Separation of Magnesium Hydroxide and Barium Sulphate from a Barium Sulphate – Magnesium Hydroxide Mixed Sludge by Carbonation: The Effect of Temperature

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Abstract

The solids that result from mine wastewater treatment usually contain elevated levels of contaminants that were originally contained in the wastewater. These must be carefully disposed of or treated to avoid shifting of the original pollutants in the waste stream to the final disposal site where they may again become free to contaminate the environment. A more reasonable approach to ultimate solids disposal is to view the sludge as a resource that can be recycled or reused. In South Africa, reverse osmosis is already being used for desalination of mine water and huge sludge volumes are also produced. The Tshwane University of Technology-Magnesium-Barium-Oxide (TUT-MBO) process and its variations is an alternative technology that offers the benefit of lower cost as magnesium hydroxide, barium hydroxide and coal are the main process raw materials. In the first stage Mg(OH)2 is dosed to raise the pH of the acid mine drainage to 9 for removal of free acid, iron(II) oxidized to iron(III) and all other metals precipitated as metal hydroxides. In the second stage Ba(OH)2 is dosed for magnesium and sulphate removal as Mg(OH)2 and BaSO4 respectively. The resultant, mixed BaSO4/Mg(OH)2 sludge is treated in a thermal stage to produce BaS and MgO.

The aim of this study was to separate magnesium hydroxide from barium sulphate, produced in the second stage of the TUT-MBO Process. Magnesium hydroxide is separated from barium sulphate through the dissolution of Mg(OH)2 with CO2 to Mg(HCO3)2. The results showed that: (a) By adding CO2 to a BaSO4/Mg(OH)2 sludge, selective dissolution of Mg(OH)2 occurred due to the relatively high solubility of Mg(HCO3)2 and the low solubility of BaSO4 and, (b) the solubility of Mg(HCO3)2 increased with decreasing temperatures and increasing pressures.

Keywords: Acid mine drainage; Precipitation; 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/day of acid mine drainage (AMD) when underground voids have filled up. This water will pollute 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, ferric hydroxide rich sludge and brine that have to be disposed at a cost on sludge disposal dumps and brine ponds.

Tshwane University of Technology (TUT) has developed innovative technologies for the neutralization and desalination of acid mine drainage while avoiding gypsum crystallization. These technologies are the Magnesium-Barium-Oxide (TUT-MBO) process and its variations namely; Magnesium-Barium-Bicarbonate (TUT-MBB) process, where magnesium bicarbonate is used instead of magnesium hydroxide, and the Ammonium-Barium (TUT-NB) process [2], where ammonium hydroxide is used instead of magnesium hydroxide to avoid the formation of mixed sludges. Laboratory and pilot studies have demonstrated that magnesium hydroxide or magnesium bicarbonate can be used for removal of metals through precipitation as metal hydroxides. In the processes, magnesium and sulphate removal is achieved by treatment with Ba(OH)2.

The TUT-MBO process and its variations offer the benefit of lower cost as magnesium hydroxide, barium hydroxide and coal are the main process raw materials [3,4]. It produces minimum amounts of sludge as process raw materials (Mg(OH)2 or Mg(HCO3)2 and Ba(OH)2) are recovered from the sludge. Sulphur, a valuable industrial raw material, can also be recovered from the sulphate removed from mine water.

The TUT-MBO process involves two stages. In the first stage, Mg(OH)2 or Mg(HCO3)2 is dosed to raise the pH of the AMD to 9 for removal of free acid, iron(II) as iron(III), and all other metals as metal hydroxides. In the second stage Ba(OH)2 is dosed for magnesium and sulphate removal as Mg(OH)2 and BaSO4 respectively. The resultant, mixed BaSO4/Mg(OH)2 sludge is treated in a thermal stage to produce BaS and MgO. To avoid this mixture it would be beneficial if BaSO4 and Mg(OH)2 could be separated prior to thermal treatment. This will allow pure BaSO4 to go to the thermal stage where it will be reduced to BaS. The Magnesium bicarbonate solution (TUT-MBB variation) can be used again in the first stage of TUT-MBO process instead of Mg(OH)2. Figure 1 shows the schematic diagram of the TUT-MBB process.

The aim of this study was to explore the separation of magnesium hydroxide from barium sulphate, produced as a mixed sludge in the second stage of the TUT-MBO process, through dissolution of Mg(OH)2 by converting it to Mg(HCO3)2 with CO2. By adding CO2 to a BaSO4/Mg(OH)2 sludge, selective dissolution of Mg(OH)2 occurs according to the following reaction:

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

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As the system becomes enriched in CO₂, the dissolution rate of Mg(OH)₂ could be influenced by its saturation level, \( \Omega \).

\[
\Omega = [\text{Mg}^{2+}][\text{OH}^-] / K_{sp}
\]

Where \( K_{sp} (T, S, p) \) is the solubility product (\( T \) is temperature, \( S \) is solubility and \( p \) is pressure) \([5]\) with the pressure dependency adjustments by Millero et al. \([6]\). 

\[
K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]
\]

**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 \([7]\), but also their dependency on ionic strength, temperature, and pressure.

