Sulphate, calcium and heavy metal removal from industrial effluents using barium carbonate

GE Trusler[1*], RI Edwards[2] and CA Buckley[1]**
[1]*Pollution Research Group, Department of Chemical Engineering, University of Natal, Durban 4001, Republic of South Africa*
[2]*Minemet CC, Department of Chemical Engineering, University of Natal, Durban 4001, Republic of South Africa*

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, calcium, magnesium, zinc and cadmium were also 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 are 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 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 mine waters 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 mine water is not new. Kun (1972) found that barium carbonate effectively removes sulphate and neutralises 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 papers 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 mine water, 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 were 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

Fig. 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 min the average amount of calcium left in solution was 9 mg/ℓ. Fig. 2 shows

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*Present address: Barplats Refineries (Pty) Ltd., PO Box 267, Brakpan 1540, Republic of South Africa.

**To whom all correspondence should be addressed.

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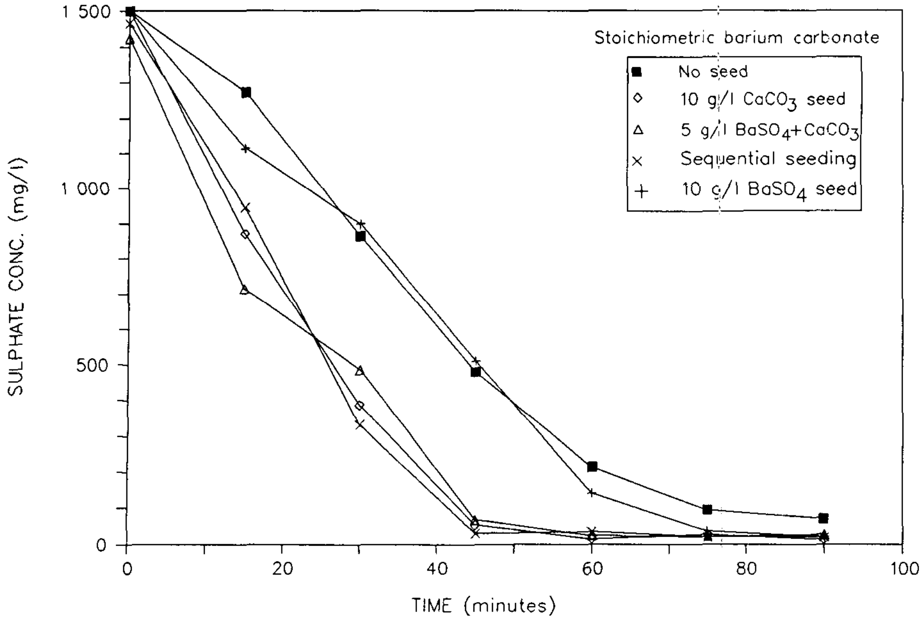

Figure 1
Sulphate removal from a calcium sulphate solution using barium carbonate: The effect of seeding

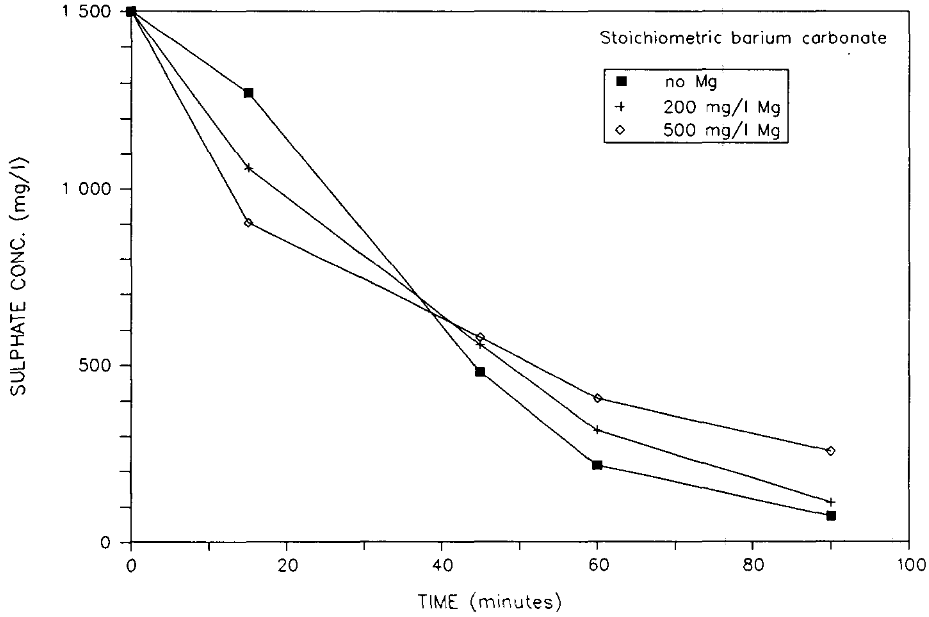

Figure 2
The effect of magnesium chloride on sulphate removal from a calcium sulphate solution

