Processing of Barium Sulphide to Barium Carbonate and Sulphur

M Masukume1,*, J P Maree2, S Ruto3 and H Joubert1

1Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
2Department of Environmental, Water and Earth Sciences, Tshwane University of Technology, Pretoria, South Africa
3Africa Remediation Technologies (Pty) Ltd, Cullinan, Pretoria, South Africa

Abstract

Gauteng Province, South Africa will have a shortfall of 400 ML/d of fresh water by 2014. This shortfall can be made up either by purchasing additional expensive water from the Lesotho Highlands Scheme or by; treating acid mine water. The CSIR ABC (alkali-barium-carbonate) Process is a most cost-effective process as the sludge produced is processed back to the process raw materials and valuable by-products, such as sulphur. Coal is the main material used in processing the sludge.

The chemical processing of barium sulphide into barium carbonate and elemental sulphur has been demonstrated on a pilot scale in batch mode. The barium sulphide was reacted with carbon dioxide at ambient temperature and atmospheric pressure to produce BaCO3 and H2S. The H2S generated, was contacted and oxidized with ferric iron solution to form elemental sulphur. Over 80% of the barium reacted during the carbonation process while all the sulphide was converted to H2S. The reaction rate of barium carbonation was found to increase with increase in CO2 flowrate. The pilot plant has produced BaCO3 and sulphur of high quality compared with commercial products in terms of reactivity and purity, respectively. The BaCO3 produced was used in acid mine drainage treatment and lowered sulphate concentration from around 2500 mg/L to 415 mg/L. The outcome of this project will assist in solving the problem of economic acid mine drainage treatment, using regenerated barium carbonate. Moreover, the project also aims to enable the generation of income through recovery of valuable by-products.

Keywords: Dissolution; Carbonation; Barium carbonate; Acid mine drainage; Sulphur

Introduction

Acid mine drainage (AMD) continues to be a serious water pollution problem in South Africa, owing to its well documented adverse effects on the environment. While there are several AMD treatment technologies that are being proposed, that include ion exchange [1] adsorption [2] freeze crystallization [3], reverse osmosis [4] and biological treatment [5-7], finding a robust and economic AMD treatment technology is still continuing. Each of these technologies has its own advantages and disadvantages which tend to limit its use.

One of the technologies with the potential of solving AMD treatment problem is the South African Council for Scientific and Industrial Research's (CSIR) Alkali-Barium Carbonate (ABC) process [8,9]. The CSIR has reported on the recovery of drinking water from Gold mine effluents via the ABC desalination process. Hence AMD could be a possible source of fresh drinking water. Moreover, the barium carbonate used in this process is recyclable by barium sulphate calcining in the presence of coal and subsequent CO2 treatment of the coal. This process not only has the benefit of generating income through the recovery of saleable by-products, thereby reducing operational costs of treatment but also allows the regeneration and reuse of a process chemical, barium carbonate. When the value of treated water and by-products exceeds the treatment cost, it is feasible to create enterprises that could provide economic benefits while solving environmental problems.

In this study, the processing of barium sulphide produced by the thermal reduction of barium sulphate sludge from the ABC process was carried out on pilot scale. The process was made up of three phases: (i) biological oxidation of ferrous iron, followed by; (ii) barium sulphide carbonation and finally, (iii) the absorption of hydrogen sulphide gas by ferric iron solution to form elemental sulphur. Sulphur is a key raw material for many manufacturing industries such as fertilizer, acids, steel, petroleum etc. Nengovhela et al. [10] have reported on the recovery of sulphur from gypsum on a laboratory scale.

Materials and Methods

Major reactors used and procedures followed during this study

Feeder: The feeder (250L) was made of chemically inert stainless steel with a turbulent stirrer of high speed. This is the stage where crude barium sulphide was dissolved in tap water (room temperature) by using a high powered stirrer and the remaining ash leached. Two batches were prepared to make up a volume of 500 L barium sulphide solution. After 10 min of mixing, the solution was allowed to settle for 5 min. The supernatant was transferred by pump to the barium carbonate reactor. The ash was removed from the feeder after every run.

