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Recovery of Drinking Water and By-products from Gold Mine Effluents

SOLLY MOTAUNG*,**, JANNIE MAREE*, MARINDA DE BEER**,
LUCKY BOLOGO*,**, DIEKS THERON† & JACOBIN BALOYI**
*Tshwane University of Technology, Pretoria, South Africa; **Natural Recourses and the Environment Operating Unit, CSIR, Pretoria, South Africa; †Sulphide Tech, Pretoria, South Africa

ABSTRACT *South Africa is a water constrained country with a large mining industry. Effluents from the mining industry, which is rich in calcium sulphate, resulted in salination of the limited amount of surface water. South Africa is also a large importer of sulphur because it is required for the manufacture of sulphuric acid. It is argued that importation of sulphur can be replaced by recovering it as a by-product during treatment of sulphate-rich effluents. The removal of acid, metals and sulphate from mine water was assessed using the CSIR ABC (Alkali-Barium-Calcium) Desalination process. The CSIR ABC Desalination process was used for neutralization and removal of the total dissolved solids content from 7600 to 400 mg/l. Metals were removed effectively through precipitation with CaS or* $Ca(HS)_2$*. The latter compound had a high solubility with higher metal removal rates compared to CaS. Sulphate remained in solution during metals precipitation with sulphide. The rate of sulphate removal during gypsum crystallization was influenced by the gypsum seed crystal content. The rate of sulphate removal during* $BaCO_3$ *treatment was influenced by pH,* $CaCO_3$ *solids and* $BaCO_3$ *solid concentration.* $Ca(HS)_2$ *was produced from CaS by passing* CO_2 *through a CaS slurry. Further* CO_2 *additions resulted in* H_2S*-stripping.* $BaSO_4$ *and* $CaCO_3$ *were converted simultaneously to BaS and CaO, respectively. The optimum temperature was 1050°C. The cost of raw materials for the treatment of water with a TDS content of 7 600 mg/l amounted to R2.21/cubic metre* (m^3)*. The potential value of the water and by-products amounted to R11.10/*m^3 *(US$1.00 = ZAR7.60).*

Background

In 1886 gold was discovered in South Africa. In the first 70 years of mining, regulations controlled mining activities. Water is pumped to the surface to enable deep underground mining. This water is generally acidic as it is produced when pyrites in the ore is exposed to air and water in the presence of iron oxidising bacteria. The National Water Act of 1956 (Department of Water Affairs and Forestry, 1956) was the first to regulate the discharge of mine water into public water courses. This was followed by the Fanie Botha Accord (1970), the Minerals and Petroleum Resources Development Act (MPRDA) (2002) and the current National Water Act (DWAF, 1998). The first neutralization plant to neutralize acid water from the ERPM mine was constructed in 1975 by Rand Mines. Permits were

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Correspondence Address: Jannie Maree, Tshwane University of Technology, Private Bag X680, Pretoria, South Africa. Email: mareej@tut.ac.za

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issued to discharge neutralized water, without desalination, into public water courses. However, as mines were closed down the pumping of water from underground to surface was terminated and water gradually filled the voids left by mining activities.

South Africa's Witwatersrand basin produces 340 million l/d of mine water, of which 50 million l/d is produced by the western basin. All the underground mining operations in the Western Basin had been closed by 1990. Figure 1 shows the position of the Western Basin. By 2004 the voids were filled and acid water started to decant. Contaminated void spaces increase with time and result in: (1) less water suitable for irrigation of crops; (2) less potable water available for local growing communities; (3) the natural drying up of river; and (4) stream bed losses. The water of mining origin in the western basin contains on average 4 800 mg/l sulphate, 800 mg/l iron(II), 100 mg/l iron(III), 230 mg/l manganese, 11 mg/l zinc, 18 mg/l nickel, 5 mg/l cobalt, 6 mg/l aluminium, 150 mg/l magnesium, some radio activity and 700 mg/l free acid (as $CaCO_3$). This acid water source creates two concerns. First, the Cradle of Humankind, World Heritage Site, is in close proximity to the decant point. Second, acid mine drainage (AMD) will flow into the Krugersdorp Nature Reserve and possibly even the Sterkfontein Caves which is the location where the earliest known hominid fossil remains were discovered.

In South Africa it is essential that a technically sound and cost-effective solution be found for the acid mine water problem. South Africa is water constrained and also has a mature mining economy with numerous mines having closed or in the process of closing down. The situation is made more complex by groundwater management units not cooperating with surface water counterparts unit at the decant points. This has an IWRM dimension on account of activities in the Orange River (Upper Vaal) Basin reporting to the Limpopo Basin via the decant. Another aspect is the fact that the problem falls between government agencies that are each unable to solve it alone. Should a technical solution be found that generates income, the acid mine water problem could be solved via economic principles rather than through government intervention via policies and legislated control measures.

In order to find a solution to this complex mine water problem, several initiatives have been launched:

(1) CSIR, with financial support from the Technology and Human Resources Industry Programme (THRIP) of the National Research Foundation (NRF), have developed several innovative processes (Appendix A). The Limestone Neutralization Process has been implemented on full-scale and plants with construction value of ZAR100 million (US$1 = ZAR7.2, October 2007) have been constructed.

(2) A study has been carried out with the aim of proposing a strategy for the management of AMD from gold mines in Gauteng (Adler & Rasher, 2007). Two broad classes of problems have been identified in the existing policy frameworks that address AMD. First, the delegation of powers between various government departments at the national, provincial and municipal levels is unclear. This problem is exacerbated by the fact that government departments lack the manpower to make frequent site visits to mines and surrounding areas to verify compliance with these guidelines. Second, the existing frameworks place the government in the position of having to be reactive rather than proactive. This is evident in the pricing structures and enforcement mechanisms used to discourage pollution using the 'polluter pays principle' (PPP), as well as the legal framework which outlines requirements for environmental impact assessments (EIAs). If the government is unable to manage public perception in addressing these issues and

