COALTECH 2020

EVALUATION OF NEW AND EMERGING MINE WATER TREATMENT TECHNOLOGIES

PART A

Evaluation of the CSIROSURE Sulphate Removal Process

EVALUATION OF THE CSIROSURE SULPHATE REMOVAL PROCESS

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1 TREATMENT PROCESS FUNDAMENTALS

1.1 Process Description

The anaerobic sulphate reduction process is based on the biological conversion of sulphate to sulphide under favourable environmental conditions:

$2CH_2O + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+$ and biomass

The reaction using ethanol as carbon/energy source:

$2C_2H_5OH + 3SO_4^{2-} \rightarrow 3HS^- + 3H_2O + 3HCO_3^- + CO_2 +$ biomass

The Sulphate Reducing Bacteria (SRB) include a wide spectrum of different bacteriological species, adapted to different substrates and different environmental conditions.

Sulphate reducing bacteria can utilise a variety of different carbon sources from complex cellulosic compounds to simple carbon compounds and can even metabolise hydrogen. The SRBs typically act in association with other bacteria when using complex natural carbon sources, such as compost, grasses etc. The industrial application of the process has focussed on simple, readily degradable carbon compounds such as acetate, methanol, ethanol and $H_2/CO/CO_2$ gas mixtures.

The SRBs are always in competition with other bacterial species, such as methanogens, for the available carbon. Process operating parameters (retention time, SO_4 : COD ratio) and environmental conditions (pH, temperature etc) dictate the outcome of the competition between sulphidogenic and methanogenic action.

The theoretical carbon requirements for sulphate reduction, expressed in terms of the COD equivalent of the carbon source are as follows:

2 mole C = 1mole SO_4

0.67 kg COD = 1 kg SO_4

Alkalinity is also generated in the process of sulphate reduction. The alkalinity production as a function of sulphate reduction is as follows:

1 mole $CaCO_3$ = 1mole SO_4

1.0 kg $CaCO_3$ = 0.96 kg SO_4

1.2 Associated Process Reactions

Most acidic mine waters contain elevated metal concentrations. The most prevalent metals in mine waters are iron (ferrous and ferric forms), aluminium and manganese. Other metals such as zinc, copper, arsenic etc may also be present at low concentrations. The biological reduction of sulphate produces sulphide. Most metal sulphides have very low solubility:

$Me^{2+} + S^{2-} \rightarrow MeS(solid)$

Metal sulphide precipitates form in the presence of sulphides and can be removed from the bulk of the mine water.

Biological sulphate reduction also results in the formation of bicarbonate and carbonate species of alkalinity. The solubility limit of calcium carbonate may be exceeded:

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(solids)$

The calcium carbonate solids will separate from the mine water stream and can be separated with the other treatment residues.

1.3 Process Conditions

Temperature

Microbiological activity is very sensitive to temperature and increases as the temperature rises. Anaerobic bacterial growth slows down substantially below 14 – 16°C. The optimum temperature for sulphate reduction may be in the range 25 – 35°C.

pH

Most SRBs, which have been isolated, are neutrophilic or only mildly tolerant of acidity. Limited reports of SRBs, which are acid tolerant have been published. For optimum growth conditions, a pH > 7,5 is typically proposed. This also relates to potential H_2S toxicity at lower pH – levels.

Nutrients

Microbial growth requires a minimum threshold of nitrogen, phosphorus and other micronutrients such as trace metals. Many mine waters are deficient in N and P and will require a supplement to allow optimum bacterial growth. The biomass yield of anaerobic biological systems in general, and biological sulphate reduction specifically, is low. The major nutrient requirements are typically expressed as a ratio to the feed COD:

COD : N : P

1.4 Process Constraints

Metals

Metals can exert an inhibitory effect on the microbiological sulphate reduction process. Metals, however, have to be present in the free form to exhibit toxic/inhibitory effects. The typical hierarchy of increasing metals inhibition is as follows :

$$Cu > Cd > Ni > Zn > Cr > Pb$$

Metals solubility in the presence of sulphide is very low for the majority of metals. The metal sulphide solubility is lower than the corresponding hydroxide or carbonate solubility for most metals, except Al, Mn and possibly Zn. Metals toxicity is, therefore, reduced by the anaerobic conditions associated with sulphate reduction and the presence of sulphide.

In fact, metal addition (such as ferric chloride) can be used to alleviate sulphide toxicity, reduce sulphide odour problems, etc.

Hydrogen sulphide

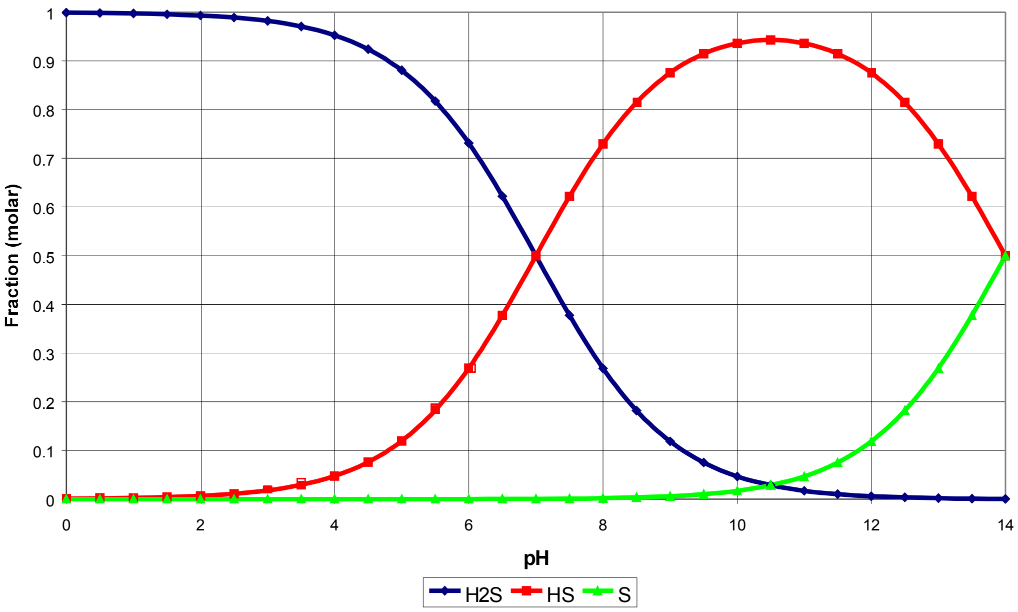
Hydrogen sulphide dissociates in water in accordance with the following equations :

$$H_2S \rightarrow H^+ + HS^- \quad , \quad K_{a1} = 7$$

$$HS^- \rightarrow H^+ + S^{2-} \quad , \quad K_{a2} = 14$$

At a neutral pH, approximately equal amounts of H_2S^- and HS may therefore be present – refer to **Figure 1**.

