

Technical Article

Treatment of Acid Leachate from Coal Discard using Calcium Carbonate and Biological Sulphate Removal

J. P. Maree¹, G. Strobos¹, H. Greben¹, E. Netshidaulu¹, E. Steyn¹, A. Christie², P. Günther², and F. B. Waanders³

¹CSIR, Water, Environment and Forestry Technology, P O Box 395, Pretoria, 0001, South Africa; ²S A Coal Estate, Anglo Coal, P O Box 2851, Witbank, 1035, South Africa; ³Director: School of Chemical and Minerals Engineering, North West University (Potchefstroom campus), Potchefstroom, 2531, South Africa (e-mail: jmaree@csir.co.za)

Abstract. An integrated approach is proposed for treating acidic coal discard leachate, consisting of CaCO_3 handling and dosing, CaCO_3 -neutralization, and biological sulphate removal. It was found that: powdered CaCO_3 can be slurried to a constant density and used to neutralize the acid water, remove Fe (II), Fe (III), and Al, and partially remove the sulphate (to saturation level); biological sulphate removal can be used to lower the sulphate to less than 200 mg/L using ethanol as the carbon and energy source; CO_2 produced during calcium carbonate treatment can be used for H_2S -stripping and; H_2S gas recovered in the sulphate removal stage can be used for iron removal.

Key words: Biological sulphate reduction; calcium carbonate; coal discard leachate; CSIR; ethanol; gypsum precipitation; iron oxidation; limestone; sulphide removal

Introduction

Since 1996, extensive research and development work has been carried out at the Navigation Section of Landau Colliery near Witbank to address problems associated with the leachate from raw coal and coal discard, including the high cost of neutralisation, the high maintenance cost in the coal processing and lime neutralization plants due to acid corrosion and scaling of equipment, and the desalination of the effluent water that is discharged into public streams.

Water is used in the coal processing plant to separate coal from waste, to grade the coal into different particle size fractions, and for dust suppression. Water leaving the processing plant contains slimes (fine coal), which are settled in a thickener. The slurried slimes are pumped to the centre of a waste dump; coarse coal discard is transported on a belt conveyor and placed around the perimeter to contain the slimes. Decanted water is returned via the penstock to the coal processing plant. Some of this water seeps through the discard dump and, together with rainwater, is collected in cut-off trenches at the base of the dump. The seepage is stored in a toe dam. A portion of the toe dam water is combined with the penstock water and other slightly polluted water prior to treatment in a primary liming plant.

In this operation, 20 000 ton per day (t/d) of raw coal is mined to produce 15 500 t/d of final product, 3 000 t/d of coal discard, and 1 500 t/d of slimes (fine coal). The dump has an area of 72.5 ha (25.6 ha under slimes and 46.9 ha under discard) and a height of 12 m. The dump contains an estimated 2.4 million tons of slimes and 4.3 million tons of discard, with the latter containing 2% pyrite (as S). The discard is responsible for most of the pollution. A number of studies have been conducted at this site since 1996 to characterize the nature and extent of pollution. The key findings were:

- Chemical leaching studies showed that 0.33 g of acid (as CaCO_3) is leached from each kg of coal.
- The rate of biological oxidation of pyrite under laboratory conditions was determined to be 148 mg of acid (as CaCO_3)/(kg·d).
- Modelling of the water network indicated that 24.1 t/d of sulphate enters the water network: 7.3 t/d originates from the feed water, 5.8 t/d from the raw coal and 11 t/d from the coal discard. Sulphate leaves the system through gypsum precipitation (11 t/d during toe seep water neutralization, 0.2 t/d in the primary neutralization plant, 4.5 t/d in the coal processing plant, and 3.2 t/d in the penstock) or with the seepage (5.1 t/d). A portion of the sulphate crystallizes out in the coal processing plant as scale on equipment, such as spirals, sieves, and pipelines, as well as on magnetite used in the separation process.
- Electron microscope studies have shown that needle-like gypsum crystals develop on the magnetite particles and interfere with the recovery of magnetite at the magnetic separators.
- The gypsum over-saturation index (OSI – values shown in brackets) indicates the likelihood of gypsum scaling (Maree et al. 2004b). The water in the coal processing plant (1.47), the thickener overflow (1.23), and the neutralization plant (1.07) are oversaturated with respect to gypsum; the return water from the penstock has an OSI of 0.99. The latter value reflects gypsum crystallization that has taken place.
- The cost of neutralization could be reduced from R0.57/m³ (1 US\$ = SA R6.50, June 2004) to R0.16/m³ by replacing unslaked lime (utilization efficiency = 60%,

purity = 90%, price = R550/t) with powdered CaCO_3 (utilization efficiency = 90%, purity = 75%, price = R110/t) (Maree et al. 2004a).