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	-	-

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

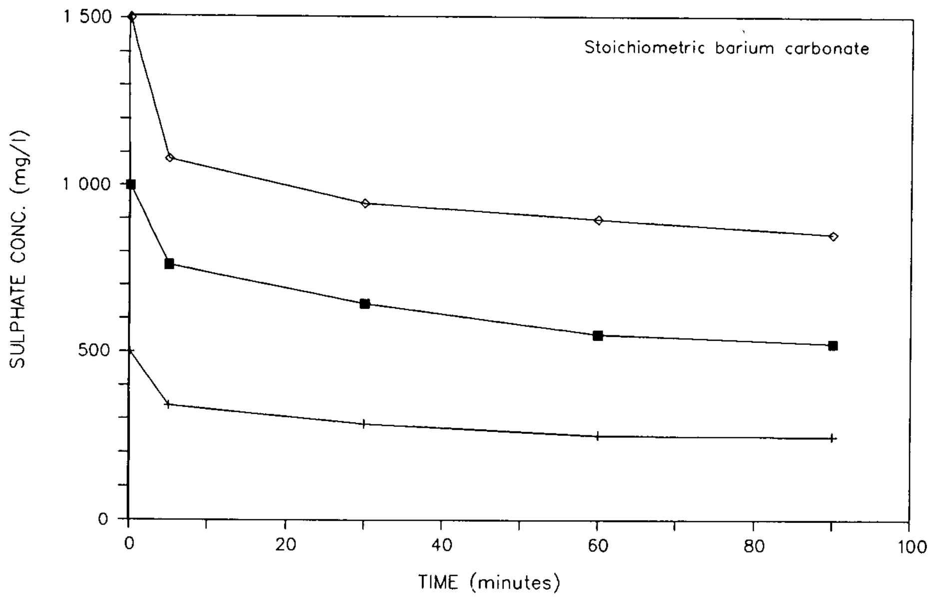

Figure 3
Sulphate removal from different concentrations of a magnesium sulphate solution using barium carbonate

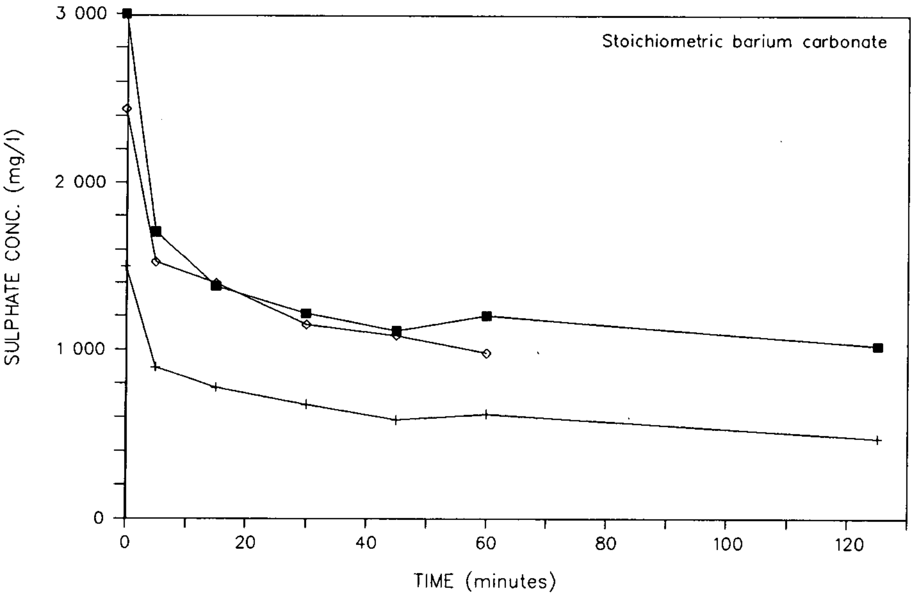

Figure 4
Sulphate removal from different concentrations of a sodium sulphate solution using barium carbonate

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 Fig. 3 using stoichiometric barium carbonate. Magnesium removal is recorded in Table 1.

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

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.

The sample of mine 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 Fig. 5.

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.

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 h. 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 h and to 120 mg/ℓ after 12 h 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 h.

TABLE 3
REACTION OF A MINE 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	-	-	-	-	-	-

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
TDS (mg/ℓ)	10 500	7 600	-	-

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 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 (Fig. 2). Sulphate removal from a magnesium sulphate solution (Fig. 3) using only barium carbonate is not as fast as that from calcium sulphate solution (Fig. 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 progresses very rapidly. The lime does not add to the TDS of the water, as calcium is precipitated as the carbonate according to reaction (2).

$$\begin{aligned}&BaCO_3 + MgSO_4 + Ca(OH)_2\\ &\rightarrow BaSO_4\downarrow + Mg(OH)_2\downarrow + CaCO_3\downarrow\end{aligned} \qquad (2)$$

Sulphate removal from a sodium sulphate solution (Fig. 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.