Figure 1 - Dissociation of Hydrogen Sulphide



The free aqueous H_2S will also be in equilibrium with the gaseous H_2S, in accordance with Henry's Law:

$$[H_2S]_{aq} = K\,[H_2S]_g$$

where:

$[H_2S]_{aq}$ = hydrogen sulphide concentration in solution (mg/ℓ)

$[H_2S]_g$ = hydrogen sulphide partial gas pressure (atm)

K = Henry's Law constant

The inhibitory form of sulphide is assumed to be free H_2S. The expression of inhibition and toxicity is, however, not straightforward. Inhibition has been correlated with both free H_2S concentrations as well as with total sulphide concentrations. It has been postulated that micro-organisms may have two inhibition thresholds, a lower one correlated with free H_2S and a higher one correlated with total sulphide.

Sulphide toxicity effects are further complicated by the difference in bacterial growth forms, suspended growth or granular/pelletised growth. Diffusion gradients set up in granular/pelletised sludge may be the reason for the lower observed toxicity, experienced in granular and pelletised forms of sludges.

The Inhibition Concentration (IC) levels of free H_2S, around a pH of 7,6 varies from approximately 100 to 180 mg H_2S/ℓ, depending on the specific substrate used by the SRBs.

2 CSIROSURE PROCESS EVALUATION

A demonstration plant for single stage biological sulphate removal was set up as part of the Coaltech Initiative. The plant was designed with a nominal treatment capacity of 200 m^3/day to achieve at least 50% sulphate reduction, treating a neutralised mine water with a sulphate concentration of 2200 – 2400 mg/ℓ.

The process evaluation was based on the operating and performance observations made at the Coaltech Demonstration Plant located at Navigation Colliery, over the period January 2000 to June 2001. **Figure 2** shows a schematic process flow diagram of the demonstration plant. **Photograms 1 to 6** depict components of the Demonstration Plant.

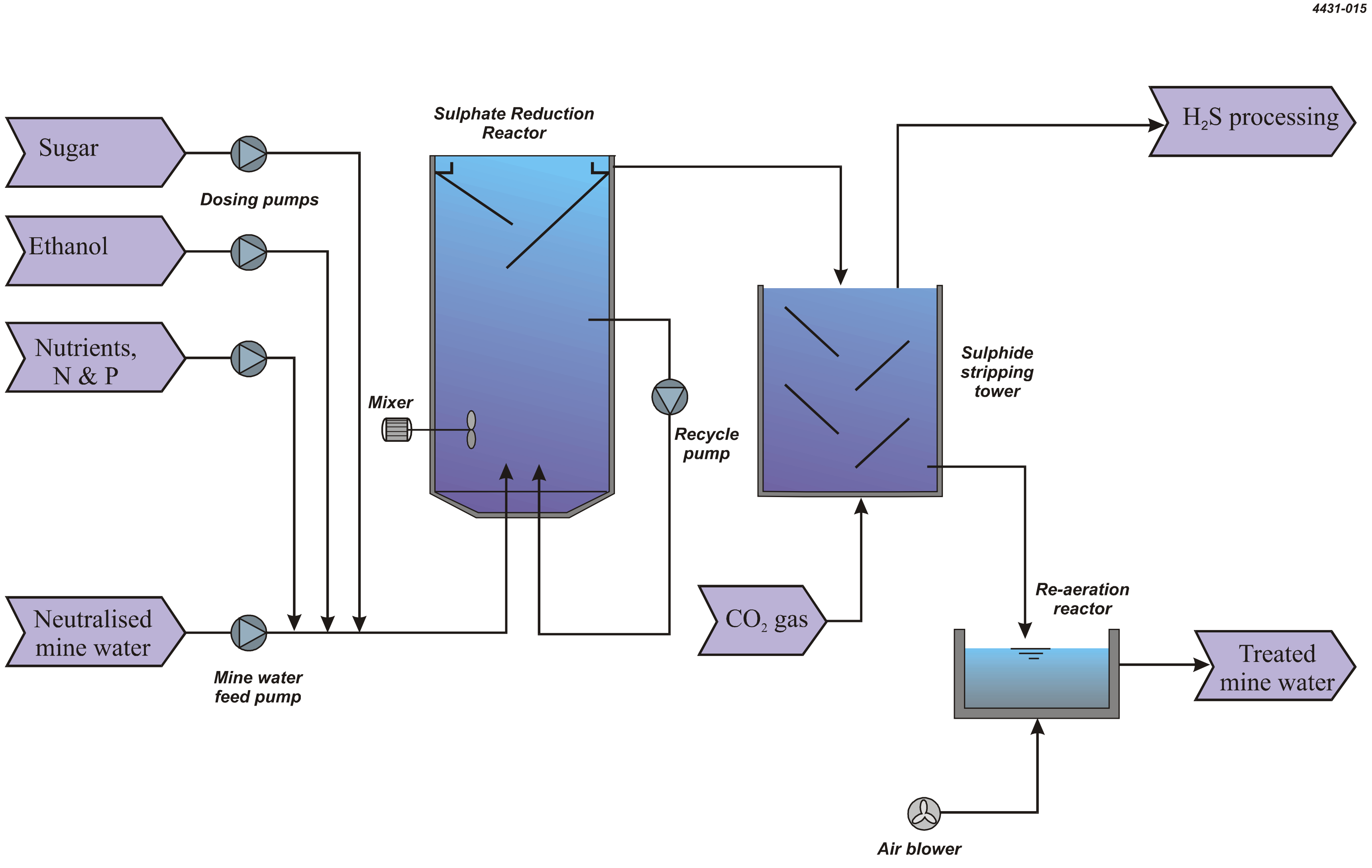
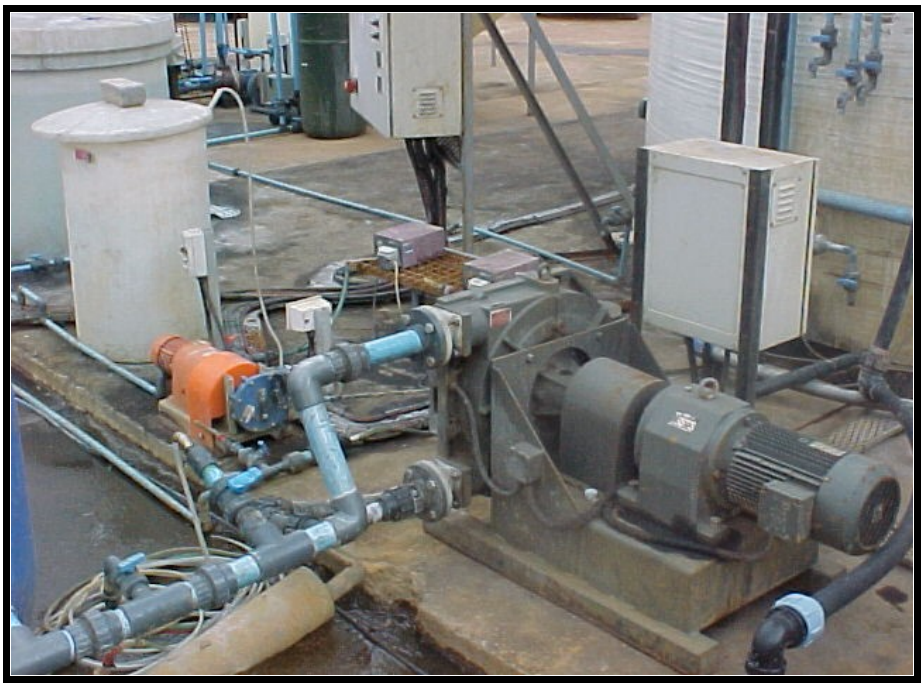