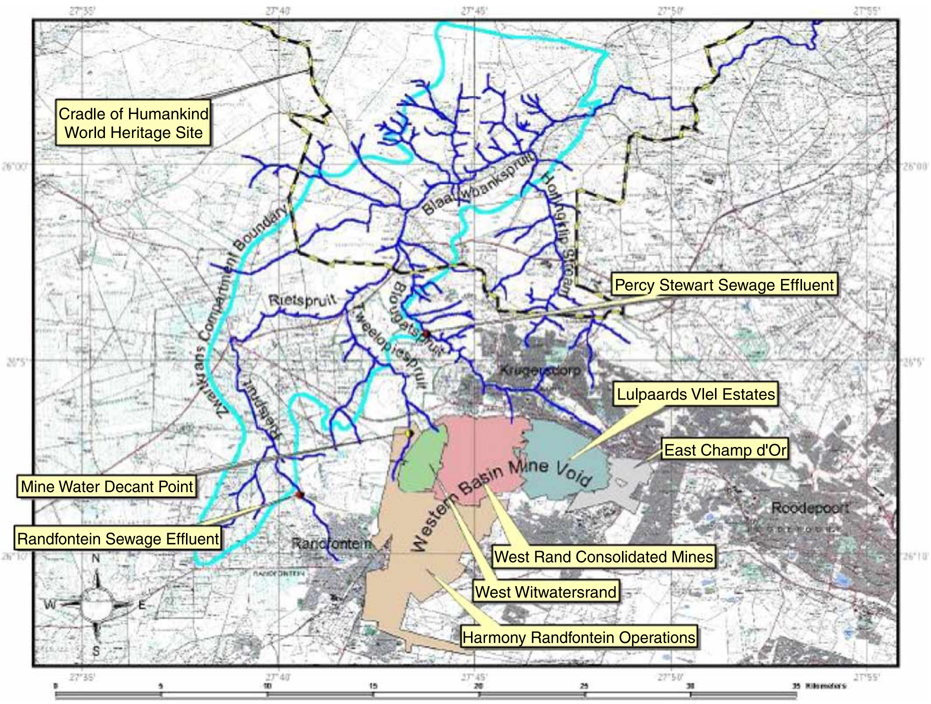

Figure 1. Site of Western Basin Mine Void and streams affected by acid mine water

working towards economically viable processes, there will be serious consequences. To make it more favourable for the mining industry to consider the utilization of new technologies for water treatment, government departments need to retain their expertise and frameworks be made more proactive. Consideration should also be given to changing the pricing structure outlined by the PPP, modifying the way in which EIAs are conducted and used, and establishing new policies and financial incentives to aid in making new water treatment facilities more sustainable over the long term.

(3) A study has been carried out to assess acid mine drainage impacts on the groundwater regime in the West Rand Basin (Hobbs & Cobbing, 2007). The study found that an understanding of the groundwater environment was obscured by complex geology. It produced sufficient evidence to question key elements of the current model put forward for decant management. The study also identified the quality of water in the receiving karst groundwater environment as comprising a mixture of acid mine drainage and treated waste water effluent.

(4) The Western Utilities Corporation (WUC) has been founded after interaction with the authorities (Department of Water Affairs and Forestry, Department of Minerals and Energy and Department of Environmental Affairs and Tourism) and the three mining houses in the Western Basin (Harmony Gold Mine, DRD and Mogale Gold) to:

- accept responsibility for resolving the AMD problem;
- eliminate/reduce water ingress into mining voids; and
- implement a treatment process for AMD at source.

Western Utility Corporation has contracted CSIR, amongst other technology suppliers, to demonstrate the CSIR ABC (Alkali-Barium-Calcium) Desalination process on pilot scale. The CSIR ABC Desalination process is designed to achieve neutralization as well as metal and sulphate removal by using the cheapest chemicals in the most efficient way. Precipitated $CaCO_3$, a by-product from the paper industry, is used for neutralization of free acid. CaS, recovered during sludge processing, is used for metal removal and further neutralization. Either BaS or $BaCO_3$ can be used for sulphate removal (Maree *et al.*, 2004; Hlabela *et al.*, 2007). $BaCO_3$ was selected because it does not require H_2S stripping from the main water stream, only from a small stream in the sludge processing stage. This novel process consists of the following stages:

- Pre-treatment using $CaCO_3$, for neutralization of the free acid and precipitation of iron(III) and aluminium(III), and CaS for precipitation of the heavy metals as sulphides:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \tag{1}$$

$$2M^{3+} + 3CaCO_3 + 3H_2O \rightarrow 2M(OH)_3 + 3CO_2 + 3Ca^{2+}(M = Fe, Al) \tag{2}$$

$$M^{2+} + H_2S \rightarrow MS + 2H^{+}(M = Fe, Mn, Ni, Co) \tag{3}$$

- Lime treatment for magnesium removal and partial sulphate removal through gypsum crystallization

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+} \tag{4}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{5}$$

$$2Al(OH)_3 + 3Ca(OH)_2 + 3CaSO_4 \rightarrow \text{Ettringite} \tag{6}$$

- pH adjustment

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \tag{7}$$

- Removal of sulphate as $BaSO_4$

$$Ca^{2+} + SO_4^{2-} + BaCO_3 \rightarrow BaSO_4(s) + CaCO_3(s) \tag{8}$$

- Processing of the $CaSO_4{\cdot}2H_2O/Mg(OH)_2$ sludge to recover CaS and CO_2

$$CaSO_4 + 2C \rightarrow CaS + CO_2 \tag{9}$$

- Processing of CaS to produce $Ca(HS)_2$, $CaCO_3$ and H_2S

$$2CaS + CO_2 + H_2O \rightarrow Ca(HS)_2 + CaCO_3 \tag{10}$$

$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2S \tag{11}$$

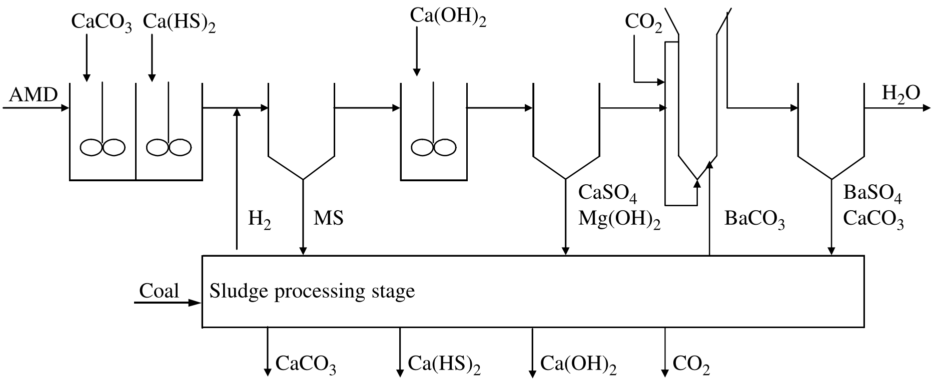

Figure 2. Process flow diagram for the CSIR ABC Desalination process

- Processing of the $BaSO_4/CaCO_3$ sludge to recover BaS and CaO (dewatering and thermal processes), and finally

$$BaSO_4 + 2C \rightarrow BaS + CO_2 \tag{12}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{13}$$

