THE CHEMICAL REMOVAL OF SULPHATES

Report to the
WATER RESEARCH COMMISSION
by the
POLLUTION RESEARCH GROUP
UNIVERSITY OF NATAL

WRC Report No 203/1/90

WATER RESEARCH COMMISSION PROJECT NO. 203

RESEARCH INTO THE CHEMICAL REMOVAL OF SULPHATES

FINAL REPORT

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WRC Report No. 203/1/90

October 1990

ISBN 0 947447 97 0

EXECUTIVE SUMMARY

The steadily increasing salt concentration in the Vaal River drainage system is becoming a serious problem due to the large scale recirculation of water, and the fact that conventional water treatment processes do not significantly reduce inorganic pollutants.

Three mines were found to contribute 55 % of the salt load to the Klip River (or 30 % to the Vaal system), the major anion being sulphate, which results from oxidation of pyrite.

A laboratory investigation has shown that these effluents can be desalinated by treatment with barium carbonate and lime.

The reaction kinetics of barium carbonate with aqueous calcium, magnesium and sodium sulphates have been investigated. Where magnesium or sodium cations are present, calcium hydroxide is required in addition to achieve complete sulphate removal.

Barium carbonate is a relatively expensive reagent, and for its use to be economically viable, it will be necessary to recover it for reuse. This could be carried out at a central facility, where barium sulphate would be reduced with coal to barium sulphide. This would be leached with water, and the solution treated with carbon dioxide to regenerate barium carbonate and generating a by-product stream of hydrogen sulphide gas. Elemental sulphur can be produced from hydrogen sulphide gas using conventional technology. High temperature reaction studies were carried out which established the basic technical feasibility of the barium recovery scheme.

The chemistry of the process has been shown to be feasible. The raw materials (coal and barium sulphate) are abundant in the Republic of South Africa while the products (water and sulphur) are in demand. Implementing the process will decrease the total dissolved solids in the Vaal Barrage benefiting all water consumers in the Pretoria-Witwatersrand-Vereeniging-Sasolburg area.

The economic benefits which would arise on implementing the system include :- 14 000 tons of sulphur (R5 600 000 - 1986); 30 000 Mℓ of water (R7 700 000 - 1985) and value added in removing 62 000 tons TDS from the Vaal Barrage (R24 800 000 - 1982) per year.

The following recommendations were made :-

- A chemical speciation program similar to Stasoft be prepared in order to aid the design of treatment processes.
- A detailed cost/benefit study be carried out in order to aid decision makers in the evaluation of the process.
- A firm of engineering contractors should assess the process technically and economically.

After a cost/benefit study and technoeconomic assessment has been undertaken, decisions can be made as to the need and direction of any further research, pilot plant evaluations or process demonstration.

ACKNOWLEDGEMENTS

Mr T. Spencer of ESKOM was involved in the concept of coupling the process to a power station. Mr. Trusler received the Durban Corporation Pollution Research Scholarship during the course of this project.

These research and development investigations were guided by a steering committee for the project which comprisved, over the period of the project, of the following members :

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Mr. P.W. Weideman	Water Research Commission
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1 INTRODUCTION

South Africa is a relatively arid country with an average rainfall of 497 mm compared to a world average of 860 mm. The rainfall is uneven and about one third of the country receives an annual rainfall of less than 300 mm. It is estimated that South Africa's exploitable surface runoff is 33 000 million m^3/annum. Present usage is about 18 000 million m^3/annum and demand is rising rapidly **(1)**.

At present there are regional water imbalances between supply and demand. The Pretoria-Witwatersrand-Vereeniging-Sasolburg (PWVS) complex is the most notable as it relies heavily on imported water from neighbouring catchments such as the Orange, Tugela, Usutu and Komati. Construction of the Lesotho Highlands Water Scheme is progressing to provide additional water.

The Vaal Catchment receives 8 % of the mean annual runoff in the country yet has the highest concentration of urban, industrial, mining and power generation development in South Africa. In 1980 it contributed 59 % of the gross national product, is home to some 5,8 million people and is the focal point for much of South Africa's future development **(2)**.

Pressure on rivers, streams and impoundments leads to water being recycled on a macroscale. One third of the water reticulated has been used before in the same basin. In the southern PWVS region 64 % of supplied water is returned in the form of effluent. As a result the total dissolved solids (TDS) level of most streams in the catchment is rising steadily.

At the Rand Water Board's (RWB) Vereeniging intake, the average TDS rose from 135 to 220 during the period 1935 to 1962 i.e. 3 mg/ℓ year. By 1979 the TDS had risen to 660 mg/ℓ which is a rise of 26 mg/ℓ year. Forecasts indicate that unless some action is taken the TDS in the Vaal Barrage could be 1 000 mg/ℓ by the end of 1990 **(3)**.

Heynike **(4)** assumed a TDS level in the Vaal Barrage of 300 mg/ℓ and calculated the total additional cost to the economy if this level should rise to 500 or 800 mg/ℓ to be 77,5 and 139,3 million Rand (1981) per annum respectively.

A large proportion of the salt influent is in the form of sulphates of calcium and magnesium and, to a lesser extent, bicarbonates.

This increasing level of mineral salt content limits the number of cycles of industrial reuse and industries require a larger quantity of water to keep discharge TDS at acceptable levels. More irrigation water is required to counteract the negative effects of salt on the soil. This increasing consumption leads to suppliers like the RWB increasing their water treatment facilities and local authorities having to increase their storage capacity to maintain a 36 hour retention volume. Higher salt levels enhance corrosion, encourage scaling in boilers and heat exchangers and serve as a substrate for organisms implicated in biocorrosion.

It is thus imperative to decrease salt addition to the Vaal River. Minewater pumpage accounts for 25 % of the salt load in the Vaal Catchment but contributes only 5 % of the flow. This research project examined the nature and sources of mineral effluents and then proposed and developed a suitable treatment process which is simple, unsophisticated and inexpensive.

The use of barium carbonate to treat high sulphate mine effluents is proposed. The barium is recycled and the sulphur is collected in the form of hydrogen sulphide.

1.1 The Effect of Removing Selected Point Sources

The Klip River contributes 54,9 % of the TDS load to the Vaal Barrage. Three mines, East Rand Premier Mine (ERPM); Durban Roodepoort Deep (DRD) and East Rand Gold and Uranium Organisation (ERGO) contribute 55 % of the TDS load but only 17 % of the flow to the Klip River.

Table 1 indicates that by treating three effluent sources with barium carbonate and lime, 42 % of the point source effluent TDS and 18 % of the total mineral load to the Vaal Barrage can be removed.

TABLE 1
The Effect of Treating Major Sulphate Contributors to the Klip River

Mines	Flow Mℓ/a	Present TDS ton/a	Removable* TDS ton/a	TDS in treated effluent ton/a
ERPM	15 150	54 900	50 000	4 900
ERGO	11 700	41 000	34 400	6 600
DRD	4 100	13 800	12 800	1 000
Total	30 950	108 700	97 200	12 500

* If the effluent were treated with barium carbonate and lime.

Western Area's expected increase in mineral contribution to the Rietspruit could also be reduced by 46 000 tons/a.

The application of a treatment process to numerous smaller effluent producers will have a lesser but still significant effect on the salt load of the Vaal River.

2 THE PROPOSED PROCESS FOR THE REMOVAL OF SULPHATES USING BARIUM CARBONATE

2.1 Process Description

The envisaged system would consist of two types of plants. A very simple water treatment plant would be located at each sulphate effluent site (Figure 1). Barium carbonate and lime would be added to the effluent to produce softened water and a precipitate. The precipitate from these local plants would be sent to a central facility where the relatively complex barium and sulphur recovery processes would take place.

At the water treatment plant, the sulphate-rich effluent is mixed with a barium carbonate/lime slurry and enters a mixed reactor. The mixing in the reactor need not be excessive but merely sufficient to maintain a uniform suspension. Calcium carbonate seed crystals encourage precipitation. About 45 minutes retention time is required. In the reactor the following reactions occur :-

$$BaCO_3 + CaSO_4 \Leftrightarrow BaSO_4\downarrow + CaCO_3\downarrow$$

$$BaCO_3 + MgSO_4 + Ca(OH)_2 \Leftrightarrow BaSO_4\downarrow + CaCO_3\downarrow + Mg(OH)_2\downarrow$$

From the reactor the slurry will enter a thickener where purified water is decanted off for use on the mine and for sale to other consumers. The thickened slurry is filtered and dried and sent to the central treatment facility.

At the central treatment facility (Figure 2) the barium sulphate/calcium carbonate mixture is mixed with pulverised coal and pelletised. These pellets are fed into a rotary kiln and reduced at 1 000 to 1 150°C. The following reactions occur :-

$$CaCO_3 \Leftrightarrow CaO + CO_2$$

$$2C + O_2 \Leftrightarrow 2CO$$

$$BaSO_4 + 4CO \Leftrightarrow \mathrm{BaS} + 4CO_2$$

The "black ash" kiln product is discharged into a wet ball or rod mill and then into a series of leaching tanks where barium sulphide is extracted with water. The insoluble portion (containing mainly ash, lime and unreacted coal) is discharged. The barium sulphide solution is reacted with the flue gas from the kiln to precipitate barium carbonate and to produce hydrogen sulphide by the following reactions :-

$$2BaS + 2H_2O \Leftrightarrow Ba(SH)_2 + Ba(OH)_2$$

$$Ba(OH)_2 + CO_2 \Leftrightarrow BaCO_3 + H_2O$$

$$Ba(SH)_2 + 2H_2O \Leftrightarrow Ba(OH)_2 + 2H_2S$$

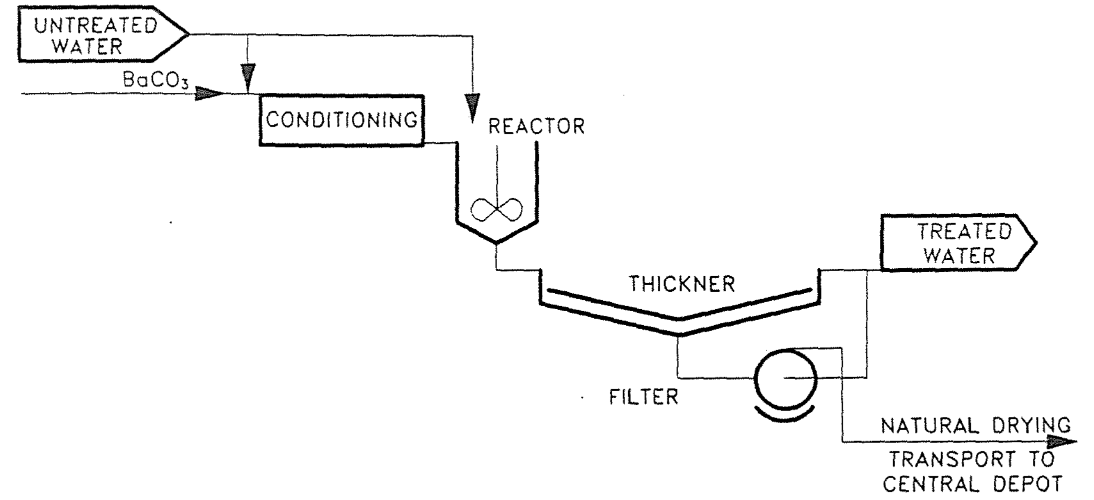

FIGURE 1 : Process Flow Diagram for the Treatment of Sulphate Rich Water with Barium Carbonate

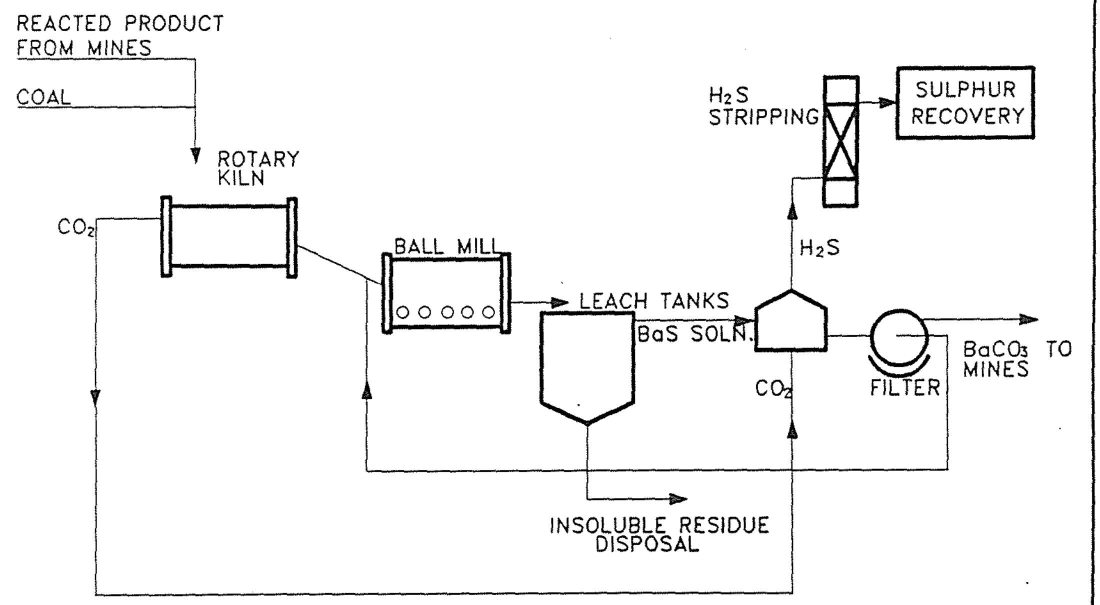

FIGURE 2 : Process Flow Diagram for the Regeneration of Barium Carbonate and the Recovery of Sulphur

The hydrogen sulphide passes through a wet scrubbing circuit and elemental sulphur is produced from the recovered gas. The barium carbonate is filtered, dried and then transported back to the local facilities for reuse.