Figure 2 : CSIR Biosure Mine Water Treatment Demonstration Plant - Process Flow Diagram

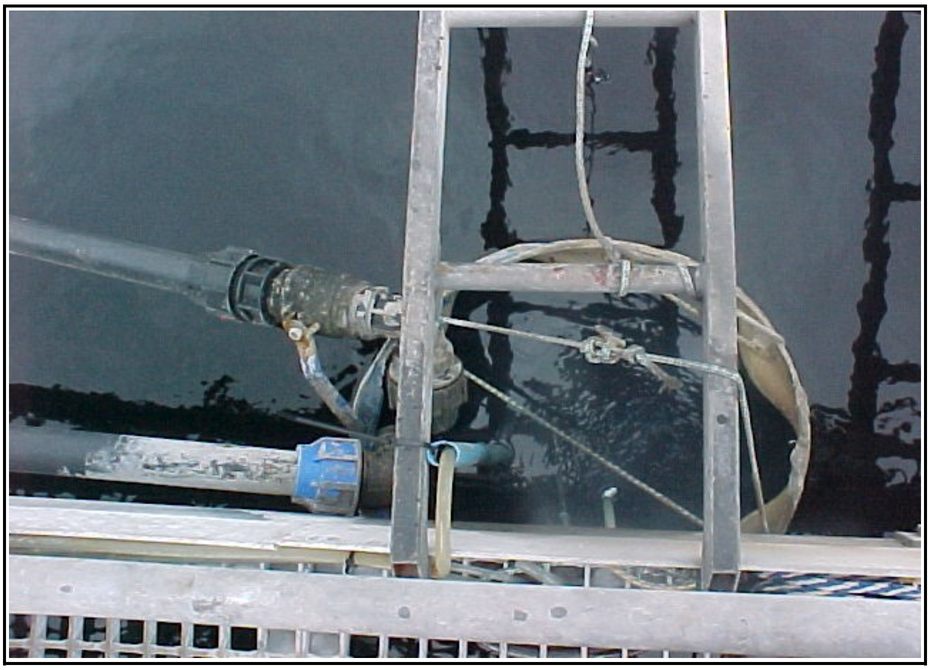
Photogram 1 : General Overview of the CSIR Demonstration Plant



Photogram 2 : Mine Water Feed Pump Arrangement

Photogram 3 : Reactor Re-Circulation Pump Installation

Photogram 4: Chemical Storage Tanks and Dosing Pumps



Photogram 5: Central stilling well and mine water feed column

Photogram 6: Sulphate reduction reactor overflow

2.1 Start-up of the process

The start-up of the process was relatively slow and was interrupted by several events. The experience gained during start-up was invaluable in developing a perspective on the process commissioning requirements for a full-scale plant.

The main process-related aspects, which require attention and management during the start-up and commissioning of a sulphate reduction process, are outlined below, based on the experience at Navigation Colliery Demonstration Plant.

Temperature

Start-up at an optimum process temperature in excess of 25°C is desirable. Attempts to start the process at lower temperatures were not satisfactory.

Biomass seeding

Anaerobic sludge is available from most municipal sewage treatment plants. This sludge is, however, not necessarily acclimated for sulphate reduction and employing such seeding sludges may slow the start-up time.

It is desirable to seed the process with an SRB acclimated sludge or at least from a municipal plant which treats a sewage containing higher sulphate concentrations ($SO_4 > 100$ mg/ℓ).

It may be advisable, on full-scale installations, to keep a strategic source of biomass. This can be utilised as a source of seeding, in the event of process failure, to achieve very rapid start-up. It is considered prudent to have at least 10% of the plant sludge inventory available in separate storage.

Acidity of feed water

Most SRBs are sensitive to low pH conditions and the start-up can be interrupted by changes in the feed water pH levels. In general, the feed into the sulphate-reducing reactor should be near neutral to ensure optimum process conditions to establish a SRB population.

This may require the dosing of an alkali during the start-up period, until the alkalinity generated in the process can be mobilised to neutralise any influent acidity.

Carbon and Nutrient feed

Consistent and reliable carbon and nutrient feeding to the reactor is essential for a smooth start-up. The SRBs typically have to acclimatise to the new carbon and nutrient substrate and may be sensitive to sudden changes in this regard. Experience gained at the

Demonstration Plant indicated that virtually complete biomass loss from the reactor can occur within 3 – 4 days, if the carbon / nutrient feed to the reactor is interrupted.

It is, therefore, essential to have redundancy and back up built into the carbon/ nutrient storage and feeding facility to limit the risk of process failure.

Gypsum formation

During the initial start-up period, the reactor may still contain high sulphate levels, before the reduction process becomes effective. If high calcium concentrations are also present, which is typical for neutralised mine water, then gypsum crystallisation may take place inside the reactor. Two negative effects may result :

- *The bio-sludge would have a high inorganic content, which would modify the sludge density and mixing/fluidisation characteristics.*
- *A reservoir of precipitated sulphate accumulates in the reactor, which first has to be removed before the sulphate reduction efficiency of the reactor will increase to target levels.*

The facility must be provided to waste excess sludge containing high gypsum levels from the reactor, especially during start-up.

Oxygen ingress

The SRB population will be inhibited at even low levels of dissolved oxygen. Introduction of air into the reactor under full-scale operational conditions, can easily take place (pump suction, inlet turbulence etc.), if proper precautions are not taken.

An audit must be done during the plant start-up to identify and eliminate any sources of air ingress into the reactor.

In general, it would appear that the sulphate reduction process can be commissioned to full production levels within 2 – 3 weeks, provided that optimum process conditions can be maintained.