- Modelling showed that the capital cost associated with neutralization and gypsum crystallization of 40 m^3/h discard leachate with an acidity of 11.5 g/L, could be reduced from R10.3 million to R3.0 million by treating streams with high pollution loads separately from streams with low pollution loads. The total volume of the less polluted streams is 3 ML/d. Only slightly lower gypsum removal is achieved this way, 8.9 t/d versus 9.5 t/d (Maree et al. 2004b).
- A modelling exercise showed that 30% of the over-saturated fraction in the primary neutralization plant and 60% in the coal processing plant crystallizes out as gypsum (Maree et al. 2004b).
- A flow of 210 m^3/h needs to be treated for the removal of sulphate to 350 mg/L in order to obtain an OSI value of 0.98 (less than 1) in the coal processing plant. A biological sulphate removal plant with this capacity has an estimated capital cost of R11.6 million (R2.3 million/(ML/d)) and a running cost of R2.54/ m^3 (Maree et al. 2004b).

Approach

As a result of these investigations and observations, an integrated process was proposed for the treatment of the site's coal discard leachate, consisting of the following stages (Figure 1):

- CaCO_3 handling and dosing system
- CaCO_3 -neutralization, which includes iron oxidation and precipitation, and neutralization
- Heating unit (not shown in Figure 1)
- Biological sulphate removal, which includes biological sulphate reduction, H_2S -stripping, aerobic treatment for removal of residual organic material, and CaCO_3 -precipitation.

This approach offers the following benefits:

- The cheapest alkali, a by-product from the paper industry, is used for neutralization of the acid and for the removal of the bulk of the sulphate concentration through gypsum crystallization. The more advanced biological process is then used only for removal of the remaining sulphate, to low concentrations.