**Materials and Methods**

Commercial grade Mg(OH)\(_2\) (60 g) and analytical grade (14 g) BaSO\(_4\) were mixed with deionized water and made up to volume (2 L). Bottled CO\(_2\) was used for dissolving Mg(OH)\(_2\). Batch studies were carried out using a completely-mixed pressurized reactor (Figure 2). It consisted of a 3 L reaction vessel equipped with a BirCraft stirrer, temperature sensor, pressure gauge, pH and conductivity control sensors. This unit was designed to handle pressures up to 10 bar and a maximum temperature of 150°C. The main body of the reactor was constructed from a Class 12 uPVC pipe with a wall thickness of 3.2 mm and an internal diameter of 560 mm. The height of the main body was 520 mm with a uPVC base and top plates that were each 65 mm thick. The dosage points were 300 mm 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. Carbon dioxide was dissolved in water, under pressure in the reactor, to lower the pH to around 6 and increase the pressure to desired levels. A pH control unit was used to control CO\(_2\) 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 effects of the following parameters were investigated: Time (0, 10, 20, 40, 60 min (measured)), Temperature (0, 10, 25, 45°C (measured and predicted)), Pressure (predicted), Mg(OH)\(_2\) concentration (60 g/L (measured and predicted)) and BaSO\(_4\) concentration (0, 14 g/L (predicted)). The default conditions were 0°C, 60 g/L Mg(OH)\(_2\), 14 g/L BaSO\(_4\). Filtered samples were collected over 0 - 60 min and analyzed for pH, alkalinity, calcium, barium and sulphate. The samples were filtered (0.45 μm membrane filter) to remove all solid material.

The total dissolved carbonate species were measured by titrating the sample with standard hydrochloric acid to pH 4.5. 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/L CaCO\(_3\)).

Magnesium hardness was determined by titration with EDTA (0.02 M) using P & R indicator and NaOH buffer. Total hardness was determined with EDTA (0.02 M) using ErichromeBlack T indicator and ammonia buffer.

Barium concentrations were determined by titrating the sample with standard 0.02 M EDTA using methylthymol blue indicator, potassium nitrate indicator and NaOH buffer (for pH 12).

The pH, conductivity and pressure in the reactor were measured directly.

**Results and Discussion**

Table 1 and Figures 3-7 show the dissolution of Mg(OH)\(_2\) (magnesium hydroxide) and BaSO\(_4\) (barite) when contacted with CO\(_2\) in water under various conditions. The Figures 3-7 contain measured values while Table 1 contains both measured and predicted values. The predictions were done using a Visual MINTEQ model \([8,9]\).

**Separation of Mg(OH)\(_2\) and BaSO\(_4\)**

The mixture of Mg(OH)\(_2\) and BaSO\(_4\) sludge produced by the TUT-MBO process cannot be separated by solubility differences due to the low solubility of both Mg(OH)\(_2\) (3.8 mg/LMg,) and BaSO\(_4\) (5.6 mg/L).
As CO₂ is produced as a waste product in the TUT-MBO process, it was decided to investigate whether Mg(OH)₂ could be separated from the almost insoluble BaSO₄ by dissolving it as Mg(HCO₃)₂ (Equation 1), by contacting the sludge mixture with CO₂. Figure 3 shows that 60 g/L Mg(OH)₂ dissolved partially when contacted with CO₂ at 1 atm. As Mg(HCO₃)₂ formed, Mg and alkalinity (Alk) values increased rapidly to 36 458 mg/L (as CaCO₃), whereafter it dropped to 21 100 mg/L (as CaCO₃). The maximum solubility value of 36 358 mg/L can be explained by the high solubility of Mg(HCO₃)₂, the intermediate product when Mg(OH)₂ is contacted with CO₂. Except for Mg(HCO₃)₂, there are also other Mg species present in the system, such as artinite, brucite, hydromagnesite, magnesite, magnesium carbonate, nesquehonite and periclase. The Visual Minteq [8,9] model showed that some of these compounds exceeded their solubilities as indicated by the positive saturation index values. Precipitation of the compounds that were over saturated would explain the observed drop in Mg(HCO₃)₂ concentration in solution from 36 358 to 21 100 mg/L Mg(HCO₃)₂ (as CaCO₃). It also showed the ionic balance between the measured calcium concentration and the total alkalinity of the system.

Over the same period the pH dropped from 9.6 to 7.6. The dissolution of Mg(OH)₂ increased with decreased pH due to the increased formation of soluble Mg(HCO₃)₂. Therefore, CO₂ dosing lowers the pH, and magnesium hydroxide is converted to Mg(HCO₃)₂.