3 REACTIONS OF BARIUM CARBONATE WITH AQUEOUS CONTAMINANTS

Barium carbonate is extremely insoluble (Ksp = $10^{-8.30}$) but barium sulphate is even more insoluble (Ksp = $10^{-9.96}$) **(5)**.

It was thus doubtful as to how readily the barium carbonate would react with the aqueous contaminants. The use of seeding and conditioning techniques increase the reaction rate. Previous proposals to increase the reaction rate have often involved the formation of the soluble barium bicarbonate. This may be formed by the addition of mineral acid to, or the bubbling of carbon dioxide through, a barium carbonate slurry. In the proposed process these routes are not feasible due to cost and the formation of soluble calcium bicarbonate.

The effluents to be treated contain three main cations : sodium, magnesium and calcium.

In the case of calcium two insoluble compounds are formed in the reaction with barium carbonate :-

$$(BaCO_3)_s + (CaSO_4)_{aq} \Leftrightarrow (BaSO_4)_s + (CaCO_3)_s$$

However, sodium and magnesium carbonates are very soluble in comparison to calcium carbonate and the efficiency of sulphate removal can be expected to be lower.

The equilibria between dilute solutions of calcium, magnesium, sodium sulphates and barium carbonate were calculated using the MINEQL computer speciation program **(6)**.

The distribution of species predicted for stoichiometric addition of barium bicarbonate to 1,56 x 10^{-2} mol/ℓ solutions of the sulphates of these three cations is given in Table 2.

TABLE 2
Efficiency of Precipitation of Anionic and Cationic Impurities

Cation type	% Precipitation		
	SO_4^{2-}	CO_3^{2-}	Cation
Calcium	100	98,9	98,9
Magnesium	98,9	1,1	24,7
Sodium	95,5	0	0

Thus in all cases, a satisfactory degree of removal of sulphate was predicted.

However, tests on synthetic solutions were able to confirm these results only in the case of calcium; much higher than predicted residual sulphates were found in the case of solutions of magnesium and sodium sulphates.

Further testwork showed this to be the result of kinetic factors; in the case of calcium ions, precipitation of calcium carbonate maintains a high driving force for the reaction throughout, but where the cations remain soluble together with carbonate, the driving force decreases rapidly.

To overcome this, lime was added in addition to the barium carbonate to remove carbonate ions associated with soluble cations. This proved very successful and in a number of tests on synthetic solutions, almost complete removal of sulphate ions was achieved.

The addition of lime has the additional benefit of removing magnesium ions as the relatively insoluble magnesium hydroxide precipitate.

In view of these encouraging results, further testwork was carried out on complex solutions simulating real mine effluents.

4 PRECIPITATION RESULTS

Simulated samples of ERGO and ERPM effluent were prepared. The mixtures were seeded with 500 mg/ℓ calcium carbonate and a 25 % stoichiometric excess of barium carbonate was used.

The results from a simulated typical ERGO effluent is given in Table 3.

TABLE 3
Salt Removal from a Simulated ERGO Effluent
Using Barium Carbonate

Time (min)	0	15	30	45	60	75	105
Total dissolved solids	3 750	2 150	1 256	1 058	1 039	970	905
Sulphate	2 300	1 306	636	484	456	403	351
Chloride	210	210	210	210	210	210	210
Iron	60	0	0	0	0	0	0
Potassium	50	40	30	30	40	40	30
Sodium	250	220	250	235	230	230	230
Calcium	560	290	50	20	20	10	10
Magnesium	140	84	80	79	83	77	74

All determinants in mg/ℓ.

A gradual reaction and incomplete removal of sulphate was observed due to the presence of sodium and magnesium, as was expected.

In a second test on a similar solution, calcium hydroxide was added in stoichiometric equivalent to the magnesium and sodium content of the solution. The beneficial effect can be seen in Table 4.

TABLE 4
Salt Removal from Simulated ERPM Effluent
Using Barium Carbonate and Lime

Time (mins)	0	15	30	45	60	75	105
Total dissolved solids	3 562	1 519	407	318	318	318	318
Sulphate	2 400	920	86	0	0	0	0
Chloride	120	120	120	120	120	120	120
Potassium	16	16	16	16	16	16	16
Sodium	180	180	180	180	180	180	180
Iron	80	0	0	0	0	0	0
Calcium	636	280	4	1	1	1	1
Magnesium	130	3	1	1	1	1	1

All determinants in mg/ℓ.

Using atomic absorption spectroscopy with a detection limit of 1 mg/ℓ, no barium was detected in the supernatant. Thus the water produced conformed to all drinking standards regarding barium.

A sample of water was obtained (15 March 1988) from ERGO to see if it would react in the same way as the simulated mixture. It appeared reddish, probably due to suspended hematite, and also contained other suspended solids. The water analysis is given in Table 5.

This water was seeded with 1 g/ℓ calcium carbonate and reacted with 6,5 g/ℓ barium carbonate and 0,8 g/ℓ calcium hydroxide. No magnesium or iron could be detected after 15 minutes of reaction time. Results for sulphate and calcium are shown in Table 6.

The size analysis of the precipitate obtained in this test is given in Table 7 for the ERGO salt removal reaction. The small proportion of crystals in the very small size ranges indicates that the predominant precipitation mechanism is one of crystal growth.

TABLE 5
ERGO Water Analysis

pH	4
Total dissolved solids	4 112
Suspended solids	126
Sulphate	2 527
Chloride	207
Calcium	653
Magnesium	152
Iron	5,6
Manganese	7,5
Sodium	242

All determinants in mg/ℓ

TABLE 6
Calcium and Sulphate Removal from ERGO Effluent with Barium Carbonate and Lime

Time (min)	0	15	30	45	60	75	90
Sulphate	1 870	1 236	372	0	0	0	0
Calcium	653	610	490	120	10	2	1

All determinants in mg/ℓ

TABLE 7
Aqueous Reaction Product
Size Analysis

Weight in Band (microns)	%
188 - 87,2	0,0
87,2 - 53,5	0,0
53,5 - 37,6	0,1
37,6 - 28,1	0,6
28,1 - 21,5	1,6
21,5 - 16,7	3,5
16,7 - 13,0	9,0
13,0 - 10,1	20,9
10,1 - 7,9	27,0
7,9 - 6,2	14,1
6,2 - 4,8	7,0
4,8 - 3,8	7,5
3,8 - 3,0	4,4
3,0 - 2,4	1,6
2,4 - 1,9	1,1

5 THE THERMAL REDUCTION OF A BARIUM SULPHATE/CALCIUM CARBONATE MIXTURE

5.1 Kinetics of Reduction

The main constituents of real precipitates will be barium sulphate and calcium carbonate.

Kinetics studies on the reduction of the sulphate to sulphide at high temperatures using coal as the reductant were carried out in an isothermal thermobalance.

Between 20 g and 30 g of equimolar mixtures of barium sulphate and calcium carbonate were mixed with finely ground Bosjesspruit coal. This coal has the analysis given in Table 8.

The rate of reduction of sulphate to sulphide was measured at a number of different temperatures. The results are shown in Figure 3. These results indicate that a satisfactory rate of reduction is obtained at temperatures below 1 250°C. In practice, temperatures above this must not be used to prevent ring formation within the kiln.

TABLE 8
Analysis of Bosjesspruit Coal

Proximate analysis (air dry basis)

H_2O	3,9 %
Ash	20,9 %
Volatile matter	21,9 %
Free carbon	53,3 %
Calorific value	31,0 MJ/kg

Mineral Matter Composition

Component	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
Mass %	43,6	26,3	6,47	1,43	1,43	11,8	3,64	0,57	0,60	4,06

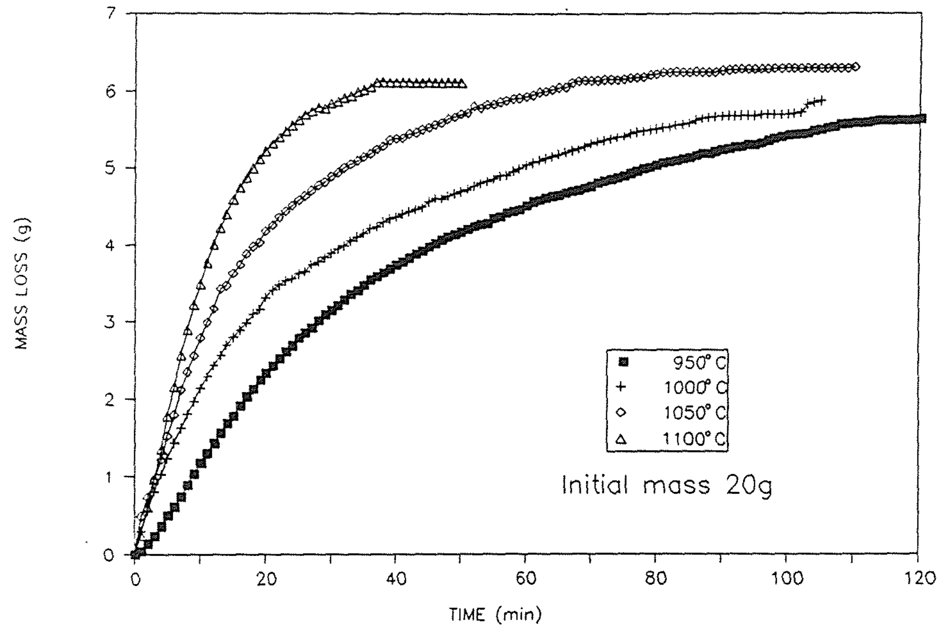

FIGURE 3 : **Reduction Kinetics of Barium Sulphate and Calcium Carbonate Using Coal as a Reductant**

5.2 Conversion of Barium into a Soluble Form

When reaction products from high temperature reductions were leached with water, it became evident that a considerable proportion (20 %) of the barium remained insoluble. This problem was initially thought to be due to incomplete reduction but even after precautions had been taken to eliminate this, some barium remained insoluble.

The insoluble fraction was a complex mixture of compounds and the cause of barium loss could not easily be determined by X-ray diffraction (XRD) analysis.

In order to determine whether and which of the components of the coal ash had this deleterious effect, each of the main constituents of the ash, i.e. SiO_2, Al_2O_3 and Fe_2O_3 were reacted separately with $BaSO_4/CaCO_3/C$ mixtures at 1 150°C. The products of these reactions were identified by X-ray diffraction, with the results given in Table 9.

TABLE 9
Products of Reaction of $BaSO_4/CaCO_3$ Mixtures with Constituents of Coal Ash

Ash constituent	Mass addition	Products obtained
SiO_2	2 %	BaS, CaO, $CaSiO_3$
Al_2O_3	2 %	BaS, $BaAl_2O_4$, CaO
Fe_2O_3	10 %	BaS, $BaFe_2O_4$, CaO

Thus, of the ash constituents, only Fe_2O_3 and Al_2O_3 will combine with barium. Barium monoaluminate is fairly soluble, and should not create a problem in the process. Barium ferrite is, however, completely insoluble, and is almost certainly the main cause of barium losses in the process.

This has obvious implications for the choice of coal which would be used as the reductant in the process.

6 THE PRODUCTION OF BARIUM CARBONATE FROM REDUCTION KILN PRODUCTS

6.1 Chemistry of Barium Carbonate Production

Barium sulphide dissolves readily in water and 10 % of the aqueous barium sulphide dissociates as shown below[7].

$$2BaS + 2H_2O \Leftrightarrow Ba(SH)_2 + Ba(OH)_2$$

Any barium oxide present will hydrolyse :-

$$BaO + H_2O \Leftrightarrow Ba(OH)_2$$

The solution is thus extremely caustic with very high pH.

When carbon dioxide is bubbled through the solution it forms carbonate ions which then precipitate insoluble barium carbonate.

$$Ba(OH)_2 + CO_3^{2-} \Leftrightarrow BaCO_3\downarrow + 2OH^-$$

The barium hydrosulphide then dissociates to maintain equilibrium between the hydroxide and the hydrosulphide ions.

$$Ba(SH)_2 + 2OH^- \Leftrightarrow Ba(OH)_2 + 2SH^-$$

$$SH^- + OH^- \Leftrightarrow H_2O + S^{2-}$$

$$H_2S \Leftrightarrow HS^- + H^+$$

As barium carbonate is precipitated, the pH of the solution falls with the result that H_2S is generated and is removed from solution.