- Processing of BaS to produce $BaCO_3$

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S \tag{14}$$

- Processing of H_2S to sulphur

$$2H_2S + SO_2 \rightarrow 2S + 2H_2O \tag{15}$$

$$S + O_2 \rightarrow SO_2 \tag{16}$$

The objectives of the present study were to demonstrate the performance of such a process on laboratory scale. The specific aims were to evaluate the CSIR ABC Desalination process (Figure 2), and to determine the efficiency of metal removal with sulphide, partial sulphate removal through gypsum crystallization, sulphate removal with $BaCO_3$, thermal treatment of $BaSO_4$ and $CaSO_4$ to recover by-products via BaS and CaS, respectively, and to compare the value of the by-products with the cost of the raw materials.

Materials and Methods

Feedstock

Acid mine water was collected from Winze 18, a decant point at Harmony Gold Mine. The water contained 4 800 mg/l sulphate and was used during batch studies. Barium carbonate (Merck) was used for sulphate removal. For H_2S-stripping studies, a 10% CaS aqueous slurry (produced from gypsum) was used. CO_2 gas (Afrox) was used for H_2S-stripping. A 1 M zinc acetate (Merck) solution was used for absorption of the stripped H_2S-gas. During the thermal studies, chemically pure $BaSO_4$ (Saarchem) was used for the BaS recovery studies.

Equipment

A 1l reactor, equipped with a glass sinter, was used for stripping of H_2S with CO_2 from a 10% CaS slurry.

Experimental Procedure

Neutralization with $CaCO_3$, lime treatment and sulphate removal with $BaCO_3$ were studied by adding $CaCO_3$, lime or $BaCO_3$ to 1 000 ml beakers containing feedstock water in the case of $CaCO_3$ dosage, or product water from the previous stage in the case of CaS, lime, CO_2 or $BaCO_3$ addition. The contents were stirred at 150 rpm. The sulphate concentration was monitored by sampling at various intervals.

Sulphide stripping was studied by placing CaS slurry in the stripping reactor (1000 ml). CO_2 was purged through the CaS slurry.

Experimental Programme

During water treatment the following parameters were varied to study their effects:

- The effect of $BaCO_3$ concentration (0, 0.5, 1, 2 times the mole equivalent of SO_4) on sulphate removal, to determine the reaction order;
- The effect of $CaCO_3$-concentration;
- The effect of pH (8.4, 11.4).

During H_2S-stripping the various reactions that take place were determined by monitoring different parameters (pH, sulphide in solution, total sulphide in solution and suspension and calcium) as a function of CO_2-addition during a batch experiment.

Analytical Procedure

Water samples were collected at various stages in the treatment process and filtered through Whatman No. 1 filter paper for sulphate, alkalinity, calcium and Fe (II) analysis. Suspended solids (SS), acidity, and pH determinations were carried out using standard procedures (APHA, 1989). Calcium was assayed using atomic absorption spectrophotometry. Acidity was determined by titration to pH 8.3 using a 0.1 N NaOH solution. Sulphide (a product from the thermal studies) was determined by mortaring and dissolving 0.5 g of the product in 100 ml deionized water followed by the iodine method for sulphide analysis (APHA, 1989).

Results and Discussion

Water Quality

Table 1 shows the chemical composition of the water after treatment in the various stages. Overall the Total Dissolved Solids (TDS) content was reduced from 7 592 mg/l in the feed water to 414 mg/l in the treated water. During $CaCO_3$ treatment free acid of 800 mg/l was removed as indicated by the increase in the pH from 2.9 to 5.8.The acidity of 100 mg/l (as $CaCO_3$) was due to the formation of HCO_3^-. Iron(III) and aluminium(III) were removed to concentrations below 1 mg/l. During CaS treatment, bivalent metals Fe, Ni and Co, were removed to concentrations less than 0.5 mg/l. Mn was removed to less than 4 mg/l. This was achieved due to the low solubility-products for FeS (17.3), MnS (14.96) and NiS (20.7) (Sillen Martell, 1964). During lime treatment, magnesium concentration was lowered from 146 to 10 mg/l and sulphate concentration was lowered from 2 310 mg/l (as SO_4). Mn was also removed to less than 1 mg/l during the lime treatment stage. During CO_2 treatment the pH was adjusted from 10.9 to 8.4.Ca^{2+} concentration was reduced from 1 040 to 948 mg/l due to $CaCO_3$-precipitation. During $BaCO_3$ treatment, sulphate concentration was reduced from 2 310 to 60 mg/l and calcium from 948 to 10 mg/l. The concentrations to which sulphate and metals are removed is governed by the solubility products of the various compounds.

Metal Removal

Preferably, metals should be removed separately from gypsum. This would allow easier recovery of valuable metals such as manganese, nickel and cobalt and also facilitate higher yields during the processing of gypsum into CaS and sulphur. Figure 3 shows the rate at which various metals and sulphate were removed during $CaCO_3$ and $Ca(HS)_2$ treatment of acid water. It was noted that the metals precipitate rapidly while gypsum remains in solution for more than 120 min before crystallization commences. This finding suggested that separate clarifiers should be provided to allow separate recovery of metal sulphides from gypsum and $Mg(OH)_2$ slurries. Inhibitors could also be added to keep gypsum in solution if required. Sodium hexametaphosphate (SHMP) is an example of a suitable inhibitor for this application.

