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-Barium-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 was one of the first countries to implement commercial scale drinking 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-Barium-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.

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 crystalization. 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, Ω [3].

$$\Omega = \left[\text{Ca}^{2+}\right]\left[\text{CO}_3^{2-}\right]/K_p$$

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].

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

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Received April 30, 2012; Accepted June 19, 2012; Published June 21, 2012

Citation: Rukuni TT, Maree JP, Zvinowanda CM, Carlsson FH (2012) The Effect of Temperature and Pressure on the separation of Calcium Carbonate and Barium Sulphate from a Mixed Sludge. J Chem Eng Process Technol 3:137. doi:10.4172/2157-7048.1000137

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Schematic flow diagram of the BaSO$_4$-CaCO$_3$ sludge separation process.

The Ca(HCO)$_3$ formed, according to Equation (1), can be precipitated as CaCO$_3$ by lowering the pressure to atmospheric conditions (Equation 2);

$$\text{Ca(HCO}_3\text{)}_{(aq)} \rightarrow \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$$

### Materials and Methods

A 2% BaSO$_4$/CaCO$_3$ slurry was prepared with a BaSO$_4$/CaCO$_3$ mole ratio of 1 as feedstock. A simulated mixed sludge was prepared using commercial grade BaSO$_4$ (28g) and analytical grade CaCO$_3$ (12 g). The salts were mixed in deionised water (2L). Bottled CO$_2$ was used for dissolving CaCO$_3$. 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 was controlled 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)**.
- **CaCO$_3$ concentration**: 6, 20 g/L (measured and predicted).
- **BaSO$_4$ concentration**: 0, 14, 23.3 g/L (predicted).

The default conditions were 0°C, 6 g/L CaCO$_3$, 14 g/L BaSO$_4$. 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 BaSO$_4$ 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 SO$_4^{2-}$/L and possible interferences are silica in excess of 500 mg/L and large quantities of organic materials. The samples were filtered to remove all undissolved substances.

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/LCaCO$_3$) [7]. The known interferences for this method are soaps, oily matter and precipitates and our samples were 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 CaCO$_3$ (calcite) and BaSO$_4$ (barite) when contacted with CO$_2$ 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 CaCO$_3$ dissolution on CO$_2$-rich water**

The dissolution rate was rapid as indicated by the fact that more than 50% of the CaCO$_3$ 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 CaCO$_3$ and BaSO$_4$**

The mixture of CaCO$_3$ and BaSO$_4$ sludge that is produced by the CSIR-ABC process cannot be separated by solubility differences due to the low solubility of both CaCO$_3$ (1.3 mg/L Ca,) and BaSO$_4$ (5.6 mg/L Ba). As CO$_2$ is produced as a waste product in the CSIR-ABC process, it was decided to investigate whether CaCO$_3$ could be separated from

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### Table 1: Effect of various parameters on the solubility of CaCO$_3$ and BaSO$_4$ in a CO$_2$-rich solution.

| Exp No | Feedstock | pH | Temperature(°C) | Pressure (atm) | CaCO$_3$ (aq) (mg/l) | Mgl Ba |
|--------|-----------|----|----------------|---------------|----------------------|--------|
|        | CaCO$_3$ (g/l) | BaSO$_4$ (g/l) | Predicted | Determined | Predicted | Determined |

| Behavior of various parameters (see Figure 3) |
|---------------------------------------------|
| 1.1  | 20 | 0 | 6.06 | 0 | 1 | 1458 | 2600 |
| Comparison of CaCO$_3$ and BaSO$_4$ when in contact with CO$_2$; pH, Ca and Ba measures and predicted (Figure 4) |
| 1.2  | 20 | 0 | 6.03 | 10 | 1 | 1228 | 2050 |
| 3.2  | 20 | 3.87 | 10 | 1 | 50 | 1.17 |
| Effect of BaSO$_4$; pH, Ca and Ba measured and predicted (Figure 5) |
| 1.1  | 20 | 0 | 6.06 | 6.26 | 0 | 1 | 1458 | 2600 |
| 2.1  | 6 | 14 | 6.01 | 6.01 | 0 | 1 | 1460 | 2801 |
| 1.2  | 20 | 0 | 6.26 | 6.29 | 10 | 1 | 1228 | 2050 |
| 2.2  | 6 | 14 | 5.94 | 5.94 | 10 | 1 | 1230 | 2560 |

| Effect of temperature on CaCO$_3$; pH and Ca predicted and measured (see Figure 6 and 7) |
|---------------------------------------------|
| 1.1  | 20 | 0 | 6.06 | 6.26 | 0 | 1 | 1458 | 2600 |
| 1.2  | 20 | 0 | 6.03 | 6.29 | 10 | 1 | 1228 | 2050 |
| 1.3  | 0 | 6.01 | 6.58 | 25 | 1 | 946 | 800 |
| 1.4  | 0 | 0.00 | 6.07 | 45 | 1 | 665 | 600 |

| Effect of temperature on CaCO$_3$ and BaSO$_4$; pH, Ca and Ba predicted and measured (see Figure 6 and 8) |
|---------------------------------------------|
| 2.1  | 6 | 14 | 6.06 | 6.01 | 0 | 1 | 1460 | 2810 |
| 2.2  | 6 | 14 | 6.03 | 5.94 | 10 | 1 | 1230 | 2560 |
| 2.3  | 6 | 14 | 6.01 | 5.98 | 25 | 1 | 947 | 1000 |
| 2.4  | 6 | 14 | 6.00 | 6.04 | 45 | 1 | 666 | 600 |