Small scale tests showed that a simulated kiln flue-gas (80 % N_2, 20 % CO_2) carbonates barium sulphide solution efficiently to produce a concentrated (10 to 20 %) stream of H_2S for conversion to elemental sulphur.

6.2 Production Methods

The production of barium carbonate by the route described here i.e. reduction of barytes to barium sulphide, leaching of the "black ash" and carbonation of the solution is an established commercial process.

Various types of equipment have been described in the literature for the various unit operations :-

(i) reduction is normally carried out in short rotary kilns at temperatures around 1 200°C. Pulverised coal is used as the fuel, and the barium sulphate agglomerated before reduction to produce a non-dusting kiln charge.

(ii) leaching is carried out on a finely milled "black ash" in agitated tanks, but a percolation type leach has also been proposed **(8)**.

(iii) The carbonation of the sulphide liquor has been the subject of many studies **(9,10,11)** and a number of different contracting devices tested.

(iv) Conversion of concentrated hydrogen sulphide streams to elemental sulphur is well-known technology and both liquid-phase and gas-phase (Claus) reactors are available for this purpose.

7 SOLIDS WASTE DISPOSAL

The main calcium product from the reduction kiln will be calcium oxide. During the leaching process this will be converted to hydrated lime and remain in the residue.

The calcium silicates are extremely insoluble and together with unreacted coal and coal ash will also remain in the residue.

The barium ferrites and unreacted barium sulphate will be lost as insoluble salts.

All insoluble solids may be easily disposed of by filtering the barium sulphide solution. The insoluble portion will include extremely inert barium compounds and lime. This slaked lime might easily be used as a neutralising agent in numerous other processes and could be a saleable product.

8 ECONOMIC CONSIDERATION

The cost of imported sulphur is R400 (1986) per ton. The treatment of 85 Mℓ/day of mine pump water containing 2 000 mg/ℓ of sulphates would produce 14 000 tons of sulphur per year, with a total value of R5 600 000 (1986) per year. The value of 85 Mℓ/day of purified water at R0,25/kℓ (1985 RWB) would be R7 700 000 per year.

The study by Heynike and McCulloch (3) has indicated that the value of removing TDS varies from R320 (1982) per ton to R450 (1982) per ton for two different scenarios. Assuming a figure of R400 per ton, then the value of removing the TDS would be R24 800 000 (1982) per year.

The barium is reused, hence saving the most expensive component. Input of raw material is in the form of barytes and coal. Coal is a cheap and readily available source of energy and reducing carbon. Barytes deposits occur in numerous places in South Africa, the largest of which is 50 km west of Pofadder in the N.W. Cape Province.

9 DISCUSSION

The contaminants distributed in a large effluent stream are concentrated into a small stream with no disposal problems. Useful water is produced from the effluent streams for use on the mines or for sale to other consumers.

Elemental sulphur is in short supply in South Africa and is imported at high cost. This process will significantly reduce the amount imported with consequent savings in foreign exchange.

The TDS and especially the sulphate level of public watercourses will be significantly lowered. The largest point source contributors of mineral load would have been almost eliminated. Together with good management to decrease the contribution by diffuse sources the cost incurred by rising TDS would be significantly reduced.

Barium is added in a very insoluble and hence non-toxic form. The chances of contaminating a product stream are minimal. Product water would always comply to the EPA recommended maximum of 1 mg/ℓ barium. Handling of the dry chemicals presents no hazard and so no control measures are necessary.

The unit operations used at the local facilities such as agitated reactors, thickeners and filters are easy to construct and maintain and are readily available. They do not require any skilled or intensive manpower to operate. At the central facility the required rotary kiln is used world-wide as the first process in the production of barium salts from barytes. Leach tanks and solution precipitation reactors are standard processing equipment. The wet scrubbing of hydrogen sulphide containing gas streams and the subsequent conversion to sulphur is also proven technology.

The observed length of strike of the Pofadder barytes deposit is 1 160 m dipping at angles between 30° and 50°. Reserves are calculated as 2 767 000 tons for every 30 m down dip (12). Numerous smaller deposits such as those in the Pietersburg area and along the Swaziland border could possibly be exploited for make-up purposes.

No pretreatment is necessary to remove the suspended solids present in the mining effluent. Most of the solids will be removed in the settler.

The sulphurous product in the form of hydrogen sulphide is produced in a small concentrated stream which is amenable to further processing such as sulphur production.

10 CONCLUSIONS

(i) The addition of barium carbonate and lime to sulphate mine effluents effectively removes all dissolved solids except for group I and VIII ions.

(ii) Calcium carbonate seed crystal enhance reaction rates.

(iii) The sulphates in the effluents are captured in the form of a concentrated hydrogen sulphide stream which is amenable to further processing into valuable sulphur products.

(iv) The barium salts may be effectively recycled with minimal make-up being required.

(v) Barium is handled in its least toxic form namely the sulphate and the carbonate.

(vi) The barium sulphate and carbonate precipitates may be readily thickened and filtered.

(vii) The presence of calcium carbonate in the reduction step enhances the recovery of water soluble barium salts by reaction with the silicates contained in the coal. It also liberates carbon dioxide which is used to carbonate the barium sulphide solution.

(viii) All unit operations are ideally suited to a mining environment.

(ix) Technology required for this process is available.

(x) The raw materials required, namely barytes and coal, exist in abundance in South Africa while the products, sulphur and water, are in demand.

(xi) The establishment of a baryte reduction kiln could pave the way for the establishment of a barium chemicals industry.

(xii) There is no solids or brine disposal problem.

11 RECOMMENDATIONS

- A chemical speciation program similar to Stasoft be prepared in order to aid the design of treatment processes.
- A detailed cost/benefit study be carried out in order to aid decision makers in the evaluation of the process.
- A firm of engineering contractors should assess the process technically and economically.

After a cost/benefit study and technoeconomic assessment has been undertaken, decisions can be made as to the need and direction of any further research, pilot plant evaluations or process demonstration.

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13 PUBLICATIONS

The following publications have resulted from the research project :-

(i) Trusler, G.E., **The Chemical Removal of Sulphates Using Barium** Salts. M.Sc. (Eng.) Thesis, University of Natal (1988).

(ii) Trusler, G.E., Edwards, R.I., Brouckaert, C.J. and Buckley, C.A., **The Chemical Removal of Sulphates.** Proceedings of 5th National Meeting, South African Institution of Chemical Engineers, Pretoria, 15 - 16 August 1988.

(iii) Edwards, R.I. and Buckley, C.A., **The Removal of Dissolved Salts from Recirculating Waters in the Vaal River Drainage System.** Proceedings of the 5th Biennial Symposium of the Ground Water Division, Geological Society of South Africa, ISBN 0-620-13620-3, 31 July - 4 August 1989.

(iv) Trusler, G.E., Edwards, R.I. and Buckley, C.A., **Sulphate, Calcium and Heavy Metal Removal from Industrial Effluents Using Barium Carbonate.** WaterSA (in press).

14 APPENDICES

*APPENDIX 1 :	**The Chemical Removal of Sulphates Using Barium Salts** - MScEng Thesis, G.E. Trusler
APPENDIX 2 :	**The Chemical Removal of Sulphates** - Paper Presented at the 5th National Meeting of the South African Institution of Chemical Engineers
APPENDIX 3 :	**The Removal of Dissolved Salts from Recirculating Waters in the Vaal River Drainage System** - Paper Presented at the 5th Biennial Symposium of the Ground Water Division, Geological Society of South Africa
APPENDIX 4	**Sulphate, Calcium and Heavy Metal Removal from Industrial Effluents Using Barium Carbonate**, Paper Submitted to WaterSA (Draft).

*This being a thesis, is not included in the final report.

WATER RESEARCH COMMISSION PROJECT NO. 203

THE CHEMICAL REMOVAL OF SULPHATES

APPENDIX 2

TO FINAL REPORT

THE CHEMICAL REMOVAL OF SULPHATES - Paper Presented

at the 5th National Meeting of the

South African Institution of Chemical Engineers

Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

October 1989

THE CHEMICAL REMOVAL OF SULPHATES

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SYNOPSIS

The steadily increasing salt concentration in the Vaal River drainage system is becoming a serious problem due to the large scale recirculation of water, and the fact that conventional water treatment processes do not significantly reduce inorganic pollutants.

Four mines were found to contribute 38% of the salt load to the system, the major anion being sulphate, which results from oxidation of pyrite.

A laboratory investigation has shown that these effluents can be desalinated by treatment with barium carbonate and lime.

The reaction kinetics of barium carbonate with aqueous calcium, magnesium and sodium sulphates have been investigated. Where magnesium or sodium cations are present, calcium hydroxide is required in addition to achieve complete sulphate removal.

Barium carbonate is a relatively expensive reagent, and for its use to be economically viable, it will be necessary to recover for reuse. This could be carried out at a central facility, where barium sulphate would be reduced with coal to barium sulphide. This would be leached with water, and the solution treated with carbon dioxide to regenerate the barium carbonate generating a by-product stream of H_2S. High temperature reaction studies were carried out which established the basic technical feasibility of this barium recovery scheme.

The chemistry of the process has been shown to be feasible. The raw materials (coal and barium sulphate) are abundant in South Africa while the products (water and sulphur) are in demand. Implementing the process will decrease the total dissolved solids in the Vaal Barrage benefiting all water consumers in the Pretoria-Witwatersrand-Vereeniging-Sasolburg area.

Paper to be presented at the 5th National meeting of the Institute of Chemical Engineers in Pretoria on 15-16 August 1988.

1 INTRODUCTION

South Africa is a relatively arid country with an average rainfall of 497 mm compared to a world average of 860 mm. The rainfall is uneven and about one third of the country receives an annual rainfall of less than 300 mm. It is estimated that South Africa's exploitable surface runoff is 33 000 million m^3/annum. Present usage is about 18 000 million m^3/annum and demand is rising rapidly[1].

At present there are regional water imbalances between supply and demand. The Pretoria-Witwatersrand-Vereeniging-Sasolburg (PWVS) complex is the most notable as it relies heavily on imported water from neighbouring catchments such as the Orange, Tugela, Usutu and Komati. Construction on the Lesotho Highlands Water Scheme is progressing to provide additional water.

The Vaal Catchment produces 8% of the mean annual runoff in the country but has the highest concentration of urban, industrial, mining and power generation development in South Africa. In 1980 it contributed 59% of the gross national product, is home to some 5,8 million people and is the focal point for much of South Africa's future development[2].

This pressure on rivers, streams and impoundments leads to water being recycled on macroscale. One third of the water reticulated has been used before in the same basin. In the southern PWVS region 64% of supplied water is returned in the form of effluent. As a result the total dissolved solids (TDS) level of most streams in the catchment is rising steadily.

At the Rand Water Board's (RWB) Vereeniging intake, the average TDS rose from 135 to 220 during the period 1935 to 1962 i.e. 3 mg/ℓ/year. By 1979 the TDS had risen to 660 mg/ℓ which is a rise of 26 mg/ℓ/year. Forecasts indicate that unless some action is taken the TDS in the Vaal Barrage could be 1 000 mg/ℓ by the end of 1990[3].

Heynike[4] assumed a TDS level in the Vaal Barrage of 300 mg/ℓ and calculated the total additional cost to the economy if this level should rise to 500 or 800 mg/ℓ to be 77,5 and 139,3 million Rand (1981) per annum respectively.

A large proportion of the salt influent is in the form of sulphates of calcium and magnesium and, to a lesser extent, bicarbonates.

This increasing level of mineral salt content limits the number of cycles of industrial reuse and industries require a larger quantity of water to keep discharge TDS at acceptable levels. More irrigation water is required to counteract the negative effects of salt on the soil. This increasing consumption leads to suppliers like the RWB increasing their water treatment facilities and local authorities having to increase their storage capacity to maintain a 36 hour retention volume. Higher salt levels enhance corrosion, encourage scaling in boilers and heat exchangers and serve as a substrate for organisms implicated in biocorrosion.

It is thus imperative to decrease salt addition to the Vaal River. Minewater pumpage accounts for 25% of the salt load in the Vaal Catchment but contributes only 5% of the flow. This paper examines the nature and sources of mineral effluents and then proposes and develops a suitable treatment process which is simple, unsophisticated and inexpensive.

The use of barium carbonate to treat high sulphate mine effluents is proposed. The barium is recycled and the sulphur is collected in the form of hydrogen sulphide.

1.1 The Effect of Removing Selected Point Sources

The Klip River contributes 54,9% of the TDS load to the Vaal Barrage. Three mines, ERPM; DRD and ERGO contribute 55% of the TDS load but only 17% of the flow to the Klip River.