Maree & Theron (2007) found that $Ca(HS)_2$ can be produced from CaS. CaS has a low solubility of 100 mg/l (as S) compared to 50 000 mg/l for $Ca(HS)_2$. As CaS first needs to be dissolved before it can precipitate metals, it was argued that $Ca(HS)_2$, being much more soluble, should precipitate metals significantly faster. Figure 4 shows that iron(II) removal is more rapid with $Ca(HS)_2$ than with CaS.

Sulphate Removal

The slow reactions that govern the sizes of the main reaction vessels are gypsum crystallization (Reaction 5), $CaCO_3$ crystallization (Reaction 7) and dissolution of $BaCO_3$ (Reaction 8). The rate of sulphate removal by gypsum crystallization may be predicted by Equation 17 (Maree *et al.*, 2004).

$$d[CaSO_4{\cdot}2H_2O]/dt = k[CaSO_4{\cdot}2H_2O](S)[C - C_0]^2 \tag{17}$$

where $d[CaSO_4{\cdot}2H_2O]/dt$ represents the rate of crystallization, k the reaction rate constant, $[CaSO_4{\cdot}2H_2O](S)$ the surface area of the seed crystals, C the initial concentration of calcium sulphate in solution and C_0 the saturated concentration of calcium sulphate in solution. Figure 5 confirmed that the higher the gypsum concentration, the higher is the

Table 1. Chemical composition of feed water before and after the various treatment stages

	Quality						
Parameter	Feed	$CaCO_3$ neutralization	CaS dosage	Lime dosage	CO_2 dosage	$BaCO_3$ addition	SO_4 addition
PH	2.9	5.8	6.8	10.9	8.4	8.5	8.3
Sulphate (mg/l SO_4)	4870	4710	4500	2300	2310	85	200
Chloride (mg/l Cl)	37	37	37	37	37	37	37
Alkalinity (mg/l $CaCO_3$)	0			300	60	65	63
Acidity (mg/l $CaCO_3$)	800	100	50				
Sodium (mg/l Na)	50	50	50	50	50	50	50
Magnesium (mg/l Mg)	147	148	146	10	10	10	10
Calcium (mg/l Ca)	613	920	1580	1040	948	10	70
Barium (mg/l Ba)						40	0.4
Manganese (mg/l Mn)	46	46	4.8	1			
Iron(II) (mg/l Fe)	949	949	11	0.01			
Iron(III) (mg/l Fe)	35	0	0	0			
Aluminium(III) (mg/l Al)	26.4	0.5					
Cobalt (mg/l Co)	5	5	0.06				
Nickel (mg/l Ni)	18	18	0.14				
Zinc (mg/l Zn)	11.9	11.9	0.15				
TDS (mg/l)	7592	6993	6378	3660	3399	280	414
Cations (meq/l)	102.5	99.2	94.8	55.0	50.4	4.1	6.5
Anions (meq/l)	102.5	99.2	94.8	55.0	50.4	4.1	6.5

Note: Ca values were adjusted to obtain ion balance.

rate of gypsum crystallization. This motivated for the introduction of sludge recirculation during the lime dosing stage.

During CO_2 addition for pH adjustment, $CaCO_3$ crystallization occurred, as indicated by the decrease in the calcium concentration. According to Loewenthal *et al.* (1986), the

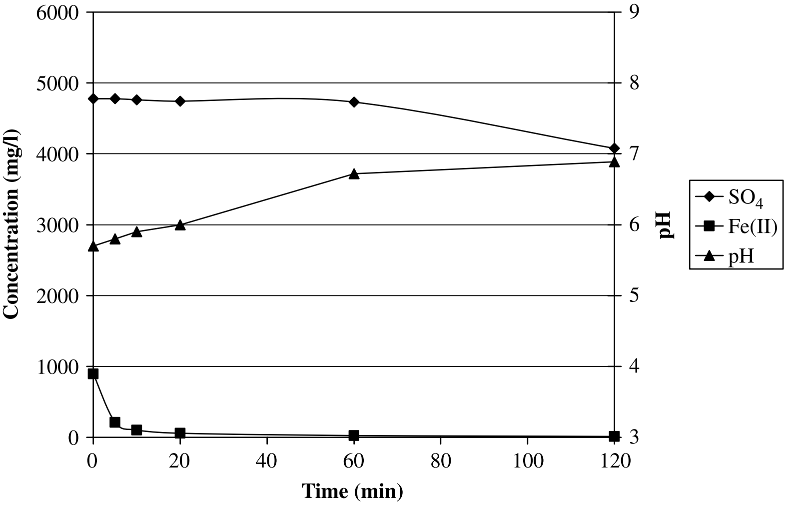

Figure 3. Rate at which Fe(II) and sulphate were removed from solution

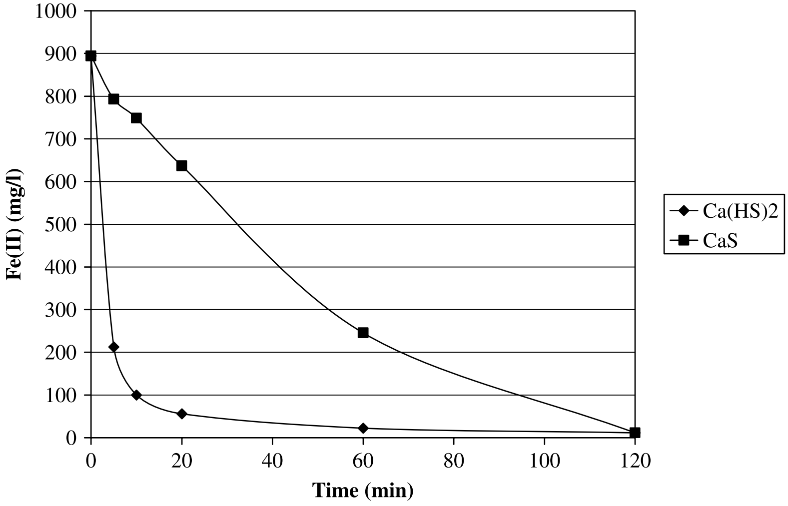

Figure 4. Comparison between CaS and $Ca(HS)_2$ for removal of metals

saturation, under-saturation and super-saturation states of $CaCO_3$ are theoretically identified by the activity product of Ca^{2+} and CO_3^{2-} species that compares with the solubility product constant, k_{sp}, for $CaCO_3$. Above the solubility product, $CaCO_3$ will precipitate from solution and below, $CaCO_3$ will dissolve. The rate of precipitation or dissolution is described by the following equation:

$$-d[Ca^{2+}]/dt = kS\left\{\left(Ca^{2+}\right)^{1/2}\left(CO_3^{2-}\right)^{1/2} - k_{sp}^{1/2}\right\}^2 \tag{18}$$

where k is the precipitation rate constant, S the surface area of $CaCO_3$ growth/dissolution sites and (Loewenthal & Marais, 1976) the activity in mol/l. The rate of precipitation depends on k, S and the term within curly brackets. Although k is affected to an unknown extent by crystal structure, S is dependent on the size, mass and structure of the crystals. By controlling S and the degree of super-saturation (term in curly brackets), the rate of precipitation or dissolution of $CaCO_3$ can be determined.

Sulphate removal with $BaCO_3$ is influenced by the following factors:

$BaCO_3$-concentration. Reaction (8), the removal of sulphate with $BaCO_3$, is the result of the following sequence of reactions:

$$BaCO_3 \rightarrow Ba^{2+} + CO_3^{2-} \tag{19}$$

$$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4 \tag{20}$$

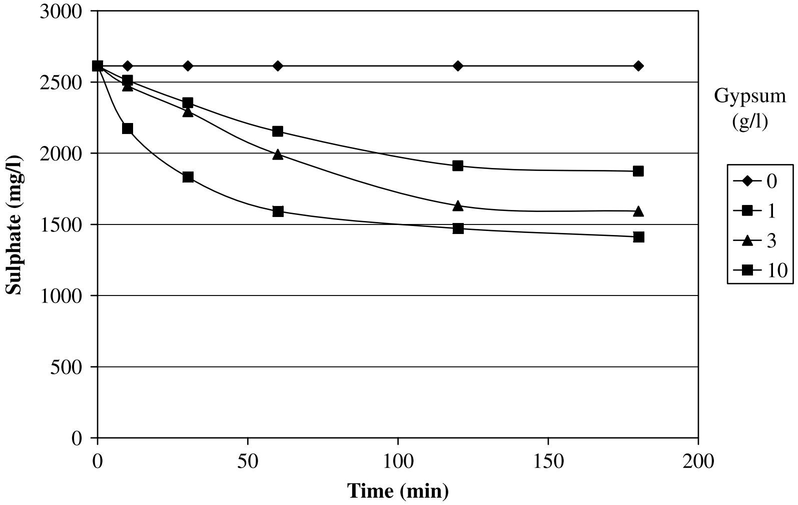

Figure 5. Effect of gypsum seed crystal addition on the rate of sulphate removal through gypsum crystallization

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{21}$$

$$Ca^{2+} + SO_4^{2-} + BaCO_3 \rightarrow BaSO_4(s) + CaCO_3(s) \tag{8}$$

The low solubility of $BaCO_3$ allows a low concentration of free Ba^{2+} ions in solution to react with SO_4^{2-}. Reaction (8) can only continue to produce Ba^{2+} if the CO_3^{2-} that is produced, is removed from solution through Reaction (21) to form $CaCO_3$. Figure 6 shows the effect of $BaCO_3$-concentration on the rate of sulphate removal. The rate of sulphate removal increased with increased $BaCO_3$ concentration. The reaction order was determined by plotting the log of the reaction rates of sulphate removal against the log of different $BaCO_3$ concentrations and was found to be first order.

A graph, ln (Reaction rate) *versus* ln [$BaCO_3$] showed a reaction rate order of 0.86 or 1.Thus, in order to achieve a rapid rate of sulphate removal it is required to dose excess $BaCO_3$.This can be achieved by using a fluidized-bed reactor. Sulphate rich water is passed though a bed of $BaCO_3$ and in contact with a high concentration of excess $BaCO_3$, to form $BaSO_4$ and $CaCO_3$.This procedure is continued until the $BaCO_3$ in the bed is exhausted whereafter it is replaced with fresh $BaCO_3$.

pH. The solubility of $BaCO_3$, like $CaCO_3$, decreases with increasing pH values. Therefore, it is expected that the rate of sulphate removal will be slower at higher pH levels, due to lower Ba^{2+} concentrations in solution. Figure 7 shows the rate of sulphate removal over the pH range 7.5 to 12.0. The ratio of $BaCO_3$:SO_4^{2-} in both cases was 1.

$CaCO_3$ concentration. The rate of $CaCO_3$ precipitation (Reaction 7) governs the rate of $BaSO_4$ precipitation (Reaction 8). $BaCO_3$ can only dissolve as fast as Ca^{2+} is removed

from solution through $CaCO_3$-crystallization. Figure 8 shows that the rate of sulphate removal with $BaCO_3$ is related to the $CaCO_3$-concentration, the higher the $CaCO_3$ crystal concentration, the faster is the rate of sulphate removal. A fluidized-bed reactor will provide a high $CaCO_3$ crystal concentration.

Effect of Polymers on Settling of Solids

Geldenhuys *et al.* (2003) determined that Flocculant 3095 is effective in promoting settling of the sludge after lime treatment. For settling of $CaCO_3$ after pH adjustment with CO_2, both a coagulant (PAC6) and a flocculant (3095) were dosed to achieve good settling of the sludge. In this application $CaCO_3$ precipitation occurred together with $BaSO_4$ precipitation. Further work is required to determine whether coagulant and flocculant additions are required.

Thermal Treatment

Gypsum treatment. Nengovhela *et al.* (2007) studied the processing of gypsum via CaS to H_2S and $CaCO_3$. The reduction of gypsum to CaS takes place at 1 100°C. A good conversion was obtained when C was reduced as reducing agent. Controlling the amount of carbon added, relative to the amount of gypsum, higher reduction was achieved when the molar ratio of gypsum to carbon was 1:3. Smaller particle size gypsum yielded higher reduction percentages due to the higher reactant surface areas for smaller particles. The reaction time between gypsum and carbon was also found to be shorter. The optimum time found was 20 min.

