The Effect of Temperature and Pressure on the separation of Calcium Carbonate and Barium Sulphate from a Mixed Sludge

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Abstract

South Africa is one of the first countries to implement full-scale mine water reclamation to drinking water quality. Reverse osmosis is already being used on full scale for desalination of mine water. However, with increased recycling of mine water, the result has been the increased generation of sludge. The Council for Scientific and Industrial Research (CSIR) has developed the Alkali-Barum-Carbonate (CSIR-ABC) process that can be used for neutralization and desalination of sulphate-rich effluents while recovering valuable by-products from the mixed sludge’s produced. A mixture of BaSO4 and CaCO3 sludge is produced as one of the by-products, which preferably needs to be separated into its components prior to thermal treatment. The aim of this study was to separate CaCO3 and BaSO4 from a CaCO3-BaSO4 mixed sludge through dissolution of CaCO3 as Ca(HCO3)2 in contact with CO2. Measured quantities of a simulated CaCO3-BaSO4 mixed sludge from the CSIR-ABC process were fed into a reactor vessel containing deionized water and pressurized CO2 was introduced. The effects of temperature and pressure with time were investigated while monitoring alkalinity, pH and calcium concentration. The findings of this study were: (1) The dissolution rate of CaCO3 was rapid i.e. from 0 to 2000mg/L in the first 20 minutes; (2) Ca(HCO3)2 had a high solubility of about 2600 mg/L when in contact with CO2 at 1atm., while BaSO4 was almost completely insoluble; (3) The solubility of Ca(HCO3)2 increased with decreasing temperature and increasing pressure; (4) CaCO3, after conversion to Ca(HCO3)2, was separated from BaSO4 in a CaCO3-BaSO4 mixed sludge; (5) Visual MINTEQ model is a powerful tool that can be used to predict the solubilities of CaCO3 and BaSO4 when contacted with CO2.

Keywords: Acid mine drainage; carbonation; Dissolution, Reclamation, Carbon dioxide, Sludge disposal

Introduction

South Africa currently faces both a shortage of water as well as a deterioration of the quality of the available water due to industrial activities such as mining and power generation. The gold mines in Gauteng are expected to decant 345 ML of acid mine drainage per day when open voids have filled up. This water will pollute the surface water resources and cause serious environmental impacts [1]. South Africa was one of the first countries to implement commercial scale drinking water reclamation from mine water using reverse osmosis. The cost of reverse osmosis amounts to R10/m3 and produces gypsum and ferric hydroxide rich sludge that has to be disposed of at a cost on sludge disposal dumps.

The CSIR-ABC process is an alternative technology and offers the benefit of lower cost as calcium carbonate, lime; barium carbonate and coal are the main process raw materials. It produces minimum amount of sludge from raw materials (BaCO3 and lime) which are recovered from the sludge. Sulphur, a valuable by-product, can also be recovered from the sulphate removed from the mine water. The CSIR-ABC process involves three stages. In the first stage CaCO3 is dosed to raise the pH of the AMD to 7 for removal of free acid, iron (II) as iron (III) and aluminium as aluminium (III). In the second stage lime is dosed to precipitate other metals, including magnesium, as metal hydroxides. Partial sulphate removal is also achieved in these two stages through gypsum crystallization. In the third stage, barium carbonate is dosed for final sulphate removal through BaSO4 precipitation and carbon dioxide is dosed to precipitate calcium as CaCO3. The resultant, mixed BaSO4/CaCO3 sludge is treated in a thermal stage to produce BaS and CaO. As a portion of the sulphide combines with calcium, the BaS yield is never higher than 85%, compared to 96% when only BaSO4 is processed in the thermal stage [2]. It would therefore be beneficial if the mixture of BaSO4 and CaCO3 could be separated prior to thermal treatment. Figure 1a shows the schematic diagram of the CSIR-ABC Process and Figure 1b shows the process flow diagram of the BaSO4-CaCO3 sludge separation process.

The aim of this study was to separate calcium carbonate from barium sulphate, produced in the third stage of the CSIR-ABC Process, through dissolution of CaCO3 with CO2. By adding CO2 to a mixed BaSO4-CaCO3 sludge, selective dissolution of CaCO3 occurs according to the following reaction:

\[
\text{CO}_2(g) + \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{HCO}_3^-(aq) + \text{Ca}^{2+}(aq)
\]

As the system becomes enriched in CO2, the dissolution rate of CaCO3 could be influenced by its saturation level, \(\Omega\) [3].

\[
\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_p}
\]

where \(K_p\) (T, S, p) is the solubility product (T is temperature, S is solubility and p is pressure) [4] with the pressure dependency adjustments by Millero et al. [5].

\[
K_p = [\text{Ca}^{2+}][\text{CO}_3^{2-}]
\]
Note: All the square-bracketed species are stoichiometric concentrations (molality or mol/kg) and disregard any complex formation or ion pairs. It is thus necessary to specify not only the pH scale used in the evaluation of the dissociation constants [6], but also their dependency on ionic strength, temperature, and pressure.