Table 1 indicates that by treating three effluent sources with barium carbonate and lime, 42% of the point source effluent TDS and 18% of the total mineral load to the Vaal Barrage can be removed.

TABLE 1 : The Effect of Treating Major Sulphate Contributors to the Klip River

Mines	Flow Mℓ/a	Present TDS ton/a	Removable* TDS ton/a	TDS in treated effluent ton/a
ERPM	15 150	54 900	50 000	4 900
ERGO	11 700	41 000	34 400	6 600
DRD	4 100	13 800	12 800	1 000
Total	30 950	108 700	97 200	12 500

* If the effluent were treated with barium carbonate and lime.

Western Area's expected increase in mineral contribution to the Rietspruit could also be reduced by 46 000 tons/a.

The application of a treatment process to numerous smaller effluent producers will have a lesser but still significant effect on the salt load of the Vaal River.

2 THE PROPOSED PROCESS FOR THE REMOVAL OF SULPHATES USING BARIUM CARBONATE

2.1 Process Description

The envisaged system would consist of two types of plants. A very simple water treatment plant would be located at each sulphate effluent site (Figure 1). Barium carbonate and lime would be added to the effluent to produce softened water and a precipitate. The precipitate from these local plants would be sent to a central facility where the relatively complex barium and sulphur recovery processes would take place.

At the water treatment plant, the sulphate-rich effluent is mixed with a barium carbonate/lime slurry and enters a mixed reactor. The mixing in the reactor need not be excessive but merely sufficient to maintain a uniform suspension. Calcium carbonate seed crystals encourage precipitation. About 45 minutes retention time is required. In the reactor the following reactions occur:

$$BaCO_3 + CaSO_4 \Leftrightarrow BaSO_4\downarrow + CaCO_3\downarrow$$

$$BaCO_3 + MgSO_4 + Ca(OH)_2 \Leftrightarrow BaSO_4\downarrow + CaCO_3\downarrow + Mg(OH)_2\downarrow$$

From the reactor the slurry will enter a thickener where purified is decanted off for use on the mine and for sale to other consumers. The thickened slurry is filtered and dried and sent to the central treatment facility.

At the central treatment facility (Figure 2) the barium sulphate/calcium carbonate mixture is mixed with pulverised coal and pelletised. These pellets are fed into a rotary kiln and reduced at 1 000 to 1 150°C. The following reactions occur:

$$CaCO_3 \Leftrightarrow CaO + CO_2$$

$$C + \frac{1}{2}O_2 \Leftrightarrow CO$$

$$BaSO_4 + 4CO \Leftrightarrow \mathrm{BaS} + 4CO_2$$

The black ash kiln product is discharged into a wet ball or rod mill and then into a series of leaching tanks where barium sulphide is extracted with water. The insoluble portion containing mainly ash, lime and unreacted coal is discharged. The barium sulphide solution is reacted with the flue gas from the kiln to precipitate barium carbonate and to produce hydrogen sulphide by the following reactions:

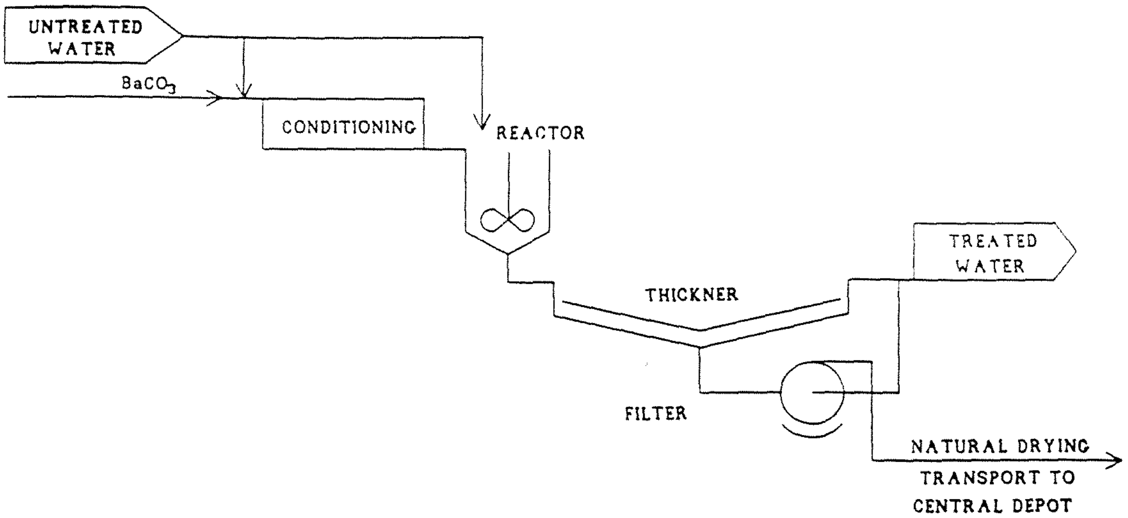

FIGURE 1 : Process Flow Diagram for the Treatment of Sulphate Rich Water with Barium Carbonate

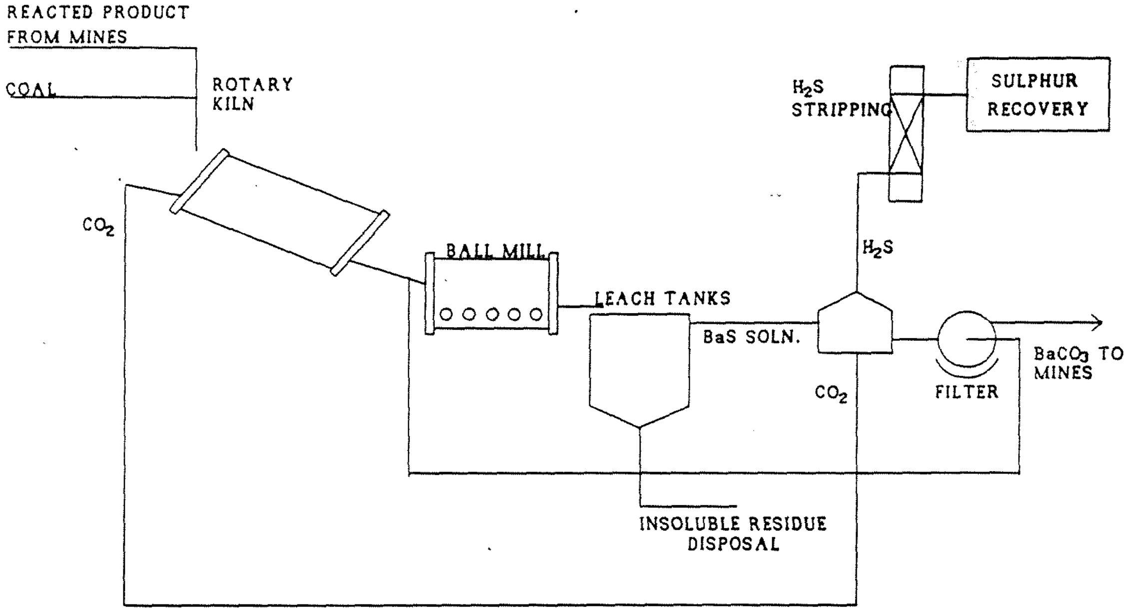

FIGURE 2 : Process Flow Diagram for the Regeneration of Barium Carbonate and the Recovery of Sulphur

$$2BaS + 2H_2O \Leftrightarrow Ba(SH)_2 + Ba(OH)_2$$
$$Ba(OH)_2 + CO_2 \Leftrightarrow BaCO_3 + H_2O$$
$$Ba(SH)_2 + 2H_2O \Leftrightarrow Ba(OH)_2 + 2H_2S$$

The hydrogen sulphide passes through a wet scrubbing circuit and elemental sulphur is produced from the recovered gas. The barium carbonate is filtered, dried and then transported back to the local facilities for reuse.

3 REACTIONS OF BARIUM CARBONATE WITH AQUEOUS CONTAMINANTS

Barium carbonate is extremely insoluble ($K_{sp} = 10^{-8.30}$) but barium sulphate is even more insoluble ($K_{sp} = 10^{-9.96}$)[5].

It was thus doubtful as to how readily the barium carbonate would react with the aqueous contaminants. The use of seeding and conditioning techniques increase the reaction rate. Previous proposals to increase the reaction rate have often involved the formation of the soluble barium bicarbonate. This may be formed by the addition of mineral acid to, or the bubbling of carbon dioxide through, a barium carbonate slurry. In the proposed process these routes are not feasible due to cost and the formation of soluble calcium bicarbonate.

The effluents to be treated contain three main cations: Na^+, Mg^{2+} and Ca^{2+}.

In the case of calcium two insoluble compounds are formed in the reaction with barium carbonate:-

$$(BaCO_3)_s + (CaSO_4)_{aq} \Leftrightarrow (BaSO_4)_s + (CaCO_3)_s$$

However, sodium and magnesium carbonates are very soluble in comparison to calcium carbonate and the efficiency of sulphate removal can be expected to be lower.

The equilibria between dilute solutions of calcium, magnesium, sodium sulphates and barium carbonate were calculated using the MINEQL programme[6].

The distribution of species predicted for stoichiometric addition of $BaCO_3$ to 1,56 x 10^{-2} mol/ℓ solutions of the sulphates of these three cations is given in Table 2.

TABLE 2 : Efficiency of Precipitation of Anionic and Cationic Impurities

Cation type	% Precipitation		
	SO_4^{2-}	CO_3^{2-}	Cation
Ca^{2+}	100	98,9	98,9
Mg^{2+}	98,9	1,1	24,7
Na^+	95,5	0	0

Thus in all cases, a satisfactory degree of removal of sulphate is predicted.

However, tests on synthetic solutions were able to confirm these results only in the case of calcium; much higher residual sulphates than predicted were found in the case of solutions of magnesium and sodium sulphates.

Further testwork showed this to be the result of kinetic factors; in the case of Ca^{2+}, precipitation of calcium carbonate maintains a high driving force for the reaction throughout, but where the cations remain soluble together with carbonate, the driving force decreases rapidly.

To overcome this, lime was added in addition to the barium carbonate to remove CO_3^{2-} associated with soluble cations. This proved very successful and in a number of tests on synthetic solutions, almost complete removal of SO_4^{2-} was achieved.

The addition of lime has the additional benefit of removing Mg^{2+} as the relatively insoluble $Mg(OH)_2$.

In view of these encouraging results, further testwork was carried out on complex solutions simulating real mine effluents.

4 PRECIPITATION RESULTS

Simulated samples of ERGO and ERPM effluent were prepared. The mixtures were seeded with 500 mg/ℓ calcium carbonate and a 25% stoichiometric excess of barium carbonate was used.

The results from a simulated typical ERGO effluent is given in Table 3.

TABLE 3 : Salt Removal from a Simulated ERGO Effluent Using Barium Carbonate

Time (min)	0	15	30	45	60	75	105
TDS (mg/ℓ)	3 750	2 150	1 256	1 058	1 039	970	905
$SO_4^=$ (mg/ℓ)	2 300	1 306	636	484	456	403	351
Cl^- (mg/ℓ)	210	210	210	210	210	210	210
Fe^{2+} (mg/ℓ)	60	0	0	0	0	0	0
K^+ (mg/ℓ)	50	40	30	30	40	40	30
Na^+ (mg/ℓ)	250	220	250	235	230	230	230
Ca^{2+} (mg/ℓ)	560	290	50	20	20	10	10
Mg^{2+} (mg/ℓ)	140	84	80	79	83	77	74

A gradual reaction and incomplete removal of sulphate was observed due to the presence of sodium and magnesium, as was expected.

In a second test on a similar solution, calcium hydroxide was added in stoichiometric equivalent to the magnesium and sodium content of the solution. The beneficial effect can be seen in Table 4.

TABLE 4 : Salt Removal from Simulated ERPM Effluent Using Barium Carbonate and Lime

Time (mins)	0	15	30	45	60	75	105
TDS (mg/ℓ)	3 562	1 519	407	318	318	318	318
SO_4^{2-} (mg/ℓ)	2 400	920	86	0	0	0	0
Cl^- (mg/ℓ)	120	120	120	120	120	120	120
K^+ (mg/ℓ)	16	16	16	16	16	16	16
Na^+ (mg/ℓ)	180	180	180	180	180	180	180
Fe^{2+} (mg/ℓ)	80	0	0	0	0	0	0
Ca^{2+} (mg/ℓ)	636	280	4	1	1	1	1
Mg^{2+} (mg/ℓ)	130	3	1	1	1	1	1

No barium was detected in solution, using AA spectroscopy with a lower concentration limit of 1 mg/ℓ, in the supernatant solution. Thus the water produced conformed to all drinking standards regarding barium.

A sample of water was obtained (15 March 1988) from ERGO to see if it would react in the same way as the simulated mixture. It appeared reddish, probably due to suspended hematite, and also contained other suspended solids. The water analysis is given in Table 5.