The use of pellets rather than the use of powder mixture resulted in better conversion of gypsum to CaS. Depending on the presence of oxygen in the muffle furnace, the reaction mixture obtained after heating at 1 100°C consisted of oxygen-containing compounds. H_2S stripping studies showed that H_2S gas could be stripped with CO_2 from a CaS-slurry with the simultaneous production of $CaCO_3$. Sulphur can be produced from the stripped H_2S. Sulphur with a purity between 95–99% was produced.

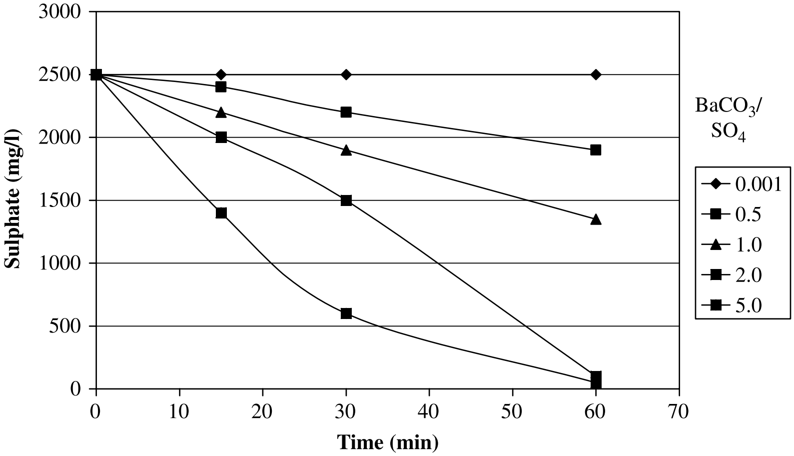

Figure 6. Effect of $BaCO_3$-solids addition on the rate of sulphate removal with $BaCO_3$

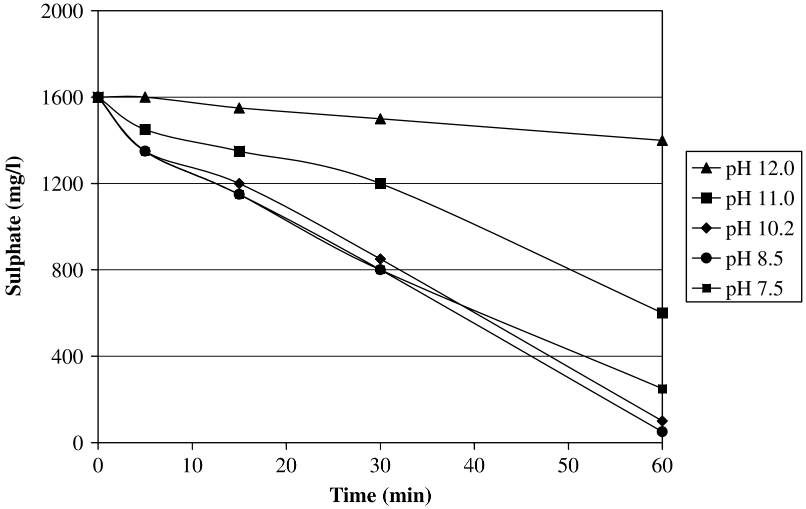

Figure 7. Effect of pH on the rate of sulphate removal with $BaCO_3$

$BaSO_4$—reduction. Hlabela *et al.* (2007) showed that $BaSO_4$ and $CaCO_3$ can simultaneously be converted to BaS and CaO, respectively. The optimum temperature was 1050°C. The [$CaCO_3/BaSO_4$] ratio has little influence on the yield of BaS.

PIPco. The PIPco process is used for the production of sulphur from H_2S. Gryka (1992) described the process where SO_2 is absorbed in a citric acid solution, which is neutralized with KOH. H_2S is absorbed in the SO_2 in the citric solution where it is converted to either $S_2O_3^{2-}$ or sulphur, depending on whether the H_2S/SO_2 mole ratio is below or above 1.

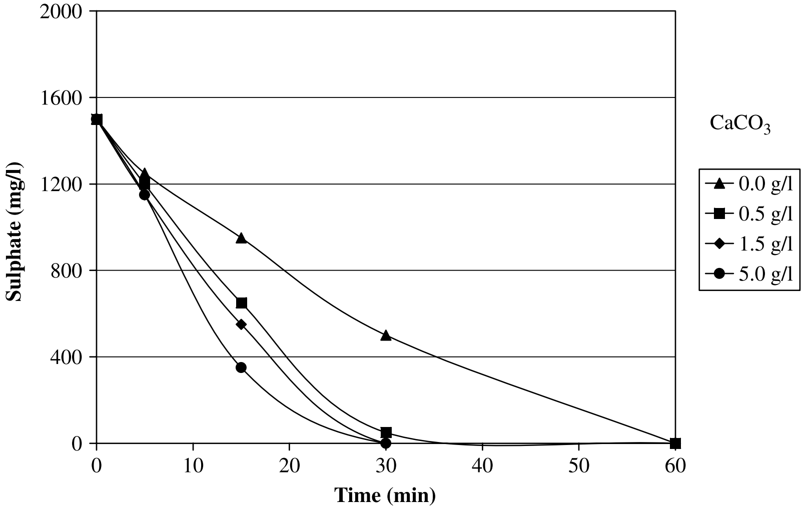

Figure 8. Effect of $CaCO_3$-solids addition on the rate of sulphate removal with $BaCO_3$

H_2S-stripping. CaS is produced when gypsum is treated with a reducing agent at elevated temperatures, as discussed above. CaS is converted via $Ca(HS)_2$ to $CaCO_3$ and H_2S when contacted with CO_2.

