recovered from the waste rock leachate.

   The THIOPAQ system is only one example of the many systems developed in biological sulphate removal with bioreactors. Many of these systems, however, have not been tested as intensively as the THIOPAQ technology in large-scale (pilot) projects and over an extended period. Some examples of other systems used in biological sulphate removal with bioreactors are discussed later (Chapter 4).

3.4.3 Constructed Wetland

Constructed wetlands can be subdivided into two main categories: free water surface (FWS) wetlands and subsurface flow (SF) wetlands (Figure 3-19). Most natural wetlands are FWS wetlands.

In FWS wetlands, the water that is treated flows over a vegetated surface from an inlet to an outlet. FWS wetlands are generally shallow basins with a subsurface barrier that prevents seepage. A submerged soil layer supports the macrophyte vegetation. An SF wetland is designed for water treatment by holding an appropriate medium in a bed or channel. The water level remains below the surface of the bed, which is planted with emergent vegetation. The volume of medium used in SF wetlands is generally larger that that in FWS wetlands. For the biological removal of sulphate from wastewaters, FWS wetlands are the most suitable.

Among the FWS wetlands a distinction is made between aerobic and anaerobic wetlands (Skousen, 1999). Aerobic wetlands usually have shallow (*e.g.* <30 cm), impermeable sediments.

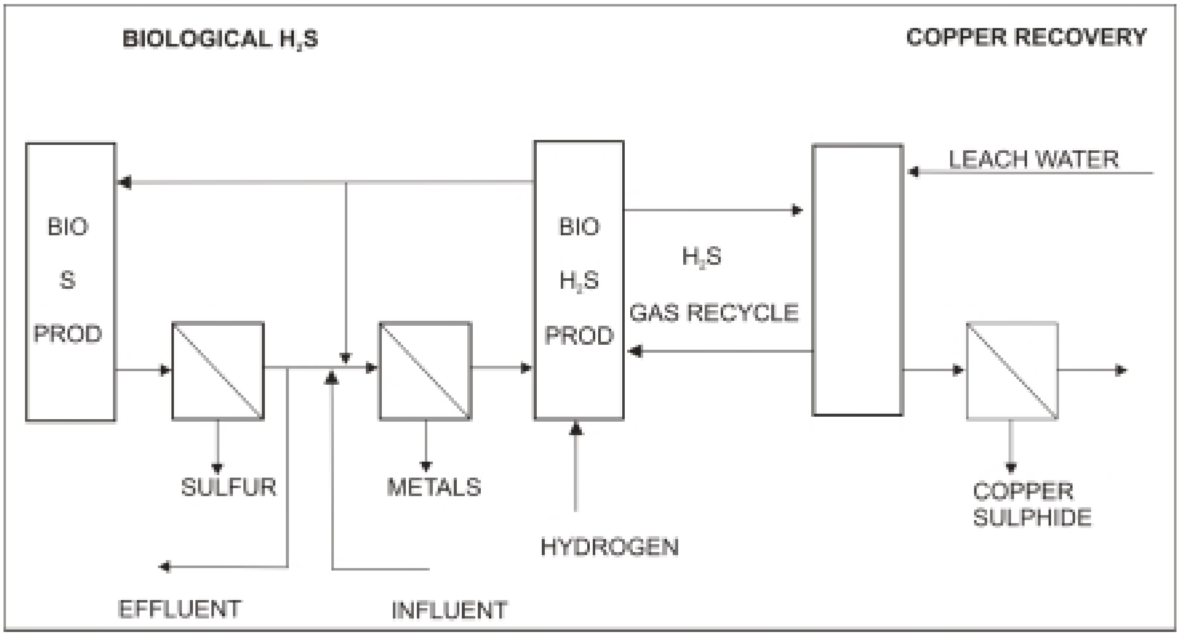
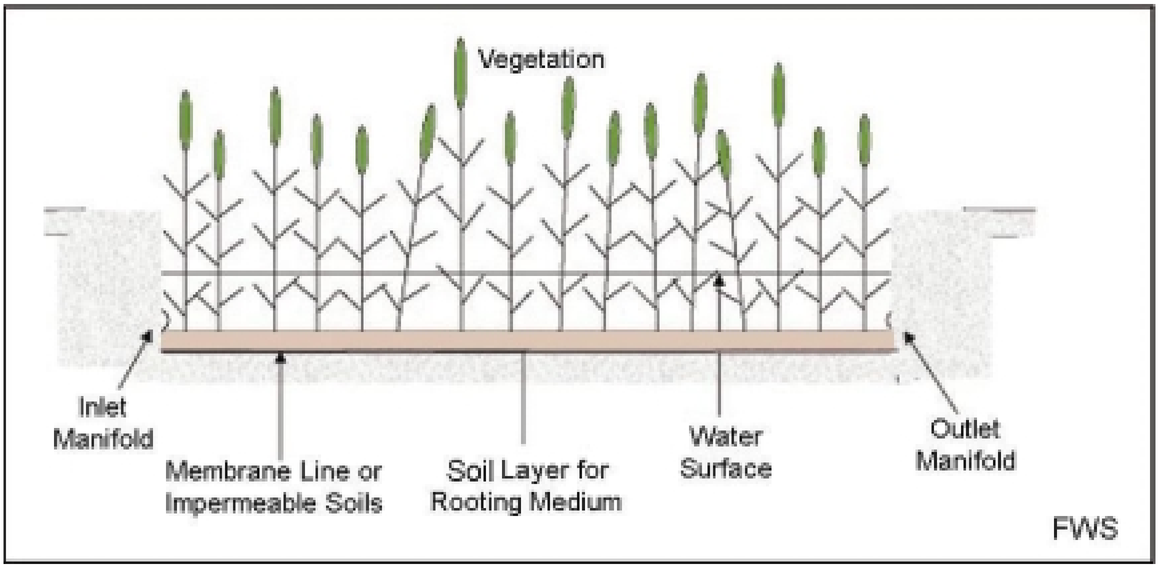


Figure 3-18: Simplified Flow Diagram of the Demonstration Plant at Kennecott

The key processes in the treatment of wastewater are concentrated in the shallow surface layer. Aerobic wetlands are used to provide residence time and aeration to enhance metal precipitation through biotic and abiotic oxidation. Usually the water has a net alkalinity. Anaerobic wetlands are characterized by relatively deep (*e.g.* >30 cm), permeable sediments that consist of a mixture of soil and various (added) organic materials. Limestone is often added to the mixture. Key processes in the treatment of wastewater involve interactions with the entire substrate. In anaerobic wetlands water flow through the organic substrate is important in the treatment process. Anaerobic wetlands are often used for the treatment of acidic water. The alkalinity used in the neutralization is derived from the dissolution of limestone and from sulphate reduction in the (anaerobic) subsurface. Metal hydrolysis and oxidation are the dominant processes in the aerobic surface layer. Anaerobic wetlands are obviously the most suitable for biological sulphate removal by sulphate reduction.



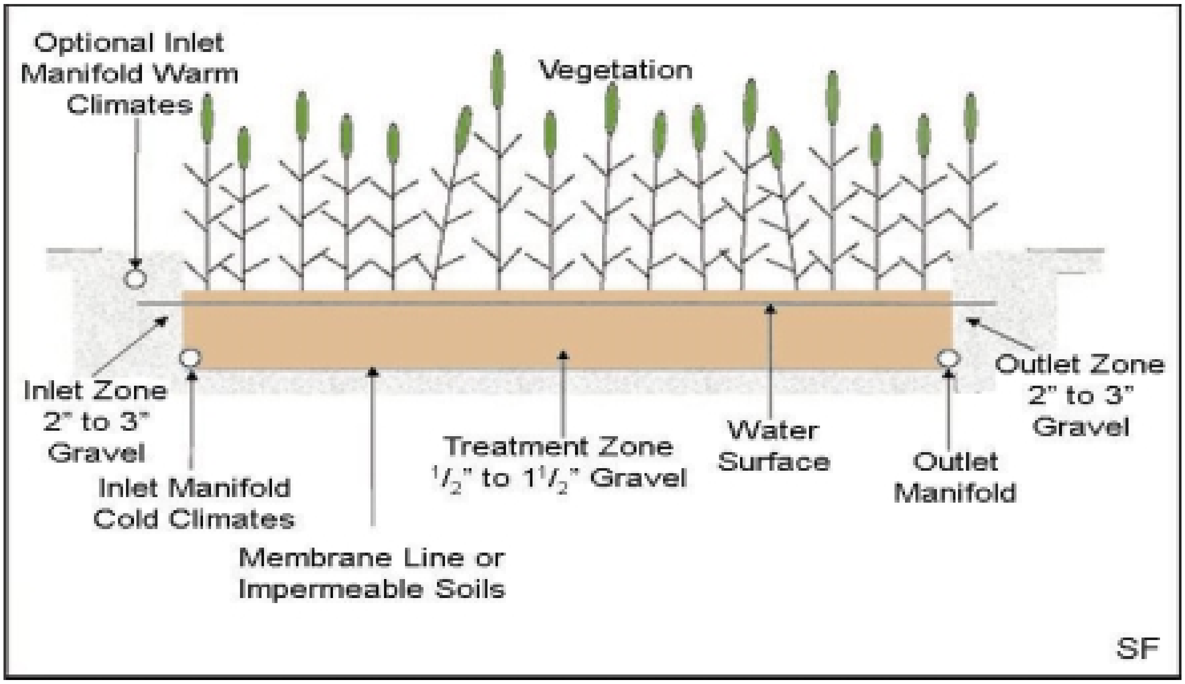


Figure 3-19: Free Water Surface (FWS) Wetland (top) and Subsurface Flow (SF) Wetland (bottom)

A schematic diagram of a constructed wetland is shown in Figure 3-20. Often the wastewater discharge is initially diverted to a small settling pond. After the settling pond the water flows into a large wetland cell, the first in a series of cells. To increase the retention time of the water to be treated, a series of baffles is used to increase the circulation path. After the last cell, there is usually a final setling pond for the precipitation and removal of solids from the treated water. The design of wetland cells is dependent on the amount of flow and the chemical composition of the flow. The cell size is based on the area required to treat the flow for a particular parameter (*e.g.* acidity).

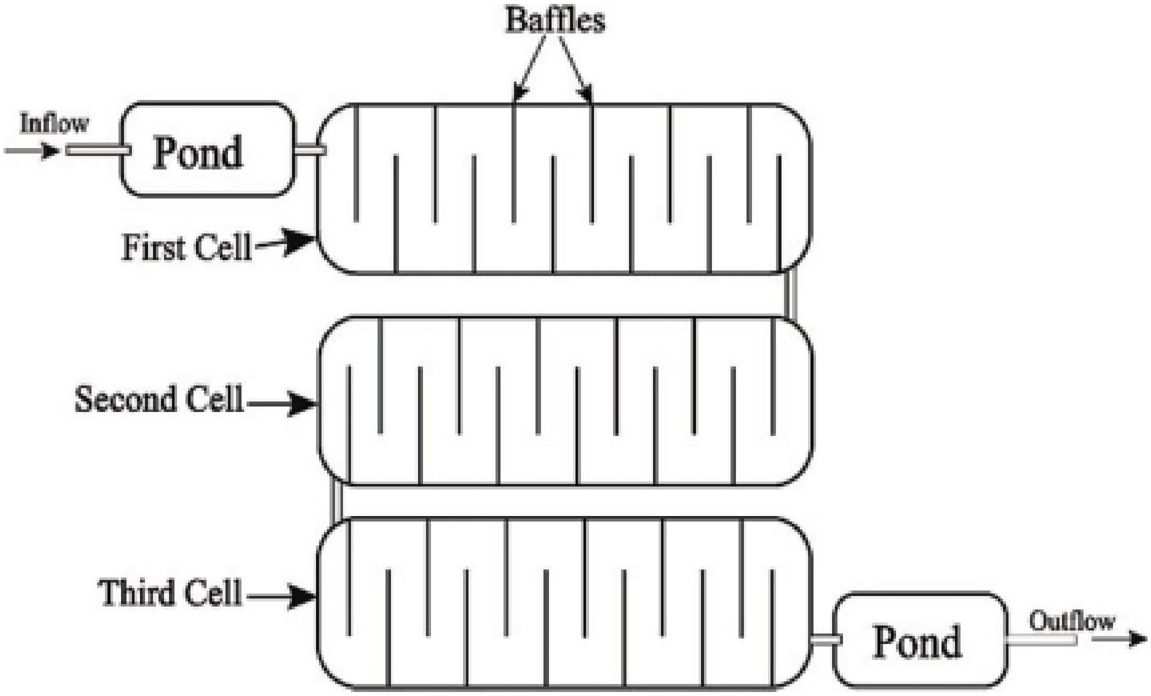


Figure 3-20: Constructed Wetland Layout

Most of the attention in the research and applications of constructed wetlands in the treatment of mine drainage is focused on acidity and dissolved metals. Biological sulphate removal in wetlands has received considerably less attention and from the few reported data on dissolved sulphate it is often not clear whether sulphate removal is due to sulphate reduction. Differences between dissolved sulphate concentrations in influents and effluents can be attributed to various processes, including sulphate reduction. Other processes that contribute to a net change of dissolved sulphate concentrations include: oxidation of reduced inorganic sulphur (RIS), hydrolysis of ester sulphates (ES), heterotrophic sulphate consumption (*e.g.* vegetation), adsorption, diffusion in sediments and mineral precipitation (*e.g.* gypsum).

More accurate estimates of sulphate reduction in wetlands are obtained by an analysis of the sulphur cycling using sediment incubation studies ($^{34}SO_4^{2-}$ radiotracer) and stable isotope

($\delta^{34}S$ and $\delta^{18}O$) analyses of sediments, rainfall and surface waters (Machemer *et al.*, 1993; Hsu and Maynard, 1999; Mandernack *et al.*, 2000). SRB bacteria prefer the lighter isotopes and produce $H_2S(g)$ that is depleted in ^{34}S relative to the orginal sulphate. The degree of isotope fractionation by bacteria is inversely proportional to the rate of sulphate reduction. A low rate of sulphate reduction will result in a large degree of isotope fractionation between sulphate and sulphide. The opposite applies to a high rate of sulphate reduction.

Several studies on constructed wetlands used in ARD treatment show that constructed wetlands do not always perform well in terms of biological sulphate removal (*e.g.* Mitsch and Wise, 1998; Hsu and Maynard, 1999). This appears to be related to their design (flow rate and size), the organic substrate used and the redox buffering provided by other oxidants (*e.g.* Fe^{3+}, NO_3^- versus SO_4^{2-}).

The design and performance assessment of constructed wetlands are largely based on the treatment efficiency for selected chemical parameters (Hedin and Nairn, 1990 and 1992; Stark and Williams, 1995; Tarutis *et al.,* 1999). The chemical parameters most often selected are acidity, iron, manganese and aluminum concentrations. Maximizing surface flow and oxidizing conditions improve treatment efficiencies for those parameters. These conditions, however, do not necessarily promote sulphate reduction, which requires less water circulation and reducing conditions (Hedin *et al.,* 1989; Eger, 1994).

In a wetland mesocosm experiment conducted to obtain wetland design parameters, sulphate reduction was stimulated by a reduction of flow rate and metal load (Stark *et al.,* 1995). A similar effect on sulphate reduction was noticed in a study on the sulphur balance of a constructed wetland to treat AMD (Machemer *et al.,* 1993). Sulphate and metal removal were inconsistent during a period with higher flow rate. Other wetland studies (Hedin *et al.,* 1989; Hsu and Maynard, 1999) suggest that a significant sulphate removal by sulphate reduction requires a larger surface area than is predicted from design criteria for the removal of iron.

Improvements in the design of constructed wetlands will enhance the conditions required for sulphate reduction. For example, the exposure of acid mine water to anoxic conditions could be increased by discharging mine effluents at the base of the (organic) substrate in constructed wetlands.

Although the quantity of organic matter in wetlands appears to be sufficient, it is not clear if the choice of organic matter substrate is particularly critical for sulphate reduction. It has been shown that the composition of the SRB population can vary among wetlands that are ecologically different (Webb *et al.,* 1998). Under laboratory conditions, these SRB populations showed remarkable differences in substrate utilization, resulting in significant differences in sulphide generation.

In a study on sulphate reduction in sediments from two different, natural wetlands (black gum and titi) sulphate loading had a different effect (Feng and Hsieh, 1998). Although sulphate reduction occurred in both sediments, sulphate loading only stimulated sulphate reduction in one of the two sediments (black gum). The other sediment could not ‘absorb’ the sulphate loading by an increase of the sulphate reduction rate. A similar response to sulphate loading was observed in a study on two different freshwater marshes (Lamers *et al.*, 2002).

It appears that the choice of organic substrate used in wetlands may be an important factor for sulphate removal. Spent mushroom substrate (SMS) appears to be well suited (except for Mn removal) as an organic substrate in constructed wetlands (Stark and Williams, 1994).

The presence of other, (energetically) more favourable electron acceptors (oxidants) than sulphate (e.g. Fe^{3+}, NO_3^-) can affect sulphate reduction in wetlands. If present in high concentrations, these oxidants can prevent sulphate reduction or oxidize sulphides produced by sulphate reduction. This effect of redox buffering has been suggested as a potential explanation for low rates of sulphate reduction in several wetland studies (Lamers *et al.*, 1998; Mitsch and Wise, 1998).

The sulphate reduction rates in natural and constructed wetlands reported in literature, range from 0.3 to 675 mg SO_4/L,day (Henin *et al.*, 1989; Machemer *et al.*, 1993; Hsu and Maynard, 1999; Edenborn and Brickett, 2001). Most of the reported values are between 30 and 150 mg SO_4/L,day. Compared to bioreactors (12 to 30 g/L,day), sulphate reduction rates in wetlands are very low.

3.4.4 Alkalinity Producing Systems

Anoxic limestone drains (ALD) and vertical-flow systems (VFS) - also called successive alkalinity-producing systems (SAPS) or reducing and alkalinity-producing systems (RAPS) - are primarily used to raise the pH and add alkalinity to acid mine water.

Anoxic limestone drains are buried cells or trenches of limestone capped with clay to prevent atmospheric exposure (Figure 3-21). The latter creates an environment, which is high in carbon dioxide and low in oxygen. This increases the dissolution of limestone and prevents the precipitation of iron hydroxide, which could inhibit limestone dissolution or clog the drain. The effluent from the ALD is often discharged into a settling pond to increase the pH (degassing) and promote metal precipitation.

Vertical flow systems are a combination of ALD and anaerobic wetlands (Figure 3-21). VFS consist of a water layer (1-3 m) over an organic compost layer (0.2-0.3 m) that is underlain by a layer of limestone (0.5-1 m). Drainage pipes below the limestone layer convey the water to an aerobic pond where pH is increased (degassing) and metals are precipitated. Water moving downwards into the organic layer becomes gradually depleted in oxygen resulting in the reduction of ferric iron and possibly the reduction of sulphate.

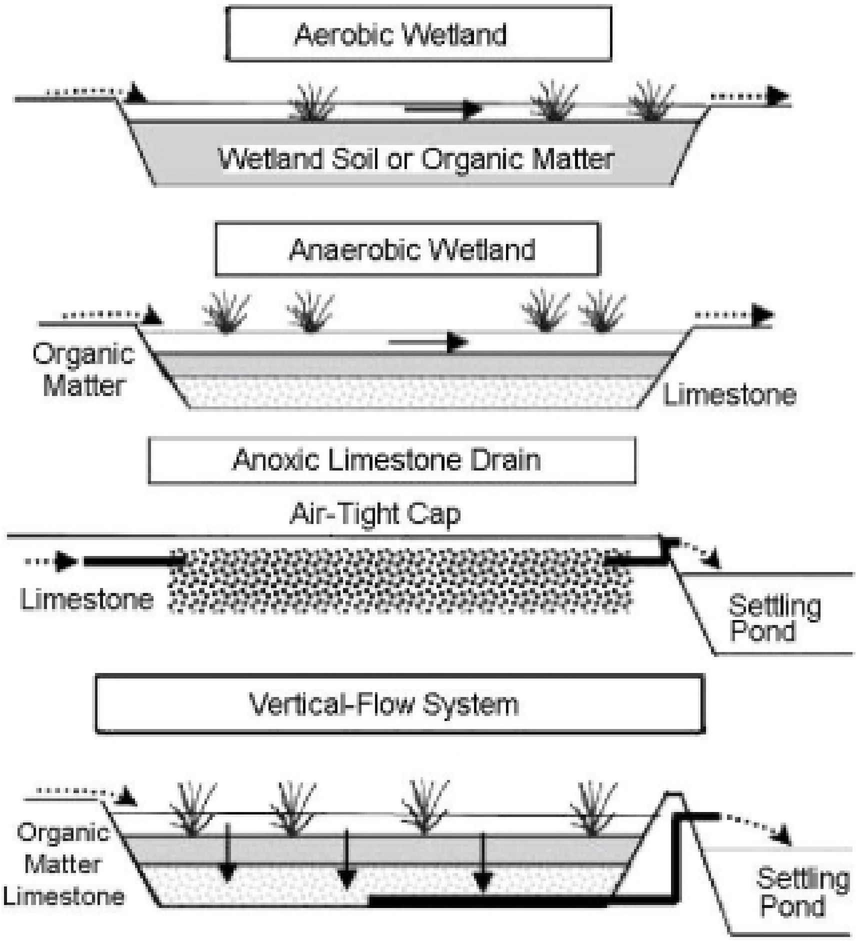


Figure 3-21: Simplified Cross-Sectional Views of the Four Major Passive Treatment Systems used in Treating Acidic Mine Drainage. Arrows represent Predominant Flows

Together with aerobic and anaerobic wetlands, ALD and VFS are the main passive treatment systems for ARD. Selection of the appropriate passive treatment system will depend on the water chemistry, flow rate, local topography and site characteristics. A flowchart for the appropriate selection of passive treatment system is shown in Figure 3-22 (Hedin *et al*, 1994).

Considering the ambient redox conditions, sulphate reduction could occur in ALD and VFS. Especially in VFS, conditions (organic layer) appear to be favourable for sulphate reduction. However, evidence of sulfate reduction in ALD or VFS is limited (Robbins *et al.*, 1999) and detailed studies have not been reported. It appears that mainly reduction of ferric iron occurs and sulphate reduction is very limited under the ambient redox conditions (*e.g.* Hedin *et al.*, 1994; Barton and Karathanasis, 1999). Depending on the circulation rate, the residence time of the water in ALD and VFS may not be sufficiently long to develop the reducing conditions necessary for sulphate reduction. Reported average retention times range from 23 hrs to 51 hrs for ALD (Hedin *et al.*, 1994) and from

4 hrs to 90 hrs for VFS (Jage *et al.*, 2001). This suggests that the design criteria of ALD and VFS, while appropriate to metal removal, may not be favourable for the development of conditions necessary for significant sulphate reduction.