This water was seeded with 1 g/ℓ calcium carbonate and reacted with 6,5 g/ℓ barium carbonate and 0,8 g/ℓ calcium hydroxide. No magnesium or iron could be detected after 15 minutes of reaction time. Results for sulphate and calcium are shown in Table 6.

TABLE 5 : ERGO Water Analysis

pH	4
TDS (mg/ℓ)	4 112
SS (mg/ℓ)	126
SO_4 (mg/ℓ)	2 527
Cl (mg/ℓ)	207
Ca (mg/ℓ)	653
Mg (mg/ℓ)	152
Fe (mg/ℓ)	5,6
Mn (mg/ℓ)	7,5
Na (mg/ℓ)	242

TABLE 6 : Calcium and Sulphate Removal from ERGO Effluent with Barium Carbonate and Lime

Time (min)	0	15	30	45	60	75	90
SO_4 (mg/ℓ)	1 870	1 236	372	0	0	0	0
Ca (mg/ℓ)	653	610	490	120	10	2	1

The size analysis of the precipitate obtained in this test is given in Table 7 for the ERGO salt removal reaction. The small proportion of crystals in the very small size ranges indicates that the predominant precipitation mechanism is one of crystal growth.

TABLE 7 : Aqueous Reaction Product Size Analysis

Weight in Band (microns)	%
188 - 87,2	0,0
87,2 - 53,5	0,0
53,5 - 37,6	0,1
37,6 - 28,1	0,6
28,1 - 21,5	1,6
21,5 - 16,7	3,5
16,7 - 13,0	9,0
13,0 - 10,1	20,9
10,1 - 7,9	27,0
7,9 - 6,2	14,1
6,2 - 4,8	7,0
4,8 - 3,8	7,5
3,8 - 3,0	4,4
3,0 - 2,4	1,6
2,4 - 1,9	1,1

5 THE THERMAL REDUCTION OF A BARIUM SULPHATE/CALCIUM CARBONATE MIXTURE

5.1 Kinetics of Reduction

The main constituents of real precipitates will be barium sulphate and calcium carbonate.

Kinetics studies on the reduction of the sulphate to sulphide at high temperatures using coal as the reductant were carried out in an isothermal thermobalance.

Between 20 g and 30 g of equimolar mixtures of barium sulphate and calcium **carbonate** were mixed with finely ground Bosjesspruit coal. This coal has the analysis given in Table 8.

TABLE 8 : Analysis of Bosjesspruit Coal

Proximate analysis (air dry basis)

H_2O	3,9%
Ash	20,9%
Volatile matter	21,9%
Free carbon	53,3%
Calorific value	31,0 MJ/kg

Mineral Matter Composition

Component	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
Mass %	43,6	26,3	6,47	1,43	1,43	11,8	3,64	0,57	0,60	4,06

The rate of reduction of sulphate to sulphide was measured at a number of different temperatures. The results are shown in Figure 3. These results indicate that a satisfactory rate of reduction is obtained at temperatures below 1 250°C. In practice, temperatures above this must not be used to prevent ring formation within the kiln.

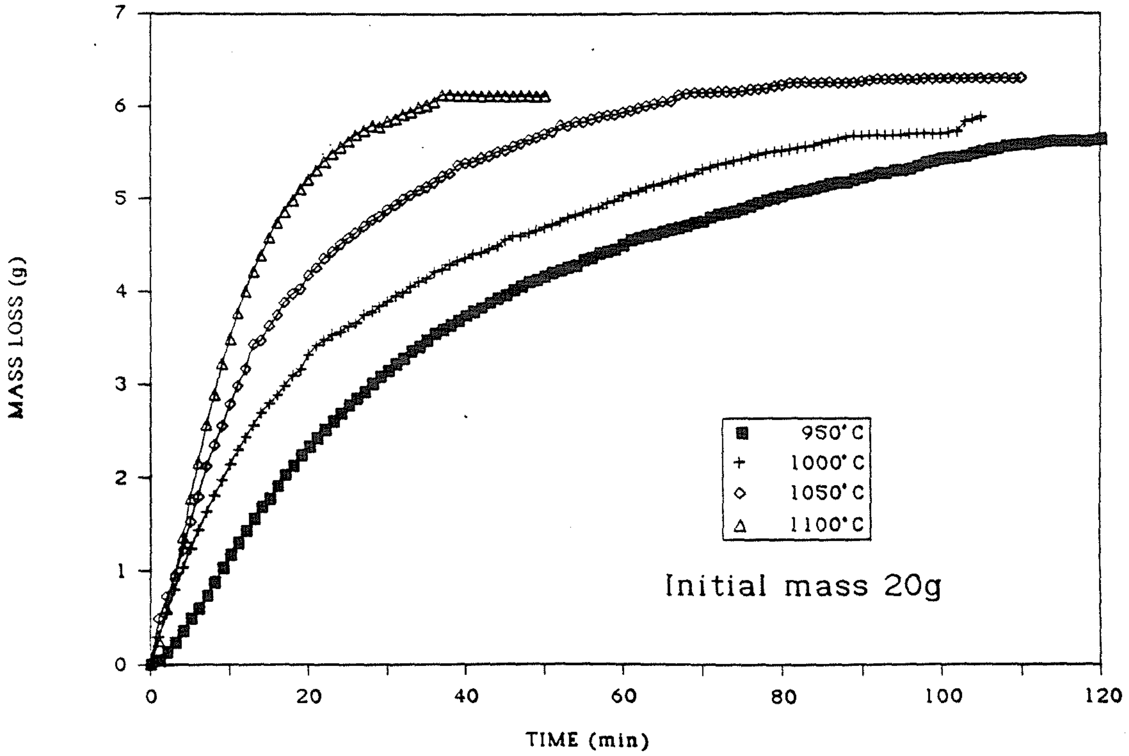

FIGURE 3 : Reduction Kinetics of Barium Sulphate and Calcium Carbonate Using Coal as a Reductant

5.2 Conversion of Barium into a Soluble Form

When reaction products from high temperature reductions were leached with water, it became evident that a considerable proportion (20%) of the barium remained insoluble. This problem was initially thought to be due to incomplete reduction but even after precautions had been taken to eliminate this, some barium remained insoluble.

The insoluble fraction was a complex mixture of compounds and the cause of barium loss could not easily be determined by XRD analysis.

In order to determine whether and which of the components of the coal ash had this deleterious effect, each of the main constituents of the ash, i.e. SiO_2, Al_2O_3 and Fe_2O_3 reacted separately with $BaSO_4/CaCO_3/C$ mixtures at 1 150°C. The products of these reactions were determined by XRD analysis, with the results given below.

TABLE 9 : Products of Reaction of $BaSO_4/CaCO_3$ Mixtures with Constituents of Coal Ash

Ash constituent	Mass addition	Products obtained
SiO_2	2%	BaS, CaO, $CaSiO_3$
Al_2O_3	2%	BaS, $BaAl_2O_4$, CaO
Fe_2O_3	10%	BaS, $BaFe_2O_4$, CaO

Thus, of the ash constituents, only Fe_2O_3 and Al_2O_3 will combine with barium. Barium monoaluminate is fairly soluble, and should not create a problem in the process. Barium ferrite is, however, completely insoluble, and is almost certainly the main cause of barium losses in the process.

This has obvious implications for the choice of coal which would be used as the reductant in the process.

6 THE PRODUCTION OF BARIUM CARBONATE FROM REDUCTION KILN PRODUCTS

6.1 Chemistry of Barium Carbonate Production

Barium sulphide dissolves readily in water and 10% of the aqueous barium sulphide dissociates as shown below[7].

$$2BaS + 2H_2O \Leftrightarrow Ba(SH)_2 + Ba(OH)_2$$

Any barium oxide present will hydrolyse:

$$BaO + H_2O \Leftrightarrow Ba(OH)_2$$

The solution is thus extremely caustic with very high pH.

When carbon dioxide is bubbled through the solution it forms carbonate ions which then precipitate insoluble barium carbonate.

$$Ba(OH)_2 + CO_3^{2-} \Leftrightarrow BaCO_3\downarrow + 2OH^-$$

The barium hydrosulphide then dissociates to maintain equilibrium between the hydroxide and the hydrosulphide ions.

$$Ba(SH)_2 + 2OH^- \Leftrightarrow Ba(OH)_2 + 2SH^-$$

$$SH^- + OH^- \Leftrightarrow H_2O + S^{2-}$$

$$H_2S \Leftrightarrow HS^- + H^+$$

As barium carbonate is precipitated, the pH of the solution falls with the result that H_2S is generated and is removed from solution.

Small scale tests showed that a simulated kiln flue-gas (80% N_2, 20% CO_2) carbonates barium sulphide solution efficiently to produce a concentrated (10 to 20%) stream of H_2S for conversion to elemental sulphur.

6.2 Production Methods

The production of barium carbonate by the route described here i.e. reduction of barytes to BaS, leaching of the "black ash" and carbonation of the solution is an established commercial process.

Various types of equipment have been described in the literature for the various unit operations:

(i) reduction is normally carried out in short rotary kilns at temperatures around 1 200°C. Pulverised coal is used as the fuel, and the barium sulphate agglomerated before reduction to produce a non-dusting kiln charge.

(ii) leaching is carried out on a finely milled "black ash" in agitated tanks, but a percolation type leach has also been proposed[8].

(iii) The carbonation of the sulphide liquor has been the subject of many studies[9,10,11] and a number of different contracting devices tested.

(iv) Conversion of concentrated H_2S streams to elemental sulphur is well-known technology and both liquid-phase and gas-phase (Claus) reactors are available for this purpose.

7 SOLIDS WASTE DISPOSAL

The main calcium product from the reduction kiln will be calcium oxide. During the leaching process this will be converted to hydrated lime and remain in the residue.

The calcium silicates are extremely insoluble and together with unreacted coal and coal ash will also remain in the residue.

The barium ferrites and unreacted barium sulphate will be lost as insoluble salts.

All insoluble solids may be easily disposed of by filtering the barium sulphide solution. The insoluble portion will include extremely inert barium compounds and lime. This slaked lime might easily be used as a neutralising agent in numerous other processes and could be a saleable product.

8 DISCUSSION

The contaminants distributed in a large effluent stream are concentrated into a small stream with no disposal problems. Useful water is produced from the effluent streams for use on the mines or for sale to other consumers.

Elemental sulphur is in short supply in South Africa and is imported at high cost. This process will significantly reduce the amount imported with consequent savings in foreign exchange.

The TDS and especially the sulphate level of public watercourses will be significantly lowered. The largest point source contributors of mineral load would have been almost eliminated. Together with good management to decrease the contribution by diffuse sources the cost incurred by rising TDS would be significantly reduced.

Barium is added in a very insoluble and hence non-toxic form. The chances of contaminating a product stream are minimal. Product water would always comply to the EPA recommended maximum of 1 mg/ℓ barium. Handling of the dry chemicals presents no hazard and so no control measures are necessary.

The unit operations used at the local facilities such as agitated reactors, thickeners and filters are easy to construct and maintain and are readily available. They do not require any skilled or intensive manpower to operate. At the central facility the required rotary kiln is a standard first processing step in producing any barium salt from barytes worldwide. Leach tanks and solution precipitation reactors are standard processing equipment. The wet scrubbing of hydrogen sulphide containing gas streams and the subsequent conversion to sulphur is also proven technology.

The barium is reused, hence saving the most expensive component. Input of raw material is in the form of barytes and coal. Coal is a cheap and readily available source of energy and reducing carbon. Barytes deposits occur in numerous places in South Africa, the largest of which is 50 km west of Pofadder in the N.W. Cape Province. The oberved length of strike of this barytes deposit is 1 160 m dipping at angles between 30° and 50°. Reserves are calculated as 2 767 000 tons for every 30 m down dip[12]. Numerous smaller deposits such as those in the Pietersburg area and along the Swaziland border could possibly be exploited for make-up purposes.

No pretreatment is necessary to remove the suspended solids present in the mining effluent. Most of the solids will be removed in the settler.

The sulphurous product in the form of hydrogen sulphide is produced in a small concentrated stream which is amenable to further processing such as sulphur production.

9 CONCLUSIONS AND RECOMMENDATIONS

(i) The addition of barium carbonate and lime to sulphate mine effluents effectively removes all dissolved solids except for group I and VIII ions.

(ii) Calcium carbonate seed crystal enhance reaction rates.

(iii) The sulphates in the effluents are captured in the form of a concentrated hydrogen sulphide stream which is amenable to further processing into valuable sulphur products.

(iv) The barium salts may be effectively recycled with minimal make-up being required.

(v) Barium is handled in its least toxic form namely the sulphate and the carbonate.

(vi) The barium sulphate and carbonate precipitates may be readily thickened and filtered.

(vii) The presence of calcium carbonate in the reduction step enhances the recovery of water soluble barium salts by reaction with the silicates contained in the coal. It also liberates carbon dioxide which is used to carbonate the barium sulphide solution.

(viii) All unit operations are ideally suited to a mining environment.