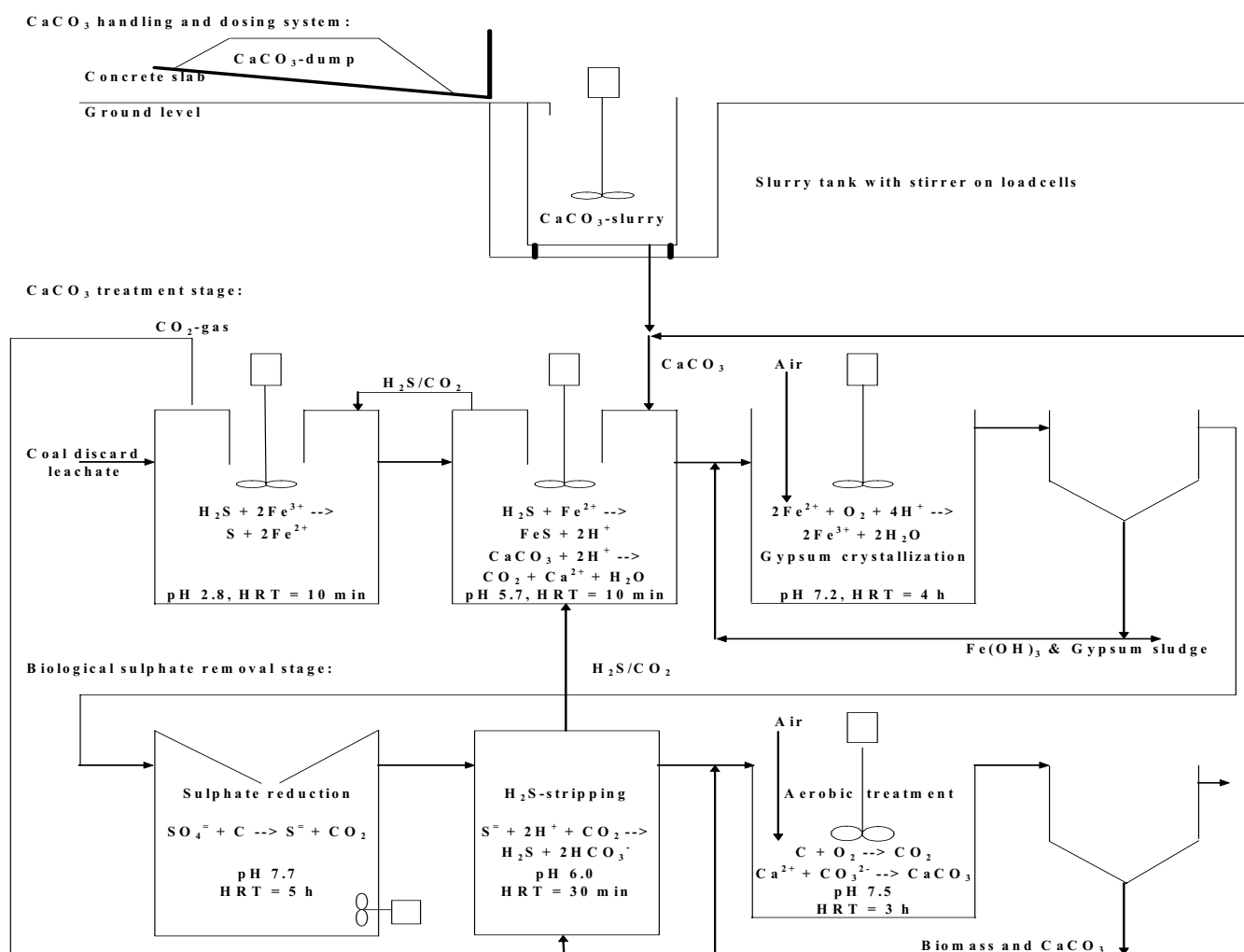


Figure 1. Process flow diagram for the treatment of coal discard leachate

- A robust biological process is used for sulphate removal to produce water suitable for use as process water that is non-scaling and suitable for discharge into public streams.
- This is an integrated process as CO_2 produced during CaCO_3 -neutralization is used for H_2S -stripping in the biological stage. The stripped H_2S -gas is transported to the CaCO_3 -neutralization stage for precipitation of iron as iron sulphide, followed by iron oxidation and precipitation of inert $\text{Fe}(\text{OH})_3$ and gypsum in the CaCO_3 -neutralization stage.

This paper addresses:

- Performance of the full-scale CaCO_3 handling and dosing system.
- Pilot-plant evaluation of CaCO_3 neutralization of the acid leachate.
- The energy utilization efficiency when feed water is contacted directly with hot coal gas.
- Pilot-plant evaluation of a biological sulphate removal plant with a capacity of $400 \text{ m}^3/\text{day}$.

Materials and Methods

Analytical

Samples were filtered through Whatman #1 filter paper. Sulphate, sulphide, alkalinity, calcium, Fe (II), mixed liquor suspended solids, volatile suspended solids, acidity, and pH determinations were carried out manually according to procedures described in Standard Methods (American Public Health Association 1985). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. The samples being analyzed for chemical oxygen demand (COD) were pre-treated with a few drops of H_2SO_4 and N_2 to strip off H_2S gas.

Feedstock

Powdered CaCO_3 , a by-product from the paper industry, was used for neutralization of acid water. It contained 25% moisture and 10% impurities (dry mass), which was mainly silica. Coal discard leachate or a synthetic solution of similar chemical composition was used as water for the CaCO_3 neutralization stage. The biological sulphate removal stage was fed with effluent from a lime neutralization plant at a rate of 8 to $16 \text{ m}^3/\text{h}$ (hydraulic retention time of 10.3 to 5.2 h), while 0.1 to 0.2 g sugar/L mine water, 0.7 to 1.0 mL ethanol B (75% ethanol, 25% propanol)/L mine water were added as the carbon and energy source. Ammonium sulphate (25 mg/L (as N)) and phosphoric acid (5 mg/L (as P)) were added to maintain the COD:N:P ratio at 1000:7:2. No trace

elements, except for 3 mg/L Fe (II), were added, as the mine feed water contains all trace elements required by sulphate-reducing bacteria. The heating unit was fed with 25 mm coal.