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

The formation of calcium carbonate nuclei seems to be the rate determining the 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 min of reaction time. If, however, some lime is added, as in the mine-water test, sulphate, calcium, magnesium and iron are almost totally removed after 90 min.

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 3 h 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.

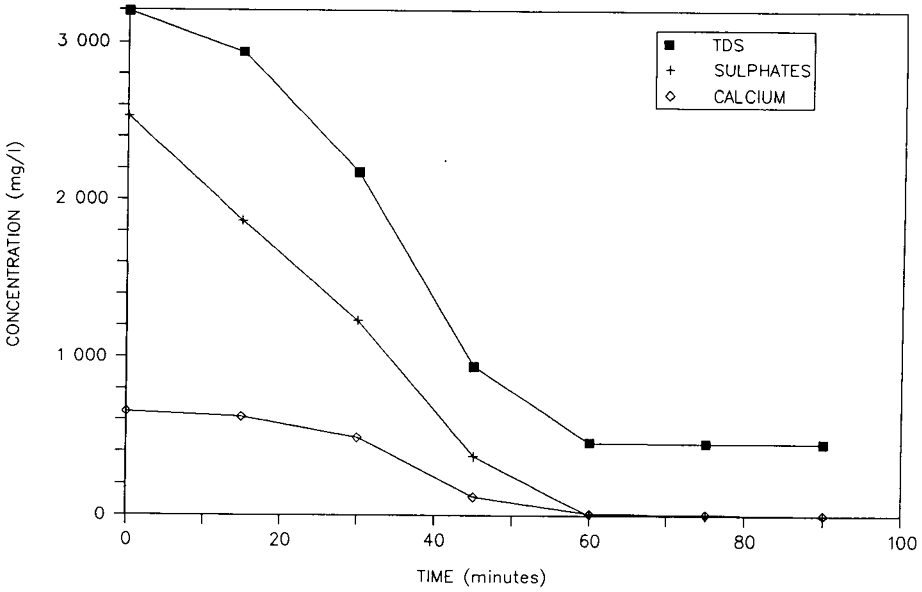

Figure 5
Sulphate removal from a mine water

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

Sulphate removal from power station cooling water (Table 5) behaves contrary to mine water 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:

$$Ca(OH)_2 + H_2S \rightleftharpoons CaS + 2H_2O \qquad (4)$$
$$2CaS + 2H_2O \rightleftharpoons Ca(HS)_2 + Ca(OH)_2 \qquad (5)$$

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/d.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 t/a of heavy metals (Claassens, 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 *et al.,* 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 *et al.,* 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.

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References

A Guide to Waste-water Management in the Tanning and Fellmongering Industries (1987) Water Research Commission Project No. 41, TT27/87. Pretoria.

CLAASSENS, GCD (1990) Director-General, Department of Water Affairs. Personal communication.

HEYNIKE, JJC (1987) Salination of Vaal River Water: Economic Effects (A Desk Study). Water Research Commission, KV2/87, Pretoria.

HEROLD, CE, MILEIKOWSKY, RN, HALL, GC and MIDGELEY, DC (1980) The numerical modelling of salinity fluctuations in the Vaal system. *Proceedings: Focus on the Vaal Symposium,* Vaal River Catchment Association. 13 March. Pretoria.

JANSON, CE, KENSON, RE and TUCKER, LM (1982) Treatment of heavy metals in wastewater. *Environmental Progress* **1**(3) 212-216.

KIM, BM (1980) Treatment of metal containing wastewater with calcium sulphide, *AIChE Symposium Series, Water-1980* **77**(209) 39-48.

KUN, LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Anglo American Research Laboratories, Project D/3/W/1.

MAREE, JP (1988) Sulphate Removal from Industrial Effluents. Ph.D. Thesis, University of the Orange Free State, Bloemfontein. 51.

OSBORN, DW (1989) Corrosion in potable water systems: The Johannesburg experience, *Water SA* **15**(1) 201-208.

Thorpes Dictionary of Applied Chemistry (1949) 4th edn., Vol **2**, Longmans, London. 229.

TRUSLER, GE, EDWARDS, RI, BROUCKAERT, CJ and BUCKLEY, CA (1988) The chemical removal of sulphates. *Proceedings of the 5th National Meeting of the South African Institution of Chemical Engineers.* Pretoria. W3-0 to W3-11.

TRUSLER, GE (1988) The Chemical Removal of Sulphates Using Barium Salts. MScEng Thesis, University of Natal, 17-20.

WHANG, JS, YOUNG, D and PRESSMAN, M (1982) Soluble sulphide precipitation for heavy metal removal from wastewater. *Environmental Progress* **1**(2) 110-113.