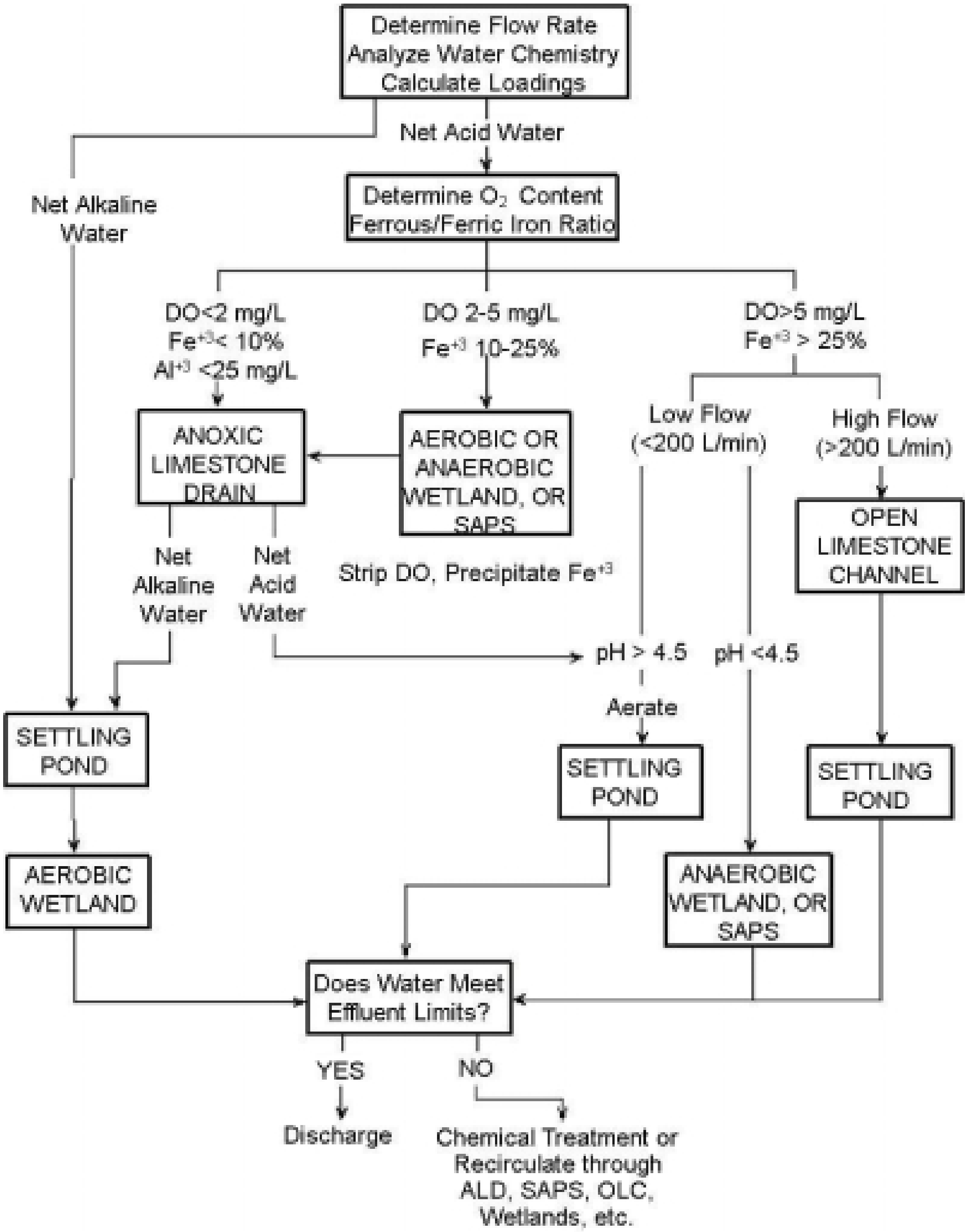
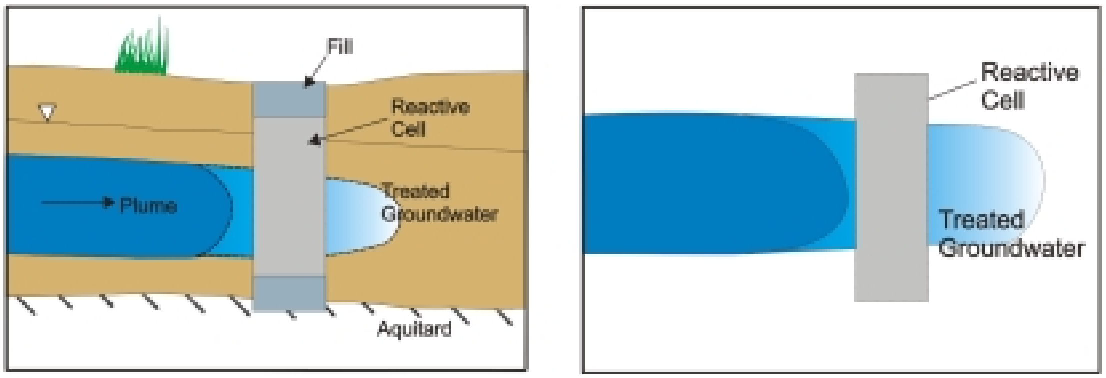


Figure 3-22: Flowchart for the Selection of an Appropriate Passive Treatment System

Despite the lack of evidence for sulphate reduction, dissolved sulphate is removed from the water in ALD and VFS. This is largely due to precipitation of gypsum and other sulphate minerals (Barton and Karathanasis, 1999; Bernier *et al.*, 2001).

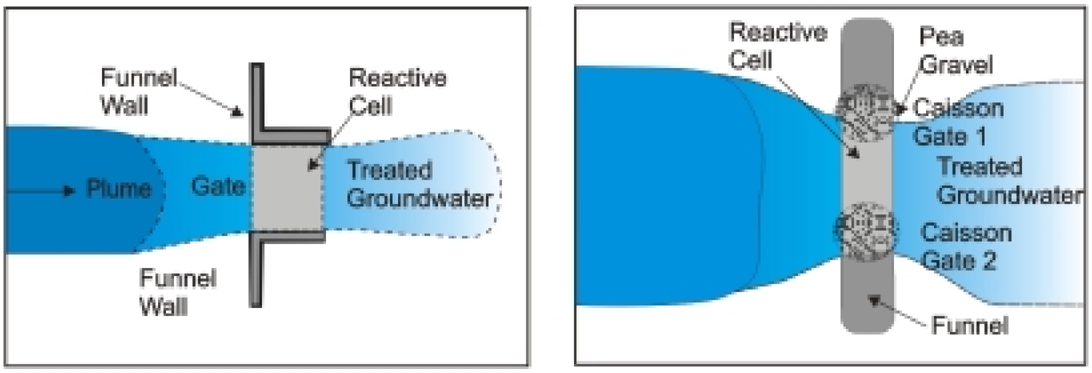
3.4.5 Permeable Reactive Barriers

A permeable reactive barrier (PBR) is a reactive zone in an aquifer, created through the addition of "reactive" material designed to interact with the contaminants in the groundwater (Figure 3-23). PBRs are constructed perpendicular to the groundwater flow path and are designed to allow contaminated groundwater to flow through them. The contaminants are either immobilized or degraded by the chemical reactions with the reactive elements of the barrier (USEPA, 1998).



(a) Elevation view of a permeable barrier

(b) Plan view of a continuous reactive barrier configuration



(C) Funnel-and-gate system (plan view)

(d) Funnel-and gate system with two caisson gates (plan view)

Figure 3-23: Different Permeable Reactive Barrier Configurations for Groundwater Treatment

Two common configurations of the barrier are the continuous reactive barrier and the funnel-and gate system (Figure 3-23). The continuous reactive barrier consists of a reactive zone only. The funnel-and-gate system uses a reactive zone flanked by impermeable walls that guide the groundwater flow to the reactive zone (Gavaskar, 1999).

For the design of a permeable reactive barrier the following issues need to be considered (USEPA, 1998; Gavaskar, 1999) (Figure 3-24):

- the suitability of the site for the application of the permeable barrier system;
- the site characteristics that affect the barrier design;
- the reaction rates or half-lives of the reactants involved;
- the location, configuration and dimensions of the barrier;
- the longevity of the system;
- the monitoring strategy; and,
- the cost

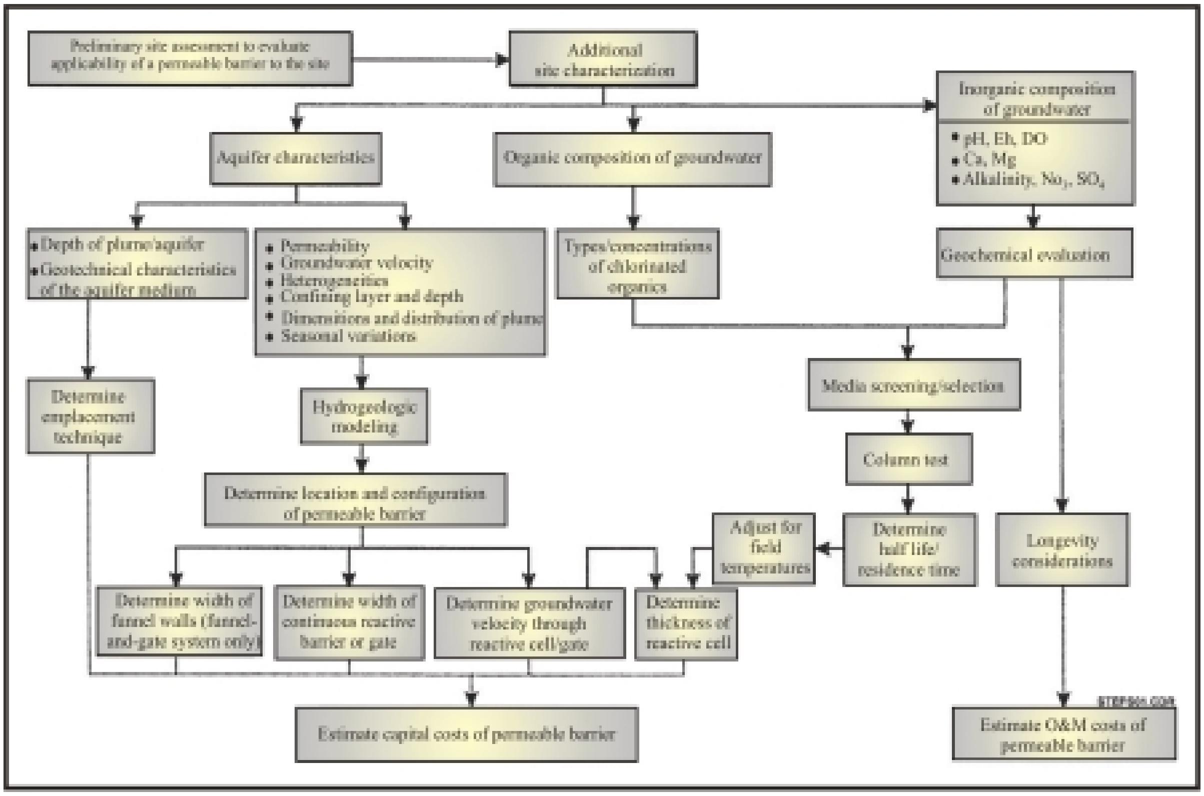


Figure 3-24: Steps in the Design of a Permeable Reactive Barrier

Reactive materials that have been successfully used in PRB applications include: zero-valent iron (elemental iron), calcite or limestone and organic materials (USEPA, 1998 and 1999; Gavaskar, 1999; Ludwig wt al., 2002; Cocos *et al.*, 2002).

Zero-iron is an electron-donor (reductant) used to reduce metal contaminants (*e.g.* Cr^{6+}, As), dehalogenate hydrocarbons or precipitate (oxy) anions in the groundwater. Calcite or limestone is used for the treatment of acidic groundwater plumes with high dissolved metal concentrations. The treatment involves neutralization of acidity and immobilization (precipitation or adsorption) of dissolved metals. Organic materials are very effective because they can be used in a wide range of physico-chemical and microbial processes that immobilize contaminants. Examples are adsorption of dissolved metals and sulphate reduction followed by precipitation of metal sulphides.

Thus far, no PRBs have been constructed to treat for sulphate specifically; however, sulphate reduction is a key process in PRBs designed to remove many trace metals. In such cases, organic matter is used as a substrate within the PRB creating an oxidant demand to the extent that sulphate reduction occurs within the barrier. The conversion of sulphate to sulphide affords an immobilization mechanism in the form of metal-sulphide precipitation provided sufficient concentrations of trace metals are available to remove the sulphide to low values. Unfortunately, few data sets focus on sulphate or even include it as an ancillary parameter.

Nevertheless, PRB is an established technology that has been tested extensively at various sites in North America. One of these applications involves the removal of high levels of dissolved iron and sulphate from contaminated groundwater at a mine site in Ontario (Benner et al., 1999; Benner *et al.*, 2002). Using a mixture of gravel and compost as reactive material, the groundwater was successfully treated *in-situ* by sulphate reduction and precipitation of iron sulphide. The average sulphate removal rate over a 38 month period was 14 mg/L,day.

It is important to note that the success of a PRB to removed sulphate (invoking sulphate reduction) require a similar sized inventory of dissolved metal with which in can precipitate, otherwise the free sulphide will remain in solution. In the absence of such a sink, sulphide will escape the system and revert back to sulphate if oxidizing conditions are encountered.

4. EVALUATION OF TREATMENT PROCESSES: CASE STUDIES

4. Evaluation of Treatment Processes: Case Studies

The following chapter presents an evaluation of each of the sulphate treatment strategies presented in Chapter 3 by way of case study. Each case study is described using a common format. The problem faced by the mining company is first defined. This is followed by a description of the sulphate treatment process chosen to address the problem and the results of that particular solution. Costs are presented followed by an assessment of the advantages, disadvantages, and where possible, potential for improvement.

4.1 Chemical Treatment with Mineral Precipitation

4.1.1 Lime and Limestone

- **Problem**

  Mine water at the Navigation coalmine near Witbank in South Africa is very acidic (pH 2.1) and high in SO_4 (3,000 mg/L), Ca (420 mg/L) and Mg (160 mg/L). Discharge of the mine water into local streams of the Upper Olifants river catchment would cause acidification and salination of the surface water resources. Sulphate removal from the mine water is required to prevent: (1) salination of surface waters, (2) scaling (gypsum), (3) biocorrosion, and (4) acid corrosion.

- **Treatment Process**

  The aim of the treatment process is to neutralize the acid mine water by adding limestone (calcium carbonate) and to improve the sulphate removal (*i.e.* achieving sulphate concentrations below the saturation level of gypsum) through the addition of lime (calcium hydroxide).

  The integrated limestone/lime process is a three-stage sulphate treatment process in which successively *limestone* (for neutralization and CO_2 production), *lime* (for $Mg(OH)_2$ and $CaSO_4 \cdot 2H_2O$ precipitation) and $CO_2(g)$ (for pH adjustment and $CaCO_3$ precipitation) are added to the feed water (Section 3.1.1). A mobile pilot plant with a capacity of 10 m^3/day was used for on-site treatment of the mine water (Figure 4-1). A special $CaCO_3$-handling and dosing system was designed and implemented for the treatment of mine water in the first stage of the process. Design details of the mobile plant and the $CaCO_3$-handling and dosing system are described by Geldenhuys *et al*. 2001.

  Waste powder limestone ($CaCO_3$) from paper industries was used in the limestone neutralization stage of the process while unslaked lime ($Ca(OH)_2$) was used for the gypsum crystallization stage. Details on the chemical composition of the limestone and lime are listed in Geldenhuys *et al*. (2001). The $CO_2(g)$ recovered from the first stage of the treatment process was used to adjust the pH in the third stage. The required contact time between the water and the limestone and lime depends on the surface area. For design purposes, a retention time (HRT) of 1 hr was required in the neutralization stage, 2.7 hrs in the gypsum crystallization stage and 0.5 hr in the calcite precipitation stage. The treatment process produced $CaSO_4 \cdot 2H_2O + Mg(OH)_2$ (2nd stage) and $CaCO_3$ (3rd stage) sludges. The $CaCO_3$ sludge was recycled to the limestone neutralization stage.

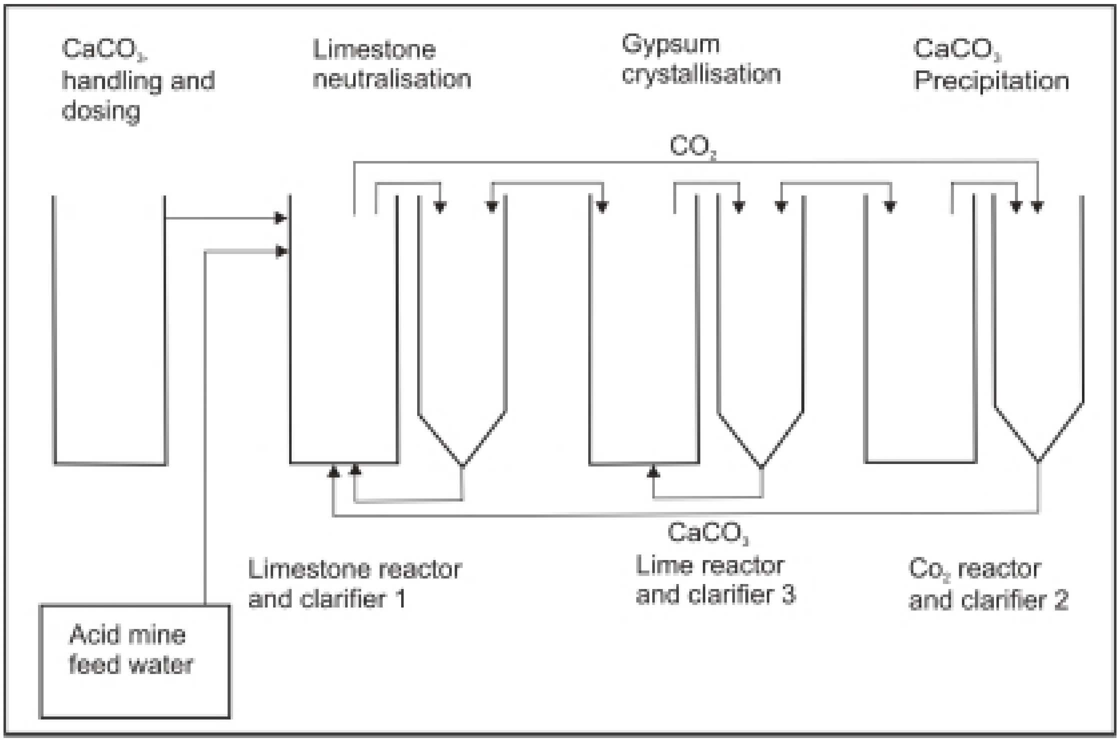


Figure 4-1: Schematic Illustration of $CaCO_3$ – Handling and Dosing System on Full Scale. Incorporated with the Limestone Neutralisation, Gypsum Crystallization and $CaCO_3$ Precipitation System at the Pilot Plant.

- **Results**

The chemical composition of the acid mine water and that of the feed water after each treatment stage are shown in Table 4-1.

From the data it is evident that treatment with limestone alone reduces the sulphate concentration to 1,900 mg/L. The successive lime treatment stage further reduces the sulphate concentration to 1,094 mg/L, well below the saturation level of gypsum. The slight increase in sulphate concentration in the third stage (1,219 mg/L) is probably caused by dissolution of some gypsum washed out from the second stage.

Table 4-1:
Chemical Composition of Feed Water and Treated Water After Each Treatment Stage

Parameter	Acid feed Water	Treated Water		
		$CaCO_3$	Lime	CO_2
pH	2.10	7.68	12.26	8.50
SO_4 (mg/L)	3000	1900	1094	1219
Ca (mg/L)	420	636	829	542
Mg (mg/L)	160	147	0	3.03
Na (mg/L)	41	40	47	46.80
Mn (mg/L)	17	13	0	0.01
Cl (mg/L)	16	17	-	-
Alkalinity (mg/L)	-3000	100	940	50

The data in Table 4-1 clearly demonstrate that improved sulphate removal is achieved when dissolved Mg is removed by $Mg(OH)_2$ precipitation at pH 12.3, after lime treatment. The Mn data indicate that the lime treatment stage could also be used to remove dissolved metals from the mine water by precipitation as metal hydroxides.

A mixed sludge of gypsum and magnesium hydroxide is the only waste product in the treatment process.

- **Costs**

Capital costs for a limestone/lime treatment plant are highly site-specific typically falling within the USD 1 to 2 M range; however, the chemical costs for the treatment process can be specified for each treatment stage. It requires 1.04 kg limestone per kg sulphate removed to reduce the sulphate concentration in the mine water to 1,900 mg/L in the limestone neutralization stage. Assuming limestone can be acquired at ~10 USD per 1000 kg, the costs would be 0.10 USD per kg sulphate removed. In the lime treatment stage 0.77 kg lime per kg sulphate removed are required to lower the sulphate concentration to 1,200 mg/L; at a cost of ~70 USD per 1000 kg lime, the costs would be 0.54 USD per kg sulphate removed. Assuming that the limestone from the third stage can be recycled, the total costs involved would range from 0.54 to 1.31 USD per kg sulphate removed or 0.94 to 2.28 USD per m^3 mine water treated to 1,200 mg/L sulphate depending on how much limestone can be recycled.

- **Advantages/Disadvantages**

The advantages of the treatment process are: (1) removal of sulphate to below the saturation level of gypsum, (2) neutralization of acidity and removal of dissolved metals, (3) elimination of scaling and corrosion problems during water reuse, (4) product water with a quality suitable for irrigation or reuse in the mine, (5) it can be used as a cost-effective pre-treatment process where sulphate needs to be removed to less than 1,200 mg/L.

The major disadvantages include: (1) the production of a mixed sludge of gypsum and magnesium hydroxide (waste product), (2) the limit to which sulphate can be removed from the mine water (~1,200 mg/L) which is still above the recommended discharge concentration (500 mg/L).

- **Future Needs/Improvements**

  To eliminate the waste product problem it would be useful to find ways to separate and recycle the sludge of gypsum and magnesium hydroxide precipitates.

- **References**

  CSIR, Division of Water, P.O. Box 395, Pretoria, 0001, South Africa.

  Website: www.csir.co.za E-mail: ajgeldenhuys@csir.co.za

4.1.2 Barium Salts

- **Problem**

  Various barium salts (*e.g.* $BaCO_3$, $Ba(OH)_2$ and BaS) can be used to remove dissolved sulphate from mine water by precipitation as barium sulphate. Compared to the other barium salts, barium sulphide has distinct advantages (discussed below), which makes it the most suitable barium salt to remove sulphate from mine water. This case study presents data generated from unidentified coal and uranium mines.

- **Treatment Process**

  The objectives of this case study on the BaS treatment process were to optimize the process and to establish technical and economical feasibility for the treatment of waters high in dissolved calcium and sulphate (Adlem, 1997; Bosman *et al.*, 1990; Maree *et al.*, 1989).

  The barium sulphide treatment process consists of three stages (Figure 4-2): (1) a sulphate removal stage, (2) a $H_2S(g)$ stripping stage, and (3) a water softening stage.

