ANGLO AMERICAN RESEARCH LABORATORIES

AARL PROJECT NO. D/3/W/1

D/3-NO. 5

WATER TREATMENT - DEVELOPMENT - ALL MINES AND COLLIERIES

REPORT NO. 5

A REPORT ON THE REDUCTION OF THE SULPHATE CONTENT OF ACID MINE DRAINAGE BY PRECIPITATION WITH BARIUM CARBONATE

The laboratory scale sulphate reduction process, using barium carbonate, described in this report was found to be uneconomic, due to slow reaction rates, excessive reagent requirements and impurities in the final products. No further work is envisaged in the near future on these lines, however, the use of more intensive mechanical mixing and grinding facilities, may improve the economics of the process.

G.S. James
MANAGER

ANGLO AMERICAN RESEARCH LABORATORIES

AARL PROJECT NO. D/3/W/1

WATER TREATMENT - DEVELOPMENT - ALL MINES AND COLLIERIES

REPORT NO. 5

A REPORT ON THE REDUCTION OF THE SULPHATE CONTENT OF ACID MINE DRAINAGE BY PRECIPITATION WITH BARIUM CARBONATE

INTRODUCTION

Acid mine drainage is polluted mainly with varying concentrations of ferrous and ferric sulphate as a result of the oxidation of pyritic material. Upon neutralisation with lime the iron is precipitated as a hydroxide and calcium sulphate then becomes the main pollutant in the clarified water. The calcium sulphate content of the water is usually in excess of the generally accepted standard for irrigation water of 1 200 mg/l total dissolved solids and 500-600mg/l sulphate. The various methods of desalination are either uneconomical or still present a pollution problem because although, the salts removed from the water are concentrated about five-fold,they are still in a solution form.

One way of removing sulphate ions from solution is to form insoluble barium sulphate by the addition of a barium salt, e.g. barium carbonate to the water. The barium carbonate might be added to the acid water, in which case the precipitate will be contaminated with iron, but the lime consumption during subsequent neutralisation will be reduced. The barium carbonate might also be added to neutralised and clarified water, when a purer precipitate will be obtained.

If the process is to be at all economical the barium sulphate precipitate must be pure enough to be of value to the ceramic industry because the imported barium carbonate which costs about R125 per ton, will be consumed at about 1,2-2,0 kg per m^3 of AMD.

In this report an account is given of the results obtained during laboratory tests on the removal of sulphates from acid mine drainage and neutralised supernate from AMD.

SUMMARY

Experiments were conducted to study the feasibility of precipitating sulphate from acid mine drainage in the form of barium sulphate. The method was found to be uneconomical as barium carbonate has to be imported at R125/ton while the recovered barium sulphate is too impure to have a commercial value. The reaction rate is slow and large reaction vessels will be required. Contamination of the effluent with barium also presents a problem.

EXPERIMENTAL

Some Coronation Colliery - Kromdraai acid water of pH 2,6 was neutralised to pH 6,8-7,2 with solid hydrated lime in a 5-litre beaker at 500 rpm stirring speed.

Another part of the acid water has been treated with hydrogen peroxide to oxidise the ferrous ion to the ferric state. This was followed by neutralisation with dry hydrated lime as above. In both cases, the precipitated ferric-ferrous hydroxides were filtered off.

1-litre quantities of the clear filtrate were treated with barium carbonate in the following way: Stoichiometric and/or half stoichiometric quantities of finely ground chemically pure barium carbonate were added to the filtrate stirred at 200 rpm with a paddle stirrer. Stirring was continued for 1,2 and/or 4 hours respectively. At the end of these reaction periods, the produced precipitates were filtered off. The filtrates and precipitates were analysed for barium, sulphate, calcium, carbonate and iron (See Tables I, III and IV).

In the second set of experiments twice the stoichiometric quantity of fine barium carbonate powder was added to (a) neutralised and (b) unneutralised acid water. The mixtures were stirred for periods of up to 24 hours. (See Table IV).

DISCUSSION

As has been mentioned in the introduction, the main aim of the experiment has been the removal of part or all of the dissolved solids by the slow reaction between barium carbonate and

calcium/.....

calcium sulphate (the reaction in the case of unneutralised acid water was mainly between barium carbonate and sulphuric acid) initiated and assisted by mechanical agitation.

Good sulphate removal was experienced when twice stoichiometric amounts of barium carbonate were used in unneutralised acid water. The reaction was completed in 6-24 hours, but the supernate was highly contaminated with barium. (See Table II). Barium contamination also occurred in the case of neutralised acid water, though the completion of the reaction required only 1-4 hours. (See Table II).

Using the stoichiometric quantity of barium carbonate, sufficient sulphate removal was accomplished in a minimum of four hours, but barium carbonate occlusion was found to be high. (See Tables I, III, IV and V).

