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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 $BaSO_4$ and $CaCO_3$ 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 $CaCO_3$ and $BaSO_4$ from a $CaCO_3$-$BaSO_4$ mixed sludge through dissolution of $CaCO_3$ as $Ca(HCO_3)_2$ in contact with CO_2. Measured quantities of a simulated $CaCO_3$-$BaSO_4$ mixed sludge from the CSIR-ABC process were fed into a reactor vessel containing deionized water and pressurized CO_2 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 $CaCO_3$ was rapid i.e. from 0 to 2000mg/L in the first 20minutes; (2) $Ca(HCO_3)_2$ had a high solubility of about 2600 mg/L when in contact with CO_2 at 1atm., while $BaSO_4$ was almost completely insoluble; (3) The solubility of $Ca(HCO_3)_2$ increased with decreasing temperature and increasing pressure; (4) $CaCO_3$, after conversion to $Ca(HCO_3)_2$, was separated from $BaSO_4$ in a $CaCO_3$-$BaSO_4$ mixed sludge; (5) Visual MINTEQ model is a powerful tool that can be used to predict the solubilities of $CaCO_3$ and $BaSO_4$ when contacted with CO_2.

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 ($BaCO_3$ 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 $CaCO_3$ 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 $BaSO_4$ precipitation and carbon dioxide is dosed to precipitate calcium as $CaCO_3$. The resultant, mixed $BaSO_4$/$CaCO_3$ 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 $BaSO_4$ is processed in the thermal stage [2]. It would therefore be beneficial if

the mixture of $BaSO_4$ and $CaCO_3$ 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 $BaSO_4$-$CaCO_3$ 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 $CaCO_3$ with CO_2. By adding CO_2 to a mixed $BaSO_4$-$CaCO_3$ sludge, selective dissolution of $CaCO_3$ occurs according to the following reaction:

$$CO_{2(g)} + CaCO_{3(s)} + H_2O_{(l)} \rightarrow 2HCO^-_{3\,(aq)} + Ca^{2+}_{(aq)} \qquad (1)$$

As the system becomes enriched in CO_2, the dissolution rate of $CaCO_3$ could be influenced by its saturation level, Ω [3].

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp} \qquad (2)$$

where K_{sp} (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].

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \qquad (3)$$

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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 $Ca(HCO_3)_2$ formed, according to Equation (1), can be precipitated as $CaCO_3$ by lowering the pressure to atmospheric conditions (Equation 2);

$$Ca(HCO_3)_{2(aq)} \rightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \qquad (4)$$
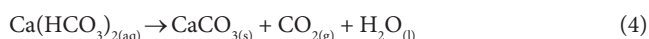
Materials and Methods

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 12unplasticised 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
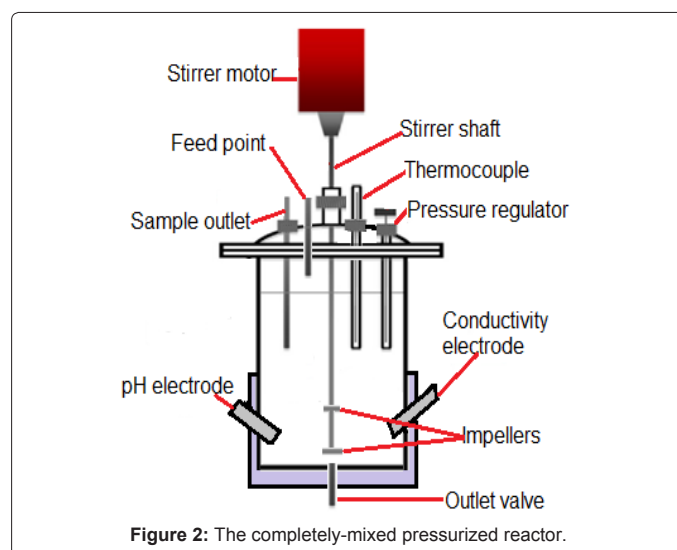

Figure 1a: Schematic diagram of the CSIR-ABC Process for neutralization, metal removal and desalination of AMD.

Figure 1b: Schematic flow diagram of the BaSO$_4$-CaCO$_3$ sludge separation process.

Figure 2: The completely-mixed pressurized reactor.

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 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 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 organic materials that may slow down the precipitation of $BaSO_4$ [7]. Correction for sample colour and turbidity was corrected by running blanks to which $BaCl_2$ 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/ $LCaCO_3$) [7]. The known interferences for this method are soaps, oily matter and precipitates and our samples where filtered to remove all undissolved substances.