(ix) Technology required for this process is available.

(x) The raw materials required, namely barytes and coal, exist in abundance in South Africa while the products, sulphur and water, are in demand.

(xi) The establishment of a baryte reduction kiln could pave the way for the establishment of a barium chemicals industry.

(xii) There is no solids or brine disposal problem.

ACKNOWLEDGEMENTS

This investigation was conducted during a research contract from the Water Research Commission entitled the Chemical Removal of Sulphates.

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WATER RESEARCH COMMISSION PROJECT NO. 203

THE CHEMICAL REMOVAL OF SULPHATES

APPENDIX 3

TO FINAL REPORT

THE REMOVAL OF DISSOLVED SALTS FROM RECIRCULATING WATERS IN THE VAAL RIVER DRAINAGE SYSTEM - **Paper Presented at the 5th Biennial Symposium of the Ground Water Division, Geology Society of South Africa**

Pollution Research Group
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October 1989

THE REMOVAL OF DISSOLVED SALTS FROM RECIRCULATING WATERS IN THE VAAL RIVER DRAINAGE SYSTEM

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ABSTRACT

The Vaal River system is the most important water supply area in South Africa. A substantial amount of water is recycled in the systems and this leads to a high TDS level. Mine pump and process waters contribute 25 % of the TDS load in a small fraction of the circulating flow.

It is proposed to remove the TDS from such waters by precipitation with barium carbonate. Sludges generated from the water precipitation process would then be treated in a central facility to regenerate barium carbonate, producing sulphur and slaked lime as by-products. This facility could advantageously be integrated with the operating of a large power station.

The efficiency of such a scheme on the water quality in the Vaal area could be equivalent to that obtained through increased inflow via the Lesotho Highlands Scheme.

Not many people now remember the alarm that greeted the publication of a small book "The Limits to Growth"(1) which pointed out the consequences of exponential growth of population and industry, in a world of finite resources. Partly, this is because the world economy came off the exponential curve within a year of publication owing to the oil crisis, and the Western World then became concerned more with the consequences of negative growth; and partly because prophets of gloom never enjoy sustained popularity.

Nevertheless, the basic tenets of the authors' thesis are undeniably true; their predictions are simply inaccurate in time-scale.

Curiously the supply of fresh water was not one of the resources considered by the above authors; in South Africa this is *the* resource which could within in a few years place limits on growth. The region is already water-short; over 60 % of the mean annual run-off is already utilised, and this almost exclusively by the 25 % of the population with Western standards of living. Quite obviously it will not be possible to raise the standard of living of even our existing population to Western standards, let alone cope with a steadily increasing one, without radical alterations to the pattern of water usage.

The traditional response to insufficient water is the construction of new impoundments but this approach is essentially short-term in nature. In the longer term the cost of harnessing new water resources can be expected to increase exponentially as the closer and more suitable dam sites are utilised. The only "permanent" solution to the problem is thus the large-scale recycling of water, since most large users (other than agricultural) do not consume the supply but merely contaminate it with organic and inorganic materials.

Large-scale recycling of water is in fact already taking place, especially in the inland regions of South Africa, but in an uncontrolled and inefficient fashion. At best, the recycled water has been treated in a conventional sewage works which removes only the bulk of the organic matter. Dissolved salts (TDS) are not removed and build up in the recirculating system. This lowers the quality of the water and has a large cost associated with problems caused by increased scaling, corrosion, increased requirements of detergents, deleterious effects on crops etc.

A major example of a large recirculation system is provided by the Vaal River system. This is the most important water supply area in South Africa, providing water to 42 % of the urban population of the Republic and contributing to 77 % of the country's mining output, 58 % of the total industrial production and 44 % of agricultural production (2).

By the year 2010 the water demand in the region will have increased to nearly 4 billion kilolitres per annum (3). At the same time the water quality in the area is deteriorating with the TDS level in the Vaal dam rising at an annual rate of 2,5 mg/ℓ (4). In 1980 the level had already reached 150 mg/ℓ, but in the Vaal Barrage region the SABS recommended maximum TDS level of 455 mg/ℓ is already being exceeded regularly. The economic cost of this increase in TDS is large ; it has been estimated that an increase in TDS from the 1980 levels to 800 mg/ℓ will cost the community over R 200 m per year(5).

When viewed in this context, the construction of large water schemes, such as the Lesotho Highlands scheme, can be seen as not primarily aimed at augmenting water supplies. Rather, this water will be used to dilute the TDS of the existing supply to acceptable levels, and to provide a medium by which excess TDS load may be flushed down to the sea. The alternative approach, to control the level of TDS in the recirculation system by inserting an effective removal step, addresses the problem more directly and has the advantage of being subject to the laws of science and not the vagaries of nature.

The most direct approach is to attempt to eliminate the root causes leading to the contamination of the water supply. This is obviously most easily done if the sources of contamination are confined to relatively few points.

Major point sources in the Vaal River System are mine pump and process waters. A number of techniques have been investigated in efforts to reduce the large TDS load which is picked up by these waters. While good technical progress has been made, it is clear that the cost of doing this will be high, and it could in fact be more effective to remove the dissolved salts from the contaminated water afterwards.

The ease with which TDS can be removed from the recirculating water depends greatly on the nature of the inorganic constituents ; Na^+ and Cl^- are intractable constituents for which no economic technology exists in this context while Ca^{2+}, Mg^{2+} and SO_4^{2-} are by comparison removed rather easily. Fortunately the major constituents of the TDS load entering the Vaal system are in the latter category, and the prospects for economic control of TDS are correspondingly increased.

A number of technologies for the removal of TDS from water of composition corresponding to those entering of Vaal system are either already commercially available or under development in South Africa. These include -:

- Ion exchange which is used where a particularly high quality water is required but the process is not suitable for high volume applications.
- Electrodialysis which has been tested on mine and power station cooling waters but found to be too expensive for large scale operation.
- Seeded slurry reverse osmosis, a variant of the established technology, designed to operate on waters where insoluble material such as gypsum will precipitate on concentration. This is under development by the Chamber of Mines and appears to be an effective but somewhat costly technique, quite different in the level of sophistication to the kind of technology traditionally used in large-scale water treatment.
- Biological processes which have received extensive investigation by the CSIR. These also involve complex flow sheets and do not appear to economically viable at this stage.

The disadvantages of these technologies have lead a number of workers in South Africa to propose the use of the simple and well-known chemical precipitation route, using a barium salt to remove sulphate, simultaneously converting Ca^{2+} and Mg^{2+} into insoluble components. The principal advantage of the technique is its simplicity which is compatible with large scale applications on unsophisticated plants. This application is however complicated by a number of factors among which are the high cost of suitable barium compounds and the high toxicity of soluble barium salts.

In our view, the second factor rules out the use of compounds such as barium sulphide which have been proposed for this application;(6) no matter what safeguards are built in, the risk of overdosing in the context of a large, unsophisticated treatment facility is simply too great. This problem can be overcome by using a barium salt of very limited solubility, such as $BaCO_3$ so that even large dosing errors could not result in an acute toxicity problem.

The stoichiometry of TDS removal using barium carbonate is extremely simple ;

$$BaCO_3 + CaSO_4 \rightarrow CaCO_3 + BaSO_4$$

both reaction products being extremely insoluble.

Thermodynamically the equilibrium in this reaction is far to the right, even though $BaCO_3$ is itself almost insoluble. However, the reaction of an insoluble substance with a dilute solution to form a more insoluble substance could be expected to be very slow. Indeed a previous worker (7) identified this as a major technological problem to be overcome, as far back as 1972.

More recently Maree *et al* (8) have reported results obtained in a joint investigation by the CSIR and Anglo-American Research Laboratories. They found very slow reaction rates; 16 x stoichiometry being required to achieve a realistic rate of sulphate removal. They ascribed this to a slow, rate-limiting step of dissolution of $BaCO_3$, the rate of this step being dependent on the surface area of the $BaCO_3$ crystals.

To overcome this, they have suggested a system in which the contaminated water is recirculated through a fluidised bed of barium carbonate particles. This would provide the high interfacial area necessary to give an acceptable rate of sulphate removal while reducing the consumption of $BaCO_3$ to somewhere near the stoichiometric requirement.

In a separate investigation at the University of Natal, Trusler (9) also studied the kinetics of sulphate removal with $BaCO_3$. His results appear to be in complete contradiction of those of Maree, showing rapid precipitation even at the stoichiometric level and only a small effect of the addition of excess reagent. This apparent contradiction is resolved by noting that $BaCO_3$ particles of very different sizes were used in the two investigations. Trusler used particles of around 5 μm in diameter; while Maree does not quote the crystal size used in his experiments, rough calculations based on both kinetic and hydrodynamic considerations indicate that his particles must be around 100 μm in diameter.

The problem of slow reaction rate can therefore also be overcome by using a reagent of high enough specific surface area, i.e. a small particle size. It will be possible to control the particle size of the reagent during the manufacturing process, but if necessary, the surface area could be increased by wet milling the product in a stirred ball mill prior to use(10).

The milled product could then be dosed to a simple conventional water treatment plant in roughly stoichiometric amounts.

Trusler found that the kinetics of sulphate removal are also affected by the nature of the cations in solution. If sulphate is present as sodium and magnesium sulphates in addition to the usually dominant $CaSO_4$, the precipitation of sulphate is greatly retarded. He showed that this could be overcome by adding hydrated lime in stoichiometric proportion to the sulphate present in excess of Ca^{2+} ions in solution. This result has been theoretically verified by Loewenthal(11). In tests using both synthetic and real high sulphate water, virtually complete removal of SO_4^{2-} Ca^{2+} and Mg^{2+} was achieved, leaving only the intractables Na^+ and Cl^- in solution.

From a technical point of view, barium carbonate precipitation is thus simple and attractive. The compound unfortunately does not occur naturally in economic quantities and must be manufactured from barytes. South Africa has large deposits of this mineral but these are located at some distance from the PWV area. However, the same technology that is commercially employed for the treatment of barytes could also be used to regenerate $BaCO_3$ for recycle from the sludge formed by treating sulphate rich waters.

The regeneration process involves the thermal decomposition of $BaSO_4$ under reducing conditions to form BaS. This is highly soluble in water but is easily decomposed by CO_2 to precipitate $BaCO_3$, forming a by-product of H_2S. H_2S can then be converted into elemental sulphur by several commercial processes, and this is a convenient and valuable by-product. The end result of a combined TDS removal and barium recycle process is thus the formation of a purified water stream, with sulphur and a slaked lime sludge as by products. Coal is the only reagent consumed in the process.

Our concept for the application of this technology is thus the treatment of sulphate-containing waters in simple low-cost facilities at convenient locations. The sludge formed at each treatment plant would be transported to a central facility where a suitable $BaCO_3$ reagent would be regenerated and the various by-products recovered.

The most effective points at which the water-treatment facilities could be located are the large mines in the area that generate significant volumes of highly contaminated water: It has been estimated (12) that these sources generate a total flow of 200 Mℓ/day which contains 25 % of the TDS load entering the Vaal System. Removal of this TDS load would have a significant impact on the whole system - it would be equivalent to increasing the inflow of high-quality water into the system by 30 - 40 %. An increase of this magnitude would be a major undertaking similar in size to the Lesotho Highlands project.

The water product from such installations would be of high quality, better in fact than that supplied by the RWB to industrial consumers in the region. It would be wasteful to allow this water to simply drain back into the Vaal Dam when it could be supplied to consumers requiring high quality water.

There are a number of such potential consumers in the region; some of the most important are the directly cooled power stations. These require large volumes of high quality cooling water. This water is evaporated, and in order to contain corrosion and scaling problems a low TDS in the make-up water is required, and considerable capital has to be invested to control TDS build-up. Mine-water treated by barium carbonate would be well-suited to this application.

Integration of this desalination scheme with a power station would have a number of subsidiary advantages :-

1) Power stations are substantial consumers of sulphur, a major by product of the process. This is converted to SO_3 which is used to increase the conductivity of the stack gas and thus increase the efficiency of electrostatic precipitation of fly-ash.

2) Many of the facilities required for the barium carbonate regeneration process are located on-site at power stations. These include coal handling facilities, steam and power, well-equipped laboratories, well-designed sludge disposal facilities etc.

In conclusion it appears to us inevitable that control of TDS build-up in the Vaal water system will be introduced. The advantage of the particular scheme presented above is the simplicity of the water treatment process. This is however offset by the complexity and probable high capital cost of the regeneration process. By integrating the scheme with the needs of a large consumer such as Eskom the overall capital and operating costs could be reduced considerably.

ACKNOWLEDGMENTS

The original work undertaken by Mr Trusler was funded by a Water Research Commission project entitled *The Chemical Removal of Sulphates*. Mr T. Spencer of ESKOM was involved in the concept of coupling the process to a power station.

