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REMOVAL OF SULPHATE FROM MINE WATER
WITH BARIUM SULPHIDE

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ABSTRACT

The Barium Sulphide Process removes sulphates from mine water by precipitating $BaSO_4$ with BaS. Barium sulphide is regenerated thermally by reducing the $BaSO_4$ with coal at 1000-1100°C for about 15 minutes. The process produces elemental sulphur and $CaCO_3$ as by-products. Laboratory studies achieve typical sulphate reductions of about 95%. Metals such as Fe, Ni, Co and Mn are also removed and pH can be increased from 1,4 to 8,3. The process has a water recovery of about 70%. For a 25 Ml/d plant (2g/l SO_4^{2-}), the capital cost is estimated at US$ 0,48m / Ml / d, while the detailed running costs amount to a net value of 27 c / m^3. This compares well with that of other processes for desalination and is less than the fresh water price for new mines in South Africa, viz. 30 c / m^3.

KEYWORDS

Acid mine water treatment; barium sulphate precipitation; barium sulphide regeneration; calcium removal; desalination; lime treatment; magnesium removal; neutralisation; sulphate removal; technical and economic evaluation.

INTRODUCTION

The oxidation of pyritic material in ore bodies and the effluents from the uranium leaching process, invariably cause mine waters, to contain significant concentrations of sulphuric acid and metal sulphates. The acidity of the water is usually neutralised, but the sulphate content of these waters is often the cause of contravention

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of effluent standards, scale formation and biocorrosion. It is estimated that in South Africa, 200 Ml/d of mining effluent, saturated with calcium sulphate, are discharged into the public streams of the Pretoria-Witwatersrand-Vereeniging triangle (Maree, 1988). This represents a sulphate load of 73 000 t/a. In a study conducted by the Department of Water Affairs (Forster, 1988) in the Eastern Transvaal, it was shown that the sulphate content in run-off water from areas with high mining activities varied between 200 and 2 000 mg/l, while in the areas of low mining activities it varied between 10 and 55 mg/l. The sulphate load in the Eastern Transvaal amounts to 12 000 t/a.

Uranium is produced by some South African gold mines as a by-product and is leached from the ore with sulphuric acid under oxidising conditions created by manganese dioxide. After solvent extraction of the uranium, the raffinate or a bleed from a recycled circuit in some cases, is neutralised with lime and discharged to the residue dams. The precipitated metal hydroxides are voluminous and constitute volumes as high as 75 percent of the raffinate volume. The neutral water constitutes the bulk of the process streams at the mine.

Acid mine drainage is also treated with lime and clarified of suspended metal hydroxides, before discharge into a public stream. Although this water is not as saline as the neutralised raffinate, it still exceeds the Effluent Act limit of 250 mS/m or 2 000 mg/l dissolved solids.

These waters can be treated by processes such as slurry recycle and precipitation reverse osmosis (SPARRO) (Chamber of Mines Research Organisation, 1988) or the biological sulphate removal process (Maree, et al., 1987; Maree and Hill, 1989). These processes are relatively expensive and therefore consideration was given to alternative means of desalination. Other promising processes in the case of sulphate-rich water entail the chemical removal of sulphate by means of soluble barium salts such as barium sulphide or barium carbonate.

Kun (1972) studied the removal of sulphate with barium carbonate and obtained good results. However, he identified three problem areas, namely the requirement of a long retention time, high concentrations of soluble barium in the treated water when more barium carbonate is dosed than stoichiometrically required, and the high cost of the barium carbonate. Volman (1984) overcame the cost problem by demonstrating that the barium sulphate produced could be reduced efficiently and economically with coal under thermic conditions to produce barium sulphide. This compound can be used directly for the process or converted to barium carbonate. Wilsenach (1986) proved the economic viability by calculating the cost of producing barium sulphide from barium sulphate at $0,08/m³ water treated, based on the treatment of 100 Ml/day with a sulphate concentration of 2 g/l. (Currency exchange rate: US$1 = R2,63). The cost of producing barium sulphide from recovered barium sulphate given by Wilsenach (1986), was updated to 1989 costs and converted to a cost per unit mass of reagent, expressed as Ba. The cost of $0,08/m³ of water treated, mentioned above, changed to $0,05/kg Ba. Wilsenach (1986) calculated