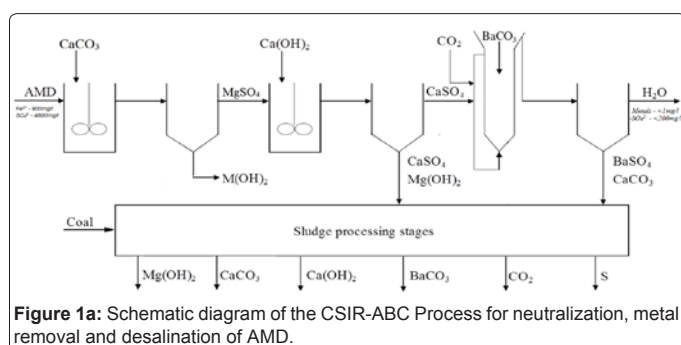Calcium hardness was determined by titration with EDTA (0.02M)
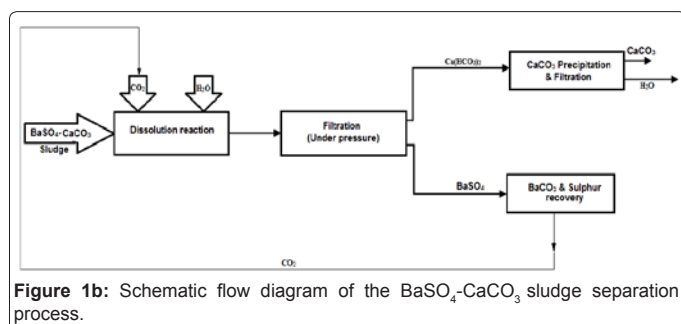
using P&R indicator and NaOH buffer. Total hardness was determined with EDTA (0.02M) using Eriochrome Black T indicator and ammonia buffer [7].

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 $CaCO_3$ (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

Exp No	Feedstock		pH		Temperature(°C)	Pressure (atm)	$CaCO_3$ (aq) (mg/l)		Mg/l Ba
	$CaCO_3$ (s) (g/l)	$BaSO_4$ (s) (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 BaSO4; 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	2.39
1.2	20	0	6.26	6.29	10	1	1228	2050	-
2.2	6	14	5.94	5.94	10	1	1230	2560	2.77
Exp 1	Effect of temperature on CaCO3; 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	20	0	6.01	6.58	25	1	946	800	-
1.4	20	0	6.00	6.07	45	1	665	600	-
Exp 2	Effect of temperature on CaCO3 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	2.39
2.2	6	14	6.03	5.94	10	1	1230	2560	2.77
2.3	6	14	6.01	5.98	25	1	947	1000	3.40
2.4	6	14	6.00	6.04	45	1	666	600	4.30
Exp 4	Effect of pressure on CaCO3; pH and CaCO3 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	-	-
Exp 5	Effect of pressure on CaCO3 and $BaSO_4$; pH, Ca and Ba predicted								
5.1	20	23.3	6.25	-	0	0.5	1107	-	2.18
5.2	20	23.3	6.06	-	0	1	1457	-	2.39
5.3	20	23.3	5.87	-	0	2	1924	-	2.63
5.4	20	23.3	5.76	-	0	3	2268	-	2.79
5.5	20	23.3	5.62	-	0	5	2795	-	2.74

Table 1: Effect of various parameters on the solubility of $CaCO_3$ and $BaSO_4$ in a CO_2-rich solution.