2.2 Process Loading

The Biosure Demonstration Plant was operated at a steady flow and the following average loading rates:

- Flow - 192 m^3/day
- HRT - 10.3 hours
- SO_4 loading rate - 5 – 6 kg SO_4/m^3/day

This was achieved at a temperature in the range of 20 – 24 °C. Initial testing indicated that at a higher reactor temperature of 30°C the following flow and loading rates may be achievable:

Flow	-	400 m^3/day
HRT	-	6 hours
SO_4 loading rate	-	10 – 12 kg SO_4/m^3/day

2.3 Process conditions

2.3.1 Carbon Requirements

The Biosure Demonstration Plant was fed a carbon substrate consisting of:

- 200 mg/ℓ sugar
- 720 mg/ℓ ethanol B (75 % ethanol and 25 % propanol)

The equivalent COD was measured to be 1 750 mg/ℓ (theoretical COD = 1 780 mg/ℓ). The theoretical carbon requirements for sulphate removal is COD : SO_4 = 0.67 on a mass basis. Efficient SO_4 removal of more than 75 – 85 % was achieved, when the carbon feed rate was increased to a ratio of:

COD : SO_4 = 0.9 –1 kg/kg

Virtually complete SO_4 removal can be achieved by further increasing the carbon feed rate to a ratio:

COD : SO_4 > 1 – 1.2 kg/kg

The sugar carbon source is relatively expensive and this type of carbon source is probably only required during start-up of the process. Sugar substrate produces high biomass production compared to other carbon sources. This is beneficial during the initial start-up to rapidly develop an adequate biomass inventory.

The effective carbon utilisation was estimated to be approximately 72 - 79 %. The ineffective utilisation of carbon substrate could be associated with competing methanogenic reactions (producing methane) or leakage of carbon substrate from the reactor. The latter appears to be the case, since high acetate concentrations were recorded in the reactor overflow.

2.3.2 Nutrient Requirements

Macronutrients, N and P have to be supplemented to support the SRB biological population. Typical nitrogen sources include urea, commercial fertilisers and various ammonium salts. The most common phosphorus source is phosphoric acid. The N and P are typically dosed in proportion to the feed COD (and therefore, indirectly to the feed SO_4).

The Biosure Demonstration Plant was operated at the following nutrient supplement levels:

COD : N : P

= 1000 : 5.5 : 1.5

2.3.3 Alkalinity

The influent mine water was already neutralised, pH > 6.5, and no further alkali addition was required. The Demonstration Plant achieved the anticipated alkalinity generation (bicarbonate form), associated with sulphate reduction. The observed alkalinity production was:

Alkalinity $CaCO_3$: SO_4 reduced

= 1 : 1 on molar basis

= 1 : 0.96 on a mass basis

High alkalinity levels in the treated mine water, 1 500 – 2000 mg/ℓ as $CaCO_3$ should be adequate to neutralise most acid mine waters, as an integral part of the sulphate removal process.

2.3.4 Biomass Inventory

The biomass inventory progressively increased from 2 500 mg/ℓ to 10 000 mg/ℓ over a three (3) month period. The biomass inventory stabilised at 10 000 mg/ℓ over extended period of operation. The sulphate removal capacity of the process also increased, since it was demonstrated that the sulphate removal depends on biomass concentration. The approximate dependency between sulphate reduction rate and biomass concentration can be expressed as:

$$R = X^{0.85}$$

Where R = sulphate reduction rate (kg SO_4/m^3/day)

X = biomass concentration (kg/m^3)

The biomass was fairly uniformly distributed in the mixed zone of the reactor. No biosolids gradients were observed as one would expect in a upflow type reactor (UASB).

2.3.5 Sulphide Production

The sulphide production paced the sulphate reduction, except for a period of time when air was fed into the top part of the reactor to enhance sulphur production.

The recorded concentration varied from 350 to 700 mg/ℓ total sulphide, and no specific adverse process response was detected. At a pH of 7.5, only 25 % of the total hydrogen sulphide would be in the free un-dissociated form, corresponding to free H_2S concentrations of 87 – 175 mg/ℓ. This may be approaching the inhibitory levels reported in the literature.

2.3.6 Sulphide Stripping

The SRR effluent contained very high sulphide concentrations, typically in stochiometric proportion to sulphate removed. The Demonstration Plant achieved very efficient sulphide stripping in a two-stage reactor:

- *Submerged packed reactor with a contact time of 20 mins.*
- *Trickling filter packed reactor with a contact time of 12 mins.*

The sulphide was effectively stripped by CO_2 gas, provided that the following molar ratio was maintained:

$$CO_2 : H_2S > 5.9 \text{ mole/mole}$$

2.4 Process Control

The Biosure Demonstration Plant did not incorporate any sophisticated control systems. The process was manually controlled by:

- *Selecting a hydraulic and sulphate loading rate and setting the appropriate mine water feed rate*
- *Setting the carbon feed and nutrient feed to pace the feed flow rate*
- *Monitoring the process performance and doing manual adjustments as necessary.*

The lack of control over critical process parameters, such as temperature, created difficulties, especially during the start-up phase of the project.

2.5 Process Performance

The Demonstration Plant achieved high levels of SO_4 removal, after the process stabilised and reliable carbon and nutrient feeds were established.

At COD : SO_4 mass feed ratio's around 0.8 – 1.0, approximately 75 –85 % SO_4 removal was achieved, resulting in residual SO_4 concentrations of 400 – 700 mg/ℓ. When the COD : SO_4

mass feed ratio was increased to 1.1 –1.2, approximately 85 – 95 % sulphate removal was achieved, giving residual SO_4 concentrations of approximately 200 mg/ℓ.

The process did respond negatively to sudden changes in process and operating parameters, such as:

- *Interruptions to carbon/nutrient feed resulting in biomass washout.*
- *Drops in temperature*
- *Introduction of air/oxygen*

The process is therefore sensitive to process changes, which result in loading and operating conditions falling outside the stable optimum range for sulphate reduction.

The product water quality in terms of SO_4 concentration did vary from day to day. This was due primarily to fluctuations in the influent mine water SO_4 concentrations. The carbon/nutrient feed rate could not be exactly paced with the influent SO_4load, due to the absence of on-line sulphate concentration monitoring.

2.6 Residue Generation

The biological process generates an excess of bio-sludge. Anaerobic processes produce little excess bio-sludge. The excess biomass production at the Demonstration Plant was estimated to be:

0.02 kg VS/kg SO_4 removed.

Calcium carbonate is also formed in the final aerobic polishing process step. Metal sulphides, which precipitate in the SRR also contribute to the total waste sludge production.

2.7 By-products production

Hydrogen sulphide is the main process by-product. This is stripped into a CO_2 gas stream for further processing by either:

- *Oxidation to sulphur; or*
- *Oxidation to sulphate*

2.8 Safety and related aspects

The Biosure process employs potentially hazardous substances (such as phosphoric acid) and flammable substances (such as ethanol). A potentially toxic gas, H_2S, is also produced in the process.