  The *sulphate removal stage* involves the addition of BaS to the feed water resulting in the precipitation of $BaSO_4(s)$; a synthetic flocculant is added to improve the sedimentation rate of $BaSO_4(s)$ in the settler. Before the reduction of $BaSO_4(s)$ to BaS(s), coal is added to the barium sulphate sludge in a 3:1 molar ratio (C: $BaSO_4$=3:1) and the sludge is dewatered to approximately 70% solids. Thermal reduction between 1000^oC and 1100^oC in a rotary kiln converts the $BaSO_4(s)$

(sludge) into BaS(s). The CO_2(g) produced during the thermal reduction can be used in the H_2S(g) stripping stage. The BaS(s) formed by thermal reduction is recycled (after dissolution in water) in the sulphate removal phase.

In the *H_2S(g) stripping stage*, the overflow from the $BaSO_4$(s) settler, which is high in dissolved calcium and sulphide, is subjected to stripping with CO_2(g) in a packed bed reactor. By adding CO_2(g) at flow rates of 0.36-4.5 L/min for 30 min, 85%-96% of the sulphides are removed. The H_2S(g) stripped from the settler overflow can be converted to S(s) or NaHS. The remaining solution from the packed bed reactor, high in dissolved calcium and bicarbonate, is diverted to a bubble bed reactor.

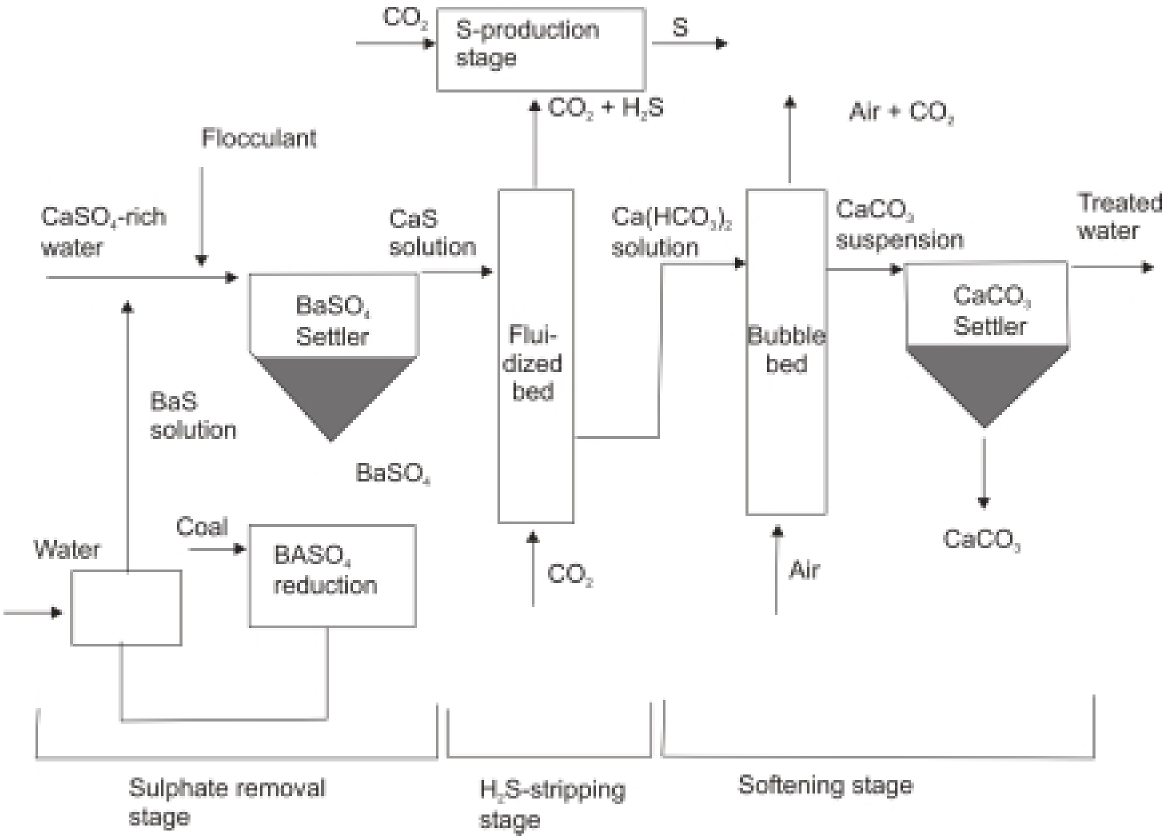


Figure 4-2: Schematic Diagram of the Integrated BaS Process

In the *water softening stage* the feed water is sparged with air to remove the CO_2(g), increase the pH (cheap alternative to liming) and promote the precipitation of $CaCO_3$(s). Precipitation of $CaCO_3$(s) is promoted by the use of seed crystals. Approximately 90% of the Ca-hardness is removed by air sparging in the reactor. The $CaCO_3$(s) suspension is diverted to a settler where relatively high grade $CaCO_3$(s) is recovered.

- **Results**

  The waters used in the barium sulphide treatment process (Bosman *et al.*, 1990) were a uranium raffinate and AMD water from a coal mine. The chemical composition of the waters before (untreated) and after the sulphate removal and $H_2S(g)$ stripping stages are shown in Table 4-2. The results show that dissolved sulphate concentrations could be reduced from as high as 17,500 mg/L (raffinate) to 175-190 mg/L. The slight increase of the sulphate concentration in the $H_2S(g)$ stripping stage is probably due to oxidation of dissolved sulphides. In addition to dissolved sulphate, dissolved calcium and magnesium are almost completely removed from the treated waters.

  The "waste" products are S or NaHS and $CaCO_3$ (sludge), which can be used in other industrial applications (*e.g.* neutralization).

Table 4-2:
Chemical Composition of Raffinate and AMD Water,
Before (untreated) and After Different Treatment Stages

		Raffinate			**AMD**		
		untreated	**$BaSO_4$**	**H2S stripping**	**untreated**	**$BaSO_4$**	**H_2S stripping**
pH		1.4	12.0	7.1	2.7	12.0	7.2
Mg	mg/L	485	4	4	125	1	10
SO4	mg/L	17,500	155	175	2,060	120	190
Ba	mg/L	-	2	1	-	2	1

- **Costs**

  The capital cost for a 25 x 10^3 m^3/day plant, capable of removing 2,000 mg/L sulphate, is estimated at approximately USD 12 M or USD 479,000 per 10^3 m^3/day (Bosman *et al.*, 1990). The rotary kiln and the sulphur production unit are the two most expensive equipment items.

  The operating costs for the 25 x 10^3 m^3/day plant amounts to approximately USD 0.36 per m^3 water. With the sulphur production unit, sulphur sales could add revenue of perhaps USD 0.09 per m^3 water. This could bring the annual operating costs down to USD 0.27 per m^3 water.

- **Advantages/Disadvantages**

  Compared to $BaCO_3$, the use of BaS in the treatment of waters high in calcium and sulphate has several advantages: (1) BaS has a shorter retention time ($BaCO_3$ dissolves slowly); (2) only $BaSO_4$ precipitates (no additional $CaCO_3$); (3) (pure) $BaSO_4$ can be directly recycled in the water treatment process after thermal reduction to BaS; (4) liming to equalize sulphate and calcium concentrations is not required in the BaS process.

The $Ba(OH)_2$ process could be the most viable in economic terms but attempts to precipitate barium hydroxide from barium sulphide water were unsuccessful due to the formation of an unknown aqueous complex.

- **Future Needs/Improvements**

  Alternative methods to improve the dewatering of the barium sulphate+coal sludge would greatly reduce the capital and operating costs associated with the thermal reduction of $BaSO_4(s)$ to $BaS(s)$.

- **References**

  Anglo American Research Laboratories Ltd., P.O. Box 106, CrownMines 2025, South Africa. Website: www.aarl.co.za

  CSIR, Division of Water, P.O. Box 395, Pretoria 0001, South Africa.

  Website: www.csir.co.za

4.1.3 SAVMIN

- **Problem**

  At the Stilfontein gold mine (Anglogold) near Vaal Reef in South Africa, 30,000 m^3 of mine drainage are pumped daily from the mine to prevent the rise of the water table in the active shafts. Most of the mine water is discharged into the nearby Koekemoerspruit. Sulphate concentrations in the mine water fluctuate between 596 to 855 mg/L and the calcium concentrations vary from 137 to 196 mg/L. Magnesium concentrations are fairly constant at 83 mg/L. Uranium and radium concentrations in the mine water are 114 µg/L and 81.9 Bq/m^3, respectively. Information on dissolved metals and the pH of the water is not available. Although the mine water is of ‘reasonable’ quality, treatment could make the water suitable for distribution as potable or high quality industrial water.

- **Treatment Process**

  The main aims of the project were to demonstrate in a pilot plant that the SAVMIN process can treat mine water to discharge (500 mg/L SO_4), potable (200 mg/L SO_4) and high quality industrial water (50 mg/L SO_4) standards and to obtain design, capital and operating costs.

  The SAVMIN process uses selective precipitation reactions to treat mine water (Section 3.1.3). The main process stages specific to this plant are shown in Figure 4-3 (Smit, 1999 and Sibilski, 2001).

  Stage 1: *Precipitation of dissolved metals and magnesium*. Using lime, the pH of the feed water is raised to pH 12.0-12.3, to precipitate dissolved (trace) metals and magnesium.

Stage 2: *Gypsum "de-supersaturation"*. Using gypsum seed crystals, gypsum is precipitated from the supersaturated solution and removed.

Stage 3: *Ettringite precipitation*. Using aluminum hydroxide, dissolved calcium and sulphate are removed from the solution by the precipitation of ettringite (a calcium-aluminum sulphate mineral).

Stages 4 and 5: *Recycling of aluminum hydroxide*. Using sulphuric acid, the ettringite slurry from stage 3 is decomposed at pH 6.5 in a solution supersaturated with gypsum (no precipitation). The resulting aluminum hydroxide is recycled to the third stage and the solution supersaturated with gypsum is contacted with seed crystals (stage 2) to precipitate and remove gypsum. The remaining solution, saturated with gypsum, is recycled.

Stage 6: *Carbonation and calcite precipitation*. Using CO_2(g), the pH of the solution from the third process stage (pH 11.4-12.4) is lowered to precipitate and remove calcite.

The SAVMIN process has been used to treat mine waters at throughputs up to 1 m^3/hr. The various precipitation reactions in the treatment process are performed in conventional stirred-tank reactors at ambient temperature and pressure. In process stages 1 and 3, lime is added with a conventional lime slaker and slurry pumping system. Sulphuric acid is added by a conventional dosing pump (stage 5). The additions of lime and sulphuric acid are controlled by industrial pH probes and monitoring systems. Because the settling rates of the precipitates are low, conventional high-flow thickeners are preferred to perform the solid-liquid separations in the treatment process. The SAVMIN process produces sludges of metal hydroxides, gypsum and calcite.

- **Results**

The chemical composition of the mine water treated with the SAVMIN process is shown in Table 4-3 for the three types of required product water. Except for the high quality industrial water, the targets for the different water quality standards of sulphate are achieved with the treatment process. The sulphate concentration of the water (69 mg/L) is only slightly higher than the target value for high quality industrial water (50 mg/L). Moreover, target values for most other dissolved substances are also achieved. Although no data on dissolved (trace) metals are reported for the project at Stilfontein, dissolved (trace) metals are effectively removed by the SAVMIN process (Smit, 1999). The uranium and radium concentrations in the mine water are reduced by 98% and 51%, respectively.

Depending on the target water quality, the treatment process produces different quantities of sludges. The quantity of metal hydroxide sludge varies from 0.98 to 1.18 kg/m^3 water, whereas that of gypsum and calcite varies from 0.67 to

2.1 kg/m^3 and 0.09 to 0.53 kg/m^3 water (Sibilski, 2001). The high-grade gypsum and calcite produced in the treatment process can be used in other industrial applications.

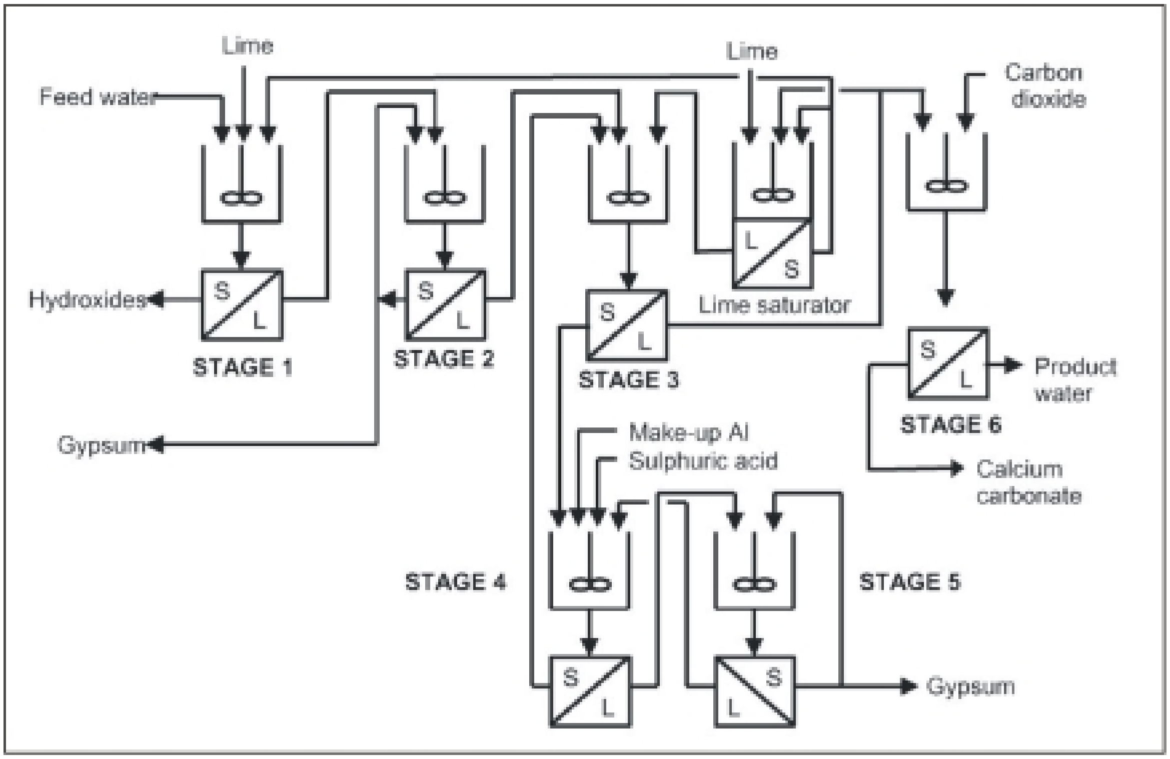


Figure 4-3: The SAVMIN Process Flow Diagram

- **Costs**

The capital cost of a 30,000 m^3/day plant to produce potable water is USD 9.4 M and is almost identical for the different water qualities. The capital costs can be reduced considerably by the use of available equipment at closed metallurgical sites.

The estimated operating costs are shown in Table 4-4 for the different water quality targets. A considerable proportion of the operating costs are consumed by the reagent costs (0.072 to 0.107/m^3). Reagent consumption depends on the concentration of sulphate and monovalent cations, which are relatively low in this case study. The monovalent cations form aqueous complexes with sulphate that can only be removed by precipitation as ettringite in the third process stage (more expensive than in first stage). The calculated reagent costs for a range of sulphate concentrations in the feed water (monovalent cation concentration of 90 mg/L) are shown in Table 4-4. In the calculations the following reagent costs (USD) are assumed: lime 39/ton; sulphuric acid 35/ton; carbon dioxide 42/ton; make-up ettringite 114/ton.

Depending on the required quality of the product water, the total operating costs vary from 0.135/m^3 to 0.17/m^3.

Table 4-3:
Typical Incoming and Outgoing Concentrations for Discharge Quality Water

	Incoming (mg/L)	Outgoing (mg/L)	% Removal	Discharge water quality target (mg/L)
SO_4	682	359	47	500
Ca	196	142	28	300
Al	<1	<1	0	20
Na	142	138	3	115
Cl	61	62	-2	140
Mg	83	<1	>99	-
K	8	11.1	-39	-
	Incoming (mg/L)	**Outgoing (mg/L)**	**% Removal**	**Potable water quality target (mg/L)**
SO_4	685	167	76	200
Ca	192	113	41	150
Al	<1	<1	0	0.5
Na	144	143	1	200
Cl	62	63	1	200
Mg	83	<1	>99	50
K	9	11	-39	100
	Incoming (mg/L)	**Outgoing (mg/L)**	**% Removal**	**High quality industrial water target (mg/L)**
SO_4	649	69	89	50
Ca	162	91	44	50
Al	<1	<1	0	-
Na	144	145	-1	-
Cl	66	65	2	40
Mg	83	<1	>99	-
K	9.4	10	-6	-

Table 4-4:
Operating Costs for the Different Qualities of Product Water (USD/m^3)

	Discharge quality	Potable	High quality industrial
Reagent	0.072	0.081	0.107
Labour	0.023	0.023	0.023
Maintenance	0.034	0.034	0.034
Insurance	0.06	0.06	0.06
Total	0.135	0.144	0.17

- **Advantages/Disadvantages**

  One of the major advantages of the SAVMIN process is the high quality of the product water that can be obtained, even at fluctuating sulphate levels in the feed water. A major disadvantage is the amount of sludge produced by the treatment process. Depending on available opportunities for industrial applications, the sludge 'problem' can be reduced considerably.

- **Future Needs/Improvements**

  To eliminate the waste product problem it would be useful to find better ways to use or recycle the different sludges produced in the treatment process.

- **References**

  Mintek, Private Bag X3015, Randburg, 2125, South Africa.

  Website: www.mintek.co.za E-mail: info@mintek.co.za

4.1.4 CESR

- **Problem**

  The cost effect sulphate removal (CESR) process is very similar to the SAVMIN process except that it uses a proprietary reagent to precipitate ettringite. The CESR process has been used successfully for several years in over 20 European plants in various industries including battery manufacturing, metal galvanizing and mining.

- **Treatment Process**

  The CESR process aims to remove dissolved sulphate and trace metals from wastewaters. However, boron, fluoride and up to 30% of chloride and nitrate have also been removed from wastewaters.

  The treatment process consists of four process steps (Section 3.1.4). The various process steps (including coagulant addition) are summarized in Figure 4-4.

  Step 1: *Initial precipitation of sulphate as gypsum*. The first process step is used when wastewaters are high in both trace metals and sulphate (>8 g/L). Adding hydrated lime while maintaining a relatively low pH (*e.g.*, pH < 10.5), precipitates sulphate alone after a mixing time of 40 to 60 minutes. Sulphate concentrations in the wastewater can be lowered to 4 to 5 g/L in the first process step.

  Step 2: *Precipitation of metals as hydroxides*. Using hydrated lime, the pH of the wastewater is raised to pH 10.5 to precipitate trace metals as metal hydroxides. After a mixing time of 40 to 60 minutes, additional gypsum is precipitated, lowering the dissolved sulphate concentration further to approximately 2 g/L.

  Step 3: *Additional sulphate removal through ettringite precipitation*. After raising the pH to 11.5 with hydrated lime, a proprietary reagent is added to precipitate ettringite, a hydrated calcium aluminum sulphate. This process step (30 to 300 minutes) achieves the final sulphate removal to the desired sulphate concentration in the wastewater. Except for a small portion used as crystallization seeds, the ettringite sludge is disposed.

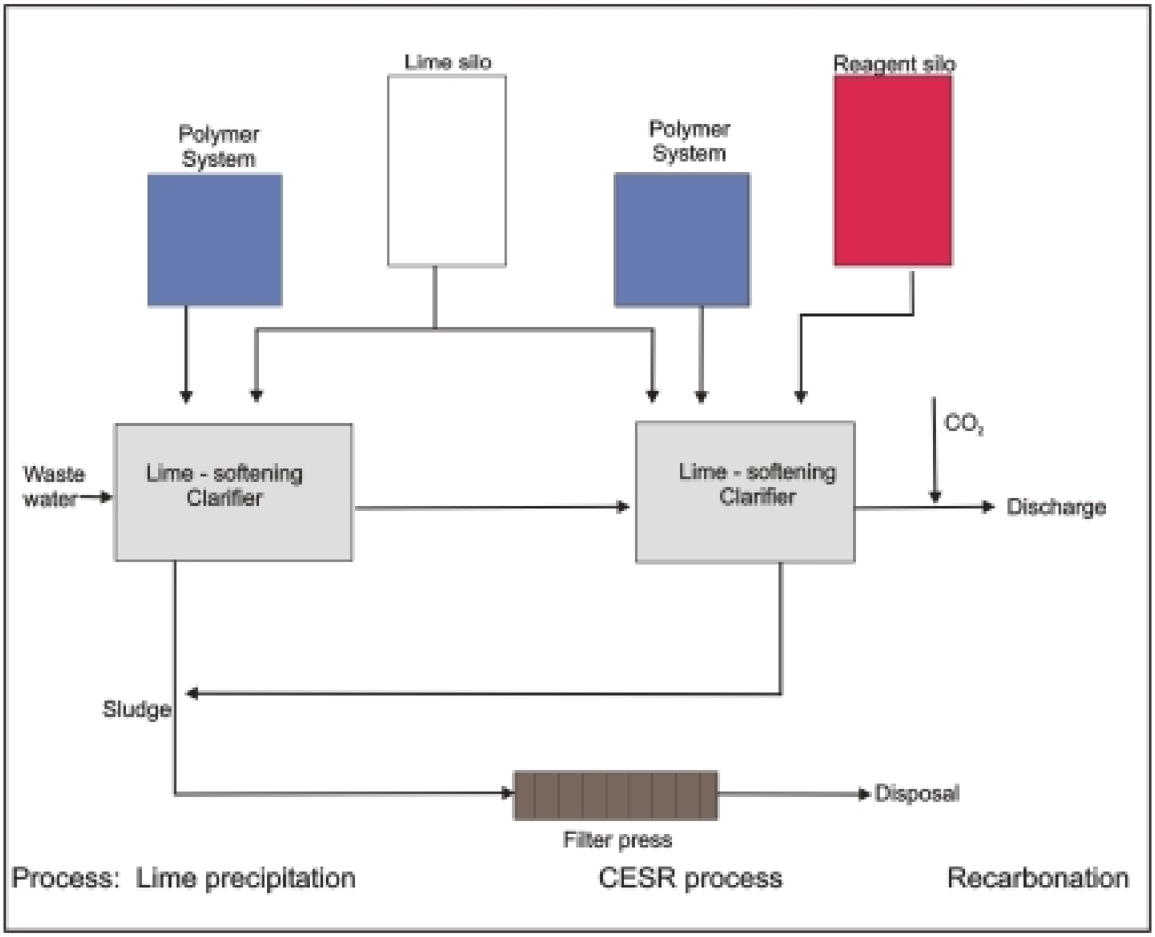


Figure 4-4: Process Flow Diagram for CESR

Step 4: *pH reduction with $CO_2(g)$*. To reduce potential scaling problems in the water distribution system, the pH of the feed water is lowered with $CO_2(g)$. The small amount of sludge produced in the final process step consists of calcium carbonate, aluminum hydroxide and minor amounts of ettringite.