Equipment

The four stages of the integrated process were studied separately.

The CaCO_3 - *handling and dosing system* (Figure 2) was evaluated on the first full-scale plant of its kind. It has a capacity of 23 t/d CaCO_3 . The plant has a sloped concrete slab onto which CaCO_3 powder is dumped and stored. The CaCO_3 powder is slurried with a water jet and collected in a slurry tank by gravity flow. A ball valve in the slurry tank maintains the water level at a specific height.

- A recycle slurry pump that withdraws CaCO_3 of higher density from the slurry tank or clear water through a water jet onto the CaCO_3 dump to maintain a constant CaCO_3 concentration. The slurried CaCO_3 is returned by gravity via the sloped concrete slab back to the slurry tank. The CaCO_3 concentration is controlled by the load cells underneath the slurry tank, which activate/stop the recycle pump at preset low/high values.
- A transfer pump, feeding slurried CaCO_3 to the neutralization reactor.

The CaCO_3 *neutralization stage* consists of a fluidised-bed reactor and a sludge separator (Table 1). Compressed air was used for iron oxidation.

The *heating unit stage* consists of: coal bunker, a speed control spiral feeder (100 kg/h), a heating unit, and a fan and water spray reactor where feed water is sprayed through 3/8 inch (1 cm) spiral jet nozzles while hot air is flowing upwards (Figure 3).



Figure 2. Limestone handling and dosing system



Figure 3. Heating unit

For the *biological sulphate reduction stage*, only the anaerobic (Figure 4) and H₂S-stripping sub-stages were evaluated on-site, as the other processes, e.g. Fe (II) precipitation with H₂S and the aerobic treatment for removal of residual organic material and CaCO₃ precipitation were known. The latter were therefore only tested in the laboratory. The anaerobic reactor consists of a completely mixed reactor (diam. = 4 m, height = 8 m, volume = 105.5 m³) with a cone in the top of the reactor to allow for sludge separation (Maree et al. 2001).

The feed rate to the anaerobic reactor was 8 to 16 m³/h and 0.3 m³/h to the H₂S-stripping stage. The reactor contents were stirred with a side entry stirrer positioned at the bottom of the reactor (260 rpm) and additional mixing was provided by a recycle pump (35 m³/h). The feed inlet pipe entered the reactor at the top from where it fed to the bottom. The reactor was inoculated with 10 m³ anaerobic digester sludge from Daspoort Sewage Works Pretoria on 6 May 2000. The temperature was approximately 17 °C.

Table 2 shows the dimensions of the two reactors operated in series used for sulphide stripping. Silica stones were used as the medium in Reactor 1, while Rashig rings were used in Reactor 2. In Reactor 1, the medium was submersed, while water trickled over the medium in Reactor 2.

Experimental

The performance of the various stages (CaCO₃ neutralization, sulphate reduction, and H₂S-stripping) was evaluated by determining the chemical composition of the feed and treated water during continuous operation.



Figure 4. Anaerobic stage of biological sulphate removal

Table 1. Dimensions of CaCO₃ neutralization pilot plant

Parameter	Value	
	Fluidised bed	Solids separation
Feed rate (L/h)	24	24
Recycle rate (L/h)	200	200
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m ² /m ³)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

Table 2. Dimensions of H₂S-stripping reactors

Parameter	Value	
	Reactor 1	Reactor 2
Diameter (m)	0.50	0.19
Height (m)	0.50	2.20
Medium height (m)	0.37	2.00
Medium	Silica stone	Rashig rings
Medium description	Submersed	Trickling
Empty volume (m ³)	0.098	0.062
Medium volume (m ³)	0.073	0.057
Feed rate (L/min)	5.00	5.00
CO ₂ feed rate (L/min)	1 to 2	1 to 2
HRT (min)	19.6	12.5