Barium carbonate reactor: The reactor (1000L) was made of fibre glass and had maximum pressure and temperature ratings of 4 bars and 50 °C, respectively. The barium carbonation process is exothermic hence fibre glass was used to allow heat loss at a faster rate. Depending on the initial mass of BaS, the solution temperature rose to a maximum of 38 °C. The barium sulphide solution was thoroughly mixed before carbon dioxide was introduced. The solution was continuously circulated using the pump. Carbon dioxide was introduced at the bottom of the reactor from a gas cylinder at a given flowrate. Quality control checks were done on this solution as the reaction proceeded; these included pH and conductivity, sulphide and barium concentration. Samples were collected at 30 minute time intervals. As the reaction proceeded, hydrogen sulphide gas was produced and stripped off through the opening on top of the reactor. The sour gas (H2S + CO2 + water vapor).

*Corresponding author: Mike Masukume, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, Private bag X680 Pretoria 0001, Tel: +27 820966980; E-mail: masukume@gmail.com

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The sour gas was led by means of a PVC pipe to the ferric iron solution. The barium sulphide containing supernatant was reused to prepare a further batch of barium sulphide solution.

**Hydrogen sulphide scrubber:** The scrubber (1000 L) was made of fibre glass and had maximum pressure and temperature ratings of 4 bar and 50°C, respectively. The barium carbonation process is exothermic hence fibre glass was used to allow heat loss at a faster rate.

The toxic hydrogen sulphide gas was contacted with the ferric iron solution at the bottom of the reactor to ensure a longer contact time and the excess gas was recycled back to the solution by a venturi. The reaction resulted in the reduction of ferric to ferrous iron with the subsequent production of elemental sulfur. The solution pH, conductivity and ferrous iron concentration were monitored as the reaction proceeded. At the end of the reaction, the solution was transferred to the sulphur settling tank for decanting.

**Biological reactor:** The biological reactor was made of polyethylene. About 700 L of 10 g/L ferrous iron solution is transferred to the biological reactor for bio-oxidation using *Acidithiobacillus ferrooxidans* bacteria. The bioreactor contained a geo-textile medium as biomass support to provide enough surface area for the bacteria to grow. The bioreactor operated at ambient temperature while solution pH was around 2. Hydroponic nutrients (300 g) containing mainly nitrogen and phosphate, were introduced at the start of the preparation of each batch. Air was continuously supplied at 56.6 L/min and 206.7 kPa and was evenly distributed through a diffuser at the bottom of the reactor. Ferrous iron concentration was monitored as the oxidation process proceeded. Figure 1 shows a typical flow diagram of the carbonation process.

**Analytical Tests**

The standard stock solutions were prepared using deionized water. The solutions were stored in glass bottles with glass stoppers. The working solutions were prepared by dilution of standard solutions.

**Ferrous iron analyses:** Filtered ferrous/ferric solution (10 mL) was pipetted into a 100 mL volumetric flask and the solution was made up to the mark using deionized water. 10 mL of this solution was pipetted into a 250 mL conical flask. This was followed by the addition of 10 mL of 0.1N sulphuric acid, and 10 mL of Zimmerman- Reinhard reagent. The solution was titrated against 0.01M sodium hydroxide solution. This was followed by the addition of 50mg of methylthymol blue indicator. The solution was titrated against 0.01M EDTA to a grey end point.

**Barium analyses:** The barium sulphide containing sample (25 mL) was pipetted into 100 mL conical flask and 75 mL deionized water added. The pH of the solution was adjusted to around 12 using 1N sodium hydroxide solution. This was followed by the addition of 50mg of methylthymol blue indicator. The solution was titrated against 0.01M EDTA to a grey end point.