The process is used at flow rates up to 1,325 L/min and can reduce sulphate concentrations in most wastewaters to less than 100 mg/L. Different sludges of mineral precipitates are produced in the four process steps: a gypsum sludge (step 1), a gypsum + metals sludge (step 2), an ettringite sludge (step 3) and a calcite + aluminum hydroxide sludge (step 4).

- **Results**

The CESR process has been tested and applied in various bench studies. Results of two bench studies are presented below.

Copper Mine Water

Results of the treatment of pit water at an active copper mine with the CESR process are shown in Table 4-5. At a 'medium reagent dosage' in the treatment process, most of the discharge limits for the treated water were reached. The best results were obtained with the highest reagent dosage but the shortest retention time. Except for iron and aluminum (high dosage, short retention time), dissolved trace metal concentrations were reduced to very low levels.

Table 4-5:
Bench Test Results with Copper Mine Water

	Feed Water (mg/L)	After Lime Treatment (mg/L)	After CESR Treatment (mg/L)			Discharge Limits (mg/L)
			High Dosage	Medium Dosage	Low Dosage	
Ca	266	808	154	208	303	
Mg	153	<1	<1	<1	<1	
Na	42	42	44	42	43	
K	8	10	13	10	10	
Cl	10	8	13	11	10	
SO_4	3,350	2,180	361	540	759	600
F	80	3.9	<0.1	<0.1	<0.1	2
TDS	4,860	3,240	677	921	1,260	1,000
pH	2.8	9.2	10.6	10.7	10.8	6 - 9
Al	220	0.3	11.8	2.3	0.6	5
Cd	1.13	0.003	<0.001	<0.002	0.001	0.1
Co	1.17	<0.01	<0.01	<0.01	<0.01	0.05
Cu	114	0.02	<0.01	<0.01	<0.01	1.0
Fe	69	<0.03	0.54	<0.03	<0.03	1.0
Mn	87	<0.01	<0.01	<0.01	<0.01	0.2
Zn	143	0.03	<0.01	<0.01	<0.01	10
As	0.009	<0.005	<0.005	<0.005	<0.005	0.1
Retention time (min)		60	70	120	180	

Berkeley Pit Water

Results of tests in which the ARD water from the Berkeley Pit in Butte, Montana was treated with the CESR process are shown in Table 4-6. Sulphate concentrations could be reduced to low levels, even at a low reagent dosage but longer retention time. Most trace metal concentrations were reduced to very low levels.

Table 4-6:
Bench Test Results with Berkeley Pit Water

	Influent (mg/L)	***After CESR Treatment (mg/L)**		
		High Dosage	**Medium Dosage**	**Low Dosage**
SO_4	8730	4	15	56
Cd	2.16	<0.001	<0.001	<0.001
Cu	193	0.05	0.02	0.01
Fe	972	0.31	<0.03	0.09
Mn	321	0.02	<0.01	<0.01
Ni	1.2	<0.01	<0.01	<0.01
Zn	603	<0.01	<0.01	0.04

***After pH adjustment**

In the first process step, approximately 1.8 kg of gypsum sludge was produced for every kg of sulphate removed from the wastewater. Approximately 5.4 kg of gypsum + metal sludge per m^3 water is produced in the second process step. Although the amount of ettringite sludge generated in the third process step is variable and not specified, it is likely comparable to that of the second process step. The amount of calcite + aluminum hydroxide sludge produced in the final process step is relatively small (0.48 kg/m^3 water).

- **Costs**

While there were no published data on the capital cost for CESR, its can be assumed to be comparable or slightly cheaper than the SAVMIN process based on their similarities. Operating costs are estimated at USD 0.79-1.58/m^3 water, for the removal of sulphate to low levels. Reagent cost for the removal of 1500 mg/L sulphate would be approximately USD 0.79/m^3 water.

- **Advantages/Disadvantages**

The major advantage of the CESR process is the high quality of the product water that can be obtained. A major disadvantage of the CESR treatment process is the relatively large amount of sludge produced compared to the similar SAVMIN process, which recycles much of the sludge.

- **Future Needs/Improvements**

To eliminate the waste product problem it would be useful to find ways to use or recycle the different sludges produced in the treatment process.

- **References**

Hydrometrics Inc., 2727 Airport Road, Helena, MT 59601, USA

Website: www.hydrometrics.com or www.wateronline.com

4.2 Membranes

4.2.1 Reverse Osmosis

- **Problem**

  Due to ongoing mining activities, an excess of mine water is generated at the Secunda coal mine (Sasol Ltd.) near Johannesburg in South Africa. The mine water (pH 8.4) is characterized by high TDS (4 g/L) and sulphate (2.2 g/L) concentrations. Because the mine water cannot be discharged into local streams, desalination of the water using a Tubular Reverse Osmosis (TRO) pilot plant was investigated (du Plessis and Swartz, 1992).

- **Treatment Process**

  The objectives of the pilot plant investigation were: (1) to demonstrate the technical feasibility of the treatment process and, (2) to obtain the required information for the design of a full-scale plant.

  A schematic representation of the TRO and pre-treatment plant is shown in Figure 4-5 (du Plessis and Swartz, 1992).

  Pre-treatment was necessary for the removal of suspended solids (174 mg/L) from the feed water. Pre-treatment involved the addition of hypochlorite to eliminate bacteria and flocculant ($FeCl_3$) to promote coagulation and settling of the suspended solids. The suspended solids were removed by clarification and dual media filtration (anthracite/sand).

  Using sulphuric acid, the pH of the pre-treated water was adjusted to between pH 5.5 and 6.5 to minimize hydrolysis of the membranes (cellulose acetate). Flocon (anti-scalant) was added (5 mg/L) to inhibit scaling (gypsum). Feed water temperature was regulated with a heat exchanger and was supplied to the module banks at a flow rate of 1.7 m^3/hr. The water recovery was controlled by a continuous adjustment of the system pressure (30-40 bar). For water recoveries of 60% and 70%, the actual fluxes (membranes) were 625 and 697 L/m^3/day, respectively. Over a test period of 1800 hrs, the average salt rejection was 96%.

- **Results**

  The chemical composition of the mine water and that of the feed water at various stages during the treatment process are shown in Table 4-7. Both flocculation and filtration reduced the suspended solids concentration in the mine water during pre-treatment. The TRO process was able to reduce the concentrations of divalent ions by 99% and those of monovalent ions by 97%. The concentrations of sulphate (2,200 mg/L) and sodium (917 mg/L) decreased to 14 mg/L and 26 mg/L, respectively. A decrease in standard flux of 5% or an increase of 10% in operating pressure was a sign that the membranes needed to be cleaned. Cleaning of membranes was necessary every 350 hrs of operation. The fact that after each cleaning the flux could be restored indicates that fouling of membranes was not permanent. However, 1800 hrs of operation is too short to evaluate permanent fouling and membrane life.

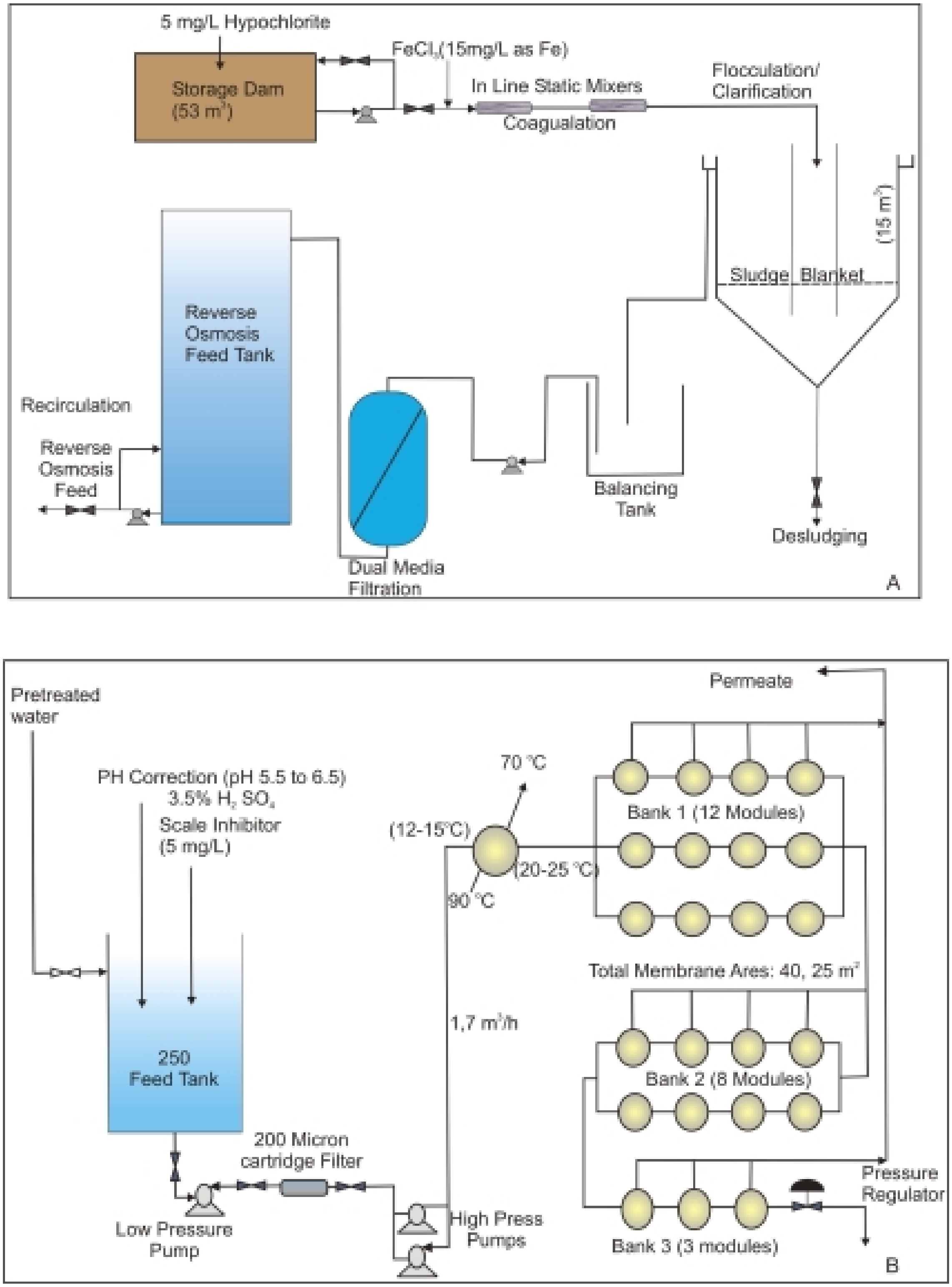


Figure 4-5: Pre-treatment for Reverse Osmosis

Table 4-7:
Quality of mine water at different stages as well as river discharge standards

		Raw mine water	Clarifier effluent	RO feed	RO concentrate	RO product	River discharge standard
pH		8.4	7.1	7.1	6.8	6.3	5.5 - 9.5
TDS	mg/L	3,959	3,919	4,092	8,720	104	-
Cl	mg/L	220	305	313	754	26	-
SO_4	mg/L	2,200	2,150	2,125	>3,000	14	-
F	mg/L	3.0	3.5	3.0	6.0	1.1	1
Na	mg/L	917	914	920	2,222	26	90
K	mg/L	8	-	-	-	-	-
SiO_2	mg/L	4.3	.-	4.3	-	-	-
Ca	mg/L	176	176	176	452	2.0	-
Mg	mg/L	80	-	-	-	-	-
Fe	mg/L	0.3	0.3	0.3	0.7	0.1	-
TSS	mg/L	174	76	47	347	<10	20
COD	mg/L	70	45	40	900	<2	75
Turbidity	NTU	9.0	6.0	0.9 - 1.5	9.0	0.9	-

- **Costs**

  For this case study there are no costs estimates available. However, costs and performance of the RO, EDR and GYP-CIX treatment technologies will be compared later (Section 4.5).

- **Advantages/Disadvantages**

  The major advantage of the RO technology is that it can treat most wastewaters and produce high quality water at variable water recoveries. However, the major disadvantage is that the lifetime of membranes is strongly affected (fouling) by the quality of the feed water. Non-scaling wastewaters (*e.g.* high in Na and Cl) are more suitable for RO treatment that many wastewaters produced in the mining industry (*e.g.* high in Ca, CO_3 and SO_4).

- **Future Needs/Improvements**

  See next section (SPARRO).

- **References**

  Sasol Mining Ltd, Private Bag X1015, Secunda 2302, South Africa.

  Website: www.sasol.com

4.2.2 SPARRO

- **Problem**

The high TDS concentration of the mine water is a major problem in the mining industry. Moreover, the high calcium and sulphate concentrations and the associated scaling problems make the mine water less suitable for treatment with RO. This prompted the Chamber of Mines of South Africa Research Organization (COMRO) to initiate research into the development of 'seeded' RO technology. The research culminated in the development of the 'Slurry Precipitation and Recycle Reverse Osmosis' (SPARRO) process, designed and patented by COMRO in 1988. This case study describes the design and testing of the SPARRO technology (Section 3.2.2) in a pilot plant.

- **Treatment Process**

The main aim of this case study was to test and evaluate the SPARRO process and additional modifications in a pilot plant using water from the ERPM gold (Pulles *et al.*, 1992 and Juby *et al.*, 1996).

Apart from the SPARRO plant, an existing pilot plant was converted into a plant designed to specifically evaluate the effects of the calcium sulphate slurry on the (tubular) RO membranes. A schematic representation of this 'membrane lifetime test' (MLT) plant and the SPARRO plant are shown in Figures 3-8 and 3-9. Over a period of five years (1989-1993), the SPARRO plant was operated and tested for 8,392 hrs. Most of the data presented represent the second phase (1990), the first real testing phase for the new membranes. The design operating criteria for the MLT and SPARRO plants are shown in Table 4-8 (Pulles *et al.*, 1992).

Table 4-8:
Design operating criteria for the SPARRO and MLT plants

Parameters	Units	Design Criteria	
		MLT	SPARRO
Product water flow rate	L/s	0.17	0.85
Feed pressure	kPa	3,000	4,000
Feed temperature to modules	ºC	27	27
Membrane flux	L/m^2/day	500	500
Product water recovery	%	85	90
Pass conversion*	%	20	50
Overall salt rejection	%	90	90
Reactor retention time	hr	4	1
Feed slurry concentration	mg/L	20,000	18,000

Note: * Pass conversion is defined as the percentage of feed water to the modules which permeates to form the product

Pre-treatment of the mine water involved the adjustment of the pH (10), addition of flocculants and clarification to remove the precipitated metals, followed by dual media filtration and final pH adjustment (pH 5-6).

After the pre-treatment stage the feed water is pumped into a storage tank. From the storage tank the feed water is pumped at a pressure of 4,000 kPa to the RO membrane module bank. Before reaching the module bank the feed water is mixed with the recycled gypsum slurry from the reactor. The mixture has a TDS concentration of approximately 7,500 mg/L. The treated water from the modules is stored. The flow concentrate from the modules (TDS 15,000 mg/L) is split into two portions. One portion is sent to the hydrocyclone and another portion is returned to the reactor. Both the overflow and underflow of the hydrocyclone are further subdivided. Using a programmable controller, one part of the flow is discharged into the reactor and another part of the flow is blowndown as brine (overflow) and as seeds (underflow). The retention time of the supersaturated concentrate in the reactor is sufficient for crystal growth and return to saturated conditions.

- **Results**

The chemical composition of the feed, product and reject (concentrate) waters in the SPARRO and MLT plants are shown in Table 4-9 (Pulles *et al.*, 1992). The data show that both plants performed well in the treatment of the mine water. The TDS (10,535 mg/L) and sulphate (6,639 mg/L) concentrations at the SPARRO plant were reduced to 336 mg/L and 152 mg/L, respectively. Also dissolved metals were effectively removed.

**Table 4-9:
Typical Performance of MLT and SPARRO Plants**

		MLT plant			SPARRO plant		
	Unit	Feed	Product	Reject	Feed	Product	Reject
pH		4.62	5.07	4.69	4.97	6.23	4.92
TDS	mg/L	7,734	342	9,013	10,535	336	14,957
Calcium	mg/L	428	16	450	467	11	478
Sodium	mg/L	767	77	911	889	72	1200
Sulphate	mg/L	4,990	155	5,971	6,639	152	9,794
Chloride	mg/L	191	17	235	273	43	462
Iron	mg/L	0.4	0.1	0.4	0.4	0.1	0.4
Manganese	mg/L	27.5	0.7	32.2	17.2	0.5	51.7

During the second phase of operation (1990), average water recoveries of 89% (MLT) and 95% (SPARRO) were achieved. Data on the membrane performance are shown in Table 4-10. The SPARRO process can be considered economically viable if the salt rejection remains above 90% and the standard membrane flux (corrected at 25°C and 4,000 kPa) is ≥550 L/m^2/day. To reduce costs, the membrane operating life should be two years.

Table 4-10:
Membrane performance data (1990) for MLT and SPARRO plants

Parameter	Unit	MLT	SPARRO
Operation	hr	4,193	3,316
Starting salt rejection	%	91.5	91.7
End salt rejection	%	93.5	92.1
Starting corrected flux	L/m^2/day	903	793
End corrected flux	L/m^2/day	545	285

Unlike the MLT plant membranes, the SPARRO plant membranes showed a drop in flux rate, below the design operating criteria (compare Table 4-8 and 4-10). The flux rate was restored to its design value after removing the last bank of membranes, which indicates that the membranes were structurally damaged. The decline in flux rate was probably caused by membrane fouling through scaling and suspended solids in the SPARRO plant (Pulles *et al.*, 1992). At the MLT plant operating conditions were less favourable for scaling.

- **Costs**

  Updated capital cost for a SPARRO plant that produces 4.0 x 10^3 m^3/day product water amount to R 16.5 M (USD 1.7 M))(Juby *et al.*, 1996). Almost 40% of the capital cost is consumed by the cost of the 5,000 membrane modules (200 spare).

  The annual operating costs (including pre-treatment) are R 2.6 M (USD 0.27 M) (excl. tax) or R 1.87 (USD 0.19) per m^3 water. Similarly, replacement of membranes (once every two years) accounts for the largest part (53%) of the annual operating costs. Electrical power amounts to 27% of the annual operating cost (Juby *et al.*, 1996).

- **Advantages/Disadvantages**

  The SPARRO technology can treat most wastewaters and produces good quality water at variable water recoveries. However, the disadvantage is that the lifetime of membranes is still affected (fouling) by the quality of the feed water. Compared to the conventional RO technology, the membrane lifetime in the SPARRO process has been improved but is still not ideal.

- **Future Needs/Improvements**

  Similar to the RO technology, more research is still required to extend the lifetime of the membranes in the SPARRO technology.

- **References**

  Chamber of Mines of South Africa Research Organization (COMRO)

  CSIR Miningtek
  P.O. Box 91230
  Auckland Park, 2006
  South Africa

  Webpage: www.csir.co.za/miningtek

4.2.3 EDR

- **Problem**

  Among mine waters a distinction can be made between waters that have a (gypsum) scaling potential and those that do not. The latter are the sodium chloride waters that predominate in the Orange Free State gold mines of South Africa. However, survey of mine waters revealed that 75% of them would exhibit scaling problems when concentrated in membrane processes (RO, EDR) at 80% water recovery. To investigate the scaling potential, a 5.8 m^3/hr Electrical Dialysis Reversal (EDR) pilot plant was operated for 6000 hrs on non-scaling mine water from a gold mine in the Orange Free State of South Africa.

- **Treatment Process**

  The objectives of the pilot plant project were to establish: (1) the technical feasibility of the EDR process, (2) the required pre-treatment for an acceptable membrane lifetime, and (3) the capital and operating costs.

  To enable a satisfactory performance of the EDR process, potential membrane foulants had to be removed from the feed water in a pre-treatment process (*e.g.* Fe and Mn <0.3 mg/L; TSS <2.5 mg/L). The pre-treatment involved: oxidation of iron and manganese with potassium permanganate, addition of a flocculant, primary filtration (dual filter) and secondary filtration (10 μm membrane). To prevent scaling by barium sulphate, an anti-scalent (sodium hexametaphosphate) was also added to the mine water.

  The membranes used in the EDR pilot plant were characterized as pH resistant (pH 1-10), resistant to fouling and impermeable to water under pressure. Other details on the EDR pilot plant are not available (Juby, 1992). A general outline of the EDR process is presented in Sction 3.2.3.

- **Results**

  The average chemical composition of the mine water, the pre-treated feed water, the product water and the brine (reject or concentrate) is shown in Table 4-11. The results show that sodium and chloride dominate the chemical composition of the mine water. In the pre-treatment of the mine water, the concentrations of dissolved iron and manganese were lowered to their target values. The TDS concentration in the mine water could be reduced from 3,200 mg/L to 640 mg/L. Also, the concentrations of dissolved chloride and sodium were significantly reduced.

  Over the period of the pilot plant operation, the average salt rejection was 80% and the average water recovery was 84%. In general the EDR plant performed well in the treatment of non-scaling mine water.

Table 4-11:
Average water composition from a 6000 hour evaluation of a 1.6 L/s EDR pilot-plant operating on brackish mine service water

Parameter	Raw mine water	EDR feed	EDR product	EDR brine
pH	6.42	6.42	6.14	5.42
Turbidity, NTU	20	0.91	0.36	0.40
TDS, mg/L	3,200	3,200	640	9,150
Cl, mg/L	1,750	1,750	375	4,990
Na, mg/L	1,400	1,400	200	3,110
Ca, mg/L	100	100	25	400
Total iron, mg/L	1.0	0.2	0.15	0.4
Total manganese, mg/L	0.6	0.3	0.16	1.1
Ba, mg/L	0.6	0.6	0.3	1.1
SO_4, mg/L	74	74	5	340

- **Costs**

  Capital and operational costs (1988) were estimated for a 4.32 x 10^3 m^3/day EDR plant with 80% salt rejection and 80% water recovery. The capital cost is estimated at R 4.68 M (USD 0.49 M) for a 50 L/sec EDR plant. Operating costs amount to R 0.50 (USD 0.05) per m^3 water and account for power (30%), membrane replacement (40%) and pre-treatment (22%). Costs of membrane replacement are based on expected membrane lifetimes of 4 yrs (anion) and 7 yrs (cation).

  Costs (2001) and performance of the EDR, RO and GYP-CIX technologies will be compared later (Section 4.5).

- **Advantages/Disadvantages**

  The EDR treatment process can be successfully applied to non-scaling mine waters. The same will probably also apply to the RO and SPARRO processes. However, for the treatment of scaling mine waters, membrane fouling remains a problem (to a variable degree) for all the three treatment technologies. Extensive pre-treatment is not an option (costs and removal limitations) and anti-scalents are only applicable at low potential scalent masses.

- **Future Needs/Improvements**

  Similar to the RO and SPARRO technologies, more research is still required to extend the lifetime of the membranes in the EDR technology.