Alkalinity was used to monitor the formation of Mg(HCO₃)₂ and includes the parameters listed in Equation (4). As the system became enriched in CO₂, the extent of dissolution decreased as a function of changes in the Mg(OH)₂ saturation state to yield both magnesium ions and Alk (Equation 1).

\[
\text{Alk} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] + [H^+] \tag{4}
\]

Figure 4 shows the contrast between the solubilities of Mg(OH)₂ (2100 mg/L as CaCO₃) and BaSO₄ (50 mg/L as CaCO₃). The results showed that, as expected, 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 Mg(HCO₃)₂ was studied. Figure 5 showed that BaSO₄ had no effect on the solubility of Mg(OH)₂ and BaSO₄ when in contact with CO₂; pH and Mg measured and predicted (Figure 4).
In the previous section it was shown that Mg(OH)₂ can be dissolved by the formation of Mg(HCO₃)₂, through CO₂ addition without affecting the low solubility of BaSO₄. The sludge separation process will be more effective at higher solubility values for Mg(HCO₃)₂. Therefore, it was decided to determine the effect of temperature on the solubilisation of Mg(OH)₂ as Mg(HCO₃)₂. According to Henry’s law (Equation 5), it was expected that the solubility should increase with decreasing temperatures. Figures 6 and 7 confirmed the validity of Henry’s law. In the case of Figure 6, only Mg(OH)₂ was present in the slurry used, whilst in Figure 7, BaSO₄ was also present. As in the previous case, it was found that BaSO₄ had no effect on the solubilisation of Mg(OH)₂ when contacted with CO₂. These figures also showed that the concentration of Mg₂⁺ in solution increased to the maximum value in the first 20 minutes and stabilized for another 20 minutes and then fell to a final stable level. This implied that at a high concentration of 60 g/L, not all of the magnesium hydroxide will be carbonated to form Mg(HCO₃)₂. The known low solubility of BaSO₄ was also reflected by the low predicted values for Ba²⁺ in solution, when BaSO₄ is contacted with CO₂. The measured “solubility” values for Mg(OH)₂ when contacted with CO₂ were lower than predicted by Visual Minteq. This can be ascribed to the high concentrations in solution which exceeded the model’s operation range.

Effect of temperature on solubility

Alaee et al. [10] showed that the air/water Henry’s Law constant (K) is defined as the ratio of the concentration of a chemical in the gas phase to its concentration in the aqueous phase.

\[ K = \frac{P}{C} \]

(6)

Where, K is in Pa.m³/mol; P, is partial pressure (Pa) and C, is aqueous concentration (mol/L).

The temperature effect on the Henry constant K can be expressed as:

\[ \ln K = \frac{P}{C} \]

(7)

Where T is temperature in K, A and B are constants of the Van’t Hoff equation.

Ten-Hulscher et al. [11] showed that B is the ratio of the enthalpy of volatilization to the gas constant, ΔHₒ/R in K⁻¹, and A is the ratio of the entropy of volatilization to the gas constant ΔSₒ/R, resulting in a dimensionless value.

Measured versus predicted solubility values

Table 1 shows a comparison of the predicted and determined values for the effect of various parameters on the solubilisation of Mg(OH)₂ and BaSO₄ in a CO₂-rich solution. The predictions were done using the Visual Minteq [8,9] model. The model was designed to simulate equilibrium and speciation of inorganic solutes in natural waters.

Temperature and sulphate: Figures 6 (experiment 1) and 7 (experiment 2) compare the solubility of Mg(HCO₃)₂ at 1 atm 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 final “solubility” of Mg(OH)₂ increases with decreasing temperature. The measured “solubility” values for Mg(OH)₂ when contacted with CO₂ were lower than predicted by Visual Minteq. This can be ascribed to the high concentrations in solution which exceeded the model’s operation range.

The results of experiment 2 in Table 1 show the predicted values for Ba²⁺ at 0°C in the treated water. The Ba²⁺ concentration increased from 6.4 to 24.3 mg/L for a temperature change of 45°C. It is preferred to have Ba²⁺ concentrations of less than 2 mg/L in treated water as this is within the expected range in natural waters. This can be achieved by allowing a low residual sulphate concentration of at least 10 mg/L in the treated water. The residual sulphate ion will act as a common ion which decreases barium solubility. Figure 8 (Experiments 4 and 5) showed that, at 25°C, a Ba²⁺ concentration of less than 2 mg/L at a
Visual Mingeq was a powerful tool to predict the "solubility" of Mg(OH)₂ and BaSO₄ when contacted with CO₂.

Thus, the TUT-MBO process offers a sustainable method for neutralization, metal removal and desalination of AMD and recovery of saleable and reusable products from the mixed sludge produced. Because Mg(HCO₃)₂ has high solubility at low temperatures and high pressure, the practical optimal operation conditions for the dissolution reaction are temperatures close to 0°C and atmospheric pressure. This is because high pressures need sophisticated reactor designs and the systems are more complicated to run that those at atmospheric pressure conditions.

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