When half stoichiometric quantities of barium carbonate were added, the reaction as well as the sulphate removal was found to be incomplete, whilst barium carbonate occlusion was still noticeable. (See Tables I, III and IV).

The results obtained show, that the reaction is only completed partially, due to the deposition of a barium sulphate/calcium sulphate film onto an unreacted and thus occluded barium carbonate particle. The paddle stirrers gave inadequate agitation and could not break down either the occluded barium carbonate particles or remove the barium sulphate/calcium sulphate film.

The solubility of barium sulphate is 2,85 mg/l at 30°C, equivalent to 1 677 mg/l barium, whilst the solubility of barium carbonate is equivalent to 3 800 mg/l of barium at 30°C. A tenfold increase in the barium content of the supernate was noted as soon as the sulphate removal reached 90-95%. This may have been due to the difference in the solubility products of barium carbonate and calcium sulphate. (Barium pollution limits of 1 mg/l barium apply in some countries, due to the poisonous nature of all soluble barium salts. There is no limit as yet in South Africa).

The price of barium carbonate at R125/tonne makes it imperative, that the reaction by-product, i.e. barium sulphate, shall be

chemically/ .....

technically pure for purchase by the ceramic industry. Though some barium carbonate, calcium carbonate and calcium sulphate impurities can be tolerated, any iron contamination which makes the colour off-white, is not permissible. In this set of experiments, all the barium sulphate precipitates were slightly yellow and contained a high percentage of unreacted barium carbonate. At this stage no further treatment, like washing with dilute hydrochloric acid to remove the small iron impurities, was performed.

CONCLUSIONS

(1) Partial sulphate reduction by the barium carbonate method is possible by the addition of stoichiometric quantities of barium carbonate to the lime neutralised acid water, if sufficient mixing is applied over a 4-hour reaction period.

(2) Twice stoichiometric barium carbonate addition to neutralised acid water increases the sulphate reduction rate and the reaction can be completed in 1-4 hours, but causes barium contamination of the supernate.

(3) Less than stoichiometric barium carbonate additions give insufficient reduction of the sulphates.

(4) As the reaction rate is low, unreacted barium carbonate causes barium contamination of the supernate.

(5) Treatment of unneutralised acid water with barium carbonate is possible, but the resultant precipitate is also too impure and the barium contaminated supernate still has to be neutralised with lime, before discharge to a watercourse.

(6) Without further treatment, the barium sulphate precipitate produced by all the above experiments, is too impure to be of commercial value. Therefore, the process is uneconomical.

INVESTIGATED AND REPORTED BY:

L.E.Kun

Bosman

D.J. BOSMAN
ACTING HEAD:WATER TREATMENT
SECTION

JOHANNESBURG
NOVEMBER 15th, 1972.
LEK/CvA

TABLE I/.....

PRELIMINARY EXPERIMENTS

NAMD TREATMENT IN 3A = Stoichiometric Quantity of Barium Carbonate
IN 3B = Half Stoichiometric Quantity of Barium Carbonate
Stirring Speed: 200 rpm
Stirring Time: 1 hour

No.	Description	pH	TDS mg/1	SO_4 mg/1	Ca mg/1	Ba mg/1	Acidity as H_2SO_4 g/1	Free Acidity as H_2SO_4 g/1	Ba %	Ca %	SO_4 %	CO_3 %
1	AMD - Turnbull	2,6	1690	1195	92	-	0,87	0,34	-	-	-	-
2	AMD - Fairview	2,7	1650	1185	75	-	-	-	-	-	-	-
3	NAMD - Fairview	6,6	1612	1170	455	-	-	-	-	-	-	-
3A	Treated NAMD - Supernate	8,1	1381	764	390	<1	-	-	-	-	-	-
3B	Treated NAMD - Supernate	7,9	1498	850	426	<1	-	-	-	-	-	-
3A	Treated NAMD - Precipitate	-	-	-	-	-	-	-	40,0	1,4	6,3	20,7
3B	Treated NAMD - Precipitate	-	-	-	-	-	-	-	41,0	0,8	7,0	22,6

AMD = Acid Mine Drainage

NAMD = Neutralised Acid Mine Drainage

TABLE II/.........

TEST SERIES NUMBER ONE

AMD and NAMD Treatment With Twice Stoichiometric Quantity of Barium Carbonate.

Stirring Speed: 200 rpm.