- **References**

  Previously: Chamber of Mines of South Africa Research Organization (COMRO)

  now: CSIR Miningtek

  P.O. Box 91230

  Auckland Park, 2006

  South Africa

  Webpage: www.csir.co.za/miningtek

4.3 *Ion-Exchange*

4.3.1 GYP-CIX

- **Problem**

  Although the GYP-CIX process can treat most mine waters with high concentrations of TDS, sulphate and calcium, it is better suited (economically) to waters with dissolved sulphate concentrations below 1,500-2,000 mg/L. The latter represents the approximate sulphate concentration in equilibrium with gypsum that precipitates after liming. At sulphate concentrations higher than 1,500-2,000 mg/L, liming is a cheaper treatment option than GYP-CIX.

- **Treatment Process**

  The GYP-CIX treatment process (Section 3.3.1) is based on conventional ion-exchange technology to remove dissolved ions from feed water. However, unlike the conventional ion-exchange technology, GYP-CIX uses $Ca(OH)_2$ and H_2SO_4 (lowest cost industrial reagents available) to regenerate the ion-exchange resins. The continuous precipitation of gypsum in the regeneration of the ion-exchange resins also allows the reuse of regeneration solutions. To handle the suspended solids in the feed water and the gypsum formed during the regeneration of the ion-exchange resins, counter current upflow columns are used. Depending on the TDS concentration of the feed water, water recoveries of 80 to 90% can be obtained.

- **Results**

The GYP-CIX process was tested in the laboratory and in mini-pilot plants to evaluate the technical feasibility and to develop design criteria for larger plants. A large pilot plant with a capacity of 11.4 m^3/hr was used to treat acid mine water at the Grootvlei mine in South Africa. The results from that large pilot plant will be discussed later along with those obtained by RO and EDR (Section 5.1).

The GYP-CIX process was also tested on mine water from the Berkeley Pit. The chemical composition of the untreated water and that of the water after pretreatment (liming) and the GYP-CIX treatment process are shown in Table 4-12. Liming and gypsum precipitation lowered the sulphate concentrations from 8,000 mg/L to 1,980 mg/L while the pH was raised from 2.7 to 8.5. The concentrations of dissolved metals (*e.g.*, Fe, Mn, Cu and Zn) were also greatly reduced by the liming pre-treatment. The sulphate concentrations in the pre-treated mine water could be further reduced to 200 mg/L by the GYP-CIX process. Similar results were obtained for the concentrations of dissolved Ca and Mg.

The main waste product from the GYP-CIX treatment process is gypsum sludge (regeneration of ion-exchange resins). By combining the cation and anion sludges, additional gypsum can be precipitated.

Table 4-12:
Results of the GYP-CIX treatment process on the Berkeley Pit water

	Untreated	Limed	GYP-CIX
pH	2.7	8.5	8.0
TDS, mg/L	10,000	3,000	350
SO_4, mg/L	8,000	1,980	200
Ca, mg;/L	490	600	50
Mg, mg/L	420	350	20
Na, mg/L	70	70	50
Fe, mg/L	1,00	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

- **Costs**

The costs involved in the GYP-CIX treatment process will depend on the quality of the feed and product waters. Starting with pre-treated (liming) mine water with a dissolved sulphate concentration of approximately 2,000 mg/L, costs will vary with the required quality of the product water. For a 136 x 10^3 m^3/day plant, the capital cost (R 250-275 M (USD 26 M-29 M), amortized at 15% over 10 yrs) will vary between R1.0/m^3 (USD 0.10/m^3) (750 mg/L SO_4) and R1.2/m^3 (USD 0.12/m^3) (250 mg/L SO_4). The corresponding operating costs vary from R1.25/m^3 (USD 0.13/m^3) to R2.50/m^3 (USD 0.26/m^3) (Robinson et al., 1998). The costs of regenerants ($Ca(OH)_2$ and H_2SO_4) make up 86% of the total operating costs. Costs (2001) and performance of the GYP-CIX, EDR and RO technologies will be compared later (Section 5.1).

- **Advantages/Disadvantages**

  The main disadvantage of the GYP-CIX process is the volume of gypsum sludge produced in the regeneration of the ion-exchange resins.

- **Future Needs/Improvements**

  To eliminate the waste product problem it would be useful to find ways to use or recycle the gypsum sludge produced in the treatment process.

- **References**

  JCI/Chemeffco

  Website: www.jci.co.za

  Bioteq Environmental Technologies Inc.,

  Suite 1150 – 355 Burrard Street, Vancouver (BC), V6C 3B8, Canada.

  Website: www.bioteq.ca

4.4 Biological Sulphate Removal

4.4.1 Bioreactor

- **Problem**

  At the Landau Colliery near Witbank in South Africa, 20,000 ton of raw coal is mined per day to produce 15,500 t/day of final product, 3,000 t/day of coal discard (2% pyrite) and 1,500 t/day of fine coal (‘slimes’). The waste products are stored on a 72.5 ha dump that contains approximately 2.4 million tons of fine coal and 4.3 million tons of discard. Due to the oxidation of pyrite, the leachate from the discard contains high concentrations of acid (pH 1.8), sulphate (8,342 mg/L) and metals (2,500 mg/L Fe). Laboratory studies have shown that 0.33 g acid (as $CaCO_3$) is leached from each kg of coal whereas the rate of (microbial) oxidation of pyrites amounts to 148 mg acid (as $CaCO_3$)/ kg, day.

  Modeling of the drainage at the site showed that 24 t/day of sulphate enters the drainage network: 7.3 t/day from the feed water, 5.8 t/day from the raw coal and 11 t/day from the coal discard.

- **Treatment Process**

The main aim of the study was to evaluate the performance of an integrated treatment approach to reduce acidity, sulphate and metal concentrations in leachate from coal discard. The integrated treatment process, shown in Figure 4-6, involves 3 stages (Maree *et al*., 2001): (1) $CaCO_3$ handling and dosing system (full-scale), (2) $CaCO_3$ treatment stage (pilot plant), (3) biological sulphate removal stage (pilot plant). The three stages of the integrated process were studied separately.

The *$CaCO_3$ – dosing and handling system* supplies powdered calcium carbonate, a by-product from the paper industry, to a slurry tank. The system has a capacity of 23 t/day $CaCO_3$ and is semi-automated. The $CaCO_3$ powder is slurried with a water jet and collected (gravity flow) in the slurry tank. The $CaCO_3$ concentration in the slurry tank is controlled by load cells, which activate or stop the (slurry) recycle pump at preset values. After mixing, the $CaCO_3$ slurry is pumped to the neutralization reactor.

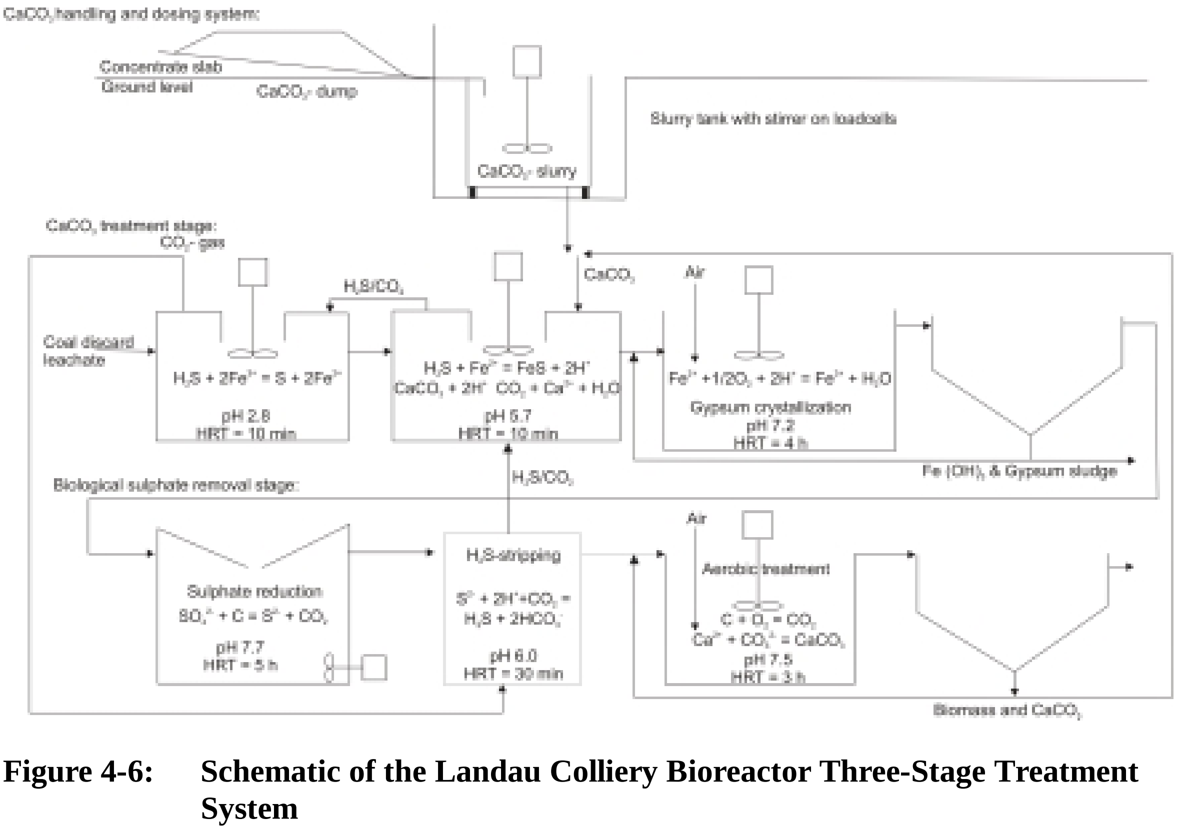


Figure 4-6: Schematic of the Landau Colliery Bioreactor Three-Stage Treatment System

The *$CaCO_3$ – treatment stage* involves reduction (Fe^{3+}/Fe^{2+}), oxidation (S^{2-}/S^0, Fe^{2+}/Fe^{3+}) and precipitation (FeS, $Fe(OH)_3$, $CaSO_4.2H_2O$) using $H_2S(g)$ stripped in the biological sulphate removal stage and $CO_2(g)$ generated in the $CaCO_3$ neutralization stage. Treatment processes are performed in fluidized-bed reactors except the precipitation of $Fe(OH)_3$ and $CaSO_4.2H_2O$ (in sludge separator). Coal discard leachate entering the $CaCO_3$ – treatment stage is sparged with H_2S(g) and CO_2(g) to oxidize H_2S to S(s) and reduce dissolved Fe(III) to Fe(II). In the following neutralization step the treated leachate is mixed with the $CaCO_3$ slurry and sparged with H_2S(g). The pH is increased to 5.7 while dissolved H_2S and Fe(II) are removed by precipitation of FeS(s). The treated leachate is then transferred to a third reactor and sparged with compressed air. The pH is raised to 7.2 and dissolved Fe(II) is oxidized to Fe(III). The leachate is supersaturated with gypsum and iron hydroxide, which are precipitated in the sludge separator. The treated supernatant from the sludge separator is then transferred to the next stage (biological sulphate removal).

The *biological sulphate removal stage* includes three steps: biological sulphate reduction, H_2S(g) stripping and aerobic treatment to remove residual organic matter (bioreactor) and to precipitate $CaCO_3$(s). The anaerobic bioreactor used is a mixed reactor (d*x*h=4*x*8 m; V=105.5 m^3) with a cone in the top to allow for sludge separation (Figure 4-7). The reactor was inoculated with 10 m^3 of anaerobic digester sludge from a sewage plant. Temperature in the reactor was

maintained at approximately 17°C. Feed water (treated leachate) from the $CaCO_3$ – treatment stage was supplied to the bioreactor at a rate of 8 to 16 m^3/hr (residence time of 5.2 to 10.3 hrs). Flow from the bioreactor to the H_2S(g) stripping step was approximately 0.3 m^3/hr. To provide a carbon and energy source for the microorganism, 0.1 to 0.2 g sugar and 0.7 to 1.0 ml ethanol B (75% ethanol+25% propanol) were added per liter of feed water. To maintain a C(OD):N:P ratio of 1000:7:2, ammonium sulphate and phosphoric acid were added as nutrients. Except for Fe(II), no trace elements needed to be added to the feed water. In the bioreactor the dissolved sulphate was reduced to sulphide by sulphate reducing bacteria. The treated water from the bioreactor was transferred to two reactors, operating in series, where it was sparged with CO_2(g) from the $CaCO_3$ neutralization step to strip the H_2S(g) from the treated water. The H_2S(g) stripping step was followed by an aerobic treatment to remove residual organic matter (bioreactor), raise the pH and precipitate $CaCO_3$(s).

- **Results**

The chemical composition of the coal discard leachate before and after the $CaCO_3$ treatment stage is shown in Table 4-13. The results demonstrate that the acidity was neutralized effectively and dissolved sulphate concentrations were reduced from 8,342 mg/L to 1,969 mg/L. Moreover, the dissolved iron concentration decreased from 2,500 mg/L to less than 60 mg/L.

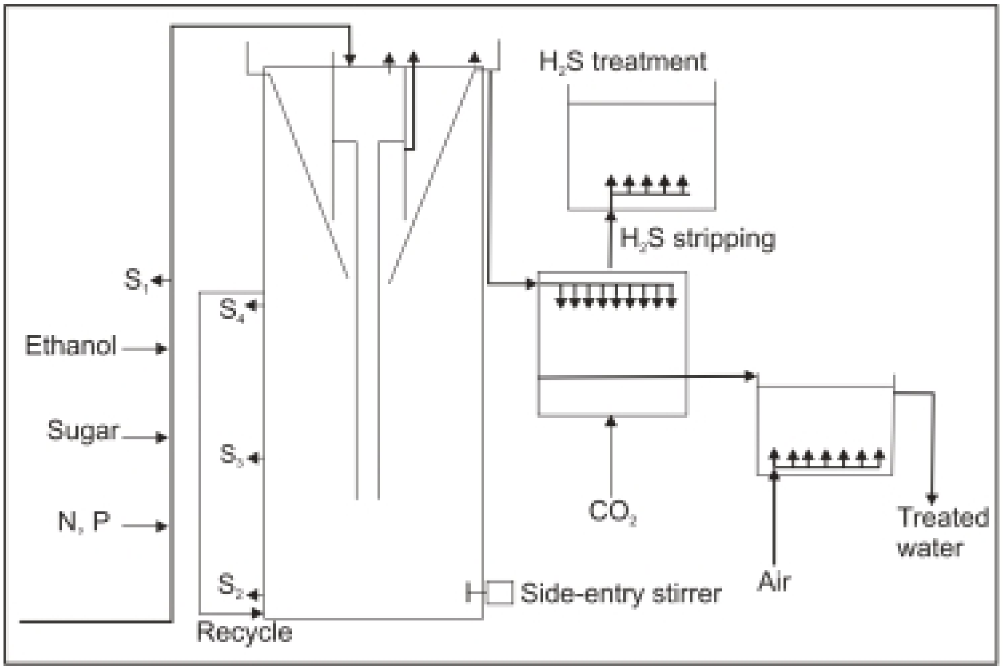


Figure 4-7: Anaerobic Bioreactor Employed for Sulphate Removal

Table 4-13:
Chemical composition of feed water and $CaCO_3$-treated water

Parameter	Feed	$CaCO_3$-Treated
pH	1.8	6.6
Acidity (mg/L $CaCO_3$)	7,300	100
Sulphate (mg/L SO_4)	8,342	1,969
Chloride (mg/L Cl)	27	30
Iron (II) (mg/L Fe)	2,500	<56
Total iron (mg/L Fe)	2,500	<56

The effects of biological sulphate reduction on the chemical composition of the feed water are shown in Table 4-14. The dissolved sulphate concentration was reduced to less than 200 mg/L resulting in a stochiometrically-equivalent increase of the dissolved sulphide concentration (606 mg/L). Alkalinity (as $CaCO_3$) increased from 60 mg/L to 2,065 mg/L. Ethanol was completely utilized in the sulphate reduction, either by complete oxidation or incomplete oxidation (acetate) of the carbon substrate. The effective utilization of the substrate is also demonstrated by the very low concentrations of fatty acids (*e.g.* formate and propanol). The sulphate reduction rate in the bioreactor increased to 12 g/L/day at a temperature of 20^{o}C and a retention time of 6 hrs.

Table 4-14:
Chemical Composition of Feed Water and Treated Water After Biological Sulphate Reduction

Parameter	Feed	Treated
pH	7.2	7.7
Sulphate (mg/L SO_4)	2,203	198
Sulphide (mg/L S)	0	606
Alkalinity (mg/L $CaCO_3$)	60	2,065
Ethanol (mg/L)	690	0
Acetate (mg/L)	0	218
Formate (mg/L)	0	5
Propionate (mg/L)	0	0
Volatile suspended solids (mg/L)	0	9,000

In the H_2S(g) stripping step, dissolved sulphide is almost completely removed from the feed water when the molar ratio of CO_2(g) to H_2S(g) exceeds 6. In the final step (aerobic treatment), the residual organic matter in the feed water (expressed as COD, mg/L O_2) is reduced to less than 30 mg/L.

Changes in the removal of sulphate in the bioreactor and the COD/SO_4-ratio in the feed water are shown in Figure 4-8 for the period from September 1 to June 26 (2001). After an initial period with low sulphate removal (30 to 50%), sulphate removal increased (>75%) due to an increase of the COD/SO_4-ratio. Assuming both partial and complete oxidation of the carbon substrate (ethanol) by SRB,

$$2C_2H_5OH + 2H^+ + SO_4^{2-} = 2CH_3COOH + H_2S(g) + 2H_2O$$

$$2CH_3COOH + 4H^+ + 2SO_4^{2-} = 4H_2CO_3 + 2H_2S(g)$$

Their combination gives:

$$2C_2H_5OH + 6H^+ + 3SO_4^{2-} = 3H_2S(g) + 4H_2CO_3 + 2H_2O$$

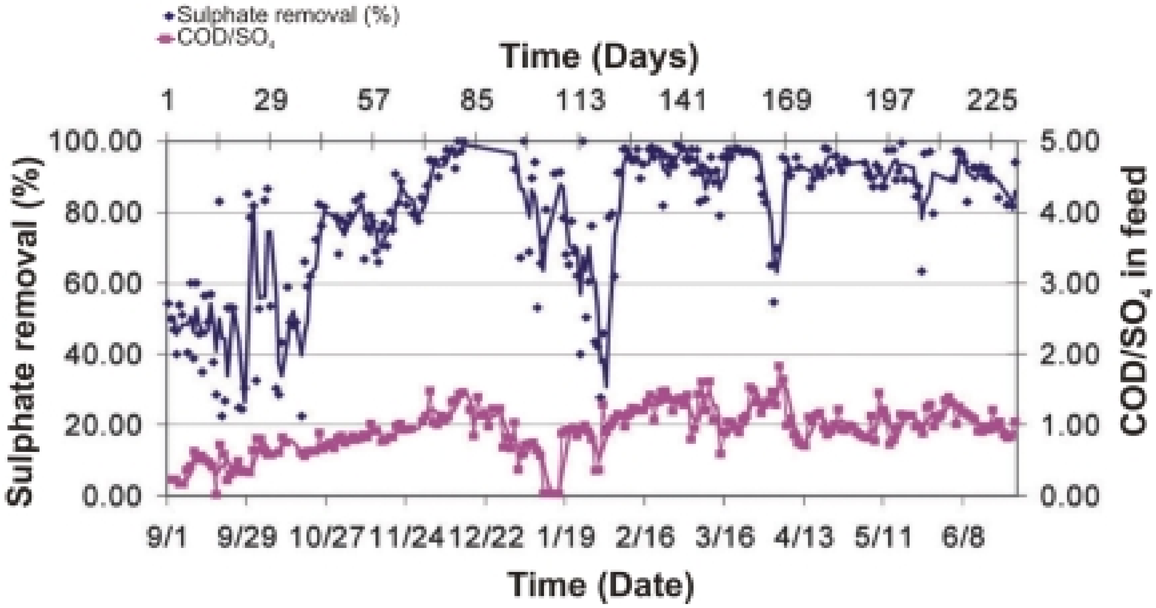


Figure 4-8: Percentage Sulphate Removal During the Period 1 September to 26 June 2001 Compared with the Ratio of COD_{feed} to $SO_{4\ feed}$

The (required) theoretical stochiometric value of the COD/SO_4-ratio is 0.67. Except for an initial period (COD/SO_4-ratio<0.67), the measured COD/SO_4-ratio varied between 1.0 and 1.2, which resulted in a high sulphate removal. The calculated, specific biomass production was 0.02 g of biomass per gram of sulphate reduced (Maree *et al.*, 2001).

Using the same reaction equation, the theoretical mass ratio between alkalinity produced and sulphate removed (Alk/SO_4-ratio) is 1.04. The measured Alk/SO_4-ratio was 1.0, which demonstrates that for the mass of sulphate reduced an equal amount of alkalinity was produced.

The waste products produced in the integrated treatment process are: (1) gypsum + iron hydroxide sludge ($CaCO_3$ treatment stage) and, (2) calcium carbonate sludge (biological sulphate removal stage).

- **Costs**

  The capital cost of a biological sulphate removal plant that can remove 2 kg sulphate per m^3 feed water was estimated to be R2.3 M (USD 0.24 M) per 1,000 m^3/day (Maree *et al.*, 2001). The corresponding operating costs would amount to R2.54 per m^3 treated water. The cost of the energy and carbon source (sugar and ethanol B) was estimated at R2.22 (USD 0.23) per m^3 treated water.

- **Advantages/Disadvantages**

  This integrated treatment process for sulphate removal from mine water (coal discard leachate) has several advantages:

  The bulk of the dissolved sulphate in the leachate is removed by gypsum precipitation using relatively inexpensive powdered $CaCO_3$ from the paper industry. An additional benefit is acid neutralization.

  The remaining dissolved sulphate is efficiently removed by biological sulphate reduction. The product water is non-scaling and suitable as process water or for discharge into surface waters.

  The CO_2(g) produced during the $CaCO_3$ neutralization step and the H_2S(g) stripped in biological sulphate removal stage are recycled and used in other steps of the integrated treatment process.

  The major disadvantage of the integrated process is the production of various sludges.

- **Future Needs/Improvements**

  The development and testing of alternatives sources of carbon and energy for use in the biological sulphate reduction step could be extremely beneficial.

- **References**

  CSIR, Division of Water, P.O. Box 395, Pretoria, 0001, South Africa.

  Website: www.csir.co.za

- **Other References**

  For the THIOPAQ technology (ref. Section 3.4.2):

  Paques B.V., P.O. Box 52, 8560 AB, Balk, The Netherlands

  Website: www.paques.nl

  The THIOPAQ technology is licensed to Bioteq Environmental Technologies Inc. and used in the Biosulphide/THIOPAQ process for the selective recovery of dissolved trace metals from effluents in the mining industry. Biogenic H_2S production is used to precipitate dissolved trace metals in effluents as metal sulphides. Although the technology could be used to remove dissolved sulphate from mine waters, it is predominately used to recover metals without necessarily removing dissolved sulphate from the effluents.

For the Biosulphide/THIOPAQ process:

Bioteq Environmental Technologies Inc.,

Suite 1150 – 355 Burrard Street, Vancouver (BC), V6C 3B8, Canada.