Results and Discussion

CaCO₃ handling and dosing system

Acidic water was neutralized effectively when powdered CaCO₃ was used (see schematic section of dosing system in Figure 1). The pH was raised from 2.9 to 6.5, acidity was reduced from 650 to 50 mg/L and iron(II) from 110 to less than 28 mg/L when 20% excess CaCO₃ was dosed. Initially problems were experienced with blocked feed and recycle pipelines as a result of grit and stone in the CaCO₃. The recycle

pipeline problem was solved by installation of a sieve in the slurry tank opposite to the inlet of the recycle pipe. Grit and stones were prevented from entering the feed line by installation of a grit separator. This unit consists of a pipe (diameter = 450 mm, length = 1.2 m) positioned vertically in the reactor with its upper end above the water level. The inlet of the feed pipe was moved from the bottom of the slurry tank to inside this pipe at a level of 800 mm below water level. This arrangement ensured that the up-flow velocity in the unit was high enough (20 m/h) to keep the fine CaCO_3 particles in suspension but low enough to allow settlement of all unwanted larger particles (coal, sand, grit and stones) before reaching the inlet of the feed line.

CaCO_3 neutralization of coal discard leachate

Limestone can be used in the integrated process for treatment of acid water. Table 3 shows the results obtained when synthetic discard leachate was treated with limestone (Maree et al. 2004c). The water was neutralised effectively and sulphate was reduced from 8 342 to 1 969 mg/L (as SO_4). It was possible to achieve complete Fe (II) oxidation by using only CaCO_3 as the neutralization agent. This differs from the standard approach where the pH is raised to 7.2 with lime where the rate of Fe (II) oxidation is fast. By using CaCO_3 , the pH of the water remains at 6 while Fe (II) is oxidised.

In this investigation, it was determined that the rate of Fe (II) oxidation is not only influenced by the Fe (II), hydroxide, and oxygen concentrations as suggested

Table 3. Chemical composition of feed (synthetic discard leachate) and CaCO_3 treated water.

Parameter	Feed	Treated
pH	1.8	6.6
Acidity (mg/L CaCO_3)	7 300	100
Sulphate (mg/L SO_4)	8 342	1 969
Ortho phosphate (mg/L P)	2.9	0.0
Chloride (mg/L Cl)	27	30
Fe (II) (mg/L Fe)	2 500	<56
Total iron (mg/L Fe)	2 500	<56

Table 4. Chemical composition of feed and treated water during 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
Mixed liquor suspended solids (mg/L)	0	13 000
SO_4 reduction rate (mg SO_4 /(L·d))	12.0	12.0

by Stumm and Lee (1961), but also by the suspended solids concentration, as suggested by Maree et al. (1998). In order to achieve complete Fe (II) oxidation, sufficient reaction time was allowed for gypsum crystallization to reach its saturation level (2 h). Aeration and sludge recirculation maintained a suspended solids concentration at 50 g/L.

Biological sulphate removal

The feed rate of the reactor varied between 8 and 16 m³/h, during a period of 300 days of continuous operation, which corresponded with a hydraulic retention time of 5.2 to 10.3 h, respectively. Table 4 shows the chemical composition of the feed and treated water.

It was noted that:

- Sulphate was removed consistently down to 200 mg/L when sufficient carbon and energy source was provided.
- Ethanol was completely utilized for either sulphate reduction or acetate production as indicated by measurement of ethanol and fatty acids. Almost no formate and propionate were formed during sulphate reduction.
- The sulphide concentration in the effluent was stoichiometrically equivalent to the sulphate concentration. The high sulphide concentrations measured in the anaerobic reactor indicated that the sulphate-reducing bacteria can achieve high sulphate reduction rates despite the high sulphide concentrations. This is contrary to the findings of McCartney and Oleskiewicz (1993) who found that sulphate reduction is inhibited by sulphide concentrations higher than 300 mg/L (as S).
- The sulphate removal rate increased to 12 g SO_4 /(L·d) at a temperature of approximately 20°C, and an HRT of 6 h. This rate may improve still further by increasing the temperature of the feed water. Good sulphate removal rates were achieved despite the fact that the most simple and cost-effective reactor type was used. This was achieved by installation of a settler in the top of the completely-mixed reactor to allow sludge separation. This design allowed for reduced capital cost without compromising on the residence time. Sulphate removal could still be achieved within 6 hours.