**Sulphur recovery reactions**

Dissolution of BaS and reaction with CO₂ to form BaCO₃ and H₂S:

\[
\text{BaS} + H₂O + CO₂ \rightarrow \text{BaCO}_3 + H₂S \quad (1)
\]

H₂S stripped and converted to elemental sulphur via the ferric iron route:

\[
H₂S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \quad (2)
\]

**Results and Discussion**

The processing of barium sulphide into saleable barium carbonate and elemental sulphur was technically demonstrated on pilot scale. The process involved the dissolution of barium sulphide, carbonation of barium sulphide solution and finally oxidation of the hydrogen sulphide by a ferric iron solution. Several control analyses were performed on the solutions during the different stages of the process as described above. The results of these analyses are described below.

**Effect of temperature on dissolution of barium sulphide (BaS)**

The effect of temperature on dissolution of BaS was monitored by measuring the changes in electrical conductivity of the BaS solution over time as shown in figure 2. While an increase in solution temperature always results in corresponding increases in dissolution rate for endothermic reactions, the results in figure 2 showed an insignificant increase possibly because BaS is readily soluble in water. Due to this small increase in solubility upon heating the barium sulphide solution, all the batches were therefore prepared using tap water at room temperature.

**Leaching tests**

The leaching tests, the results of which are shown in figure 3, were carried out in order to dissolve all the barium sulphide present together.
with process ash and to ensure that the residual ash was safe for disposal. The second run (Figure 3) showed that all the BaS was dissolved in the first run and an insignificant amount remained in the ash which posed no risk when disposed to the environment.

**Efficiency of the barium carbonation process**

The barium sulphide solution was reacted with carbon dioxide at ambient temperature to form barium carbonate and hydrogen sulphide. Tables 1 and 2 show the results of chemical analyses checks where the solution pH, conductivity, sulphide and barium concentrations were monitored during barium carbonation and the oxidation of \( \text{H}_2\text{S} \) gas by the ferric iron solution.

The results (Table 1) showed that over 80% of the dissolved barium reacted with the \( \text{CO}_2 \) whilst all the sulphide was converted to \( \text{H}_2\text{S} \). The results (Figure 3) showed that the rate of barium carbonation was dependant on \( \text{CO}_2 \) flowrate. An increase in \( \text{CO}_2 \) flowrate from 7 to 15 L/min resulted in a corresponding increase in carbonation reaction rate (Figure 4). Hence \( \text{CO}_2 \) concentration is the major rate limiting factor in this reaction. A high flow rate of \( \text{CO}_2 \) also aided in stripping of \( \text{H}_2\text{S} \) from the barium carbonate reactor. As indicated in figure 5, the solution pH decreased as the reaction proceeded and the carbonation process was stopped when the solution pH reached 6.3 (Figure 6). Based on laboratory studies, a solution pH below 6.3 resulted in the undesired formation barium bicarbonate.

**Barium carbonate reactivity**

The barium carbonate produced was characterised for reactivity. Figure 7 shows reactivity of commercial and Cullinan pilot plant barium carbonate with synthetic calcium sulphate rich water over time. Results from figure 7 showed that the barium carbonate from the Cullinan pilot plant compared well with a commercial product in terms of reactivity.

**Efficiency of the barium carbonate produced on AMD treatment**

The \( \text{BaCO}_3 \) produced was used in acid mine drainage treatment and lowered sulphate concentration from around 2500 to 415 mg/L. Table 3 shows a summary of the performance of barium carbonate produced on AMD treatment. The sulphate removal efficiency of 83.4% compares well with the results reported employing the CSIR ABC desalination process that utilised commercial \( \text{BaCO}_3 \) as reported by Motaung et al. [9] and Mulopo [11].

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**Figure 3:** Leaching tests on barium sulphide. Solid load = 40kg/500 L. BaS dissolution was monitored by the electrical conductivity of the solution.