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WATER RESEARCH COMMISSION PROJECT NO. 203

THE CHEMICAL REMOVAL OF SULPHATES

APPENDIX 4

TO FINAL REPORT

SULPHATE, CALCIUM AND HEAVY METAL REMOVAL FROM INDUSTRIAL EFFLUENTS USING BARIUM CARBONATE

Paper Submitted to WaterSA (Draft)

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October 1989

SULPHATE, CALCIUM AND HEAVY METAL REMOVAL FROM INDUSTRIAL EFFLUENTS USING BARIUM CARBONATE

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ABSTRACT

This paper presents results obtained from reacting barium carbonate with calcium, magnesium and sodium sulphate solutions and sulphate containing industrial and mining effluents.

Sulphate removal was very effective when the sulphate ions were associated with calcium. When they were associated with magnesium or sodium the addition of lime aided sulphate removal. The rate of sulphate removal from a calcium sulphate solution was retarded by the presence of magnesium ions. Sulphate removal from a power station cooling water was enhanced by the addition of sulphuric acid. In addition to sulphate; calcium, magnesium, zinc and cadmium were removed from solution by barium carbonate.

Calcium sulphide could be produced as a by-product of a barium carbonate regeneration process. This sulphide could be used to treat heavy metal containing effluents.

INTRODUCTION

The total dissolved solids (TDS) content of the Vaal River System is rising rapidly. This is due to the fact that salts are being added to the system and that water and TDS is being recycled. Conventional water treatment plants remove most of the organic constituents of industrial and domestic effluents but little, if any, of the dissolved salts.

The increasing level of TDS leads to an increase in water consumption and places a limit on the amount of industrial reuse. Heynike (1987) assumed a TDS level in the Vaal Barrage of 300 mg/ℓ and estimated that if this level should rise to 800 mg/ℓ the additional cost to consumers would be R252,7 M (1983) per annum.

Herold *et al.* (1980) found that just less than half of the salt being added to the system was from point sources. The actual proportion varies from year to year. It was noted by Trusler *et al.* (1988) that three mines contribute 42 % of the point source effluent TDS and 18 % of the total mineral load to the Vaal Barrage in 4 % of the volumetric flow. The major anionic constituent of these mine pump waters is sulphate which is associated with calcium, magnesium and sodium.

The presence of sulphates in waters enhances corrosion, encourages scaling in boilers and heat exchangers and serves as a substrate for organisms implicated in biocorrosion.

There appears to be a close relationship between the sulphate content of reticulated water and the number of repairs to water mains (Osborn,1989).

A process has been developed whereby minewaters may be effectively treated at source with barium carbonate using existing waterworks technology. The sludge would be sent to a central facility which recycles barium and produces elemental sulphur and lime as by-products (Trusler, 1988).

Once a barium regeneration facility has been established, soluble barium salts could also be sold for use in treating numerous other sulphate effluents and process waters such as those from zinc plants, metal plating factories, power station cooling water and pulp and paper manufacturers.

The central facility may also be used to manufacture soluble calcium sulphide for treatment of heavy metal containing effluents.

The concept of the use of barium carbonate to treat acidic minewater is not new. Kun (1972) found that barium carbonate effectively removed sulphate and neutralised acid mine drainage. It was however found that barium carbonate was too expensive, the reaction rate was too slow and that barium contaminated the product water. This paper shows that the long reaction period required for precipitation has been solved by using small barium carbonate particles, seeding the mixture with calcium carbonate and adding lime to ensure that all sulphate ions are associated with calcium ions. The barium is recycled to reduce costs and to provide income from the production of elemental sulphur. Product water also contains very little soluble barium.

In this paper the reaction of barium carbonate with various simulated and actual sulphate effluents is given and the experimental findings are discussed.

The potential for producing soluble calcium sulphide and its use for treating heavy metal containing effluents is examined.

EXPERIMENTAL

Solutions of calcium, magnesium and sodium sulphate were prepared from analytical reagents and samples of neutralised minewater, partially neutralised underground water, a zinc plant effluent and power station cooling water were collected.

All the feed solutions were reacted in a batch stirred reactor at ambient temperatures. The sulphate ions in solution were determined gravimetrically and the metal ions determined by using an atomic absorption spectrophotometer after the solutions had been filtered through glass microfibre filters (size GF/C). The average particle size of barium carbonate used was 4,5 μm and it was added in a 20 % (mass) slurry form to prevent particle agglomeration.

Aqueous Sulphate Removal

Figure 1 shows the rate of sulphate removal from a calcium sulphate solution and the effect of various types of seed crystals using a stoichiometric amount of barium carbonate. After 90 minutes the average amount of calcium left in solution was 9 mg/ℓ. Figure 2 shows the rate of sulphate removal using stoichiometric barium carbonate from a calcium sulphate solution after magnesium has been added in the form of magnesium chloride. The rate of sulphate removal from three concentrations of a magnesium sulphate solution is shown in Figure 3 using stoichiometric barium carbonate. Magnesium removal is recorded in Table 1.

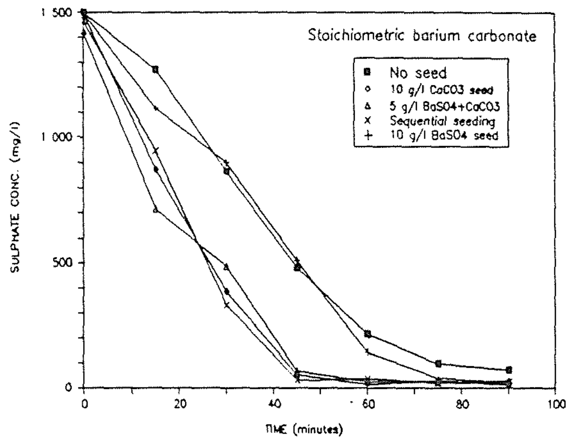

FIGURE 1 : Sulphate Removal from a Calcium Sulphate Solution Using Barium Carbonate : The Effect of Seeding

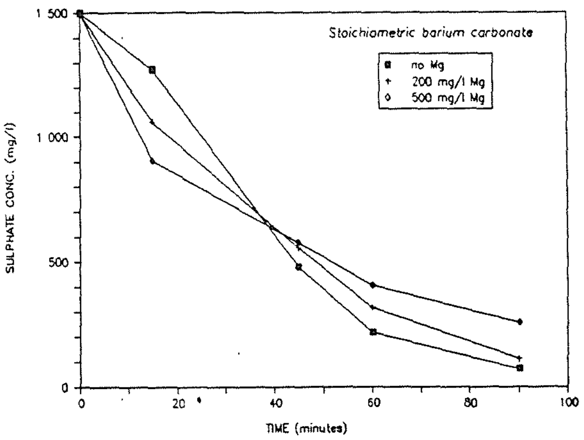

FIGURE 2 : The Effect of Magnesium Chloride on Sulphate Removal from a Calcium Sulphate Solution

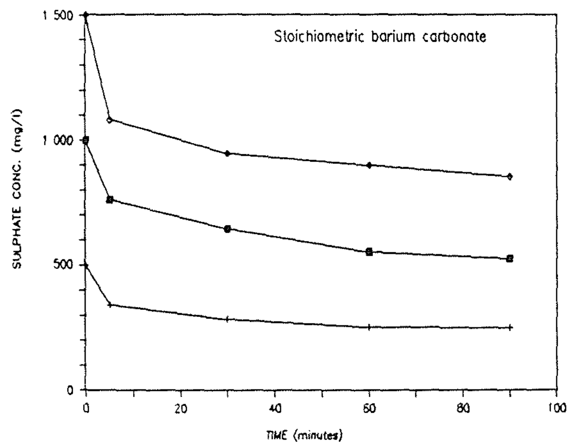

FIGURE 3 : Sulphate Removal from Different Concentrations of a Magnesium Sulphate Solution Using Barium Carbonate

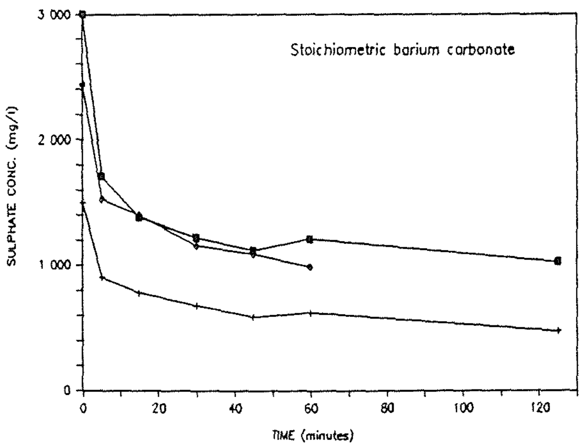

FIGURE 4 : Sulphate Removal from Different Concentrations of a Sodium Sulphate Solution Using Barium Carbonate

TABLE 1
Sulphate and Magnesium Removal from Magnesium Sulphate Solutions Using Stoichiometric Barium Carbonate (mg/ℓ)

Time (min)	Reaction with $BaCO_3$		Reaction with $BaCO_3$		Reaction with $BaCO_3$ and equivalent CaO	
	SO_4	Mg	SO_4	Mg	SO_4	Mg
0	1 000	256	1 500	380	2 000	512
5	761	119	1 080	-	-	-
15	-	119	-	-	152	-
30	645	117	947	-	<10	3
60	553	124	900	195	-	-

The rate of sulphate removal from three concentrations of a sodium sulphate solution using stoichiometric barium carbonate is shown in Figure 4. In the sodium sulphate solution containing 2 440 mg/ℓ the residual sulphate level fell to 620 mg/ℓ after 3 days and 320 mg/ℓ after 14 days.

A sample of partially neutralised underground mine water was reacted with a 25 % stoichiometric excess of barium carbonate and seeded with 1 g/ℓ calcium carbonate. The results are given in Table 2.

TABLE 2
Reaction of Partially Neutralised Underground Mine Water with Barium Carbonate
(25 % stoichiometric excess)

Determinant	Raw	Reaction Time (min)		
		30	60	90
pH	4,5	-	-	9,5
SO_4 (mg/ℓ)	1 627	1 167	676	397
Ca (mg/ℓ)	580	425	180	46
Mg (mg/ℓ)	97	45	40	10
Na (mg/ℓ)	130	100	100	100
Fe (mg/ℓ)	0	0	0	0

The sample of mine pump water was reacted with a 25 % excess of barium carbonate and 0,811 g/ℓ calcium hydroxide. The mixture was seeded with 1 g/ℓ calcium carbonate. The results of the experiment are given in Table 3 and Figure 5.

TABLE 3
Reaction of a Mine Pump Water with Barium Carbonate and Equivalent Lime (25 % stoichiometric excess)

Determinant	Raw	Time (min)					
		15	30	45	60	75	90
pH	4,1	10,55	10,57	10,58	11,60	11,65	11,65
SO_4 (mg/ℓ)	2 527	1 870	1 236	372	<10	<10	<10
Ca (mg/ℓ)	653	610	490	120	10	2	1
Mg (mg/ℓ)	152	0	0	0	0	0	0
Fe (mg/ℓ)	5,6	0	0	0	0	0	0
Mn (mg/ℓ)	7,5	-	-	-	-	-	-
Na (mg/ℓ)	242	-	-	-	-	-	-
Cl (mg/ℓ)	207	-	-	-	-	-	-

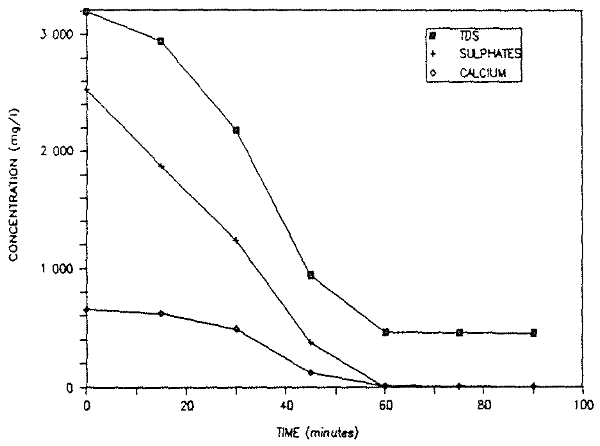

FIGURE 5 : Sulphate Removal from a Mine Pump Water

A zinc plant effluent was reacted with a 25 % stoichiometric excess of barium carbonate and 1 g/ℓ calcium oxide. This did not lead to complete sulphate removal and thus in another experiment the effluent was first stirred with excess lime and filtered before being reacted with excess barium carbonate. The results are presented in Table 4.