An $\text{Alk}_{\text{produced}}/\text{SO}_{4\text{removed}}$ -ratio = 1.0 was measured, which corresponds well with the theoretical ratio of 1.04 (Reactions 2 or 3). Alkalinity values as high as 2000 mg/L were measured with an equal reduction in the sulphate content.



▪ The biomass distribution was uniform, bottom to top, in the reactor. During the start-up period more sludge occurred in the lower part of the reactor due to the presence of heavy chemicals and gypsum. The biomass concentration increased from 2 500 mg/L on at the start of the period to 10 000 mg/L where it stabilized. The specific biomass production was calculated to be 0.02 g biomass/g SO_4 removed.

Figure 5 shows the percentage sulphate removal and the $\text{COD}_{\text{feed}}/\text{SO}_4$ ratio with time. Sulphate removal increased from between 30 % and 50 % during the period before day 48 to above 75% after day 48 (Figure 2, sulphate line). The improved sulphate removal with time can be ascribed to the increased value for the $\text{COD}_{\text{feed}}/\text{SO}_4$ ratio with time (Figure 2, $\text{COD}_{\text{feed}}/\text{SO}_4$ line). Before day 48, this value was lower than the theoretical value of 0.67 (Reactions 2 or 3: $2\text{C} \equiv 2\text{O}_2 \equiv 1 \text{SO}_4$; $24 \text{ g C} \equiv 64 \text{ g O}_2 \equiv 96 \text{ g SO}_4$). Thereafter, this value increased to between 0.8 and 1.2 (except for the period around day 135 when the ethanol feed pump failed).

The utilization efficiency of the energy source (ethanol and sugar) and its cost are calculated in Table 5.

It was noted that:

- At a dosage of 0.1 g/L sugar and 0.72 g/L ethanol B (75 % ethanol + 25 % propanol), 2.0 g/L sulphate was removed. This represented a utilization efficiency of 75%.
- The measured COD value of 1.75 g/L (as O_2) agreed well with the calculated value of 1.78 g/L (as O_2).
- The energy source cost associated with the removal of 2.0 kg/ m^3 sulphate amounted to R2.22/ m^3 . This cost could be reduced further should by partial replacement of ethanol and sugar with carbon monoxide. Carbon monoxide could be recovered when coal off-gas is used for heating of feed water.

Heating of feed water

The plant was operated at a flow rate of 9 m^3/hr and an average water inlet temperature of 15°C. The feed water was effectively heated from 15°C to 30°C. Heat transfer from the gas to the water was more than 99% effective. The exit temperature of the gas was approximately equal to the inlet temperature of the water. The heat transfer from the coal to the water was approximately 75 to 90 %. Heat losses were due to incomplete combustion of coal and disposal of hot ash. Figure 6 shows the total heat transfer efficiency in the period August to September 2003.

Table 6 gives a summary of the energy balance over the direct contact heat exchanger column. It can be

seen that the spray column is a very effective configuration to establish heat transfer. Due to back mixing, the column allows complete heat transfer between the water and the gas.

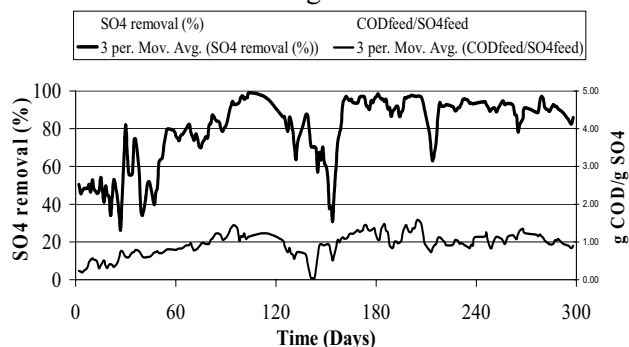


Figure 5. Percentage sulphate removal over a period of 9 months, compared with the ratio of the chemical oxygen demand of the influent water (COD_{feed}) to the SO_4

Table 5. Comparison between measured and calculated chemical oxygen demand (COD) values