Figure 9 shows the relationship between the concentrations of the various species versus time when CO_2 was added at a flow rate of 520 ml/min. The initial CaS concentration in the slurry was 1 250 mmol/l and the pH of the slurry was 12.2. CaS has a low solubility, as indicated, before CO_2 was added. During CO_2 addition the pH dropped from 12.2 to 8.2. It was further noted that:

- The sulphide concentration in the slurry reactor reached a maximum concentration of 650 mmol/l (20 800 mg/l S) due to the formation of $Ca(HS)_2$ in solution (reaction 10). The difference of 458 mmol/l $Ca(HS)_2$ (1 250 mmol/l−792 mmol/l) was present as a solid due to its solubility. Total sulphide values were also measured. These values showed that 1 175 mmol/l sulphide was in solution and in suspension at the end of Phase 1 and that it was completely stripped at the end of Phase 2.
- With further CO_2 addition, the pH dropped further to 7.5 and sulphide was stripped completely (to less than 16 mg/l S) (Reaction 11).
- During the first phase of the reaction the molar ratio of [sulphide: calcium] in solution was 2. This confirmed that $Ca(HS)_2$ formed before H_2S was stripped off with further CO_2 addition.
- The molar ratio of [sulphide in solution: CO_2 added during the first phase] is 1.0. This showed that CO_2 absorbs rapidly during the first phase of the reaction. This is due to the high absorption capacity of CO_2 and the low solubility of $CaCO_3$ at high pH values.
- The molar ratio of [CO_2 added: sulphide removed] during the second phase of the reaction was 2.3. This was higher than the expected stoichiometric value of 1.0. This lower utilization efficiency of CO_2 was due to the lower pH where the solution has a lower absorption capacity for CO_2 than at higher pH values. The low mixing intensity also played a role.

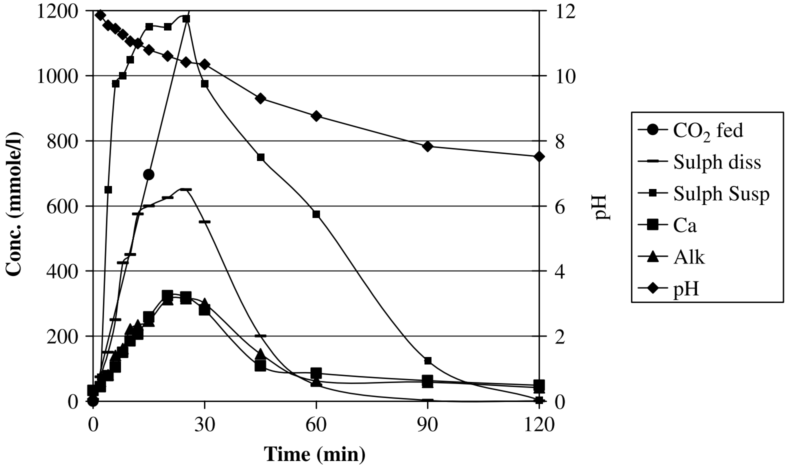

Figure 9. Sulphide stripping with CO_2 from a CaS slurry

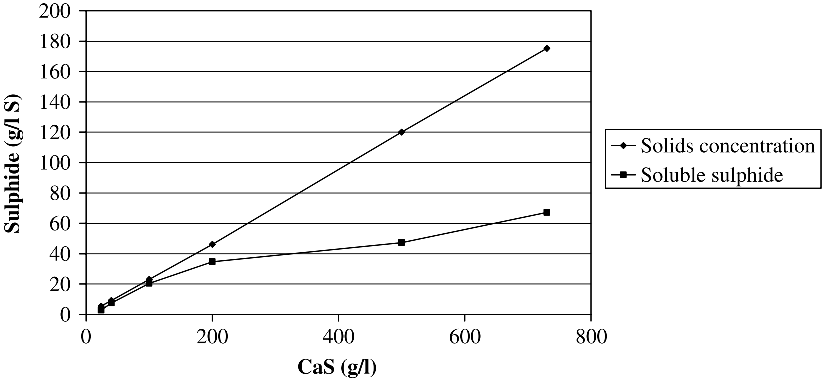

Figure 10. Solubility of $Ca(HS)_2$

The solubility of $Ca(HS)_2$ is influenced by the CaS dosage and by temperature. Figure 10 shows that $Ca(HS)_2$ dissolves rapidly up to a concentration of 20 g/l (as S). With higher dosages of CaS, the soluble sulphide concentration can increase to 40 g/l (as S), and to 60 g/l with very high CaS concentrations. Figure 11 shows that temperature has only little effect on the solubility of $Ca(HS)_2$.

Economic Feasibility

Table 2 shows the cost of raw material, the value of treated water and chemical products, the running cost, estimated capital cost and calculated internal return of revenue (IRR) value. The total running cost of treating the feedstock water amounted to R2.21/m^3 (US\$1.00 = ZAR7.60) of treated water, compared to the value of R11.10/m^3 for the products. The latter value excluded the potential value of metals that may be recovered.

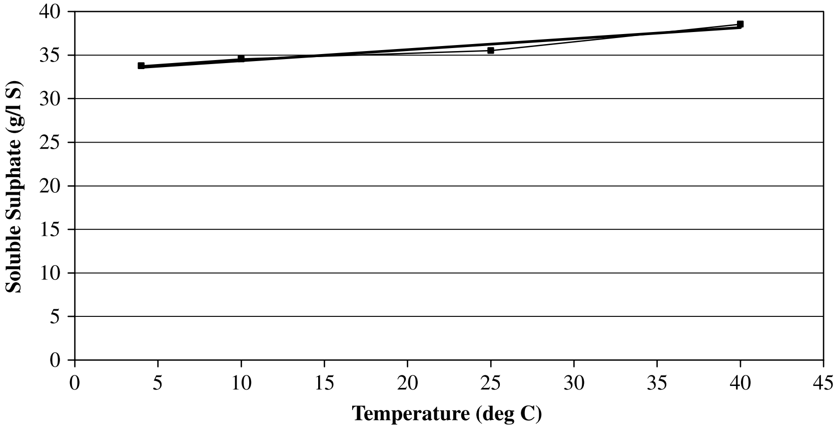

Figure 11. Effect of temperature on the solubility

Table 2. Economic feasibility of if the CSIR ABC Desalination process for a 50 Ml/d treatment plant