The Ca(HCO₃)₂ formed, according to Equation (1), can be precipitated as CaCO₃ by lowering the pressure to atmospheric conditions (Equation 2);

\[ \text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \] (4)

Materials and Methods

A 2% BaSO₄/CaCO₃ slurry was prepared with a BaSO₄/CaCO₃ mole ratio of 1 as feedstock. A simulated mixed sludge was prepared using commercial grade BaSO₄ (28g) and analytical grade CaCO₃ (12 g). The slats were mixed in deionised water (2L). Bottled CO₂ was used for dissolving CaCO₃. The composition and the behaviour of the simulated sludge was the same as that of the real sludge due to the fact that all possible impurities (metals) in the real sludge are removed in the pre-treatment stage of the CSIR-ABC process using limestone and lime.

Batch studies were carried out using a completely-mixed pressurized reactor (Figure 2). It consisted of a 3L reaction vessel equipped with a BirCraft stirrer, temperature sensor, pressure gauge, pH and conductivity control sensors. This unit was designed to withstand pressures of up to 10bar and a maximum temperature of 150°C. The main body of the reactor was constructed from a Class 12 unplasticised polyvinyl chloride (uPVC) pipe with a wall thickness of 3.2mm and an internal diameter of 560mm. The length of the pipe was 520mm with uPVC base and top plates that were each 65mm thick. The dosage points were 300mm above the effluent off-take point that was fitted at the bottom of the reactor. Calcium carbonate and barium sulphate were first fed into the reactor from the top and deionized water was pumped into the reaction vessel with a Watson-Marlow pump with continuous stirring. Pressurized carbon dioxide was dissolved in water in the pressurized reactor, to lower the pH to around 6 and increase the pressure to desired levels. A pH control unit was used to control CO₂ dosage by monitoring the pH. At the end of the reaction the solution was filtered under pressure and the filtrate released from the pressure vessel through a valve.

The effect of the following parameters was investigated:

- Time: 0, 10, 20, 40, 60 min (measured).
- Temperature: 0, 10, 25, 45°C (measured and predicted).
- Pressure (predicted).
- CaCO₃ concentration: 6, 20 g/L (measured and predicted).
- BaSO₄ concentration: 0, 14, 23.3 g/L (predicted).

The default conditions were 0°C, 6 g/L CaCO₃, 14 g/L BaSO₄. Filtered samples were collected over the time period 0-60 min and analysed for pH, alkalinity, calcium, barium and sulphate. The samples were filtered (0.45μm membrane filter) to remove all solid material.

Sulphate concentration was measured in the effluent water. The sample was conditioned using a glycerine conditioning reagent, and solid barium chloride was added and mixed. The turbidity of the BaSO₄ suspension was measured using a turbidity meter and the reading was compared with a calibration curve to determine the sulphate concentration. The minimum detectable concentration is approximately 1mg SO₄²⁻/L and possible interferences are silica in excess of 500 mg/L and large quantities organic materials that may slow down the precipitation of BaSO₄ [7]. Correction for sample colour and turbidity was corrected by running blanks to which BaCl₂ was not added.

The total dissolved carbonate species were measured by titrating the sample with standard hydrochloric acid to pH 4.3. The volume of acid was used to calculate the total alkalinity of the sample. From this calculation, the carbonate and hydroxide species concentrations were calculated, and the total carbonate species concentration (as mg/LCaCO₃) [7]. The known interferences for this method are soaps, oily matter and precipitates and our samples where filtered to remove all undissolved substances.

Calcium hardness was determined by titration with EDTA (0.02M)
using P&R indicator and NaOH buffer. Total hardness was determined with EDTA (0.02M) using Eriochrome Black T indicator and ammonia buffer [7].

Barium concentrations were determined by a Spectro Arcos Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Filtered samples were diluted using deionised water and analysed while alternating with blanks to eliminate the occurrence of carry-over effect [7]. The instrument’s estimated detection limit for barium is 2 µg/L and the upper limit of the effective calibration concentration range is 50 mg/L.

The pH, temperature, electrical conductivity and pressure were measured in situ.