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the cost of barium sulphide production to be 3,5 times higher if
production rates are ten fold less, (10 Ml/day instead of 100 Ml/day
water treated). The economic study described in this paper was based
on treating 25 Ml/d of sulphate rich water (2 g/l). It was estimated
that this would be the approximate size of a plant required at a
certain point source of pollution, such as a mine.

Trusler et al. (1988) gave further attention to the use of barium
carbonate for sulphate removal and suggested an integrated process
which includes the recovery of barium carbonate and lime. They also
noted that incomplete sulphate removal is obtained in the barium
carbonate route when sulphate ions are not completely associated with
calcium ions. They overcame this problem by dosing a calcium salt,
such as lime or calcium chloride, to equalise the sulphate and
calcium concentrations.

Maree, et al., (1989), developed a barium carbonate method in a
two-stage fluidised bed reactor system to overcome the other problems
identified by Kun (1972), namely the long retention time and the high
barium concentration in the treated water. However, the barium
carbonate process was found to be unsuitable for water containing
metals, as is the case with some mine waters. The barium carbonate
crystals became inactive when coated with metal hydroxide
precipitates. Maree et al. (1989) also saw a disadvantage of the
barium carbonate process in the separation of barium sulphate and
calcium carbonate, which precipitate simultaneously.

For these reasons the barium sulphide process was chosen for an
investigation of its suitability for treatment of sulphate-rich mine
waters.

The aims of the study were to establish the technical and economical
feasibility of the process, for which purpose the following
parameters were determined:

1. Quality of product water.
2. Volume of product water and residue sludge produced.
3. Optimum conditions for $BaSO_4$ reduction in the thermic
    regeneration stage.
4. Development of a detailed process flowsheet and
    determination of the major equipment and treatment costs.

MATERIALS AND METHODS

The waters used for the study were a uranium process raffinate and an
acid mine drainage (AMD) from a coal mine. These waters were
neutralised with lime and clarified whereafter sulphate was removed
by adding barium sulphide.

Technical barium sulphide powder (Riedel-De Haën) was used during the
investigation for the precipitation of sulphate. The barium was
added to the test waters in solution form to eliminate the
possibility of barium sulphide particles being covered by

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precipitated barium sulphate.   Barium sulphide has a solubility of 116 g/l (Maree, et al., 1989), but was used at a concentration of 25 g/l, because some crystallisation took place at higher concentrations.

Laboratory grade calcium hydroxide was used for the tests.

The stages of treatment are as follows (see Figure 1):

Stage 1:   Mixing and aeration of acidic water with lime.
           Metal hydroxides and surplus calcium sulphate
           precipitate. Solids/liquid separation by
           sedimentation with sludge thickening for sludge
           disposal and further treatment of liquid.
Stage 2:   Dissolution of barium sulphide to form barium
           hydroxide plus hydrogen sulphide.
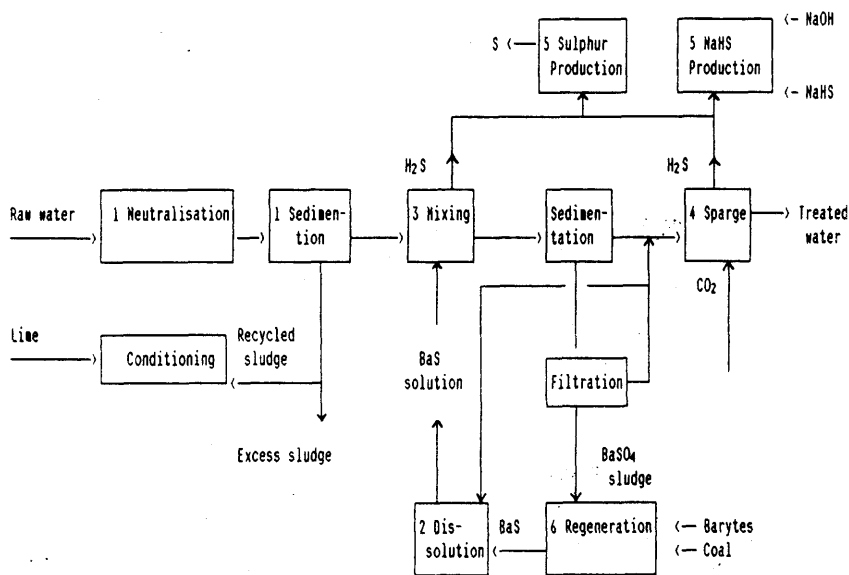
Figure 1: Schematic flowsheet for the Barium Sulphide Process