TABLE 4
Reaction of a Zinc Plant Effluent with Barium Carbonate
(25 % stoichiometric excess)

Determinant	Raw	1 g/ℓ CaO + $BaCO_3$ for 180 min	Liming filtrate	Liming filtrate + $BaCO_3$
pH	5,1	8,6	12,5	12,5
SO_4 (mg/ℓ)	6 800	4 600	1 300	<10
Ca (mg/ℓ)	520	16	-	-
Mg (mg/ℓ)	850	-	-	-
Na (mg/ℓ)	60	-	174	88
Fe (mg/ℓ)	0,2	-	-	-
Cd (mg/ℓ)	17	Trace	Trace	Trace
Mn (mg/ℓ)	308	60	-	-
Zn (mg/ℓ)	1 150	Trace	Trace	Trace
TS (mg/ℓ)	12 190	-	-	-
TDS (mg/ℓ)	10 500	7 600	-	-

Water from the cooling circuit of a power station was reacted with 1,98 g/ℓ barium carbonate and 0,656 g/ℓ calcium oxide for 3 hours. In a second test 2,616 g/ℓ barium carbonate and 12,6 mmol/ℓ of sulphuric acid was used. The acid was sequentially added. Results are given in Table 5. In a simulated version of the same water the sulphate level dropped to 235 mg/ℓ after 3 hours and 120 mg/ℓ after 12 hours upon reacting with barium carbonate and lime. The simulated effluent treated with only barium carbonate had a sulphate level of 400 mg/ℓ after 3 hours.

TABLE 5
Reaction of a Power Station Cooling Water with Barium Carbonate (25 % stoichiometric excess)

Determinant	Raw	$BaCO_3$ + CaO	$BaCO_3$ + H_2SO_4
pH	7,7	11,5	7,1
SO_4 (mg/ℓ)	774	646	197
Ca (mg/ℓ)	121	318	54
Mg (mg/ℓ)	22	0	9
Na (mg/ℓ)	373	-	-
Fe (mg/ℓ)	0,6	0	0

DISCUSSION

Sulphate Removal

It was found that barium carbonate is very effective in removing sulphates from a calcium sulphate solution. The low level of sulphates left in solution and the relatively fast reaction time occurs because in addition to barium sulphate precipitation there is a simultaneous precipitation of calcium carbonate. This aids the dissolution of barium carbonate as shown in reaction (1) .

$$BaCO_3 + CaSO_4 \rightarrow BaSO_4\downarrow + CaCO_3\downarrow \qquad (1)$$

The formation of magnesium sulphate ion pairs retards the rate of sulphate removal from a calcium sulphate solution containing magnesium (Figure 2).

Sulphate removal from a magnesium sulphate solution (Figure 3) using only barium carbonate is not as fast as that from calcium sulphate solution (Figure 1) due to the greater solubility of magnesium carbonate. If sufficient lime is added to the solution so that magnesium is precipitated as the hydroxide both sulphate and magnesium removal progress very rapidly. The lime does not add to the TDS of the water because calcium is precipitated as the carbonate according to reaction (2).

$$BaCO_3 + MgSO_4 + Ca(OH)_2 \rightarrow BaSO_4\downarrow + Mg(OH)_2\downarrow + CaCO_3\downarrow \qquad (2)$$

Sulphate removal from a sodium sulphate solution (Figure 4) is initially very fast but then comes to an apparent equilibrium at higher than the expected level. It was found that if the reaction proceeded for a number of days the level of sulphates continued to drop. It thus appears that the kinetics are extremely retarded if the carbonate species are not removed from solution.

$$BaCO_3 + Na_2SO_4 = BaSO_4\downarrow + Na_2CO_3 \qquad (3)$$

The formation of calcium carbonate nuclei seem to be the rate determining step during the initial part of the reaction. The addition of calcium carbonate seed nuclei speeds up the reaction. The provision of barium sulphate nuclei has no effect on the rate of sulphate removal. It seems reasonable to assume that if precipitation nuclei are provided and there is sufficient agitation then the rate determining step is the dissolution of barium carbonate or resistance at the product crystal interface.

The reaction of barium carbonate with the partially neutralised underground water (Table 2) shows that barium effectively neutralises the water and removes most of the TDS but that sulphate removal is not complete after 90 minutes of reaction time. If however, some lime is added, as in the mine pump water test ; sulphate, calcium, magnesium and iron are almost totally removed after 90 minutes.

It was seen that treating a zinc plant effluent with barium carbonate (Table 4) effectively neutralised it and removed all the zinc and most of the calcium and manganese. The time required for effective sulphate removal is longer than the three hours allowed in the experiment. If the zinc effluent is well treated with lime and then reacted with barium carbonate; sulphate, zinc and cadmium are almost totally removed.

Sulphate removal from power station cooling water (Table 5) behaves contrary to minewater in that sulphate removal with barium carbonate is not very effective if lime is added. Magnesium is however, removed at the high pH. Lowering the pH with sulphuric acid appears to aid sulphate and calcium removal. More soluble barium salts could be used for effluents which require a very long reaction time. Sulphate removal from synthetic solutions containing the same salts is much more effective. It appears as though some additive to power station cooling water, such as anti-scalant and anti-bacterial reagents, has a severe impact on sulphate removal by precipitation.

Heavy Metal Removal

During the process of regeneration of barium carbonate, hydrogen sulphide gas and a lime/ash slurry are produced as by-products (Trusler, 1988). If the hydrogen sulphide is bubbled through a slurry of this lime/ash mixture, soluble calcium sulphide would form (Thorpe, 1949). The reaction progresses rapidly due to the high alkalinity of the solution and the extreme solubility of calcium sulphide. The following reactions occur :-

$$Ca(OH)_2 + H_2S \Leftrightarrow CaS + 2H_2O \qquad (4)$$

$$2CaS + 2H_2O \Leftrightarrow Ca(HS)_2 + Ca(OH)_2 \qquad (5)$$

Calcium sulphide solutions of varying concentrations are used as a sheep dip, a fungicide or an insecticide. The tanning and fellmongering industries use approximately 660 kg/day/1 000 hides of sulphide salts for their depilatory characteristics (A Guide to Waste-Water Management in the Tanning and Fellmongering Industries, 1987).

Of particular interest in the South African context is the possible use of soluble sulphides to treat heavy metal containing effluents. Effluent discharged from the metal plating industry in the Vaal Barrage catchment contains approximately 74 tons/year of heavy metals (Claasens,1990). The use of calcium sulphide as a heavy metal removal agent has been investigated and it has been found to be effective (Kim, 1980).

Metal containing effluents are often treated using the traditional hydroxide process but in many respects the use of sulphide precipitation is superior.

The low solubility of metal sulphides improves metal removal efficiency. The metal sulphide sludge is also three times less subject to leaching and therefore disposal is easier and safer (Whang,Young and Pressman, 1982). The possibility of amphoteric metal hydroxides redissolving is eliminated.

Sulphide precipitation is also more practical than hydroxide precipitation in that it directly reduces the hexavalent chrome to its trivalent state thus eliminating the need for pH control (Janson,Kenson and Tucker, 1982).

Complexed metal cyanides form free cyanide once the heavy metals have been removed making them more amenable to biodegradation.

Compared to the hydroxide the sulphide route is relatively insensitive to most chelating agents and performs well on many complexed heavy metals. Calcium sulphide produces precipitates which settle easily with the calcium acting as coagulant (Maree, 1988).

Calcium sulphide may thus be used in the soluble sulphide precipitation technique as a replacement for the traditional sodium sulphides.

CONCLUSIONS

Sulphates are effectively and quickly removed from a number of industrial effluents using barium carbonate, especially if the sulphates are associated with calcium. If magnesium is present in solution, the pH needs to be raised enough to allow magnesium to precipitate out as the hydroxide, to obtain effective sulphate and magnesium removal.

Barium carbonate removes almost all zinc and cadmium ions from a zinc plant effluent and with effective lime pretreatment all sulphate. To obtain effective sulphate removal from a power station cooling water using barium carbonate, the addition of a mineral acid such as sulphuric acid is necessary.

Calcium sulphide may be produced from by-products of the regeneration process. It may be directly sold for agricultural use or used to remove heavy metals from waste-water.

ACKNOWLEDGMENTS

This work was performed as part of a project funded by the Water Research Commission entitled *The Chemical Removal of Sulphates.*

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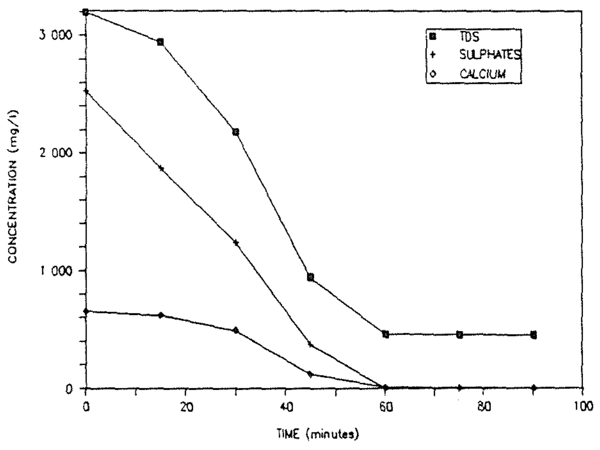
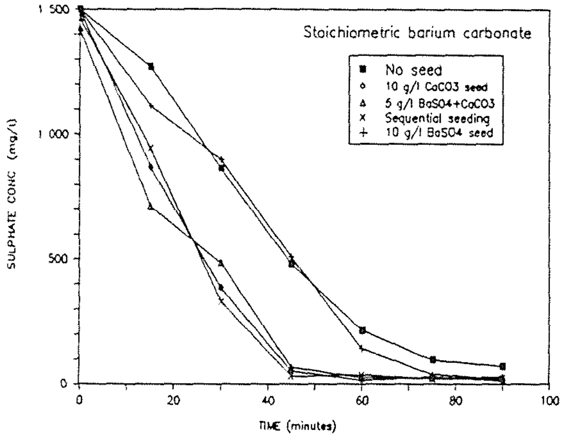
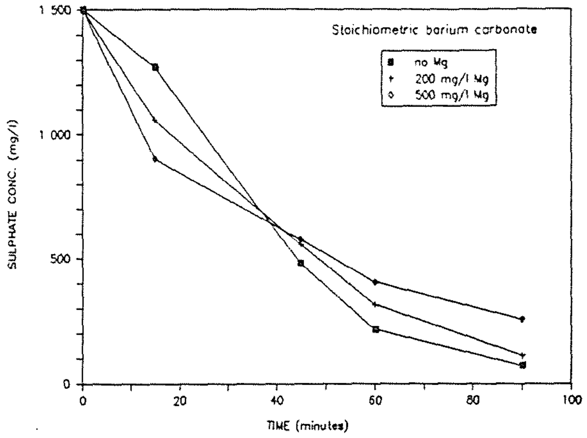
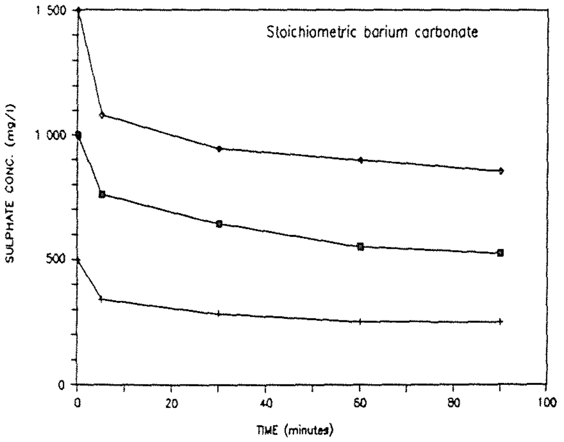
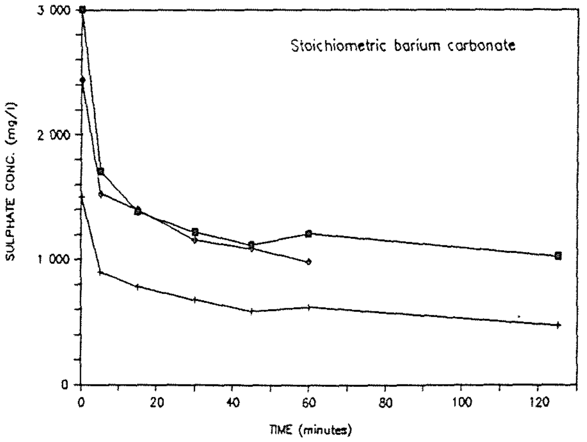

TDS
SULPHATES
CALCIUM
CONCENTRATION (mg/l)
3 000
2 000
1 000
0
0
20
40
60
80
100
TIME (minutes)


Stoichiometric barium carbonate
■ No seed
◇ 10 g/l CaCO3 seed
△ 5 g/l BaSO4+CaCO3
× Sequential seeding
+ 10 g/l BaSO4 seed
SULPHATE CONC (mg/l)
1 500
1 000
500
0
0
20
40
60
80
100
TIME (minutes)


Stoichiometric barium carbonate
■ no Mg
+ 200 mg/l Mg
◇ 500 mg/l Mg
SULPHATE CONC. (mg/l)
1 500
1 000
500
0
0
20
40
60
80
100
TIME (minutes)


Stoichiometric barium carbonate
SULPHATE CONC. (mg/l)
1 500
1 000
500
0
0
20
40
60
80
100
TIME (minutes)


Stoichiometric barium carbonate
SULPHATE CONC. (mg/l)
3 000
2 000
1 000
0
0
20
40
60
80
100
120
TIME (minutes)