On the small scale of the Demo Plant, no specific automated warning systems were implemented. Demonstration Plant operating personnel were alerted to the potential hazards and precautions were taken to prevent contact with hazardous and flammable materials.

3 FULL-SCALE TREATMENT PLANT CONCEPTUAL DESIGN AND COSTING

The potential application of the treatment technology to a full-scale installation was investigated, based on the interim results of the CSIRosure Demonstration Plant.

The potential application was taken to be one of the three regional mine water treatment facilities proposed by one of the previous Coaltech projects (Task 6.8.2) The specific regional facility is for one of Acid Mine Water in the Brugspruit Catchment, which is projected to have a modular size of 5 Mℓ/day at the following projected average mine water quality:

Conductivity = 560 mS/m
pH = 2.8
TDS = 4 210 mg/ℓ
Calcium = 580 mg/ℓ
Magnesium = 200 mg/ℓ
Sodium = 50 mg/ℓ
Sulphate = 2 530 mg/ℓ
Chloride = 55 mg/ℓ
Iron ≤ 100 mg/ℓ
Aluminium ≤ 20 mg/ℓ
Manganese = 27 mg/ℓ

The conceptual integrated sulphate removal process is shown in **Figure 3-A**.

The conceptual treatment process design was based on achieving the following product water quality targets:

- *Sulphate, $SO_4 \leq 200$ mg/ℓ*
- *pH range 6.5 – 8*
- *Iron ≤ 1 mg/ℓ*
- *Aluminium ≤ 1 mg/ℓ*
- *Manganese ≤ 1 mg/ℓ*

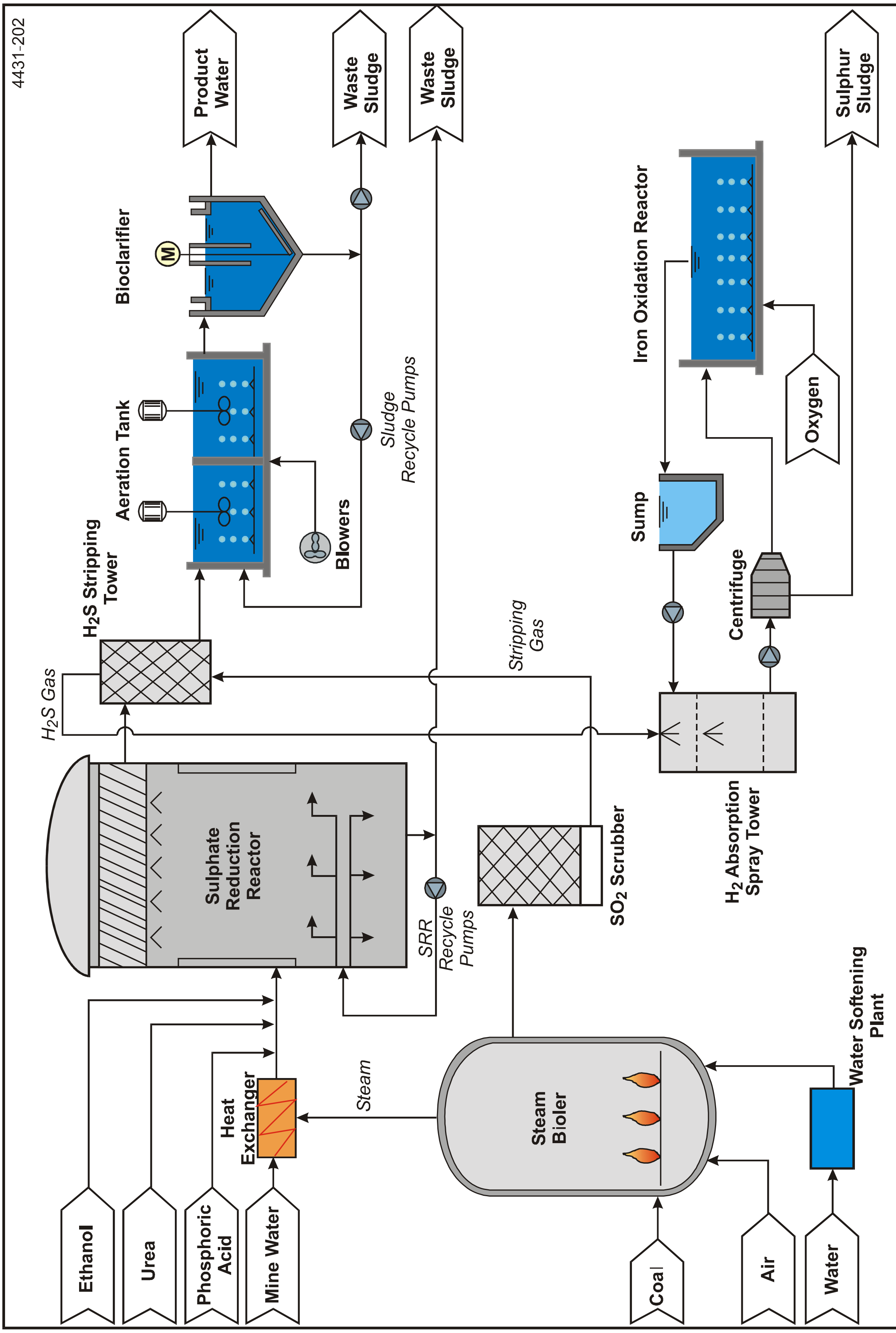


Figure 3 - A : Biological Sulphate Removal Process - Integrated Process Flow Diagram

3.1 Process Design Criteria

3.1.1 Temperature

The temperature will be controlled at 25°C – 30 °C for optimum biological sulphate. The mine water heating requirements would be based on the following seasonal variation in temperature:

Winter = 14°C

Summer = 23°C

3.1.2 Sulphate Reduction Reactors

The sulphate reduction reactor was based on the following hydraulic and sulphate loadings:

HRT = 8 hours

SO_4 = 9 kg SO_4/m^3/day

3.1.3 Sulphide Scrubbers

The sulphate scrubber was designed for the following design loading rates:

- *H_2S volumetric loading = 54 kg H_2S/m^3/day*
- *Hydraulic loading = 26 m^3/m^2/hour*
- *Gas loading = 420 m^3/m^2/hour*

3.1.4 Iron Oxidation Reactors

The sulphide spray tower was designed for the following loading rates:

- *H_2S volumetric loading = 32 kg H_2S/m^3/day*
- *Hydraulic loading = 1.3 m^3/m^2/hour*
- *Gas loading = 150 m^3/m^2/hour*

3.1.5 Iron Oxidation Reactor

The iron oxidation reactor design was based on having pure oxygen available. The following loading rates were used:

- *Hydraulic retention time = 6 hours*
- *Iron oxidation rate = 1.5 kg Fe/m^3/day*