Parameter	Energy source			Total
	Sugar	Ethanol B	Propanol	
Dosage (g/L)	0.1	0.72		0.10
Purity (%)	100	75	25.00	
Dosage (g/L)	0.1	0.54	0.18	0.82
COD value (g O_2/g)	1.12	2.09	2.40	
COD (g O_2/L) (calculated)	0.11	1.13	0.43	1.67
COD (g O_2/L) (measured)				1.75
SO_4 equivalent (g/L)				2.51
SO_4 removed (g/L)				2.00
COD utilization efficiency (%)				80
Carbon source price (R/t)	2384	2750		
Carbon source cost (R/ m^3)	0.24	1.98		2.22

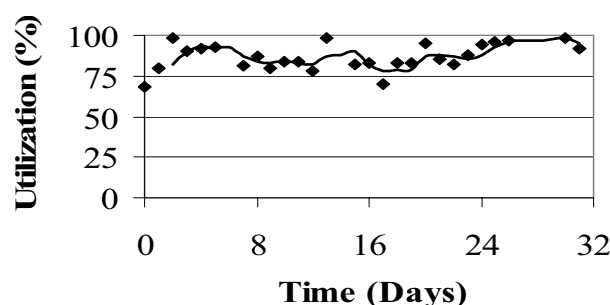


Figure 6. Total heat transfer efficiency in the period 17 August to 20 September 2003

Table 6. Energy balance over the direct contact heat exchanger column

Parameter	Value
Feed rate (m^3/h)	9
Temperature increase ($^{\circ}\text{C}$)	11
Gas temperature inside furnace ($^{\circ}\text{C}$)	365
Temperature of exit gas ($^{\circ}\text{C}$)	17
Coal feed (kg/h)	17
Energy load feed (kJ/h)	470400
Energy absorbed (kJ/h)	426995
Efficiency (%)	89

Table 7. Determination of the flow rate ratio of CO₂-gas to H₂S-rich water required for complete H₂S-stripping, with water fed at 5 L/min, CO₂ fed at 1 L/min, and H₂S set at 364 mg/L S and at 80 mg/L S after Reactor 1

Parameter	Exp No			
	1	2	3	4
HRT (min): Reactor 1	19.6	19.6	19.6	19.6
Reactor 2	12.5	12.5	12.5	12.5
H ₂ S after Reactor 2	0	62	8	0
CO ₂ into Reactor 2 (L/min)		0.1	0.3	0.5
CO ₂ feed (mmol/min)	44.6	49.1	58.0	67.0
H ₂ S removed	8.9	9.4	11.1	11.4
CO ₂ /H ₂ S-ratio	5.03	5.20	5.22	5.89

Sulphide removal

Sulphide can be removed through direct conversion of sulphide to sulphur in the anaerobic reactor by controlled oxygenation or by H₂S-stripping downstream of the anaerobic reactor. The disadvantage of the former option is that sulphur needs to be separated from the water in order to prevent back oxidation to sulphate. Care should be taken to avoid any introduction of air into the process as this will result in sulphide oxidation. Another attractive technology is removal of sulphide by stripping with CO₂-gas. This is a feasible option, provided that CO₂-gas is available (e.g. gas from the aerobic stage or CO₂-gas produced during limestone neutralization of acid water or from coal when the feed water is heated).

Table 7 shows that sulphide is removed effectively from the effluent of the anaerobically treated water by passing it through two stripping units in series. Sulphide can be reduced from 364 mg/L (as S) down to 0 mg/L when the molar ratio of CO₂-gas to sulphide in solution exceeds 5.9.

Aerobic treatment

Laboratory studies showed that the residual organic material in the effluent from the H₂S stripping stage can be removed to less than 30 mg/L (as O₂).

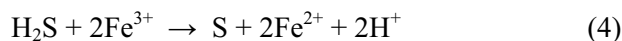
H₂S processing

H₂S-gas recovered from the anaerobic stage can be processed effectively by contacting it with discard leachate that is rich in Fe (II) and Fe (III). Table 8 shows the effect obtained when H₂S is contacted with untreated discard leachate at pH 2.8 and with CaCO₃ treated leachate at pH 5.7. It is noted that at a low pH of 2.8, the Fe (II) concentration increases as a result of sulphur production (Reaction 4), while at a pH of 5.7, it decreases due to FeS precipitation (Reaction 5).