Website: www.bioteq.ca

4.4.2 Constructed Wetland

- **Problem**

The Big Five pilot wetland at Idaho Springs in Colorado (US) was designed as a passive treatment system to remove dissolved metals from the mine drainage flowing from the Big Five Tunnel. The hypothesis was that the dissolved metals are removed by precipitation as metal sulphides and that almost all the sulphide produced by sulphate reduction is consumed in the precipitation reaction.

- **Treatment Process**

The main objective of this particular case study was to verify that almost all the sulphide produced was used in the precipitation of metal sulphides (Machemer *et al.*, 1993). This required: (1) determination of the specific (chemical) forms in which S occurs in the wetland substrates, (2) construction of a mass balance for the various forms of S in the wetland, (3) measurement of sulphate reduction rates and metal sulphide production rates in laboratory incubations

The original structure of the Big Five wetland consisted of three treatment cells (A, B and C in Figure 4-9). Rebuilding of part of the wetland (1989) included three new treatment cells: B-upflow, B-downflow and E-downflow (Figure 4-9). The original cell B was modified to evaluate upflow and downflow water treatment effectiveness. In the downflow configuration, mine water flows in over the top of the substrate and exits at the bottom of the substrate. The opposite applies to the upflow configuration. Cell E was filled to a depth of 1 m. with substrate from the original cell B. The two new B cells received a new substrate of fresh mushroom compost (0.67 m) and were left without vegetation. Cell E had only limited vegetation. Mine drainage from the Big Five Tunnel was diverted to the individual cells and effluent was collected at the exit of each cell. Flow rates of effluent from each cell are presented in Table 4-15. There was no water flow between the different cells.

Emission of $H_2S(g)$ at the surface (Stock Tank) and below the surface (Funnel Collectors) was measured in cell A (Figure 4-9).

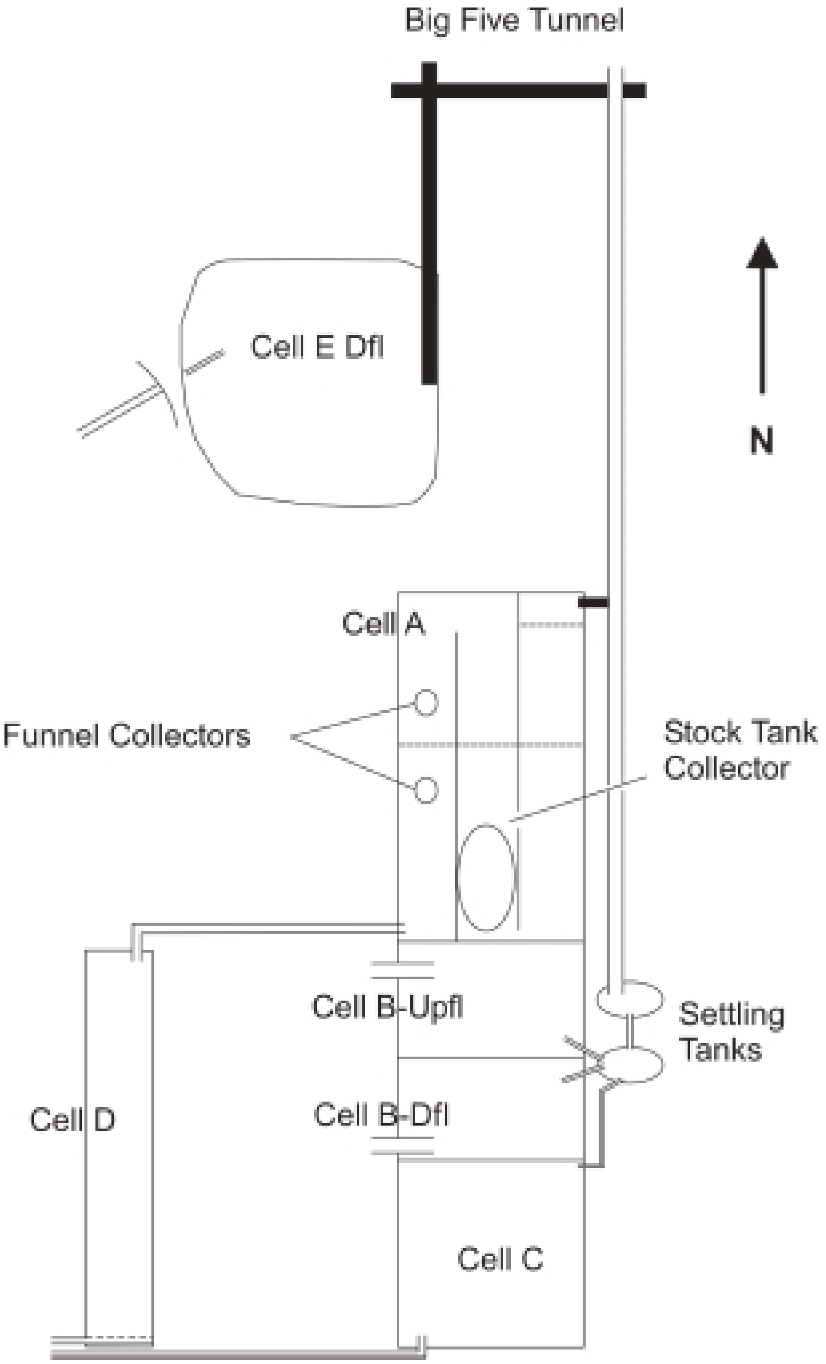


Figure 4-9: Layout of the Big Five Wetland treatment cells. Mine drainage flows directly into cells A and E-Downflow. The mine drainage flows through two settling tanks before flowing into cells B-Upflow, B-Downflow, and C. The locations of the H_2S gas collectors are indicted

Table 4-15:
Chemical Composition of the Mine Drainage Influent and Treatment Cell Effluents

Parameter	**Mine drainage** (summer)	**Mine drainage** (winter)	**Cell A** (summer)	**Cell B-Upflow** (summer)	**Cell B-Upflow** (winter)	**Cell B-Downflow** (summer)	**Cell E-Downflow** (summer)
pH	3.01	2.98	4.95	6.65	3.98	6.01	6.17
Eh (mV)	645	656	310	230	542	380	88
SO_4 (mg/L)	1,700	1,700	1,680	1,540	1,690	1,570	1,560
Na (mg/L)	44.3	44.5	46.5	58.9	47.8	42.3	54.4
Ca (mg/L)	376	371	384	414	406	441	452
Mg (mg/L)	140	145	151	149	152	143	161
K (mg/L)	8.20	7.78	20.2	120	33.6	22.2	42.1
Al (mg/L)	3.68	4.36	0.335	<0.0342	3.85	0.188	<0.061
Fe (mg/L)	43.1	43.3	27.0	5.15	26.6	9.22	7.00
Mn (mg/L)	31.3	30.3	31.3	19.9	30.2	29.8	29.0
Zn (mg/L)	9.05	9.20	2.86	0.363	7.58	3.36	<0.043
Cu (mg/L)	0.556	0.598	<0.035	<0.035	0.338	<0.037	<0.035
Ni (mg/L)	0.180	0.190	0.090	0.076	0.194	0.212	<0.020
Cd (mg/L)	0.0263	0.0306	<0.0026	<0.00092	0.0243	<0.0032	<0.0082
Pb (mg/L)	0.0169	0.0222	<0.0035	<0.0034	0.00806	<0.0034	<0.0034
Cl (mg/L)	6.29	10.9	8.36	52.3	15.2	8.32	19.8
Temperature (°C)	15.0	12.2	12.8	14.6	5.9	13.9	14.7
Cell Flow (L/min)			0.86	0.56	0.18	0.59	0.69

- **Results**

The mean chemical composition of the mine drainage and the effluents from the treatment cells are presented in Table 4-15 for the period April-September 1990 (11-15 measurements).

The summer results in Table 4-15 show a small but significant removal (~10%) of dissolved sulphate from water flowing through cell E and cells B (upflow and downflow), possibly due to sulphate reduction. Dissolved trace metal concentrations were greatly reduced in the effluents from the treatment cells whereas the pH increased from 3.0 to 6.0-6.7.

Measurements of $H_2S(g)$ emissions demonstrate that the amount of sulphide produced daily in the substrate was three orders of magnitude larger than the amount of sulphide lost per day by emission from the surface (cell A). This difference was greater in the winter than in the summer.

Sequential extractions and mineralogical analyses showed that the content of AVS + elemental sulphur in the substrate of cell A increased substantially over a 10 month period whereas the pyritic and organic sulphur contents did not change significantly. This suggests that sulphate reduction and precipitation of acid volatile sulphides (AVS) was an important metal removal process in the wetland.

Using substrate from cell B (upflow), sulphate reduction was studied in a serum bottle experiment. Nearly all the sulphide produced was converted into a solid AVS precipitate, most likely an amorphous metal sulphide. The dissolved sulphide concentration was very low. Assuming a 1:1 molar correlation between reduced sulphate and precipitated AVS, the increase in AVS appears to balance the observed decrease in dissolved sulphate with time.

Using the available data and a measured sulphate reduction rate of 1.2 mmol/L, day (115 mg/L/day), a sulphur balance was constructed for cell E (Figure 4-10). The results demonstrate that sulphate removal by sulphate reduction and precipitation of metal sulphides is small but significant. Except for dissolved manganese and aluminum, all dissolved trace metals in the mine drainage can be removed by sulphate reduction and precipitation of metal sulphides. Compared to the amount of solid-phase metal sulphides and dissolved sulphate, the amount of dissolved sulphide is very small. Yet, the production of dissolved sulphide is sufficient to remove most of the dissolved (trace) metals from the mine drainage.

- **Costs**

  There are no costs available for this case study. However, it may be clear that capital and operating costs are considerably less that those for the other sulphate treatment technologies discussed earlier.

- **Advantages/Disadvantages**

  The results of this case study show that constructed wetlands can be highly effective in removing dissolved metals from mine drainage; however, they may be considerably less effective in removing dissolved sulphate. In this case study the dissolved sulphate concentration could only be reduced by approximately 10%.

- **Future Needs/Improvements**

  More research, particularly on the design of wetlands, is required to determine the full potential of wetlands for the biological removal of dissolved sulphate from mine drainage.

- **References**

  Colorado School of Mines

  1500 Illinois St., Golden (CO), 80401, US

  Website: www.mines.edu

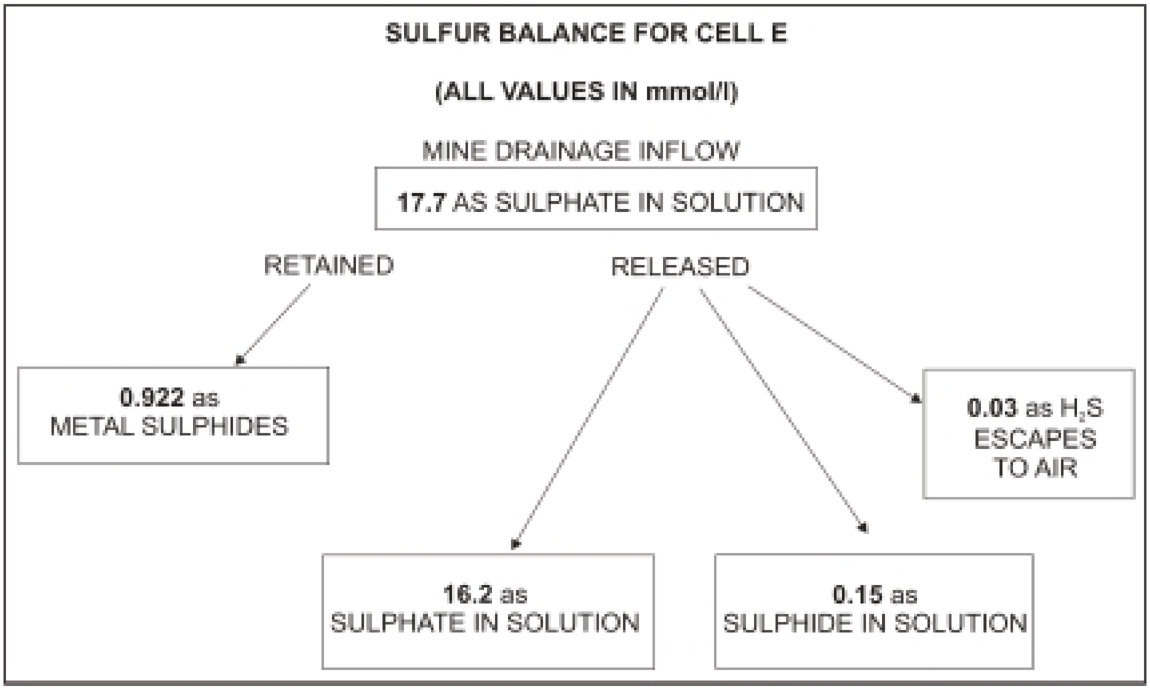


Figure 4-10: Sulphur balance for cell E-Downflow in mmol/l. The 2% (0.4 mmol/l) of Inflowing SO_4 not Accounted for is Within Analytical Error

- **Problem**

  Biological sulphate reduction is an important process in the remediation of acid mine drainage by constructed wetlands. However, very little detailed information on sulphate reduction in wetlands are available; in most cases, influent and effluent concentrations are the only data available. Moreover, our knowledge of the effectiveness of wetlands in promoting sulphate reduction is limited. A better knowledge is required to improve the design of constructed wetlands for the remediation of acid mine drainage by biological sulphate reduction.

- **Treatment Process**

  The objective of this case study was to provide more detailed information on the process of biological sulphate reduction in a constructed wetland using stable isotopes (^{34}S and ^{32}S) to trace microbial activity (Hsu and Maynard, 1999).

  The study was conducted in Wills Creek wetland near Linton in Ohio (US). The wetland was constructed in 1994 to remediate acid mine drainage from underground abandoned coal mines in the area. Wills Creek is a staged wetland that consists of an aeration area, a settling pond and a series of three cells (Figure 4-11). The settling pond and cells 1 and 2 (planted with *Typha*) are surface flow systems. Cell 3 (unvegetated) has a subsurface flow system, promoting anaerobic conditions. Before entering the aeration area and settling pond, the acid mine drainage is treated in anoxic limestone drains. Other characteristics of the wetland cells are listed in Table 4-16. The wetland was designed to have a retention time of 3 to 5 days.

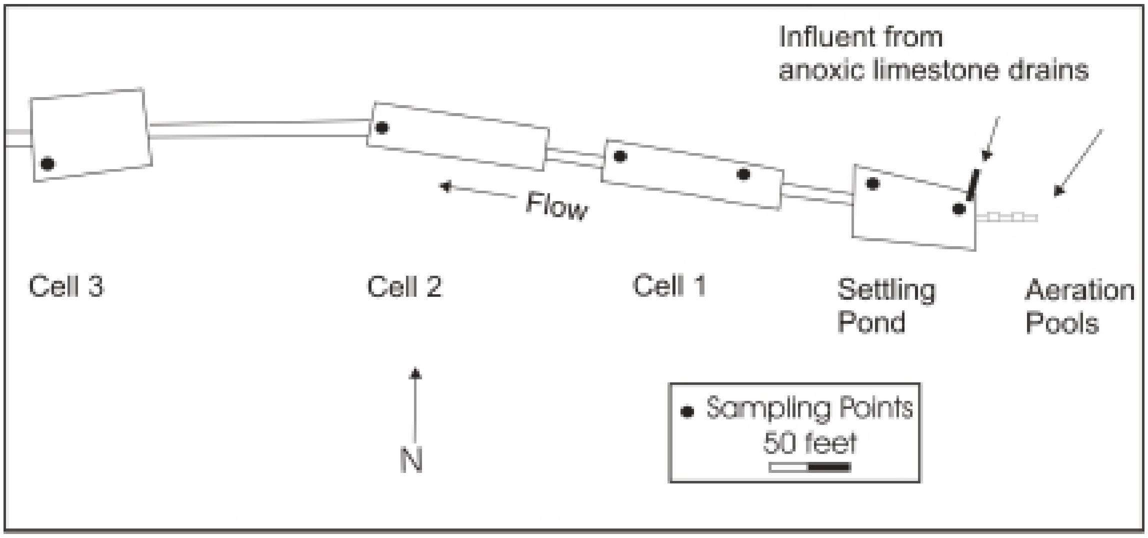


Figure 4-11: The layout of the Wills Creek Wetland into three different cells. The original design was to have all of the input flow through the aeration pool, but additional seeps were discovered after construction began and these were fed directly into the settling pond through anoxic limestone drains

Table 4-16:
Dimensions of the Wills Creek constructed wetland cells

	Surface area (m^2)	Water depth (m)	Water volume (m^3)	Initial substrate
Settling pond	314	1.52	478	
Cell 1	255	0.08	19.5	mushroom compost /lime
Cell 2	255	0.08	19.5	manure/lime
Cell 3	312	0.76	238	limestone/Fermway [a]
Total volume = 755m^3; surface area of composted cells = 822m^2				

[a] Fermented mixture of chicken/cow manure

Soil and water samples were collected over a five-year period (1995-1999) and represent dormant and productive seasons. Soil samples were taken at the surface and at approximately 15 cm depth.

- **Results**

The chemical composition of the wetland influents and effluents are shown in Table 4-17. The results show that the constructed wetland was not effective in removing dissolved sulphate from the mine drainage. Dissolved sulphate concentrations in the wetland cells ranged between 200 and 1,000 mg/L with little variation between cells for a given sampling period, except for June 1997. The average total sulphur concentration in the soil was 1.28 % and about 2/3 of the total sulphur was in the form of sulphide.

The sulphur isotope fractionation was calculated from the difference between the $\delta^{34}S$ value for dissolved sulphate and the $\delta^{34}S$ value for iron sulphides (AVS or pyrite). Because pyrite is the stable end product, pyrite values (CrRS) were used to determine the fractionation. The sulphur isotopes showed a large fractionation, which indicates that sulphate reduction rates were low (Table 4-18). The isotopic fractionation between sulphate and sulphide ($\Delta^{34}S$) was then used to calculate the sulphate reduction rate (R in moles/L,yr) using the following empirical equation (Maynard, 1980):

$$\text{Log } R = -0.084\ \Delta^{34}S + 0.36$$

Using the measured isotopic fractionation values, the biological sulphate reduction rates in the constructed wetland were estimated to range from 0.001 to 0.75 moles/L, yr (0.3-197 mg/L, day). Contrary to the wetland design, the estimated biological sulphate reduction rate was the highest in wetland cell 1 followed by cell 3 (anaerobic) and then cell 2.

Although biological sulphate reduction was occurring at low rates, dissolved sulphate concentrations were not decreasing as the water flowed through the wetland. Geochemical modeling results (PHREEQC) showed that the water in the wetland cells was supersaturated or close to saturation with respect to two minerals: alunite and gypsum. These two minerals were also detected by x-ray diffraction in soil samples from cells 1 and 2. This indicates that the concentration of dissolved sulphate in the wetland was controlled by the solubility of the two minerals.

The top of the substrate in the wetland cells was coated with an oxidized layer of iron oxides, calcium- and aluminum sulphates that isolated the wetland soil from the overlying water. SRB in the soil used the sulphate from the oxidized layer and not the dissolved sulphate from the overlying water. Hence, the dissolved sulphate concentration in the overlying water was not affected by sulphate reduction but was instead controlled by the solubility of the sulphate minerals.

Finally, it is interesting to note that the highest sulphate reduction rate occurs in the wetland cell (1) with the most suitable substrate: spent mushroom compost (Table 4-16).

Table 4-17:
Water chemistry in Wills Creek wetland system

	pH	Conductivity μS/m	Fe mg/L	Mn mg/L	SO_4 mg/L	SO_4/S.C.
10/25/94						
ALD	6.15	1,422	24	1.21	570	0.401
Cell 1 outlet	6.9	1,351	6.71	1.55	55	0.407
Cell 3 outlet	7.09	1,349	0.08	0.4	482	0.357
12/19/94						
ALD	6.18	1,780	40	1.68	640	0.360
Cell 1 outlet	6.82	1,450	11.1	1.47	615	0.424
Cell 3 outlet	6.92	1,420	1.44	0.78	585	0.412
5/22/95						
ALD	6.72	1,740	28.1	3.895	645	0.371
Cell 3 outlet	7.13	1,350	1.21	1.74	546	0.404
8/1/95						
ALD	6.65	1,149	8.32	1.01	396	0.344
9/1/95						
Cell 3 outlet	7.10	1,240	0.95	0.79	488	0.394
10/4/95						
ALD	6.35	1,204	17.1	1.98	547	0.454
Cell 3 outlet	7.00	1,179	0.41	0.44	474	0.402
3/14/96						
ALD	6.62				581	
Cell 1 outlet	6.47				624	
Cell 3 outlet	6.61				815	
8/21/96						
ALD					313	
Cell 1 outlet					296	
Cell 3 outlet					315	
3/20/97						
ALD	5.95				224	
Cell 1 outlet	5.80				254	
Cell 3 outlet	6.40				241	
4/30/98						
ALD	6.07				516	
Cell 1 outlet	6.07				616	
Cell 3 outlet	5.94				607	
6/7/99						
ALD	5.85	1,293			494	0.382
Cell 1 inlet	3.18	1,815			1086	0.598
pore water	5.85	1,795				
Cell 2 inlet	3.28	1,689			914	0.541
Cell 3 outlet	3.28	1,596			844	0.529

Table 4-18:
Sulphur isotope values (per mil) of sulphate and sulphides at Wills Creek

	Sulphate	**FeS (AVS)**	**FeS_2 (CrRS)**	**Fractionation (Sulphate-Pyrite)**
7/24/95				
Settling Pond	-2.57			
Cell 1, A2	-2.44	-13.20	-12.32	9.88
Cell 2	-3.14			
Cell 3	-2.46	-28.99	-30.11	27.65
3/13/96				
Settling Pond	-4.47			
Cell 1, A2	-3.22	-21.26	-20.73	17.51
Cell 2	-3.52			
Cell 3	-4.34	-36.47	-30.45	35.11
8/20/96				
Settling Pond	-3.56			
Cell 1, (n=2)	-3.50	-14.28	-16.37	12.87
Cell 2	-5.12		-44.06	38.94
Cell 3	-3.85	-30.87	-33.78	29.93
3/19/97				
Settling Pond	-3.56			
Cell 1, (n=2)	-3.35	-29.29	-25.88	22.53
Cell 2	-3.09	-41.04	-43.12	40.03
Cell 3	-2.41	-32.05	-30.82	28.41
6/7/99				
Settling Pond				
Cell 1, (n=4)	-3.62	-26.51	-29.66	26.04
Cell 2	-3.47	-21.86	-23.77	20.30
Cell 3	-2.72	-33.13	-34.48	31.76
Cell 1 avg	-3.23	-20.91	-20.99	17.76
Cell 2 avg	-3.69	31.45	-36.98	33.29
Cell 3 avg	-3.16	-32.30	-33.73	30.57
System avg	-3.36	-28.22	-30.57	27.21

- **Costs**

  There are no costs available for this case study. However, it may be clear that capital and operating costs are considerably less that those for the other sulphate treatment technologies, discussed earlier.