**Results and Discussion**

Table 1 and Figure 3-6 show the dissolution of CaCO₃ (calcite) and BaSO₄ (barite) when contacted with CO₂ in water under various conditions. The Figure 3-6 contain measured values while Table 1 contains both measured and predicted values. The predictions were done using a Visual MINTEQ model [8].

**Kinetics of CaCO₃ dissolution on CO₂-rich water**

The dissolution rate was rapid as indicated by the fact that more than 50% of the CaCO₃ that dissolved was already in solution when the first sample was collected after 10 min (Figure 3). The dissolution rate is influenced by particle size, pressure and temperature.

**Separation of CaCO₃ and BaSO₄**

The mixture of CaCO₃ and BaSO₄ sludge that is produced by the CSIR-ABC process cannot be separated by solubility differences due to the low solubility of both CaCO₃ (1.3 mg/L Ca) and BaSO₄ (5.6 mg/L Ba). As CO₂ is produced as a waste product in the CSIR-ABC process, it was decided to investigate whether CaCO₃ could be separated from it was decided to investigate whether CaCO₃ could be separated from

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**Table 1: Effect of various parameters on the solubility of CaCO₃ and BaSO₄ in a CO₂-rich solution.**

<table>
<thead>
<tr>
<th>Exp No</th>
<th>Feedstock</th>
<th>pH</th>
<th>Temperature(°C)</th>
<th>Pressure (atm)</th>
<th>CaCO₃ (aq) (mg/l)</th>
<th>Mg/l Ba</th>
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<tbody>
<tr>
<td></td>
<td>CaCO₃ (g/l)</td>
<td>BaSO₄ (g/l)</td>
<td>Predicted</td>
<td>Determined</td>
<td>Predicted</td>
<td>Determined</td>
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**Exp 1** Effect of BaSO₄; pH, Ca and Ba measured and predicted (Figure 5)

<table>
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<tr>
<th>Exp 2</th>
<th>Effect of temperature on CaCO₃; pH and Ba measured and predicted (see Figure 6 and 7)</th>
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**Exp 3** Effect of pressure on CaCO₃; pH and CaCO₃ predicted (see Figure 9)

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**Exp 5** Effect of pressure on CaCO₃ and BaSO₄; pH, Ca and Ba predicted

<table>
<thead>
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<th>Exp 5</th>
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The pH, temperature, electrical conductivity and pressure were measured in situ.
the almost insoluble BaSO₄ by dissolving it as Ca(HCO₃)₂ (Equation 1), by contacting the sludge mixture with CO₂.

Figure 3 shows that CaCO₃ dissolved when contacted with CO₂ at 1atm. Ca and Alkalinity (Alk) values increased rapidly in stoichiometric concentrations from the low solubility of CaCO₃ to the high solubility of Ca(HCO₃)₂ (2600 mg/L Alk, as CaCO₃) and 2650 mg/L Ca (as CaCO₃). Over the same period the pH dropped from 8.7 to 6.2. Due to the ease of alkalinity measurements, they were used to monitor the formation of Ca(HCO₃)₂ and includes the parameters listed in Equation 5. Figure 3 also shows the ionic balance between the measured calcium concentration and the total alkalinity of the system. As the system became enriched in CO₂, the extent of dissolution decreased as a function of changes in the CaCO₃ saturation state to yield both calcium ions and alkalinity (Equation 1). The solubility of CaCO₃ decreases with an increase in pH. Therefore, increasing CO₂ input into the reaction lowers the pH and calcium carbonate becomes more susceptible to dissolution. In this study, the pH was lowered to 6 and this enabled CO₂⁻ to associate with protons, while driving the solubility equilibrium toward the formation of HCO₃⁻.

\[
\text{Alk} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] + [\text{H}^+] \quad (5)
\]

Figure 4 shows the contrast between the solubilities of CaCO₃ (2200 mg/L; Ca as CaCO₃) and BaSO₄ (50 mg/L as Ba). The results showed that BaSO₄ does not dissolve when contacted with CO₂ and consequently there were negligible losses of BaSO₄ due to dissolution. The effect of BaSO₄ on the rate of formation and solubility of Ca(HCO₃)₂ was studied. Figure 5 showed that BaSO₄ had no effect on the solubility of Ca(HCO₃)₂. This is because BaSO₄ has a very low solubility. The known low solubility of BaSO₄ was also confirmed by the low predicted values for Ba²⁺ in solution, when contacted with CO₂ (Table 1).