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Stage 3: Mixing of neutralised and clarified solution with barium sulphide. Barium sulphate precipitates.

Stage 4: The solution is acidified with carbon dioxide to pH 6,5 - 7,0 for sparging and recovery of hydrogen sulphide, yielding the process product (treated water).

Stage 5: Conversion of hydrogen sulphide to sulphur or sodium bisulphide.

Stage 6: Regeneration of barium sulphate with coal to produce barium sulphide. As mentioned above, technical grade and not regenerated BaS was used in the water treatment stages.

Voluminous sludges produced in Stage 1 required sludge recycle and conditioning with the alkali for sludge densification. The batch laboratory test, as described by Bosman (1983), is based on the High Density Sludge process as developed by the Bethlehem Steel Corp. (Kostenbader and Haines, 1970).

Thermic regeneration of $BaSO_4$ to BaS was studied in a tube furnace by reducing 5 g samples of pelletized technical grade $BaSO_4$ and anthracite in the ratio 3:1 $C:BaSO_4$ on a molar basis. Coal (mined in the Wesselsnek area) was used in later studies.

RESULTS AND DISCUSSION

Water Quality

The chemical composition of the untreated waters before and after neutralisation appears in Table I. The quality of the waters after BaS addition is given in Table II. It is evident that the sulphate content of the raffinate as well as the AMD sample was reduced to less than 200 mg/l. As a result of the BaS addition, the actual

Table I: Chemical composition of the waters in the study.

	Raffinate		Acid Mine Drainage	
	Untreated	Neutralised & clarified	Untreated	Neutralised & clarified
pH	1,4	9,3	2,7	8,5
Conductivity mS/m	-	600	-	275
Acidity to pH 8,3	10 700	-	710	-
Alkalinity to pH 4,8	-	180	-	50
Dissolved solids	27 900	4 210	2 940	3 120
Sulphate	17 600	3 080	2 060	1 970
Chloride	265	255	5	5
Calcium	615	515	345	625
Magnesium	485	250	125	110
Sodium	320	305	25	25
Potassium	120	120	ND	ND
Ferrous Iron	1 300	ND	ND	ND
Ferric Iron	700	ND	ND	ND
Total Iron	2 000	0,8	40	0,5
Manganese	1 800	1,4	20	1,1
Aluminium	570	<0,5	60	1,7
Copper	6	<0,5	ND	ND
Cobalt	11	<0,5	ND	ND
Nickel	26	<0,5	ND	ND

ND: Not determined

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Table II: Effect of barium sulphide addition on water quality.

Treatment	Raffinate			Acid Mine Drainage		
	Lime	Barium	Carbon Dioxide	Lime	Barium	Carbon Dioxide
Stage	1	3	4	1	3	4
pH	9,3	12,0	7,1	8,5	12,0	7,2
Calcium (mg/l)	515	400	110	625	485	140
Magnesium (mg/l)	250	4	4	110	1	1
Sulphate (mg/l)	3 080	155	175	1 970	120	190
Barium (mg/l)	1	2	1	1	2	1

reductions were 94 and 90 % respectively. This difference has probably resulted from a slight difference in barium sulphide dosage between the two tests.