**Figure 4:** Effect of \( \text{CO}_2 \) flowrate on carbonation reaction rate.

**Table 1:** Results of analytical monitoring during the barium carbonation process.

| Time (min) | \( \text{CO}_2 \) flowrate (L/min) | Conductivity (mS/cm) | pH  | Ba (g/L) | Ba removal (%) | Sulphide (g/L) as BaS | Sulphide removal (%) |
|-----------|---------------------------------|----------------------|-----|----------|----------------|------------------------|----------------------|
| 0         | 7                               | 20.3                 | 12.7| 17.6     | -              | 20.2                   | -                    |
| 30        | 7                               | 14                   | 12.1| 14.9     | 15.4           | 19.4                   | 4.2                  |
| 60        | 7                               | 11                   | 8.3 | 11.5     | 34.6           | 16.9                   | 16.7                 |
| 90        | 7                               | 8.3                  | 7.7 | 10.1     | 42.3           | 14.4                   | 29.2                 |
| 120       | 7                               | 7.2                  | 7   | 7.4      | 57.7           | 10.1                   | 50                   |
| 150       | 7                               | 5.5                  | 6.5 | 6.8      | 61.5           | 8.5                    | 58.3                 |
| 180       | 7                               | 5                   | 6.4 | 5.4      | 69.2           | 2.5                    | 87.5                 |
| 210       | 7                               | 3.4                  | 6.3 | 3.4      | 80.8           | 0                      | 100                  |

**Table 2:** Results of analytical monitoring during oxidation of \( \text{H}_2\text{S} \) by ferric iron solution.

| Time (min) | \( \text{CO}_2 \) flowrate (L/min) | \( \text{CO}_2 \) used/Sulphide removed | pH   | Conductivity (mS/cm) | Fe(II) (mg/L) | Fe(II) formed (eq) |
|-----------|---------------------------------|----------------------------------------|------|----------------------|---------------|---------------------|
| 0         | 7                               | -                                      | 2.3  | 8.8                  | 167.6         | -                   |
| 30        | 7                               | 3.8                                    | 2.2  | 8.9                  | 167.6         | -                   |
| 60        | 7                               | 1.9                                    | 2.2  | 8.7                  | 167.6         | -                   |
| 90        | 7                               | 1.6                                    | 2.2  | 8.9                  | 446.8         | 2.8                 |
| 120       | 7                               | 1.3                                    | 2.1  | 10.3                 | 2625          | 24.2                |
| 150       | 7                               | 1.3                                    | 1.6  | 13.8                 | 3071.8        | 28.6                |
| 180       | 7                               | 1.1                                    | 1.5  | 16.7                 | 3295.2        | 30.8                |
| 210       | 7                               | 1.1                                    | 1.4  | 20.5                 | 4132.9        | 39.1                |
Conclusions

A process was investigated for manufacturing barium carbonate by reacting barium sulphide with carbon dioxide, on a pilot scale. The pilot plant produced BaCO₃ and sulphur of high quality compared with commercial products.

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Table 3: Summary of the performance of barium carbonate produced in the present project on AMD treatment.

Feed of BaCO₃ (ml/min) | Commercial BaCO₃ | Cullinan BaCO₃
---|---|---
10 | | |
10 | | |
10 | | |

Raw water

| pH | 7.7 | 7.9 | 9.9 |
| Conductivity (mS/cm) | 9.4 | - | 9.5 |
| Sulphate (mg/L) | 2485 | 2500 | 2500 |
| Ca (mg/L) | 3360 | - | 3270 |
| Mg (mg/L) | 32 | - | 24.5 |

Treated water

| pH | 10.5 | 10 | 10 |
| Conductivity (mS/cm) | 9 | 9 | 9 |
| Sulphate (mg/L) | 419 | 415 | 410 |
| Ca (mg/L) | 820 | 960 | 724 |
| Mg (mg/L) | 67.4 | 33.5 | 37.1 |
| Ba (mg/L) | 238.8 | 239.8 | 238.6 |

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