| Effect of pressure on CaCO$_3$; pH and CaCO$_3$ predicted (see Figure 9) |
|---------------------------------------------|
| 4.1  | 20 | 0 | - | 6.25 | 0 | 0.5 | 1108 | - |
| 4.2  | 20 | 0 | - | 6.06 | 0 | 1 | 1458 | - |
| 4.3  | 20 | 0 | - | 5.87 | 0 | 2 | 1926 | - |
| 4.4  | 20 | 0 | - | 5.76 | 0 | 3 | 2271 | - |
| 4.5  | 20 | 0 | - | 5.68 | 0 | 4 | 2553 | - |
| 4.6  | 20 | 0 | - | 5.62 | 0 | 5 | 2798 | - |

| Effect of pressure on CaCO$_3$ and BaSO$_4$; pH, Ca and Ba predicted |
|---------------------------------------------|
| 5.1  | 20 | 23.3 | 6.25 | - | 0 | 0.5 | 1107 | - |
| 5.2  | 20 | 23.3 | 6.06 | - | 0 | 1 | 1457 | - |
| 5.3  | 20 | 23.3 | 5.87 | - | 0 | 2 | 1924 | - |
| 5.4  | 20 | 23.3 | 5.76 | - | 0 | 3 | 2268 | - |
| 5.5  | 20 | 23.3 | 5.62 | - | 0 | 5 | 2795 | - |
the almost insoluble BaSO_4 by dissolving it as Ca(HCO_3)_2 (Equation 1), by contacting the sludge mixture with CO_2.

Figure 3 shows that CaCO_3 dissolved when contacted with CO_2 at 1atm. Ca and Alkalinity (Alk) values increased rapidly in stoichiometric concentrations from the low solubility of CaCO_3 to the high solubility of Ca(HCO_3)_2 (2600 mg/L Alk, as CaCO_3) and 2650 mg/L Ca (as CaCO_3). 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(HCO_3)_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 CO_2, the extent of dissolution decreased as a function of changes in the CaCO_3, saturation state to yield both calcium ions and alkalinity (Equation 1).

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

Figure 4 shows the contrast between the solubilities of CaCO_3 (2200 mg/L; Ca as CaCO_3) and BaSO_4 (50 mg/L as Ba). The results showed that BaSO_4 does not dissolve when contacted with CO_2 and consequently there were negligible losses of BaSO_4 due to dissolution. The effect of BaSO_4 on the rate of formation and solubility of Ca(HCO_3)_2 was studied. Figure 5 showed that BaSO_4 had no effect on the solubility of Ca(HCO_3)_2. This is because BaSO_4 has a very low solubility. The known low solubility of BaSO_4 was also confirmed by the low predicted values for Ba^{2+} in solution, when contacted with CO_2 (Table 1).

### Effect of temperature and pressure on solubility

In the previous section it was shown that CaCO_3 can be dissolved through CO_2 addition without affecting the low solubility of BaSO_4. The sludge separation process will be more effective at higher solubility values for CaCO_3. Therefore, it was decided to determine the effect of pressure and temperature on the solubility of CaCO_3. 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(HCO_3)_2 in the presence of BaSO_4 as well as in the absence of BaSO_4 was investigated. It was found that BaSO_4 had no effect on the solubility of CaCO_3 when contacted with CO_2.

### 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 CaCO_3 and BaSO_4 in a CO_2-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(HCO_3)_2 at 1atm CO_2 when no BaSO_4 and 14 g/L BaSO_4, respectively, were
present over the temperature range 0–45°C. Both sets of results showed that the solubility of CaCO$_3$ 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(HCO$_3$)$_2$ in the absence and presence of 23.3 g/L BaSO$_4$. It was noticed that the solubility of CaCO$_3$, when contacted with CO$_2$ increased with increasing pressure (Figure 9). The model also showed, as in the case of the temperature studies above, that BaSO$_4$ had no influence on the solubility of CaCO$_3$ when contacted with CO$_2$ (compare Expt 4 with Expt 5, Table 1). The practical implications of these findings are that the solubility of CaCO$_3$, when contacted with CO$_2$ 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 CaCO$_3$ is directly related to the separation rate from the mixed sludge. Figure 10 shows the dissolution rate of the CaCO$_3$ with temperature from a CaCO$_3$-BaSO$_4$ mixed sludge in a CO$_2$-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 CaCO$_3$ from the mixed sludge while increased temperature leads to a significant decrease in the dissolution rate of CaCO$_3$.

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 CaCO$_3$ in the presence of CO$_2$ is fast at low temperature and high pressure;
- CaCO$_3$ has a high solubility of about 2600 mg/l when in contact with CO$_2$ at 1 atm, while BaSO$_4$ is almost completely insoluble;
- The solubility of CaCO$_3$ increases with decreasing temperature and decreasing pressure;
- The Visual MINTEQ model was a powerful tool used to predict the solubility of CaCO$_3$ and BaSO$_4$ when contacted with CO$_2$;
- CaCO$_3$ can be separated from BaSO$_4$ in and CaCO$_3$-BaSO$_4$ mixed sludge.

The cost of this process is low because all the process raw materials (CO$_2$ and the CaCO$_3$-BaSO$_4$ 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

Financial support from THRIP and the use of the laboratory facilities at Tshwane University of Technology are gratefully acknowledged.

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