the almost insoluble $BaSO_4$ by dissolving it as $Ca(HCO_3)_2$ (Equation1), by contacting the sludge mixture with CO_2.
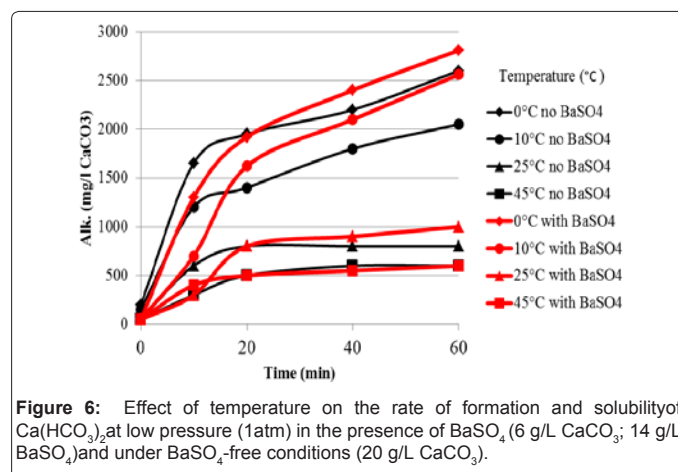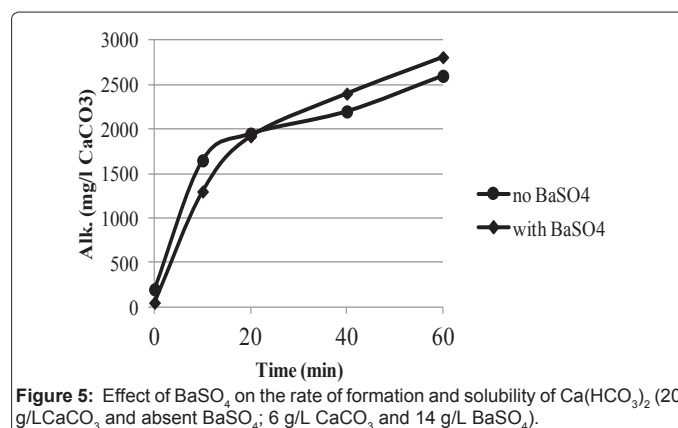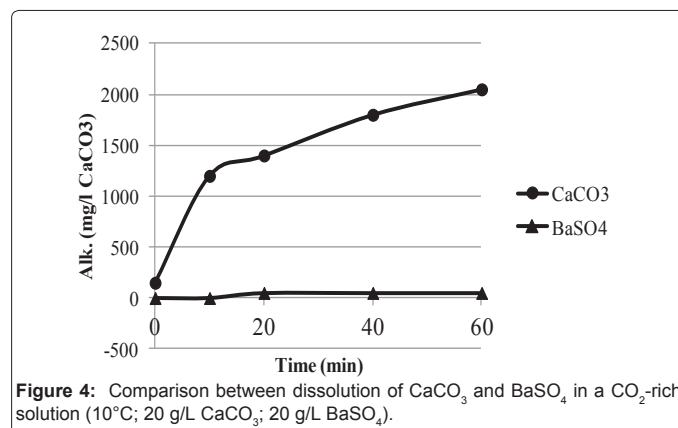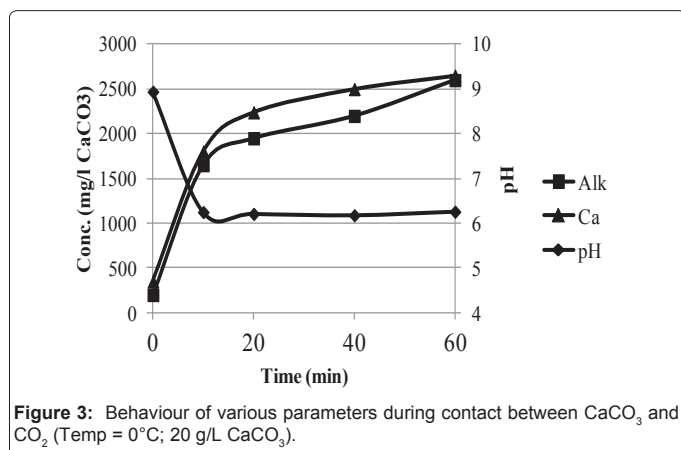
Figure 3 shows that $CaCO_3$ dissolved when contacted with CO_2 at 1atm. Ca and Alkalinity (Alk) values increased rapidly in stoichiometric concentrations from the low solubility of $CaCO_3$ to the high solubility of $Ca(HCO_3)_2$ (2600 mg/L Alk, as $CaCO_3$) and 2650 mg/L Ca (as $CaCO_3$). Over the 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).The solubility of $CaCO_3$ decreases with an increase in pH. Therefore, increasing CO_2 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 CO_3^{2-} to associate with protons, while driving the solubility equilibrium toward the formation of HCO_3^-.

$$Alk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] + [H^+] \qquad (5)$$

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.

Figure 3: Behaviour of various parameters during contact between $CaCO_3$ and CO_2 (Temp = 0°C; 20 g/L $CaCO_3$).

Figure 4: Comparison between dissolution of $CaCO_3$ and $BaSO_4$ in a CO_2-rich solution (10°C; 20 g/L $CaCO_3$; 20 g/L $BaSO_4$).

Figure 5: Effect of $BaSO_4$ on the rate of formation and solubility of $Ca(HCO_3)_2$ (20 g/L$CaCO_3$ and absent $BaSO_4$; 6 g/L $CaCO_3$ and 14 g/L $BaSO_4$).

Figure 6: Effect of temperature on the rate of formation and solubilityof $Ca(HCO_3)_2$at low pressure (1atm) in the presence of $BaSO_4$ (6 g/L $CaCO_3$; 14 g/L $BaSO_4$)and under $BaSO_4$-free conditions (20 g/L $CaCO_3$).