The effect of the three stages of treatment on other constituents of the water is also shown in Table II. These results show a significant reduction in the calcium content (precipitated as $CaCO_3$) and virtually complete removal of magnesium (precipitated as magnesium hydroxide by the alkalinity of the barium sulphide solution in Stage 3). This process also has the ability to remove other metals such as Fe, Ni and Co, as shown by Maree et al (1989). The balance of ions in the product water consists of sodium, potassium and chloride (not affected by the treatment) and bicarbonate, which constitute the rest of the anions. Table II shows that after carbonation, the pH of the water had reached 7,1 and 7,2 for the two waters respectively. With further softening (to remove the excess calcium carbonate) the pH can be raised to 8,3.

The increase in the sulphate content in both cases during carbonation has probably resulted from the oxidation of sulphides by the air used for sparging hydrogen sulphide.

Overdosage of barium is controlled by adding the barium sulphide solution in increments after the addition of approximately 90 percent of the stoichiometric amount. Small samples of the supernatant solution were tested with barium sulphide for further precipitation, before additional incremental dosages were made. When no further precipitation was observed, an additional 5 percent by volume of untreated water was added, to precipitate any excess barium. Some refinement of this control method needs to be worked out, especially for a continuous full-scale process.

The fine precipitates of mainly barium sulphate and calcium carbonate that formed after barium sulphide and CO_2 addition respectively, were separated from the solutions by filtration. Alternative, more economic separation methods may be either centrifugation or the formation of larger particles by operating the two stages with seed

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crystal beds. This technique is well-known for calcium carbonate precipitation and should be tested on barium sulphate.

Sludge densification

The neutralisation of acid mine water containing significant quantities of metal sulphates, invariably produce voluminous sludges. This was the case with the two waters used in the tests. These sludges were reduced in volume by application of the sludge densification process described above. Figure 2 gives the sludge volumes produced from raffinate per test cycle as densification proceeded. Sludge densification tests were not carried out on the AMD because of relatively small sludge volumes in this case and the assumption that similar densification rates will be obtained.
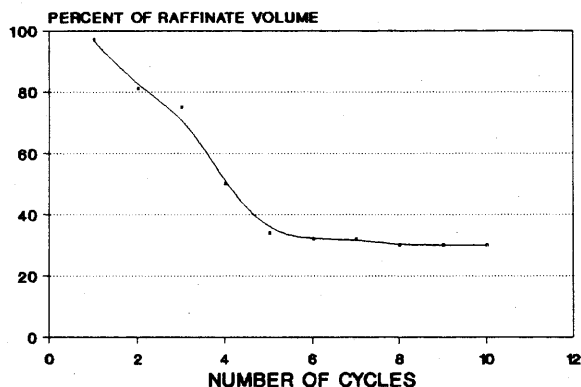
*Figure 2:* *Raffinate sludge densification by sludge recycle.*

Sludge densification in Stage 1 of the treatment process resulted in a sludge volume of 30 percent of the volume of raffinate treated. The moisture content of the barium sulphate sludge was 1 percent. Therefore, the volume of product water was 69 percent of the untreated water.