Raw material (t/d):		*Products (t/d):*	
$CaCO_3$ (70%)	160.850	Water	49500
Coal (80%)	113.49	Sulphur	43.89
$BaSO_4$ (95%) (10% losses)	21.78	$CaCO_3$ (pure)	72.38
		$CaCO_3$ (impure)	72.38
		$MgCO_3$ (pure)	22.95
		Nickel	0.80
		Cobalt	0.20
Utilization (%)		*Recovery (%)*	
$CaCO_3$ (70%)	90.00	Water	99.0
Coal (80%)	95.00	Sulphur	95.0
$BaSO_4$ (95%) (10% losses)	100.00	$CaCO_3$ (pure)	90.0
		$CaCO_3$ (impure)	90.0
		$MgCO_3$ (pure)	90.0
		Nickel	90.0
		Cobalt	90.0
Price (R/t):		*Price (R/t):*	
Gypsum	0.00	Water	3.00
Coal	400.00	Sulphur	1 000.00
$BaSO_4$ (95%)	1 200.00	$CaCO_3$ (pure)	1 500.00
		$CaCO_3$ (impure)	220.00
		$MgCO_3$ (pure)	2 500.00
		Nickel	165 000.00
		Cobalt	247 500.00
Cost (R/d):		*Value (R/d):*	
Gypsum	0	Water	148 500
Coal	45 395	Sulphur	43 893
$BaSO_4$ (95%)	26 131	$CaCO_3$ (pure)	108 574
Electricity	9 750	$CaCO_3$ (impure)	15 924
Manpower	9 750	$MgCO_3$ (pure)	57 371
Maintenance	19 500	Nickel	132 165
		Cobalt	48 448
Total cost (R/a)	*40 341 689*	*Total income (R/a)*	*202 529 309*
Total cost (R/m3)	*2.21*	*Total income (R/m3)*	*11.10*
Cost of plant (R)	284 694 974		
IRR	132%		

Conclusions

The following conclusions were made from this study:

- The CSIR ABC (Alkali-Barium-Calcium) Desalination process can be used for neutralization of AMD and lowering of the total dissolved solids content from 7600 mg/l to 400 mg/l.
- Metals can be removed effectively through precipitation with CaS or $Ca(HS)_2$. The latter compound has a high solubility resulting in higher metal removal rates compared to CaS.
- Sulphate remains in solution during metal precipitation with sulphide.

- The rate of sulphate removal during gypsum crystallization is influenced by the gypsum seed crystal concentration.
- The rate of sulphate removal during $BaCO_3$ treatment is influenced by pH, $CaCO_3$ solids and $BaCO_3$ solids concentrations.
- $Ca(HS)_2$ can be produced from CaS by passing CO_2 through a CaS slurry. Further CO_2 addition results in H_2S-stripping.
- $BaSO_4$ and $CaCO_3$ can be simultaneously converted to BaS and CaO respectively. The optimum temperature found was 1050°C.
- The cost of raw materials for the treatment of water with a TDS content of 7600 mg/l amounted to R2.21/m^3. The potential value of the water and by-products amounted to R11.10/m^3.

Acknowledgements

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Appendix A. Patents and Full-Scale Applications

Limestone Neutralization

Maree, J. P. (2000) *Limestone Handling and Dosing System*, South Africa (Patent No. 2001/7086), Botswana (BW/A/2001/00014 - Pending), Zambia (24/2001 - Pending), United States of America (US 6,592,246 B2).

Maree, J. P. & Clayton, J. A. (1991) (15 July) *Treatment of Water* ($CaCO_3$ neutralization), United States of America (Patent No. 5,156,746), South Africa (Patent No. 91/5516), Australia (Patent No. 639 192), Canada (No. 2 047 432-7).

Maree, J. P. (1997) *Integrated Iron Oxidation and Limestone Neutralization*, Republic of South Africa (98/5777), Australia (Patent No. 732237), United States of America (6,419,834), Canada (2 294 058), Germany (698110927-08), Great Britain (1012120).

Maree, J. P. (2003) *Integral Chemical/Biological Process*, South Africa (2003/1362), Australia (2001279996 – Examination Requested), Canada (2,418,472 – Examination Requested) EPO (1,313,668), USA (US 6,863,819), China (01816205.3), Great Britain (1,313,668), France (1,313,668), Germany (1,313,668)

Maree, J. P. (2003) Underground neutralization of acid mine water. Provisional Patent.

The patents on limestone neutralization have been implemented on full-scale by Anglo Coal at several of its mines in Witbank area, BCL in Botswana and Ticor, Empangeni. The following plants have been constructed and are in operation: Limestone handling and dosing system at Navigation – 2001; Limestone handling and dosing system at Kromdraai – 2003; Limestone and lime treatment and gypsum crystallization plant at Ticor, Empangeni – 2001; Limestone neutralization, iron(II)-oxidation and gypsum crystallization plant at BCL, Botswana – 2003; Limestone/lime treatment, Namakwa Sands - 2005; Limestone/lime treatment, Illuka Resources - 2006. These plants were the first of its kind in the world and offer the following benefits:

- Reduction in alkali cost (50%)
- Simple to operate
- Chemical is safe to handle.

The value of the plants that were constructed was R100 million.

Biological Sulphate Removal

Maree, J. P. (1987) *Biological Treatment of Water*, United States of America (Patent No. 4,839,052), Australia (Patent No. 69859/87), South Africa (Patent No. 87/1661), (Filed: 6 March 1987).

Maree, J.P and Gerber, A. (1997) *Single Stage Sulphate Removal*, South Africa (Patent No. 98/6902) and United States of America (Patent No. 6,306,302)

Maree, J. P. (1990) *Sulphate-Nitrate Process*. Canada (Patent No. 2,025,433) (Filed 19 September).

Barium Process

Maree, J. P. (1989) *Treatment of Water* (BaS process), Republic of South Africa (Patent No. 90/1889), 28 November, Canada (Patent No. 2 012 266 8) and United States of America (Patent No. 5,035,807).

Hydrogen Sulphide Processing

Maree, J. P. (1990) *H_2S Oxidation*, South Africa (Patent No. 90/8981).

Gypsum Treatment

Maree, J. P. (2004) *Treatment of Sulphur Dioxide-Containing Gas*, Provisional patent.

Fluoride Removal

Maree, J. P. & Buiseman, G. (2006) *Fluoride Removal*, Provisional Patent No. 2006/08539

Metal Removal

Maree, J. P. (2006) *Metal Removal with Calcium Sulphide*, to be filed in April 2007.
Maree, J. P. & Theron, D. J. (2007) Metal removal with Calcium Sulphide, RSA Patent Application 2007/3791.