3.1.6 Aerobic Polishing Reactors

The aerobic polishing reactor would be based on the step-feed activated sludge process, using the following design criteria:

- *Aerobic SRT = 4 days*
- *Maximum Biomass concentration = 2500 mg/ℓ*

The bio-clarifier process design criteria would be as follows:

- *Upflow rate = 0,8 m/hour*
- *Solids loading rate = 6 kg/m^2/hour*

3.1.7 Carbon storage and feeding

The conceptual design was based on the use of Ethanol B as carbon source with the following design criteria:

- *Storage capacity = 14 days*
- *COD : SO_4 mass ratio = 1 kg/kg*

3.2 Treatment Process Description

3.2.1 General Process Description

The proposed treatment involves sulphate reduction by anaerobic bacteria to sulphide in the Sulphate Reduction Reactor (SRR) at 25 - 30 °C. The sulphide will then be stripped from the water stream with a CO_2 rich gas, generated during heating of the feed mine water. The effluent from the stripping column will be aerobically polished to remove residual COD. In the aerobic polishing reactor, $CaCO_3$ will be precipitated that can be used as a neutralisation agent.

Therefore, the following processes will take place on the main mine water stream:

- *Heating of the feed water to 25 - 30 °C by combustion of coal*
- *Sulphate reduction in a Sulphate Reduction Reactor combined with integral settling tank*
- *Sulphide stripping with a carbon dioxide/nitrogen gas stream*
- *Aerobic polishing whereby residual solids/organics are removed from the water*

On a side stream, three processes will be employed for the conversion of sulphide in the stripping gas to sulphur. These three processes include:

- *Sulphide rich gas contacted with an iron(III) solution to produce sulphur*

- *Separation of suspended sulphur particles from the water stream with a centrifuge*
- *Iron(II) oxidation back to iron(III)*

Provision is also made to dose a carbon substrate and nutrients to the SRR and Iron Oxidation Reactor, flocculant to the aerobic bioclarifier and the sulphur separation stages, and $CaCO_3$ slurry to the sulphur dioxide-scrubbing column for treatment of the off-gas from coal burning.

The overall process flow diagram is shown in **Figure 3.2.1 (a) - A**. The plant layout is shown in **Figure 3.2.1 (b) – A**.

The individual unit treatment processes are described in some detail in the next sections.

3.2.2 Temperature Control

The optimum operating temperature in the SRR is 25 - 30 °C. The feed water temperature may vary between 14 and 23 °C, therefore, it has to be heated to obtain the optimum temperature for sulphate reduction. A coal-fired boiler will generate steam. The boiler will have a two-fold function:

- *Steam generation to heat the feed mine water*
- *CO2 generation for stripping of H_2S from the SRR effluent*

Steam will be contacted via a shell and tube heat exchanger with the feed mine water. The rate of steam flow will be controlled by the temperature probe in the feed water line. Condensed steam will be recycled to the boiler. If the stripping gas requirement exceeds the heating requirement, more than the required steam will be generated and excess steam will be vented to the atmosphere.

Boiler feed water will be prepared through a boiler feed water treatment plant (softening unit) from either potable water or product water. Only a small make-up stream of boiler feed water will be required, as the condensate is returned to the boiler. Boiler feed water pumps will supply water to the boiler. There will be two (2) pressure relief systems on the steam boiler. One safety relief valve, which will release steam if the pressure goes too high as well as a operational relief valve which will release excess steam if the stripping gas requirement exceeds the heating requirement. The boiler gas will be extracted via fans from where it will pass through the SO_2 scrubbing stage.

Figure 3.2.2 – (A) shows a process flow diagram of the mine water heating system.

Figure 3.2.1 (a) - A

Figure 3.2.1 (b) – A

Figure 3.2.2 – (A)

3.2.3 CO_2 rich gas generation and scrubbing

The CO_2 rich gas will be generated in the steam boiler. The gas will be treated in an SO_2 scrubbing tower, while the excess is released to atmosphere. The stripping gas will be contacted with limestone slurry in the SO_2 scrubber. The limestone slurry will be stored in a limestone day tank equipped with a mixer. Limestone slurry will be supplied from sludge generated in the aerobic polishing reactor. The slurry will be dosed with a dosing pump into the SO_2 scrubbing tower together with make-up water from the product water line. The scrubbing water will be recycled with the SO_2 scrubber recycle pumps. The temperature in the scrubbing tower will be high (>80 °C), depending on the gas temperature and flow. The gas from the boiler will flow through the scrubbing tower and pass through a demister to the H_2S stripping column. A bleed stream will be taken from the scrubbing water circuit through a manual control valve to the waste sludge sump.

3.2.4 Anaerobic Sulphate Reduction

In the anaerobic SRR , sulphate rich mine water is fed together with ethanol-b (a mixture of ethanol - and propanol, sugar and nutrients. Provision is also made to inject steam into the recycle line at a Venturi steam injector. The reactor is inoculated with anaerobic sewage sludge and sulphate-reducing bacteria are selected through operating at the specific environmental conditions. Sulphate is biologically reduced by the anaerobic oxidation of ethanol in a complete mixed reactor or up-flow anaerobic sludge blanket (UASB) system. The relevant chemical reaction for ethanol oxidation and sulphate reduction is:

$$3SO_4^{2-} + 2CH_3CH_2OH \rightarrow 3H_2S + 6HCO_3^-$$

The products of this reaction remain in solution and it is necessary to remove the residual H_2S and alkalinity. The net result is that sulphate is reduced to sulphide and that bicarbonate is produced, which results in an increase in alkalinity.

The reactor can be operated either as an UASB reactor or as a complete mixed reactor. Two sets of inlet nozzles to the reactor make provision for these two options. Recycle pumps will mix the reactor. Sludge is retained by lamella settling plates positioned inside the reactor and baffles will be placed underneath the lamella to prevent turbulence and sludge washout. The overflow channels of the reactor will be capped to prevent H_2S gas escaping to the atmosphere. The SRR off gas will be abstracted with fans, from where it will go to the H_2S stripping tower.

Waste anaerobic sludge can periodically be discharged to the waste sludge sump, where it will be thickened and be available for re-use in the anaerobic reactor.

Figure 3.2.4 - A shows the process flow diagram of the sulphate reduction process.

3.2.5 Sulphide Stripping

The effluent from the SRR reactor is fed to a packed column, where it is contacted with a CO_2 rich gas stream. A counter-current flow configuration will be used. The CO_2 dissolves in the water and replaces the H_2S in solution. H_2S gas is thus transferred to the gas phase. The following reaction takes place.

$$CaS(aq) + 2CO_2(g) + 2H_2O(aq) \rightarrow Ca(HCO_3)_2(aq) + H_2S(g)$$

The stripping columns will consist of tall packed (cross flow media) towers. A demister will prevent the carry-over of aerosols into the gas flow. The released H_2S is a gas and needs to be precipitated in a solid form, because it cannot be vented to the atmosphere.