BaS regeneration studies

The results of preliminary thermic reduction studies of $BaSO_4$ to BaS appear in Figures 3 and 4. It is clear from Figure 3 that the optimum temperature for reduction is between 1 000 and 1 100°C. This confirms observations made by Lozhkin et al (1974) and Dimitrova et al (1972). After 15 minutes, more than 90% conversion of $BaSO_4$ to BaS had been achieved (Figure 4). It must be remembered that this was for the reduction of small quantities of $BaSO_4$ under laboratory conditions: on a commercial scale the retention time needed for efficient regeneration might be longer. Further studies on a laboratory and pilot scale (considering possible chemical interferences, varying reagent ratios, types of coal and measuring conversion versus time at different temperatures) will contribute to a greater understanding of the kinetics and will lead
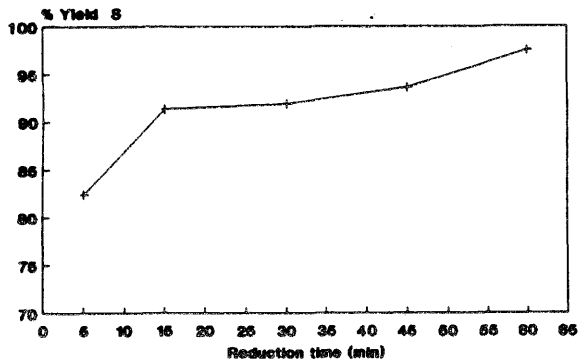
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Temp. vs BaSO4 reduction efficiency
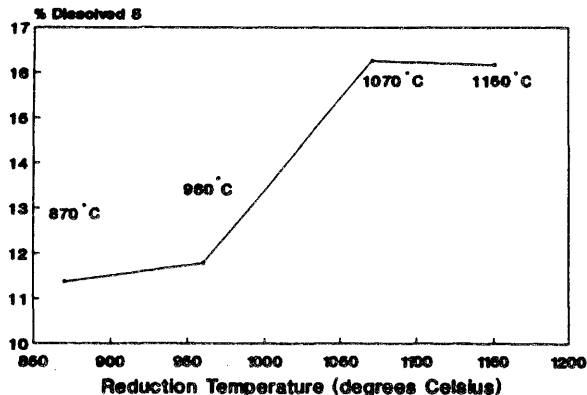
Figure 3: The effect of temperature on BaSO4 reduction. The optimum temperature is between 1000°C and 1100°C.

BaSO4 reduction with increasing retention time

Figure 4: The effect of retention time on BaSO4 reduction. After approximately 15 minutes, greater than 90% reduction was achieved.

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to improved predictions of the conditions required on full scale.

PROCESS FLOWSHEET: TECHNICAL FEATURES

Having proved the technical viability of the process in the laboratory, a more detailed flowsheet was drawn up and the major equipment items that would be needed were identified. The plant costed was to treat 25 Ml/d of water containing 2 g/l of sulphates. Pre-treatment with lime was not included in the exercise and the effluent entering the process was assumed to be neutral. This assumption has support in that at most mines, this pre-treatment facility already exists.

The proposed flowsheet is shown in Figure 5 and the mass flows are given in Table III. The following technical features are of note:

(1) The raw water is mixed in-line with the BaS solution; the formation of $BaSO_4$ is fairly rapid and an in-line mixer avoids the use of an extra vessel. Experimentation with addition of milled coal to the in-line mixer is presently underway in an attempt to improve the settle-ability of the sludge. The coal may be used in the BaS regeneration step.

(2) The $BaSO_4$ is settled in a gravity thickener (underflow 300 kg/m^3 solids) and further dewatered with a rotary drum vacuum filter producing a filter cake with 35% moisture.

(3) Sulphides in the overflow from the thickener are stripped off with a mixture of CO_2 and air. Since $CaCO_3$ precipitates in this stage, it is planned to run the stripper as a fluidised bed of seed $CaCO_3$ crystals that can continually be drawn off.

(4) The H_2S is converted to sulphur by means of oxidation with iron (III). The iron (III) is regenerated biologically by Thiobacillus ferrooxidans.

(5) Residual carbonate is precipitated as $CaCO_3$ in the softening stage with lime.

(6) In the BaS regeneration step, the $BaSO_4$ filter cake is dried, then pelletized with milled coal (if the latter has not already been added upstream).

(7) The pelletized $BaSO_4$ and coal is fed to a rotary kiln, additional pulverised coal being burnt as fuel.