- **Advantages/Disadvantages**

  The results of this case study show that the use of stable isotopes can very useful in determining the relative contribution of biological sulphate reduction to the removal of dissolved sulphate from acid mine drainage in constructed wetlands. Relying only on input and outputs of dissolved sulphate is often insufficient to determine the causes of the apparent malfunctioning of constructed wetlands in removing sulphate from acid mine drainage. Moreover, the use of stable isotopes can be a powerful tool in developing new designs for constructed wetlands exclusively aimed at sulphate removal from acid mine drainage.

- **Future Needs/Improvements**

  More research, particularly on the design of wetlands, is required to determine the full potential of wetlands for the biological removal of dissolved sulphate from mine drainage.

- **References**

  Ohio Dept of Natural Resources, Division of Mineral Resources Management, 1855 Fountain Square, Building H-3, Columbus (OH), 43224, US

  Website: www.dnr.state.oh.us

4.4.3 Alkalinity Producing Systems

- **Problem**

  In 1989, a 1,022 m^2 surface flow wetland was constructed in McCreary Co., Kentucky (US) to treat acid mine drainage from an abandoned mine in the Jones Branch watershed. After a year of good performance, the treatment efficiency of the wetland was reduced due to insufficient utilization of the treatment area, inadequate alkalinity production and metal overloading. To improve the performance of the Jones Branch wetland, a renovation project was implemented. The renovation project involved the design of two anoxic limestone drains (ALD) and a series of anaerobic subsurface drains that promote vertical flow of mine water through a successive alkalinity producing system (SAPS) of limestone beds overlain by organic compost.

- **Treatment Process**

  The main objective of this case study was to evaluate the design and operating efficiency (water quality) of the renovated constructed wetland (Barton and Karathanasis, 1999).

  The original wetland consisted of two sequential ponds with 15 and 10 cells, respectively. Renovation of the wetland involved: removal of the existing substrate, installation of an ALD, converting the original surface flow design to an alternating surface/subsurface flow system and addition of a new substrate (50 cm hay/manure compost on top of 30 cm of crushed limestone). A plan of the renovated wetland is shown in Figure 4-12.

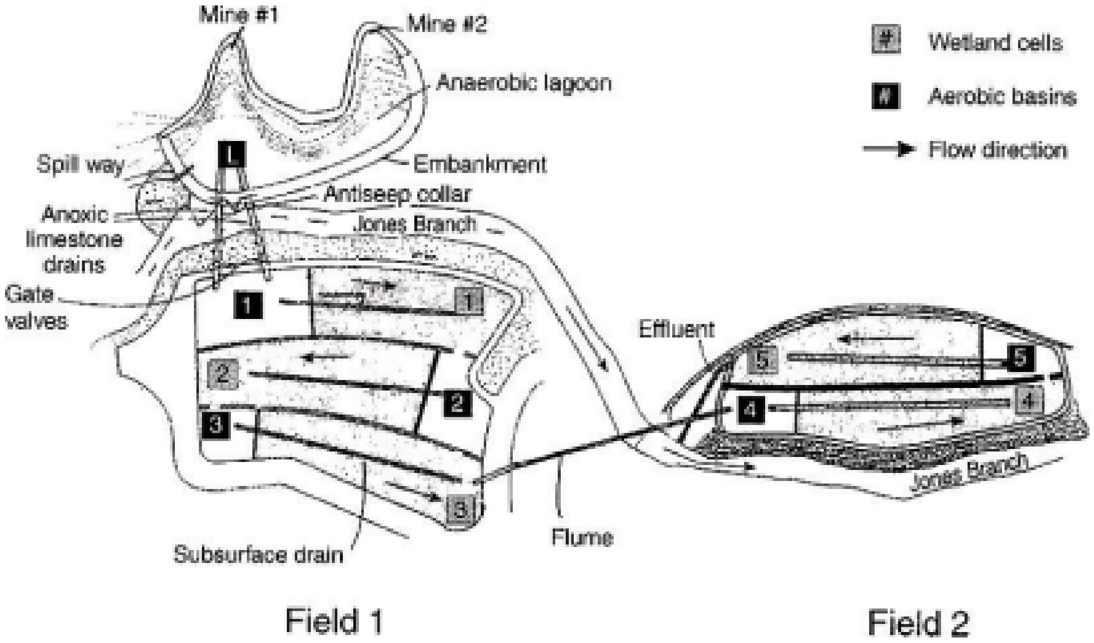


Figure 4-12: Schematic of Renovated Wetland to Treat AMD

Seepage from the mine was collected in an anaerobic lagoon and diverted to the wetland via two, submerged ALD. The outlets of the ALD contained valves to control flow rate and water level. In the wetland, the mine drainage flows through a series of five alternating aerobic and anaerobic treatment zones. Each aerobic treatment zone consists of a precipitation basin without substrate and plants. Water from the precipitation basin flows into the subsurface of the anaerobic treatment zone containing new substrate planted with *Typha*. After the first wetland cell (aerobic and anaerobic zone), the process is repeated in four other wetland cells, divided over two fields.

The main aim of the new treatment was to generate enough alkalinity in the ALD and anaerobic zones to promote metal precipitation and to neutralize the acidity produced by metal hydrolysis in the aerobic zone. Sulphate removal by biological sulphate reduction was not considered in the new treatment design.

Three water samples were collected twice a week from June 1995 to December 1996 at the anaerobic lagoon, the aerobic basins and the anaerobic zones of cells 3 and 5. Substrate samples were collected in both the aerobic and anaerobic zones of each wetland cell. Also, the interstitial and supernatant water was collected for chemical analyses.

- **Results**

Surface water quality data for influent and effluent samples after the wetland renovation are presented in Table 4-19. The results show that the renovated wetland performed well. The acidity of the mine drainage was neutralized, dissolved metal concentrations were greatly reduced and even dissolved sulphate concentrations were reduced by more than 50%. This reduction in dissolved sulphate concentration could be due to biological sulphate reduction. However, data on the chemical composition of interstitial and surface waters, collected at various sampling locations, do not indicate that significant biological sulphate reduction occurred in the wetland (Table 4-20). Concentrations of dissolved sulphide in surface and interstitial waters were low (<5 mg/L) and there was no geochemical or mineralogical evidence for the formation of iron sulphide. Moreover, considering the ambient redox conditions (measured Eh), sulphate reduction by SRB is not likely to occur. Using the chemical composition of the interstitial and surface waters, geochemical modeling revealed that all interstitial and some surface waters were saturated or close to saturation with gypsum. The occurrence of gypsum was confirmed by the SEM/EDAX analyses of mineral precipitates and substrate samples. These findings indicate that the removal of dissolved sulphate from the mine drainage is due to gypsum precipitation rather than biological sulphate reduction.

- **Costs**

There are no costs available for this case study.

- **Advantages/Disadvantages**

Although alkalinity-producing systems have the potential to promote biological sulphate reduction under anoxic conditions, their current design is probably not suitable. Prolonged exposure to reducing conditions would require a longer retention time of the feed water for sulphate reduction to occur.

In their current design, alkalinity-producing systems will only contribute to the removal of dissolved sulphate from mine drainage by the precipitation of gypsum.

Table 4-19:
Post-renovation influent and effluent water quality and flow data from July 1995 to October 1996 for the Jones Branch wetland. (n= number of samples)

Parameter	Units	Average		Standard Deviation		n
		Influent	Effluent	Influent	Effluent	
pH		3.38	6.46	0.45	0.99	26
Eh	mV	260.6	159.3	63.2	109.6	25
Sulphate	mg/L	3,034	1,352	569	730	26
Sulphide	mg/L	1.2	1.2	1.8	1.6	26
DO	mg/L	1.5	3.8	0.9	1.7	25
Fe(II)	mg/L	787	19.5	109	55.5	26
Total Fe	mg/L	787	37.3	121	75.2	26
Mn	mg/L	10.9	5.6	2.1	3.1	26
Al	mg/L	12.6	0.2	4.1	0.2	26
Ca	mg/L	261	264	47	128	26
Alkalinity	mg/L[a]	0	141	0	90	26
Acidity	mg/L[a]	2,244	119	337	206	26
Flow	L/min	37.1	26.1	14.4	18.7	26

[a] $CaCO_3$ equivalent

- **Future Needs/Improvements**

  It would be useful to develop alternative designs for alkalinity producing systems that are better suited for the biological removal of sulphate from mine drainage.

- **References**

  USDA Forest Service, Southern Region

  1700 Bypass Road, Winchester (KY), 40391, US.

  Website: www.southernregion.fs.fed.us

Table 4-20:
Surface water and porewater solution chemistry for post renovation samples at the Jones Branch wetland. (interstitial solutions: n=8; surface water samples: n=26, L anaerobic lagoon; B (#) aerobic precipitation basin C (#) anaerobic zone (wetland)

Parameter	**Sample Site**										
	L	**B1**	**B2**	**B3**	**B4**	**B5**	**C1**	**C2**	**C3**	**C4**	**C5**
							Interstitial Solution				
pH	3.51	3.93	5.53	6.20	6.04	5.36	5.76	6.35	6.62	7.15	7.71
Eh (mV)	269.1	176.7	67.7	-10.1	48.2	97.9	78.1	-14.3	6.8	-28.1	-72.5
SO_4 (mg/L)	1879	2038	1655	1315	985	1001	1079	823	745	585	522
Fe(II) (mg/L)	579	585	400	257	156	46	207	64	60	20	2.2
Fe(III) (mg/L)	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Al (mg/L)	4.3	1.9	0.5	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Ca (mg/L)	172	225	250	233	184	192	218	190	194	169	193
Mn (mg/L)	12	12	8.8	6.0	5.5	0	7.7	7.1	4.9	2.2	1.6
Alk (mg/L)^a	0	0	18.1	33.7	25.3	75.0	70.2	153.7	230.3	421.9	635.8
							Surface Water				
pH	3.38	3.20	3.19	4.62	5.96	4.83	-	-	6.07	-	6.46
Eh (mV)	260.6	294.8	345.4	246.8	83.8	169.1	-	-	264.3	-	159.3
SO_4 (mg/L)	2060	2143	1274	979	790	860	-	-	787	-	1031
Fe(II) (mg/L)	500	524	56	23	8.4	6.1	-	-	22	-	13
Fe(III) (mg/L)	<0.6	1.1	5.6	0.6	<0.6	<0.6	-	-	<0.6	-	<0.6
Al (mg/L)	3.8	3.0	1.4	0.5	0.3	0.3	-	-	<0.3	-	<0.3
Ca (mg/L)	158	168	162	143	133	133	-	-	158	-	173
Mn (mg/L)	11	12	8.2	6.6	5.5	5.5	-	-	6.6	-	5.5
Alk (mg/L)^a	0	0	0	39.0	112.5	35.9	-	-	198.5	-	141.1

[a] $CaCO_3$ equivalent

4.4.4 Permeable Reactive Barrier

- **Problem**

At the Nickel Rim mine site (Falconbridge Ltd) near Sudbury (On) in Canada, a groundwater plume, high in dissolved sulphate and iron concentrations, flows from an inactive tailings impoundment into an adjoining alluvial aquifer (Figure 4-13). In addition to the groundwater flow from the tailings impoundment, the alluvial aquifer also receives locally recharging acidic surface water. To promote precipitation of metal sulphides and generate alkalinity through biological sulphate reduction, a full-scale reactive barrier was installed in August 1995 (Benner et al., 1999).

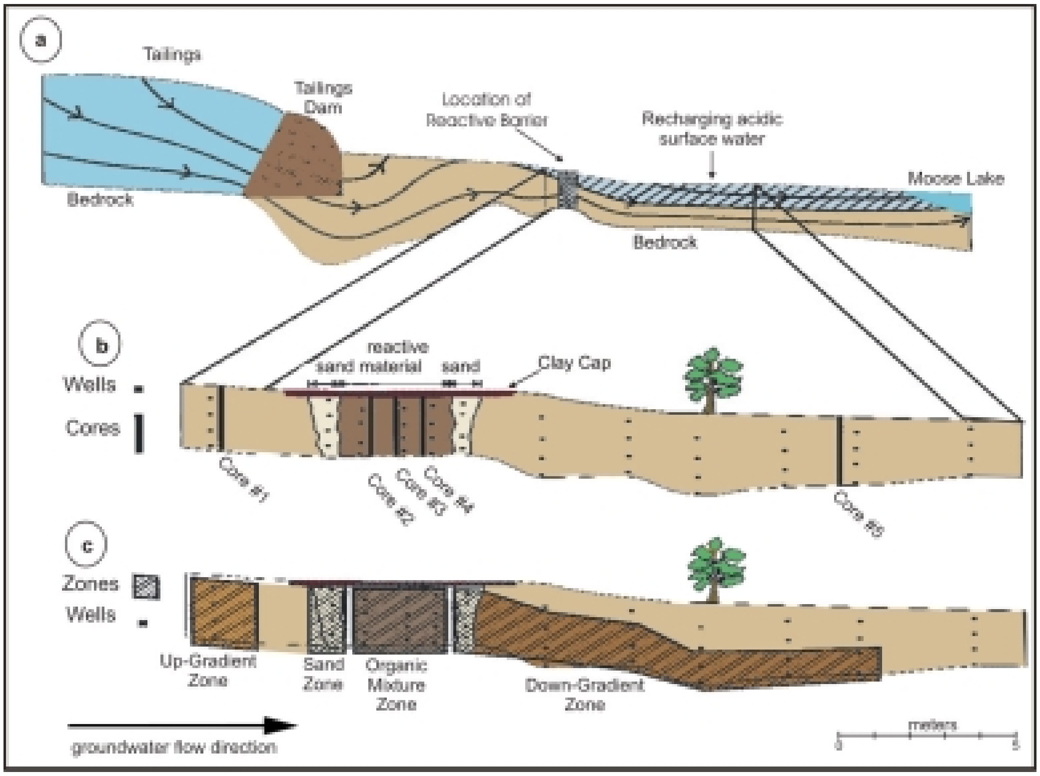


Figure 4-13: Cross-sectional profiles of aquifer and reactive barrier: (a) shows flow lines for the Nickel Rim aquifer prior to the installation of the reactive barrier determined by field-collected data and flow modeling form Brain (200), (b) sample well and core locations in aquifer and reactive barrier, and (c) location of geochemically distinct zones along groundwater flow path

- **Treatment Process**

The objectives of this case study were to present results of 3 yr of monitoring, to define rates of dissolved sulphate and iron removal, and to describe spatial and temporal variations in barrier performance (Benner et al., 2002).

The reactive barrier extends 20 m across the aquifer and is 3.5 m deep and 4 m thick. The barrier was keyed to the bedrock at the base and at the sides. The reactive material consisted of a mixture of municipal compost (20 vol%), leaf mulch (20%), wood chips (9%), gravel (50%) and limestone (1%). Zones of sand (1 m thick) were also installed at both sides of the barrier and a protective clay cap was placed over the barrier to minimize oxygen diffusion and infiltration of water into the barrier (Figure 4-13). Groundwater velocity was approximately 15 m/yr.

- **Results**

Within the aquifer, four distinct zones can be distinguished: the up-gradient zone, the sand zone, the organic mixture zone and the down-gradient zone (Figure 4-13). Chemical analyses of groundwater samples collected at vertical well nests along the flow path in September 1996 were used to construct cross-sectional profiles of selected dissolved constituents (Figure 4-14).

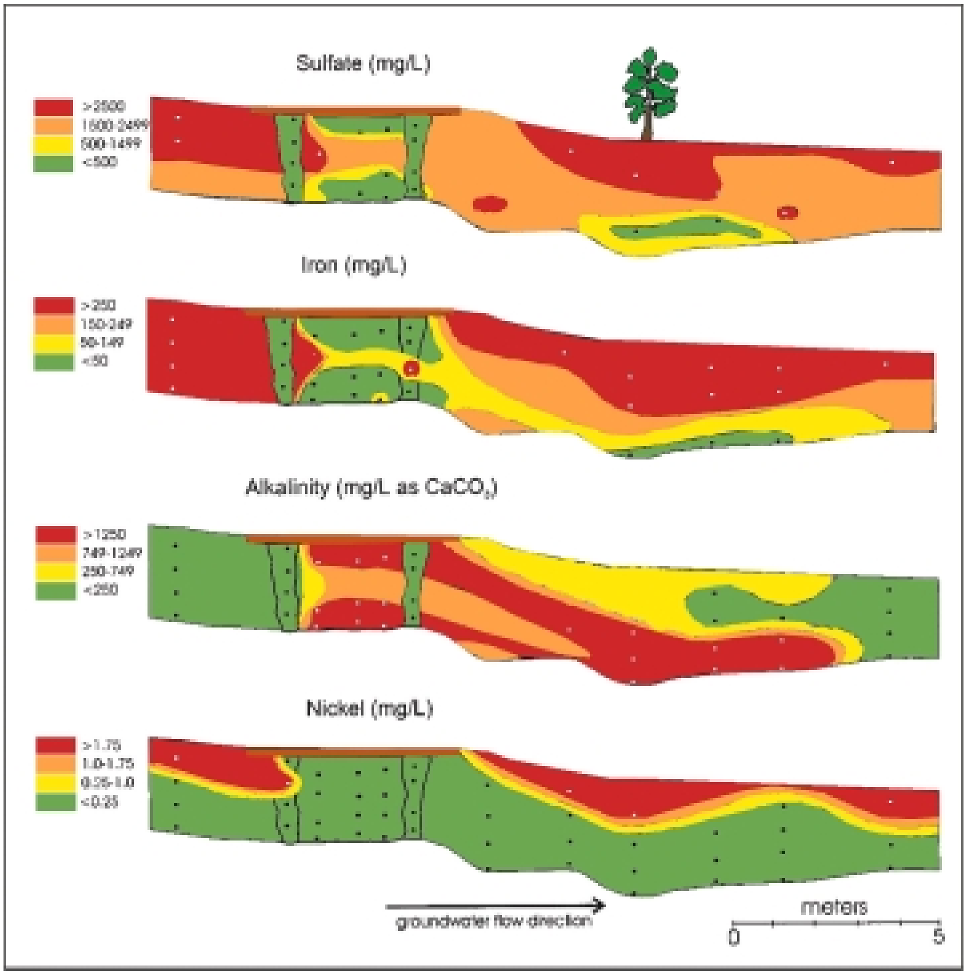


Figure 4-14: Cross-Sectional Profiles of Dissolved Constituents for September 1996: SO_4, Fe, Alkalinity (as $CaCO_3$), and Ni

The groundwater in the upgradient zone was characterized by high concentrations of sulphate (2,500 to 5,200 mg/L), iron (250 to 1,350 mg/L) and nickel (0.12 to 30 mg/L). The pH varied between 2.8 and 5.9 and the alkalinity (as $CaCO_3$) ranged between 60 and <1 mg/L.

In the sand zone, the alkalinity increased to 150 mg/L, probably due to dissolution of calcite. The corresponding decrease in the dissolved sulphate concentrations to 3,200 mg/L was likely caused by gypsum precipitation. Although dissolved sulphide concentrations were low, sulphate reduction could also explain the observed increases in alkalinity and pH and the decreases in dissolved sulphate and iron. The cause of the decrease in dissolved nickel concentrations cannot be attributed to the precipitation of a specific mineral phase.

After groundwater entered the organic mixture zone, the average concentrations of sulphate decreased (840 mg/L) whereas the average alkalinity (2,300 mg/L) and sulphide concentration (17 mg/L) increased. The average populations of SRB were 10^5 times greater than in the up-gradient zone. SEM/EDX analysis of black precipitates revealed the presence of poorly crystalline mackinawite, which provided a sink for dissolved iron (reduced to 80 mg/L). The pH increased from 6.2 (sand zone) to 6.7. Concentrations of nickel decreased to less than 0.1 mg/L, probably due to precipitation of nickel sulphide (millerite).

After the treated groundwater exited the reactive barrier, the dissolved sulphide concentration in the down-gradient zone decreased to an average of 0.14 mg/L. Despite these low concentrations of sulphide there was evidence that sulphate reduction still occurred (black precipitates). Populations of SRB were 10^3 times greater than in the up-gradient zone while alkalinity was still produced, resulting in water supersaturated with respect to calcite.

As a result of the reactive barrier the groundwater was treated in three different ways: (1) generation of alkalinity, (2) elimination of acid-generating potential, and (3) removal of trace metals. Moreover, precipitation of carbonates within the barrier and down gradient of the reactive barrier provided additional (solid-phase) buffering capacity against future (surface) influx of acidity.

Computer transport modeling based on changes in the dissolved chloride concentrations with time, indicated that the average residence time within the barrier is 90 days. Modeling also suggested that flow velocities through the middle of the barrier are approximately three times faster than at the top and at the base.

Using the change in vertically averaged concentrations between up-gradient and down-gradient groundwater well nests, an overall rate of sulphate and iron removal could be calculated. Changes in vertically averaged sulphate and iron concentrations with time are shown in Figure 4-15 for well nests up gradient and down gradient of the barrier. Also the differences between up-gradient and down-gradient concentrations of sulphate and iron were plotted versus time. These data indicate that the concentrations of sulphate and iron removed, decreased linearly with time (Figure 4-15). Using an average residence time of 90 days, the concentrations removed were converted to a removal rate. The results show that, 38 months after installation of the barrier, the sulphate- and iron removal rates had decreased from respectively 58 to 40 mmol/L, yr and 38 to 18 mmol/L, yr. Assuming that the sulphate removal was entirely due to sulphate reduction, the maximum sulphate reduction decreased from 15.3 to 10.5 mg/L, day.

- **Costs**

  The US Environmental Protection Agency performed an economic analysis of the implementation of permeable reactive barriers at a number of sites, including the Nickel Rim mine site (USEPA, 2002). According to their analysis, the capital costs (design and construction) were approximately USD 65,000. The annual operating and maintenance costs were USD 30,000. The costs of the site characterization and the reactive media were estimated at respectively USD 25,000 and USD 15,000.

- **Advantages/Disadvantages**

  The major advantage of the reactive barrier technology is probably the limited operating and maintenance it requires once it is installed and functioning.

- **Future Needs/Improvements**

  At present there is little information about the long-term performance of the permeable reactive barrier technology. It is also unknown if or when the reactive media needs to be replaced.