The water, from which the H_2S stripped, is then further treated to remove residual COD and to precipitate $CaCO_3$.

3.2.6 Aerobic Polishing and Calcite Harvesting

The product from the H_2S stripping column is fed to an aerobic reactor, which is aerated and stirred mechanically.

Residual COD is degraded by aerobic bacteria and CO_2 is produced. The calcium bicarbonate is converted to calcium carbonate and precipitated, as follows:

$$2Ca(HCO_3)_2(aq) + O_2(g) \rightarrow 2CaCO_3(s) + 2H_2O(aq)$$

$$COD + O_2(g) \rightarrow CO_2(g) + H_2O(aq)$$

This will take place in the two aerobic reactor basins. Air will enter the bottom of the reactor through a diffusion system. The solids will also be kept in suspension by mixers, positioned on the aeration reactors.

The aeration basin overflows by gravity to the aerobic bioclarifier. The clarifier will be a centre drive configuration. Sludge will either be recycled or pumped away for disposal.

The limestone sludge produced can be utilized as a neutralization agent.

Figure 3.2.6 – (A) shows a process flow diagram of the aerobic polishing process.

Figure 3.2.4 - A

Figure 3.2.6 – (A)

3.2.7 Sulphide Oxidation

The sulphide rich gas stream is contacted with an iron(III) solution in a spray tower. The recycle Fe III-rich stream, which is pumped from the recycle sump, will be divided into several streams that are sprayed into the different column sections. The H_2S gas will enter the column from the bottom and flow through each column section, counter-current to the water. H_2S is absorbed into the water stream and reacts with the iron(III) according to the following reaction:

$$3H_2S(g) + 6Fe^{3+}(aq) \rightarrow 3S(s) + 6\,Fe^{2+}(aq) + 6H^{+}(aq)$$

The gas stream exits the top column through a demister. Sulphur is produced as a suspension in the iron(III) water stream. The water stream with the suspended sulphur exits the column at the bottom and flows into the centrifuge feed sump – refer to **Figure 3.2.7 - A.**

3.2.8 Sulphur Separation

Sulphur solids will be separated from the water stream by means of a centrifuge. Prior to entering the centrifuge, the water is collected in the centrifuge feed sump. From the feed sump, it is pumped by the centrifuge feed pumps to the centrifuge. The feed pumps will be controlled by an input signal from a level sensor in the feed sump. There will be an overflow from the centrifuge feed sump to the recycle sump. Prior to entering the centrifuge and the centrifuge feed pumps, provision is made to dose a polymer to aid in coagulation of the sulphur particles. In the centrifuge, the solid and liquid phases will be separated and a sulphur cake will be produced – refer to **Figure 3.2.7 - A**.

3.2.9 Iron Oxidation

After the centrifuge, the water stream will enter the Iron Oxidation Reactor. Oxygen will be blown into the reactor. The reactor will be packed with a plastic medium. The following reaction catalysed by bacteria, will take place:

$$4Fe^{2+}(aq) + O_2(g) + 4H^{+}(aq) \rightarrow 4\,Fe^{3+}(aq) + 2H_2O(aq)$$

Figure 3.2.7 – (A)

Provision will also be made to dose urea and phosphoric acid as nutrients for the bacterial action. The water will overflow back into the recycle sump from whence it will be pumped by the recycle pumps to the Sulphide Absorption Spray Columns. A level sensor in the sump will protect the recycle pumps. There will be an overflow from the recycle sump to the sludge sump. The sump will be kept full by means of a product water line and float valve. The make-up ferrous sulphate will also be dosed directly into this sump – refer to **Figure 3.2.7 - A**.

3.2.10 Chemicals Make-Up and Dosing

Chemicals that need to be dosed to the SRR include:

- *Ethanol-b*
- *Sugar*
- *Phosphoric acid*
- *Urea*

Chemicals to be dosed to the Iron Oxidation Reactor are:

- *Ferrous sulphate*
- *Phosphoric acid*
- *Urea*
- *Oxygen*

It will also be necessary to dose polymer to the sulphur separation and aerobic stages and limestone slurry to the SO_2 scrubbing tower.

The make-up and dosing facilities for each of these chemicals include the following:

- ***Ethanol-b***

Delivered by tanker to bulk storage tanks and dosed with dosing pumps. Flow will be measured with a rotameter. The Ethanol dosing will be interlocked with the mine water pumps that will stop pumping, if ethanol dosing ceases.

- ***Sugar***

Sugar will be delivered and stored in bags. It will be manually charged to the sugar make-up tank where it will be dissolved in product water. The make-up tank will be equipped with a mixer. There will be a strainer in the dosing line before the dosing pump from where the sugar solution will go directly into the mine water feed line.

- ***Phosphoric acid***

The phosphoric acid will be delivered in bulk storage delivery containers, from where it will be dosed directly with a phosphoric acid dosing pump into the mine water feed line. Flow will be measured with a rotameter. Phosphoric acid will also be dosed manually into the Iron Oxidation Reactor.

- ***Urea***

Urea will be made up through manual addition of bags into the urea make-up tank. From there it will be dosed into the feed mine water line to the Sulphate Reduction Reactor. It will also be dosed to the Iron Oxidation Tank.

- ***Ferrous sulphate***

Ferrous sulphate will be made up manually in a make-up tank equipped with an agitator, where it will be dosed with the ferrous dosing pumps.

- ***Polymer***

Polymer will be manually made up in the polymer make-up tank, equipped with an agitator, from where it will be dosed to the sulphur stream. A separate polymer make-up and dosing facility will supply polymer to the Aeration Tank.

- ***Oxygen***

Oxygen will be delivered in bulk to the site and injected into the Iron Oxidation Reactor.

- ***Limestone slurry***

Limestone slurry will be supplied from the sludge generated in the Aeration Tank. Approximately 90% of the solids content of this sludge will be limestone.

3.3 Treatment Residue Disposal

3.3.1 Solid Waste Streams

The waste sludge from the Sulphate Reduction Reactor will be collected in the waste sludge sump from where it will be pumped to disposal.

The following table gives the treatment sludge production, based on the average mine water flow quality:

Type of sludge	Production (ton TS/day)
1. Anaerobic waste sludge:	
– Metal hydroxides	1.3
– Biomass	0.2

Type of sludge	Production (ton TS/day)
2. Aerobic waste sludge:	
– Limestone	6.5
– Biomass	0.8
3. Sulphur sludge	3.9
Total	**12.7**

The limestone sludge can be utilized in the further neutralisation of acid mine water streams. The sulphur sludge will be co-disposed with the limestone sludge. The excess alkalinity in the limestone sludge will prevent the onset of the acidic conditions required for sulphur oxidation. The large mass of limestone sludge will also effectively encapsulate the sulphur sludge, thus eliminating oxygen ingress and preventing sulphur oxidation.