(8) The kiln products are dry-milled, the BaS being leached out to give a solution of approximately 24% BaS on a mass basis. The insoluble ash-related compounds are dewatered and disposed of as solid waste.
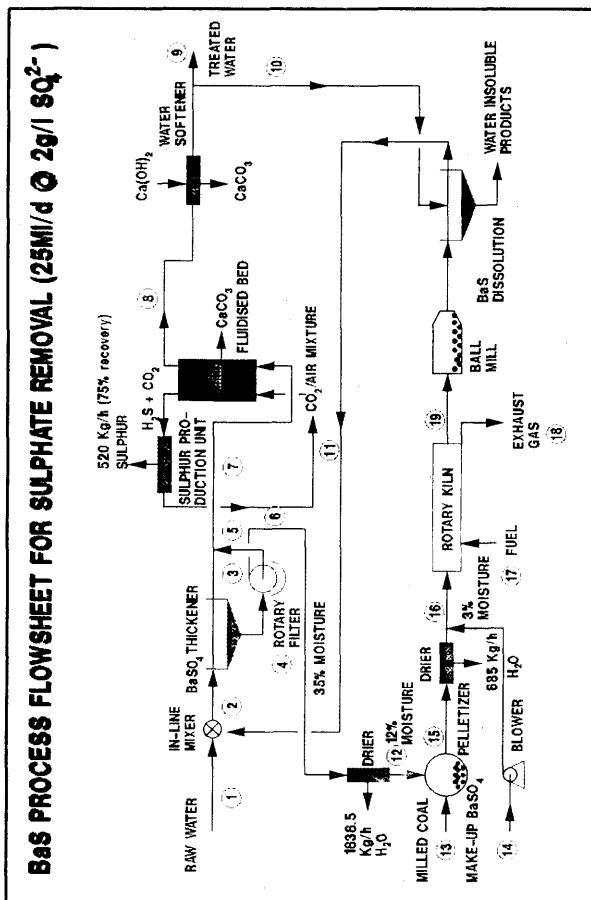
Figure 5: A more detailed BaS process flowsheet for a plant treating 25 Ml/d of sulphate-rich water (2g/1).

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STREAM	COAL (Kg/h)	N₂ (Kg/h)	O₂ (Kg/h)	CO₂ (Kg/h)	H₂O (kg/h)	BaS (Kg/h)	BaSO₄ (Kg/h)	SO₄²⁻ (Kg/h)	Sulphide (Kg/h)	Cales CaCO₃ (Kg/h)	TOTAL (Kg/h)	Temp (°C)	Press (atm)	COMMENTS
1					1 042 500			2 083		2 083	1 848 868	15	1	25 ml/d @ 2g/l SO₄
2					1 053 500		5 063		695	2 088	1 061 346	15	1	
3					1 036 643				695	2 088	1 039 426	15	1	
4					16 875		5 063				21 938	15	1	Underflow 300kg/m³ BaSO₄
5					14 150						14 150	15	1	
6					2 725		5 063			2 088	7 788	15	1	35% moisture in cake
7					1 050 793				695	2 088	1 053 576	15	1	
8					1 050 793					966	1 051 761	15	1	Assume all S stripped
9					1 039 775					516	1 040 291	15	1	
10					11 018					5	11 023	15	1	24% m/m BaS stream
11					11 018	2 673					14 691	15	1	
12					868		5 063				5 951	15	1	12% H₂O for pelletization
13	868		3 245				563				1 431	15	1	
14	868	11 355	3 245		826		5 025				14 600	15	1	
15	868	11 355			826		5 025				7 361	15	1	Pellets 5% moisture
16	868	11 355			203		5 025				21 296	15	1	
17	870										870	15	1	Pulverized coal
18		11 355		6 370	203	3 673	563				17 928	100	1	To stack
19											4 236	100	1	Products milled to facilitate BaS dissolution

Table III: Mass flows for the 25 Ml/d BaS process flowsheet.

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As more information regarding the above unit operations is gained, the existing flowsheet will be refined if necessary.

ECONOMIC VIABILITY

To evaluate the economic feasibility of this treatment process, the equipment was sized and detailed capital and operating costs for the above flowsheet were calculated.