No.	Description	Stirring time Hours	pH	TDS mg/l	SO$_4$ mg/l	Ca mg/l	Ba mg/l	Total Fe mg/l
4	NAMD - Turnbull	-	7,0	2052	1169	410	-	<1
4A	Treated NAMD - Supernate	1	7,0	1178	696	263	<1	<1
4B	Treated NAMD - Supernate	2	7,6	410	218	93	<1	<1
4C	Treated NAMD - Supernate	4	8,0	108	11	19	12	<1
4D	Treated NAMD - Supernate	6	8,1	130	10	18	10	<1
4E	Treated NAMD - Supernate	24	8,4	52	16	15	13	<1
5	AMD - Fairview	-	2,7	1650	1185	75	-	-
5A	Treated AMD - Supernate	1	3,2	1572	799	75	<1	-
5B	Treated AMD - Supernate	2	4,1	1446	745	25	<1	-
5C	Treated AMD - Supernate	4	4,2	1200	725	23	<1	-
5D	Treated AMD - Supernate	6	4,3	1020	617	21	<1	-
5E	Treated AMD - Supernate	24	4,3	850	520	19	<1	-

AMD = Acid Mine Drainage

NAMD = Neutralised Acid Mine Drainage

TABLE III/........

TABLE III

TEST SERIES NUMBER TWO

Description	Stoichiometric Quantity of Barium Carbonate Added	Stirring Speed rpm	Stirring Time Hours	pH	TDS mg/1	SO_4 mg/1	Ca mg/1	Ba mg/1	Total Fe mg/1	CO_3 %	Tot Fe %
NAMD - Turnbull	-	-	-	6,8	1384	912	370	-	<1	-	-
Treated NAMD - Supernate	1	200	1	7,8	1156	747	358	<1	<1	-	-
Treated NAMD - Precipitate	1	200	1	-	-	-	-	-	-	22,1	0,
Treated NAMD - Supernate	1	200	2	7,9	1132	743	315	<1	<1	-	-
Treated NAMD - Precipitate	1	200	2	-	-	-	-	-	-	19,6	0,
Treated NAMD - Supernate	1	200	4	7,9	992	604	285	<1	<1	-	-
Treated NAMD - Precipitate	1	200	4	-	-	-	-	-	-	17,5	0,
Treated NAMD - Supernate	½	200	1	7,9	1296	806	358	<1	<1	-	-
Treated NAMD - Precipitate	½	200	1	-	-	-	-	-	-	19,0	0,
Treated NAMD - Supernate	½	200	2	7,9	1278	823	348	<1	<1	-	-
Treated NAMD - Precipitate	½	200	2	-	-	-	-	-	-	20,3	0,
Treated NAMD - Supernate	½	200	4	7,9	1266	770	335	<1	<1	-	-
Treated NAMD - Precipitate	½	200	4	-	-	-	-	-	-	14,3	0,

AMD = Acid Mine Drainage

NAMD = Neutralised Acid Mine Drainage

TABLE IV/...........

TEST SERIES NUMBER THREE

.	Description	Stoichiometric Quantity of Barium Carbonate Added	Stirring Speed rpm	Stirring Time Hours	pH	TDS mg/1	SO_4 mg/1	Ca mg/1	Ba mg/1	Total Fe mg/1	CO_3 %	Tot Fe %
	O + NAMD - Turnbull	-	-	-	6,7	1430	921	370	-	<1	-	-
	Treated O + NAMD - Supernate	1	200	1	7,9	1360	828	358	<1	<1	-	-
	Treated O + NAMD - Precipitate	1	200	1	-	-	-	-	-	-	22,6	0,
	Treated O + NAMD - Supernate	1	200	2	7,9	1354	801	356	<1	<1	-	-
	Treated O + NAMD - Precipitate	1	200	2	-	-	-	-	-	-	23,3	0,
	Treated O + NAMD - Supernate	1	200	4	7,7	1162	665	315	<1	<1	-	-
	Treated O + NAMD - Precipitate	1	200	4	-	-	-	-	-	-	18,5	0,
	Treated O + NAMD - Supernate	½	200	1	8,0	1426	875	390	<1	<1	-	-
	Treated O + NAMD - Precipitate	½	200	1	-	-	-	-	-	-	25,4	0,
	Treated O + NAMD - Supernate	½	200	2	7,8	1392	841	363	<1	<1	-	-
	Treated O + NAMD - Precipitate	½	200	2	-	-	-	-	-	-	21,3	0,
	Treated O + NAMD - Supernate	½	200	4	7,9	1338	796	374	<1	<1	-	-
	Treated O + NAMD - Precipitate	½	200	4	-	-	-	-	-	-	15,3	0,

O + NAMD = Oxidised and Neutralised Acid Mine Drainage.

TABLE V/......

TABLE V

BULK SAMPLE

No.	Description	pH	TDS mg/1	SO_4 mg/1	Ca mg/1	Ba mg/1	Total Fe %	SO_4 %	Ca %	Ba %	CO_3 %	Total Fe %
8	NAMD - Fairview	6,6	1612	1070	455	-	<1	-	-	-	-	-
8A	Treated NAMD - Supernate	7,8	926	591	277	<1	<1	-	-	-	-	-
8A	Treated NAMD - Precipitate	-	-	-	-	-	-	23,1	4,9	51,3	14,7	0,2

NAMD Treated with Stoechiometric Quantity of Barium Carbonate and Stirred at 500 rpm for 4 Hours.

oOo