- **References**

  - Dept of Earth Sciences, University of Waterloo, Waterloo (On), N2L 3G1, Canada

  Website: www.uwaterloo.ca

  - US EPA, Office of Research and Development/Technology Innovation Office

  Website: www.epa.ov/tio/remed.htm

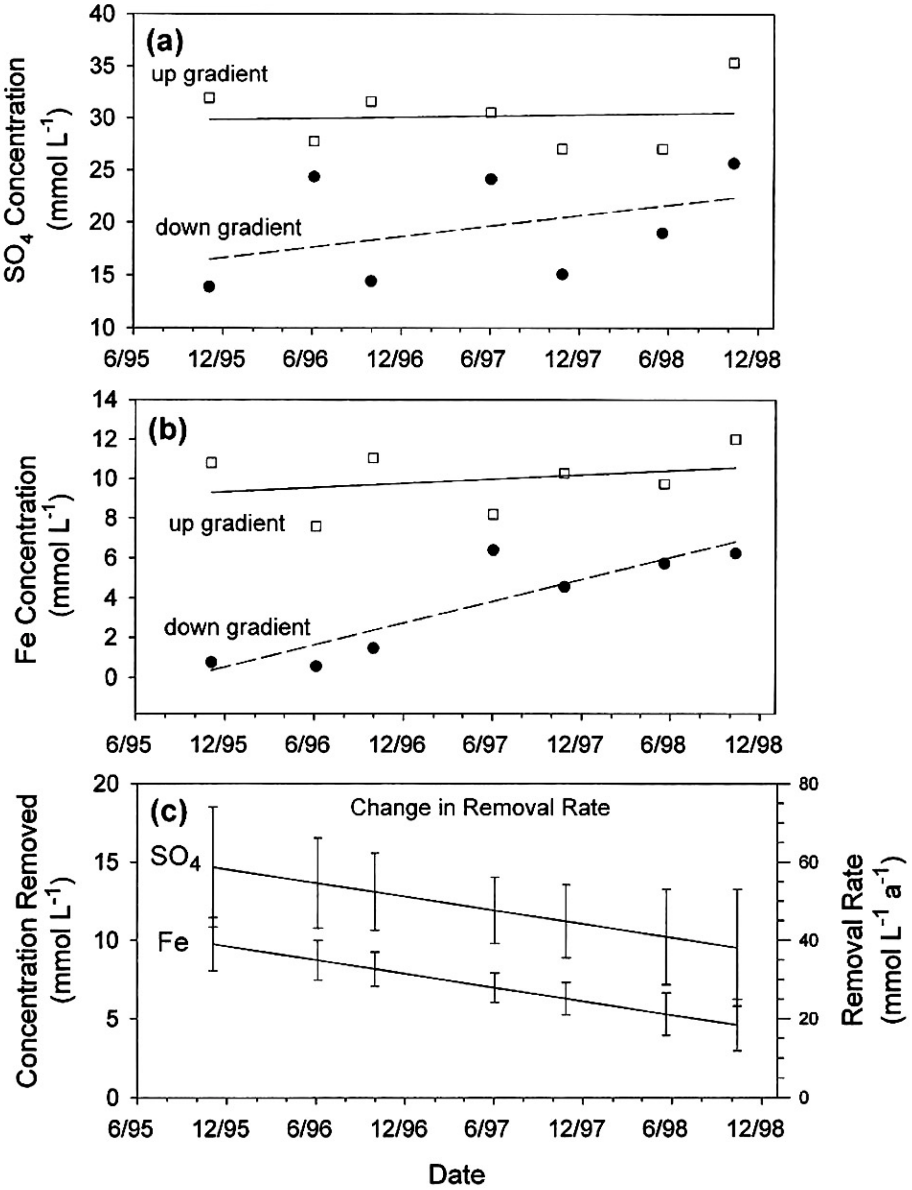


Figure 4-15: **(a) Vertically averaged concentrations of SO_4 in the well nests RW23 (up gradient) and RW26 (down gradient) versus time. (b) Vertically averaged concentrations of Fe in the well nests RW23 (up gradient) and RW26 (down gradient) versus time. (c) Removal of SO_4 and Fe based on the difference between RW23 and RW26 (up gradient – down gradient) concentrations versus time. Error bars reflect one standard error**

5. DISCUSSION AND CONCLUSIONS

5. Discussion and Conclusions

5.1 Comparison of RO, EDR and GYP-CIX

While the variability in site-specific conditions makes it is difficult to directly compare the different treatment processes, there was one well-documented study in which three approaches were tested to treat sulphate in mine water (Schoeman and Steyn, 2001). This case study documents the efficacy and cost of RO, EDR and GYP-CIX at the Griitvkeu Proprietary Mines Ltd. In South Africa and is therefore included in this chapter.

Grootvlei Proprietary Mines Ltd. (South Africa) is discharging approximately 80 to 100 x 10^3 m^3/day mine water into the Blesbokspruit watershed. The mine water from the underground works is of poor quality and requires treatment before discharge into the river. To select the most appropriate technology, various treatment processes were tested at the site. An evaluation of the performance and economics of the RO, EDR and GYP-CIX treatment processes for the Grootvlei mine water is presented below (Schoeman and Steyn, 2001).

The various stages used in the treatment processes are summarized in the upper fields of Table 5-1. The RO treatment Grootvlei feed water by RO requires the greatest degree of pretreatment of the three processes in direct contrast to CYP-CIX, which requires none. The performance and economics of the three treatment processes are evaluated for various scenarios ranging from best to worst case anticipated for the mine site. The scenarios are summarized in the lower portion of Table 5-1, and are based on:

- the composition of the feed water;
- the water recovery after treatment; and;
- the composition of the product water.

The economics of the treatment processes are evaluated for plants with a feed water capacity ranging from 45 to 80 x 10^3 m^3/day.

The compositions of the feed and product waters are shown in Table 5-2a to Table 5-2c for each scenario in each treatment process. The performance in water treatment is comparable among the three treatment processes. It should be noted that all three treatment processes are comparable in that they produce high quality drinking water.

The economic evaluation of the three treatment processes is based on estimates of capital cost, operating costs and capital costs for the disposal of brine, generated in each treatment process (Table 5-3). Cost estimates are made for the different scenarios and for treatment plants with different feed water capacities.

Table 5-1:
Process Stages and Case Scenarios used in the Treatment of Grootvlei Mine Water

Process Stages	**RO**	**EDR**	**GYP-CIX**
Pretreatment	Aeration Lime + soda ash addition Flocculation + settling pH adjustment (H_2SO_4) Sand filtration Sludge dewatering RO feed tank	Aeration Lime addition Filtration pH adjustment (H_2SO_4)	Not necessary
Treatment specs.	Anti-scalant dosing Cartridge filtration (TSS) Membrane cleaning	Feed water temp. 35°C 2 or 4-stage EDR process	Degassing to remove alkalinity Ion-resin regeneration
Post-treatment	pH adjustment (lime) Disinfection	pH adjustment (lime) Disinfection	none
Brine disposal	Evaporation ponds Thermal evaporation	Evaporation ponds Thermal evaporation	Evaporation ponds Thermal evaporation
Waste product	Pretreatment sludge	Pretreatment sludge	Regeneration sludge
Case Scenarios	RO	EDR	GYP-CIX
Feed water composition	1. Best case 2. Probable case 3. Worst case	1. Best case - low TDS 2. Worst case - high TDS 3. Worst case - high TDS	1. Best case 2. Probable case 3. Probable case 4. Worst case
Feed water capacity	80 x 10^6 liter / day 65 x 10^6 liter / day 45 x 10^6 liter / day	80 x 10^6 liter / day 65 x 10^6 liter / day 45 x 10^6 liter / day	80 x 10^6 liter / day 65 x 10^6 liter / day 45 x 10^6 liter / day
Water recovery	1. 85 % 2. 85 % 3. 85 %	1. 80 % 2. 65 % 3. 65 %	1. 88.2 - 91.3 % 2. 79.0 - 82.4 % 3. 58.1 - 68.3 % 4. 54.0 - 58.2 %
Product water composition	Product 1 Product 2 Product 3	Product 1 - potable Product 2a - non-potable Product 2b - potable	Product 1 (TDS<240) Product 2 (TDS<700)

Note: Refer to following tables for descriptions of various feed and product water compositions

Table 5-2a:
Composition of Feed and Product Waters in RO Treatment of Grootvlei Mine Water

	Best Case		Probable Case		Worst Case	
(mg/L)	Feed I	Product 1	Feed II	Product 2	Feed III	Product 3
TDS	2,100	51	4,130	113	4,920	113
pH	10.0	6.1	10.0	6.5	10.0	6.0
SO_4	1,207	24	2,328	41	2,887	49
Ca	20	0.4	38	0.7	49	0.8
Mg	4.5	0.1	6.5	0.1	11	0.2
Na	650	16	1,250	35	1,450	35
K	21	1.0	23	1.2	35	1.5
Cl	178	7.0	178	15	272	14
Alk	5.0	2.1	254	20	178	12

Table 5-2b:
Composition of Feed and Product Waters in EDR Treatment of Grootvlei Mine Water

	Best Case		Worst Case		Worst Case	
(mg/L)	Feed I	Product 1	Feed II	Product 2a	Feed II	Product 2b
TDS	1,972	126	4,178	1,519	4,178	246
pH	7.0	7.0	6.0	5.9	6.0	5.4
SO_4	1,182	72	2,660	944	2,660	207
Ca	350	18	650	211	650	45
Mg	80	4.9	200	73.9	200	16
Na	150	14	330	147	330	39
K	21	1.4	24	7.8	24	2.1
Cl	188	16	287	116	287	30
Alk	0	0	25	18	25	6.4

Table 5-2c:
Composition of Feed and Product Waters in GYP-CIX Treatment of Grootvlei Water

	Feed Water				Product Water	
(mg/L)	Feed I best	Feed II probable	Feed III probable	Feed IV worst	Product 1	Product 2
TDS	1,999	2,714	3,451	4,472	<240	<700
pH	4.5	6.0	6.1	5.8	8-9	8-9
SO_4	1,182	2,037	2,523	2,827	<50	<250
Ca	200	340	432	500	<40	<50
Mg	80	152	182	200	<20	<50
Na	150	271	330	330	<25	<100
K	-	21	0.02	-	<5	<10
Cl	188	188	287	287	<70	<150
Alk	-	51	20	-	<50	<100

Table 5-3:
Economic Evaluation[1] of the Treatment of Grootvlei Mine Water

Costs	RO	EDR	GYP-CIX
Capital cost			
- 80·x 10^6 liter / day			
Best Case			USD 26.7 M
Probable Case	USD 31.8 M		USD 26.7 M
Worst Case	USD 35.0 M	USD 44.4 - 53.3 M	USD 26.7 M
- 65·x 10^6 liter / day			
Best Case			USD 22.2 M
Probable Case			USD 22.2 M
Worst Case		USD 36.1 - 43.3 M	USD 22.2 M
- 45·x 10^6 liter / day			
Best Case	USD 20.4 M		USD 16.7 M
Probable Case	USD 22.7 M		USD 16.7 M
Worst Case	USD 24.0 M	USD 30.0 M (non-pot.)	USD 16.7 M
Operating cost			
Best Case	USD 0.43 / m^3	USD 0.44 / m^3	USD 0.24-0.31 / m^3
Probable Case	USD 0.71 / m^3		USD 0.44-0.52 / m^3
Probable Case			USD 0.54-0.55 / m^3
Worst Case	USD 0.88 / m^3	USD 0.48 / m^3	USD 0.55-0.60 / m^3
Brine disposal[2]			
- 80·x 10^6 liter / day			
Evaporation ponds	USD 13.6 M	USD 31.8 M	USD 41.8 M
Thermal evap.	USD 18.0 M	USD 42.0 M	USD 55.1 M
- 65·x 10^6 liter / day			
Evaporation ponds	USD 11.1 M	USD 25.8 M	USD 34.0 M
Thermal evap.	USD 14.7 M	USD 34.2 M	USD 44.9 M
- 45·x 10^6 liter / day			
Evaporation ponds	USD 7.6 M	USD 10.2 M	USD 6.2 M
Thermal evap.	USD 10.2 M	USD 13.6 M	USD 8.2 M

[1] all costs based on 1996 prices corrected for 2001 (1 USD = R 4.50)
[2] calculated for worst case scenarios

Irrespective of scenario or plant capacity, the capital cost is lowest for the GYP-CIX technology, followed by the RO process and then the EDR process. Capital costs of brine disposal generally increase in the order of RO<EDR<GYP-CIX. Brine disposal by evaporation in (unlined) ponds is less expensive than enhanced (thermal) evaporation. Using an 80 x 10^3 m^3/day plant to treat the worst-case water of the Grootvlei mine, the *total* capital cost for the RO process (USD 48.6-53.0 M) will be significantly less than those for the GYP-CIX (USD 68.5-81.8 M) or EDR (USD 76.2-95.5M) processes.

The differences between the operating costs of the three treatment technologies vary with the scenario used (Table 5-3). For the worst-case scenario, the operating costs of the EDR process are the lowest while those of the RO process are the highest. A more comprehensive estimate of the annual operating costs (worst-case scenario) is presented in Table 5-4. In addition to the operating costs specific to each treatment process, costs for brine disposal and savings through the sale of drinking water are used in the estimate of the annual operating costs. The annual operating costs for the EDR (USD 6.7 M) and GYP-CIX (USD 8.6 M) treatment processes are considerably less than those for the RO process (USD 17.2 M). This may favour the use of the EDR and GYP-CIX processes for the treatment of water from the Grootvlei mine.

Table 5-4:
Annual Operating Costs[1] for the Treatment of Worst-Case Grootvlei Mine Water

		RO	EDR	GYP-CIX
Annual operating costs				
RO:	USD 0.88/m^3	USD 21.9 M		
EDR:	USD 0.48/m^3		USD 9.0 M	
GYP-CIX:	USD 0.60/m^3			USD 9.6 M
Brine disp.:	USD 0.19/m^3	USD 0.82 M	USD 1.9 M	USD 2.5 M
Annual savings				
Drinking water:	USD 0.22/m^3	USD 5.5 M	USD 4.2 M	USD 3.5 M
Total annual operating cost		**USD 17.2 M**	**USD 6.7 M**	**USD 8.6 M**

[1] for plant with 80,000 m^3 feed water per day

5.2 Comparison of Sulphate Treatment Processes

The most important characteristics of the sulphate treatment processes used in the case studies (section 4) are summarized in Table 5-5a to Table 5-5c for the different types of treatment technology.

When comparing costs of the different treatment processes it should be noted that: (1) estimated costs depend strongly on the specific process design, local market prices and local labour costs; (2) cost estimates were made at different times and have not been updated. Considering these limitations, the reported capital and operating costs should be used with caution.

Among the processes that use chemical treatment with mineral precipitation (Table 5-5a), the limestone/lime and SAVMIN processes appear to be the most suitable for sulphate removal from mine water. Although the limestone/lime process can only reduce sulphate concentrations to 1200 mg/L, it is inexpensive and therefore useful as a pretreatment process for other, more expensive treatment processes. The more expensive SAVMIN process, can reduce sulphate concentrations to very low levels. Both processes also remove (trace) metals from mine water. The BaS and CESR processes are probably the most expensive and the CESR process produces the largest amount of sludge. Compared to other types of treatment technology (Table 5-5b and Table 5-5c), chemical treatment processes with mineral precipitation produce the largest amount of sludge. The development of new techniques to reduce or recycle these sludges would make the chemical treatment processes much more attractive.

Among the treatment processes that use membranes or ion-exchange (Table 5-5b), only the GYP-CIX process and possibly the SPARRO process are suitable for the treatment of scaling mine waters (high in SO_4 and Ca as opposed to high in Na and Cl). The major advantage of these specific processes is that they produce high quality water that can be used or sold as drinking water. A major disadvantage is the production of brine that requires additional cost for disposed. Operating costs of the GYP-CIX process and possibly the SPARRO process could be greatly reduced if the water pretreatment involved the limestone/lime treatment process.

The bioreactor and the permeable reactive barrier appear to be the most efficient among the treatment processes that use biological sulphate removal. Although the processes operate on different scales and have different applications, both show the greatest potential for sulphate removal from mine water. Operating costs of the bioreactor could be further reduced by developing alternative, less-expensive carbon and energy sources. The latter could also contribute to the long-term performance of the permeable reactive barrier which is not known yet. Treatment processes that use biological sulphate removal have the added benefit of removal of trace metals by precipitation of metal sulphides.

Constructed wetlands and alkalinity producing systems are the least efficient sulphate removal processes. Whereas it is questionable as to whether any substantial sulphate reduction occurs in alkalinity producing systems, the contribution of reduction to the sulphate removal in constructed wetlands appears to be limited; the contribution of mineral precipitation (gypsum) in wetlands appears to be more important. The limited extend of sulphate reduction in constructed wetlands may be related to their design, originally based on the removal of other dissolved elements (*e.g.* Fe, Mn). Hence, new designs may have to be developed if constructed wetlands are to be used specifically for sulphate removal by sulphate reduction. Despite the limited degree to which sulphate is removed, trace metals are very effectively removed by sulphate reduction in constructed wetlands as considerably less sulphate reduction is required to remove the trace metals.

Table 5-5a:
Summary of case studies on chemical treatment processes with mineral precipitation

	Limstone/Lime	BaS	SAVMIN	CESR
	2001	1990	1999-2001	2001 ?
Pretreatment	no	no	no	no
Feed water	SO_4: 3,000 mg/L	SO_4: 27,500 mg/L	SO_4: 649 mg/L	SO_4: 29,100 mg/L
Product water	SO_4: 1,219 mg/L	SO_4: 190 mg/L	SO_4: 69 mg/L	SO_4: 190 mg/L
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[1]	unknown (low)	USD 0.48 M per 10^3 m^3/day (Δ SO_4: 2,000 mg/L)	USD 0.31 M per 10^3 m^3/day	unknown
Operating costs[1]	USD 0.10 / m^3	USD 0.36 / m^3 (Δ SO_4: 2,000 mg/L)	USD 0.17 / m^3	USD 0.79 / m^3 (Δ SO_4: 1,500 mg/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

[1] Assuming South African R 1 = USD 0.104 or R 9.62 = USD 1.00 (Nov. 2002)

Table 5-5b:
Summary of case studies on treatment processes using membranes and ion-exchange

	RO	**SPARRO**	**EDR**	**GYP-CIX**
	2001	1992-1994	2001	2001
Pretreatment	yes	yes	yes	no
Feed water	SO_4: 4,920 mg/L	SO_4: 6,639 mg/L	SO_4: 4,178 mg/L	SO_4: 4,472 mg/L
Product water	SO_4: 113 mg/L	SO_4: 152 mg/L	SO_4: 246 mg/L	SO_4: <240 mg/L
Brine production	yes	yes	yes	yes
Sludge production	low	low	low	low-moderate
Monitoring	low-moderate	low-moderate	low-moderate	low
Maintenance	high	high	high	moderate
Capital cost	USD 0.44-0.53 M[1] per 10^3 m^3/day	USD 0.52 M[2] per 10^3 m^3/day	USD 0.56-0.67 M[1] per 10^3 m^3/day	USD 0.33-0.37 M[1] per 10^3 m^3/day
Operating costs	USD 0.88 / m^3	USD 0.22[2] / m^3	USD 0.48 / m^3	USD 0.60 / m^3
Advantages	- drinking water quality	- drinking water quality - improved membrane life	- drinking water quality	- drinking water quality
Disadvantages	- scaling problems - short membrane life	- short membrane life	- scaling problems - short membrane life	- production of sludges
Improvements	- not suitable for scaling waters	- membrane life	- not suitable for scaling waters	- recycling of sludges

[1] Calculated from capital costs for plants with feed of 45-80 10^3 m^3/day (worst-case scenario Grootvlei mine water)
[2] Costs based on 1992 prices (S.A.), conversion used: South African R 1 = USD 0.104 or R 9.62 = USD 1.00 (Nov. 2002)

Table 5-5c:
Summary of case studies on treatment processes using biological sulphate removal

	Bioreactor	**Constructed Wetland**	**Alk. Producing Systems**	**Permeable Reactive Barrier**
	2001	1993/1999	1999	1999-2002
Pretreatment	yes	yes	yes	no
Feed water	SO_4: 8,342 mg/L	SO_4: 1,700 mg/L	SO_4: 3,034 mg/L	SO_4: 2,500-5,200 mg/L
Product water	SO_4: 198 mg/L	SO_4: 1540 mg/L	SO_4: 1,352 mg/L	SO_4: 840 mg/L
Sludge production	low-moderate	no	no	no
Monitoring	moderate-high	low	low	low
Maintenance	moderate	low	low	low
SO_4 reduction rate	12-30 g/L,day	0.3-197 mg/L,day	0 mg/L,day	max. 10.5-15.3 mg/L,day
Capital cost	USD 0.24 M[1] per 10^3 m^3/day (Δ SO_4: 2,000 mg/L)	unknown (low)	unknown (low)	USD 65,000
Operating costs	USD 0.27[1] / m^3 (Δ SO_4: 2,000 mg/L)	unknown (low)	unknown (low)	USD 30,000 / yr
Advantages	- also trace metal removal - recycling of H_2S and CO_2	- 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	- no sulphate reduction ?	- long-term performance ?
Improvements	- recycling of sludge - cheap C + energy source	- specific design requird	- specific design requird	- alternative reactive media

For the removal of sulphate from mine water the following treatment processes appear to be the most suitable:

- Limestone/lime (largely as pretreatment process)
- SAVMIN
- GYP-CIX
- Biological sulphate removal by bioreactor or permeable reactive barrier

Among these four treatment processes, sulphate removal by biological sulphate reduction has the greatest potential. The major advantages of biological sulphate reduction are: (1) both sulphate and trace metals can be reduced to very low levels; (2) the amount of waste produced is minimal; (3) capital cost are relatively low and operating costs can be drastically reduced by the development of inexpensive carbon and energy sources; (4) trace metals in mine drainage can be selectively recovered and sold for additional savings.

5.3 Conclusions

Based on an extensive review of available treatment technologies that can be used for sulphate removal from mine drainage, the following main conclusions can be made:

- Existing treatment technologies for mine drainage are generally poorly documented and not readily available. A better organization and exchange of information could greatly improve and guide future advances in the development of better and less expensive treatment technologies.
- Although stringent guidelines for sulphate concentrations in mine water do not exist, it is relatively easy to combine the removal of trace metals with the removal of sulphate using existing treatment processes (*e.g.* SAVMIN, GYP-CIX or Biological Sulphate Reduction).
- Chemical treatment processes with mineral precipitation are generally the least expensive but produce the largest quantities of sludge. Improved methods to reduce or recycle sludge need to be developed.
- Except for the SPARRO process, membrane treatment processes are not well-suited to the treatment of scaling mine waters. Even with the production of high quality (drinking) water, operating costs are presently very high. If prices of drinking water increase sharply in the future, operational costs for membrane treatment processes will decrease accordingly due to increased savings by the sale of drinking water.
- Treatment processes that use ion-exchange (GYP-CIX) are a good alternative for membrane treatment processes if scaling mine waters need to be treated. The frequency of ion-resin regeneration can be reduced by pretreatment of the mine water (*e.g.* limestone/lime process). Similar to the water produced in membrane treatment processes, water produced by the GYP-CIX process can be sold as drinking water.
- Among the treatment processes that use biological sulphate reduction, the bioreactor and permeable reactive barrier are the most efficient. An added benefit of biological sulphate reduction is the removal of trace metals from the mine water.

For an improvement of the efficiency of biological sulphate removal in constructed wetlands and alkalinity producing systems, additional research and development of their design is required.

- For the removal of sulphate from mine water, the limestone/lime process (as pretreatment), the SAVMIN process, the GYP-CIX process and biological sulphate reduction in a bioreactor or permeable reactive barrier appear to be the most suitable treatment processes.
- Among the four suitable treatment processes, sulphate removal by biological sulphate reduction has the greatest potential. The major advantages of biological sulphate reduction are: (1) both sulphate and trace metals can be reduced to very low levels; (2) the amount of waste produced is minimal; (3) capital cost are relatively low and operating costs can be drastically reduced by the development of inexpensive carbon and energy sources; (4) trace metals in mine drainage can be selectively recovered and sold for additional savings.

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