Effect of temperature and pressure on solubility

In the previous section it was shown that CaCO₃ can be dissolved through CO₂ addition without affecting the low solubility of BaSO₄. The sludge separation process will be more effective at higher solubility values for CaCO₃. Therefore, it was decided to determine the effect of pressure and temperature on the solubility of CaCO₃. According to Henry’s law, it was expected that the solubility should increase with decreasing temperatures. Figure 6 confirmed the validity of Henry’s law [9,10]. In Figure 6, the effect of temperature on the rate of formation and solubility of Ca(HCO₃)₂ in the presence of BaSO₄ as well as in the absence of BaSO₄ was investigated. It was found that BaSO₄ had no effect on the solubility of CaCO₃ when contacted with CO₂.

Measured versus predicted solubility values

Table 1 shows a comparison of the predicted and determined values for the effect of various parameters on the solubility of CaCO₃ and BaSO₄ in a CO₂-rich solution. The predictions were done using the Visual MINTEQ (2000) model. The model was designed to simulate equilibrium and speciation of inorganic solutes in natural waters.

Temperature

Figure 7 and 8 (Expt 1) (Expt 2) compare the solubility of Ca(HCO₃)₂ at 1atm CO₂ when no BaSO₄ and 14 g/L BaSO₄, respectively, were
present over the temperature range 0-45°C. Both sets of results showed that the solubility of CaCO₃ increases with decreasing temperature. The measured values at the lower temperatures (0° and 10°C) were higher than the predicted values. These differences indicate that the Visual MINTEQ (2000) model can be improved further. However, it is a very useful tool as it can predict trends for a large number of compounds.

**Pressure**

As the results in the above section showed, the Visual MINTEQ(2000) model can predict trends, it was used to predict the effect of pressure on the solubility of Ca(HCO₃)₂ in the absence and presence of 23.3 g/L BaSO₄. It was noticed that the solubility of CaCO₃ when contacted with CO₂ increased with increasing pressure (Figure 9). The model also showed, as in the case of the temperature studies above, that BaSO₄ had no influence on the solubility of CaCO₃ when contacted with CO₂ (compare Expt 4 with Expt 5, Table 1). The practical implications of these findings are that the solubility of CaCO₃, when contacted with CO₂ increases with decreasing temperature and increasing pressure. The CSIR-ABC Process offers a sustainable method for neutralization, metal removal and desalination of acid mine drainage and recovery of by-products from the mixed sludge produced.

**Separation rate**

In this study, it was found that the dissolution rate of CaCO₃ is directly related to the separation rate from the mixed sludge. Figure 10 shows the dissolution rate of the CaCO₃ with temperature from a CaCO₃-BaSO₄ mixed sludge in a CO₂-rich solution. The highest rate of separation was recorded at 0°C. Figure 10 also shows that lower temperatures favour high rates of separation of the CaCO₃ from the mixed sludge while increased temperature leads to a significant decrease in the dissolution rate of CaCO₃.

**Conclusions**

The results of this study will contribute to the improvement of the CSIR-ABC Process design to meet the criteria for maximum value of treated water and by-products coupled with reduced running and sludge disposal costs. The conclusions drawn from this work were:

- The dissolution rate of CaCO₃ in the presence of CO₂ is fast at low temperature and high pressure;
- CaCO₃ has a high solubility of about 2600 mg/l when in contact with CO₂ at 1 atm., while BaSO₄ is almost completely insoluble;
- The solubility of CaCO₃ increases with decreasing temperature and decreasing pressure;
- The Visual MINTEQ model was a powerful tool used to predict the solubility of CaCO₃ and BaSO₄ when contacted with CO₂;
- CaCO₃ can be separated from BaSO₄ in and CaCO₃-BaSO₄ mixed sludge.

The cost of this process is low because all the process raw materials (CO₂ and the CaCO₃-BaSO₄ sludge) are waste products of the CSIR-
ABC process (Figure 1a and 1b). It is also foreseen that the cost can be kept low in other applications by producing CO₂ on-site by burning coal and scrubbing the off-gas in water rather than purchasing pure CO₂. From the reaction equilibrium and the results of this study, it is apparent that decreasing the temperature and increasing CO₂ pressure will result in a better conversion of CaCO₃ to Ca(HCO₃)₂. However, high pressure systems are more complex to run and require sophisticated reactor designs and special construction material which will ultimately increase costs. Because Ca(HCO₃)₂ has high solubility when contacted with CO₂ at low temperatures and high pressure, the practical, optimal operation conditions for the dissolution reaction are temperatures close to 0°C and pressures as close as possible to atmospheric depending on the application.

Acknowledgments

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References