Table IV: PURCHASED EQUIPMENT COSTS FOR 25 Ml/d PLANT (2 g SO_4^{2-}/l)

	1990 cost (US$)
Rotary kiln	817 000
BaS leaching vessels	39 000
$BaSO_4$ thickener	161 000
Filter	152 000
H_2S stripper	132 000
Ball mill (coal)	22 000
Ball mill (kiln products)	47 000
Sulphur production unit	1 088 000
TOTAL PURCHASED EQUIPMENT COST	**2 458 000**

Table V: CAPITAL COST ESTIMATE FOR 25 Ml/d PLANT (2 g SO_4^{2-}/l)

Direct costs	Cost (US$)
Purchased equipment	2 450 000
Installation	984 000
Instrumentation	689 000
Piping	763 000
Electrical	246 000
Buildings	541 000
Yard improvements	216 000
Services	1 353 000
Land	138 000
	7 430 000
Indirect costs	
Engineering and supervision	787 000
Construction	837 000
	1 624 000
Contractor's fee	453 000
Contingency	905 000
Fixed capital	10 412 000
Working capital	1 561 000
TOTAL CAPITAL INVESTMENT	**11 973 000**

Table VI: RUNNING COSTS FOR 25 Ml/d PLANT (2 g SO_4^{2-}/l)

A Direct costs	Cost (US$)
Raw materials	1 519 000
Operating labour	150 000
Supervisory and clerical labour	15 000
Utilities	304 000
Maintenance	208 000
Operating supplies	21 000
Lab. charges	15 000
	2 232 000
B Fixed charges	
Depreciation (over 20 years)	521 000
Local Taxes	208 000
Insurance	104 000
	833 000
C Plant overheads	
General plant upkeep, payroll overheads, medical services, safety & protection and storage	186 000
D Administration costs	56 000
TOTAL RUNNING COST	**3 307 000 p.a.**

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The costs of the major equipment items are given in Table IV. It is clear that the rotary kiln and the sulphur production unit are the two most expensive items. Together, they constitute just over three-quarters of the total equipment cost. This emphasises how important it is to optimise the operation of these pieces of equipment.

Table V shows a breakdown of the total capital investment required for a 25 Ml/d plant removing 2 g/l of sulphate. It includes items such as installation, instrumentation, piping, engineering and supervision, etc. The total amount is $11,97m or $479 000 / Ml / d. A detailed list of all the components making up the total annual operating cost for the 25 Ml/d plant appears in Table VI. It amounts to 36 c/m^3 water treated. However, with the sulphur production unit, there is a potential revenue of 9 c/m^3 from sulphur sales. The net running cost for the plant is hence 27 c/m^3. This is 3 cents cheaper than the current water price for the new mines in RSA of 30 c/m^3 which shows that it is economically viable to treat the used water as opposed to simply purchasing fresh water. The treatment cost of the BaS process also compares well to that of alternative desalination processes, eg. the SPARRO process (a reverse osmosis process developed by the Chamber of Mines, RSA) costs 46 c/m^3 to run. Considering the possibility of additional revenue from calcium carbonate sales and the savings from not having to pay penalties for pollution of surface waters, the profit margin might be even larger.

CONCLUSIONS

Neutralisation with lime and precipitation of metals, followed by treatment with barium sulphide to remove sulphates, is the recommended process for acid mine waters.

The sulphate content of neutralised mine water was reduced by more than 94 percent (less than 200 mg/l in the product), or 99 percent if based on the sulphate content of raffinate before neutralisation. The calcium contents of the raffinate and AMD were reduced by 80 and 60 percent respectively, while all metals and virtually all the magnesium were removed.

Sodium, potassium and chlorides are not affected by the process and remain, together with bicarbonate, in solution. However, substantial desalination took place and the product quality complies well with effluent standards.

The capital cost of the BaS process is $479 000/ Ml / d, the net operating cost amounting to 27 c/m^3 (including the revenue from sulphur sales). These figures compare well to those for other sulphate-rich water desalination processes.

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ACKNOWLEDGEMENTS

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