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 1atm., while $BaSO_4$ is almost completely insoluble;
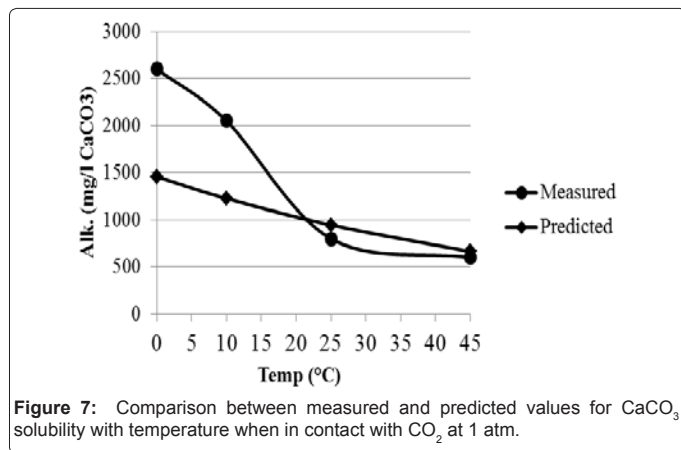

Figure 7: Comparison between measured and predicted values for $CaCO_3$ solubility with temperature when in contact with CO_2 at 1 atm.
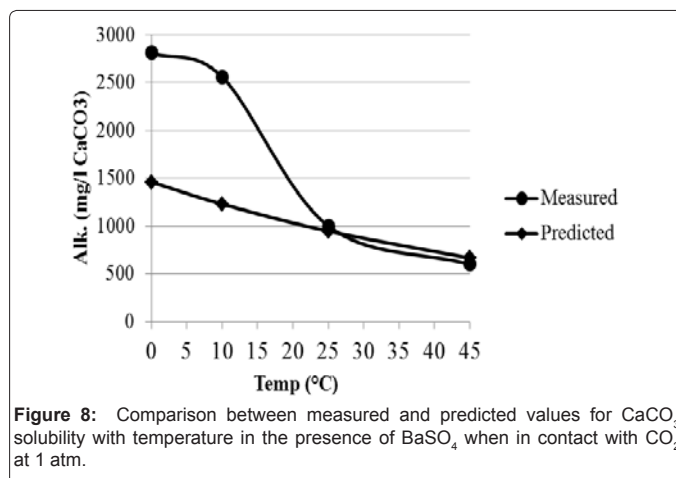

Figure 8: Comparison between measured and predicted values for $CaCO_3$ solubility with temperature in the presence of $BaSO_4$ when in contact with CO_2 at 1 atm.
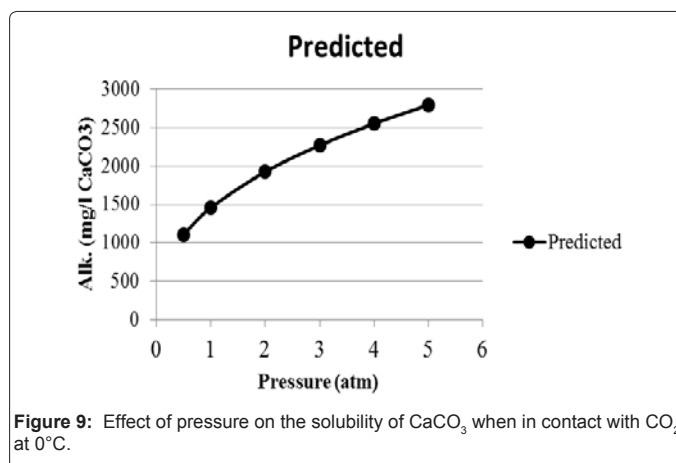

Figure 9: Effect of pressure on the solubility of $CaCO_3$ when in contact with CO_2 at 0°C.
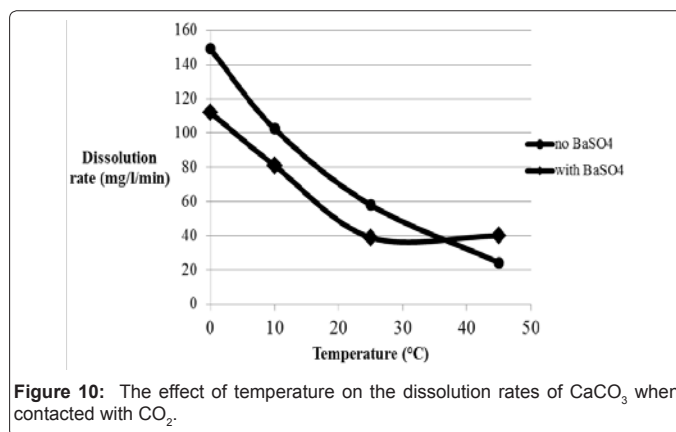

Figure 10: The effect of temperature on the dissolution rates of $CaCO_3$ when contacted with CO_2.

- 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 CO_2 on-site by burning coal and scrubbing the off-gas in water rather than purchasing pure CO_2. From the reaction equilibrium and the results of this study, it is apparent that decreasing the temperature and increasing CO_2 pressure will result in a better conversion of $CaCO_3$ to $Ca(HCO_3)_2$. However, high pressure systems are more complex to run and require sophisticated reactor designs and special construction material which will ultimately increase costs. Because $Ca(HCO_3)_2$ has high solubility when contacted with CO_2 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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