Table 8. Treatment of H₂S-rich gas with iron-rich discard leachate

Condition	Iron(II) (mg/L)	
	Feed	Treated
Discard leachate		
Low pH (2.8)	4 189	7 316
Neutral pH	3 910	1 229

By passing H₂S gas through discard leachate at low pH followed by discard leachate at pH 5.7, as suggested in Figure 1, sulphur and FeS, respectively, are formed as products from H₂S. The S and FeS and residual Fe (II) in the discard leachate, are oxidised to Fe (III) and H₂SO₄ in the Fe (II)/gypsum crystallization reactor to form inert products, namely, ferric hydroxide and gypsum, after neutralization with CaCO₃.



This approach offers the following benefits:

- Small reactor vessels are required as the reactions are fast.
- Only inert sludges are produced, namely ferric hydroxide and gypsum. The mass of sludge is low. By treating 3 MI/d of sulphate rich water for the removal of 1 500 mg/L sulphate, the gypsum production amounts to 8.1 t/d. This is insignificant when compared to the coal waste production of 4 500 t/d.
- Sufficient Fe (II) and Fe (III) are available in the discard leachate for processing of the H₂S (6.0 t/d iron (as SO₄) while only 4.5 t/d iron (as SO₄) is required.

Conclusions

1. Calcium carbonate powder can be slurried to a constant density and used to treat acid water, despite elevated levels of Fe (II). The water can be completely neutralized, precipitating (Fe (II), Fe (III) and aluminium), and lowering sulfate concentrations (to saturation level).
2. The biological sulphate removal process can be used for removal of sulphate to less than 200 mg/L using ethanol as the carbon and energy source. Feed water to the biological stage can be contacted directly with hot coal gas to increase the temperature to 25 °C.
3. CO₂ produced during calcium carbonate treatment can be used for H₂S-stripping and H₂S gas recovered in the sulphate removal stage can be used for iron removal.

Acknowledgements

We sincerely thank the following organisations for their financial and logistical support of the research reported in this paper:

- Anglo Coal (Navigation Section of Landau Colliery), which provided financial support, the necessary infrastructure at the mine, and general assistance.
- The National Research Foundation, which provided funding through their Technology and Human Resources for Industry Programme for CSIR projects on neutralisation and sulphate removal.
- The CSIR who provided substantial financial support for the research programme.

References

American Public Health Assoc (1985) Standard Methods for the Examination of Water and Wastewater. 12th Edition, American Public Health Assoc, NY

Maree JP, de Beer M, Strydom WF, Christie ADM (1998) Limestone neutralisation of acidic effluent, including metal and partial sulphate removal. Proc, International Mine Water Assoc Symp, Johannesburg, South Africa, 6 - 13 Sept, p 449-460

Maree, JP, Strobos, G, Greben, H, Günther, P and Christie ADM (2001) Biological treatment of mine water using ethanol as energy source. Conf on Environmentally Responsible Mining in South Africa, Muldersdrift, South Africa, 25 – 28 Sept

Maree JP, de Beer M, Strydom WF, Christie ADM, Waanders FB (2004a) Neutralizing coal mine effluent with limestone to decrease metals and sulphate concentrations. *Mine Water and the Environment* 23(2): 81-86

Maree JP, Günther P, Strobos G, Waanders FB (2004b) Optimization of effluent treatment at a coal mine by process modelling. *Mine Water and the Environment* 23(2): 87-90

Maree JP, Hagger MJ, Strobos G, Hlabela, P, Cronje H, van Niekerk A, Wurster, Nengovhela R, and Waanders FB (2004c) Neutralization of acid leachate at a nickel mine with limestone. *Mine Water and the Environment* (in this issue)

McCartney DM, Oleszkiewicz JA (1993) Competition between methanogens and sulphate reducers: effect of COD: sulphate ratio and acclimation. *Wat Environ Res* 65: 655-664

Stumm W, Lee GF (1961) Oxygenation of ferrous iron. *Ind Eng Che* 53(2): 143 – 146

Received June 17, 2004; accepted September 4, 2004