3.3.2 Off-Gas Treatment

The off-gas from the Sulphate Reduction Reactor will be extracted with the fans and will be discharged to the H_2S Absorption Spray Tower.

The off gas from the H_2S Absorption Spray Tower will be blown to a depth of 0.5 m below the water surface into the Aeration Tank to capture and oxidise any fugitive H_2S gas, preventing its release to the atmosphere.

3.4 Capital Expenditure

The capital expenditure for the 5000 m^3/day treatment module was estimated based on January 2002 cost indices. The capital expenditure cost estimates was done at an indicative level of accuracy (± 30 %). The capital investment for a specific plant site would be site specific and would depend on the local situation related to:

- *Local geotechnical and founding conditions*
- *Access to the site*
- *Provision of site services such as water, sanitation, electrical power and communications*
- *Infrastructure requirements to deliver the acid mine water to the treatment plant site in terms of pumping, piping and storage*
- *Final disposal of the treatment plant residues and sludges*

The capital cost estimates must therefore be considered in the light of the above qualifications. The capital cost estimate is as follows:

Plant Component	Civil/Building Works	Mechanical Equipment	Electrical/ Instrumentation Equipment
1. Mine water collection and storage	346 000	289 000	249 000
2. Boiler installation with softening plant	41 000	3 168 000	249 000
3. SO_2 scrubber and associated equipment	62 000	459 000	187 000
4. Sulphate reduction reactor and associated equipment	1 954 000	818 000	374 000
5. H_2S stripping tower	62 000	916 000	62 000
6. Aerobic polishing plant	684 000	1 675 000	623 000
7. H_2S Absorption Spray Tower	83 000	3 990 000	343 000
8. Iron Oxidation Reactor	407 000	545 000	93 000
9. Site pipe work and services	122 000	3 326 000	0
10. Project management and engineering	557 000	1 848 000	401 000
Sub Totals	**4 318 000**	**17 034 000**	**2 581 000**
Total (excluding VAT)			**23 933 000**

The total estimated capital cost for a 5 000m^3/day sulphate reduction plant is R23.9 million.

3.5 Operating and Maintenance Costs

The operating and maintenance costs were calculated to include the major components of:

- *Chemicals*
- *Electrical power*
- *Coal energy*
- *Operating personnel and labour*
- *Maintenance and repair*

The operating and maintenance costs reflect the price indices of January 2002.

3.5.1 Chemical Usage

The chemical usage is estimated on the basis of the average mine water flow and load conditions.

The chemical usage is summarised below:

Chemical type	Consumption (kg/day as pure)	Solution (%)	Unit cost (R/kg as chemical)	Daily cost (R/day)
Ethanol	5 024	95	3.2	16 923
Sulphate reduction - urea	122	100	2.35	288
Sulphate reduction – phosphoric acid	49	85	4.5	260
Aerobic polishing – urea	78	100	2.35	184
Aerobic polishing– phosphoric acid	77	85	4.5	410
Aerobic polishing – polymer	5	100	35	175
Sulphide oxidation – ferrous sulphate	184	10	1.26	2 321
Sulphide oxidation – polymer	2	100	35	79
Sulphide oxidation – oxygen	2 157	100	0.65	1 402
Total				**22 043**

3.5.2 Electrical power

The installed power and the power drawn from each major individual mechanical equipment item were estimated. The electrical power cost was estimated using a unit rate of :

R0.12 /kWhr

The estimated installed power and the daily energy cost are summarised below:

Equipment item	Number installed	Installed power kW/unit	Operating hours/day	Daily power cost R/day
Feed water treatment plant	1	25	24	57.60
Boiler feed water pumps	2	17	12	39.17
Boiler	1	37	24	85.25
Off-gas fans	2	7.5	12	17.28
SO_2 scrubber recycle pumps	2	11	12	25.34
Limestone agitator	1	1.5	24	3.46
SRR recycle pumps	3	11	8	25.34
Off-gas fans	2	2.2	12	5.07
Urea make-up tank mixer	1	1.1	4	0.42
Urea dosing pump	1	0.5	24	1.15
Phosphoric dosing pump	1	0.5	24	1.15
Ethanol dosing pump	1	0.5	24	1.15
Sugar make-up tank mixer	1	1.2	4	0.46
Sugar dosing pump	1	0.5	4	0.19

Equipment item	Number installed	Installed power kW/unit	Operating hours/day	Daily power cost R/day
Air blowers	2	110	12	253.44
Absorption gas blowers	1	11	24	25.34
Aeration tank mixers	2	22	24	101.38
Clarifier bridge drive	1	1.5	24	3.46
Sludge recycle pumps	2	11	12	25.34
Limestone sludge pumps	2	11	12	25.34
Centrifuge feed pumps	2	30	12	69.12
Centrifuge	1	55	24	126.72
Spray tower recycle pumps	2	17	12	39.17
Oxygen dissolution mixer	1	11	24	25.34
Waste sludge sump mixer	1	4.5	24	10.37
Waste sludge pumps	2	22	12	50.69
Total				**1 018**

3.5.3 Coal energy

The estimated coal consumption and cost are as follows:

- *Coal usage = 5 ton/day*
- *Unit cost = R100/ton pebble coal*
- *Daily cost = R500/day*

3.5.4 Operating personnel and labour

The cost associated with operating personnel and labour was based on a reasonable assessment of the staffing requirements for a treatment plant. The proposed categories of operating personnel and labour and associated monthly cost are summarised below:

Personnel Category	Number	Unit Cost (R/Month)	Monthly Cost (R/Month)
Plant superintendent	1	9 000	9 000
Process operators	4	6 500	26 000
Process assistants	2	4 500	9 000
Labourers	5	2 000	10 000
Total cost			**54 000**

3.5.5 Maintenance cost

Planned and preventative maintenance and associated repair work are costed as a fraction of the capital investment into different components of the plant. The estimated annual maintenance cost is summarised below:

Infrastructure component	**Capital expenditure** **R**	**Annual allowance for maintenance** **%**	**Annual maintenance cost** **R/year**
Civil & building works	4 318 000	0.5	21 600
Mechanical equipment	17 034 000	2	340 700
Electrical & instrumentation	2 581 000	3	77 400
Total	**23 933 000**		**439 700**

3.5.6 Operating and Maintenance Cost Summary

The different operations and maintenance cost component are summarised as follows:

Cost component	**Daily cost** **(R/day)**	**Unit cost** **(R/m^3)**
1. Chemicals	22 043	4.41
2. Electrical power	1 018	0.20
3. Coal	500	0.10
4. Operating personnel	1 775	0.35
5. Maintenance	1 205	0.24
Total	**R26 541**	**5.30**