

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 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 $BaSO_4$ respectively. The resultant, mixed $BaSO_4/Mg(OH)_2$ 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 CO_2 to $Mg(HCO_3)_2$. The results showed that: (a) By adding CO_2 to a $BaSO_4/Mg(OH)_2$ sludge, selective dissolution of $Mg(OH)_2$ occurred due to the relatively high solubility of $Mg(HCO_3)_2$ and the low solubility of $BaSO_4$ and, (b) the solubility of $Mg(HCO_3)_2$ increased with decreasing temperatures and increasing pressures.

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

Introduction

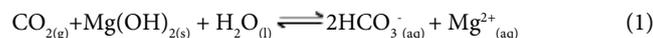
South Africa currently faces both a shortage of water as well as a deterioration of the quality of the available water due to industrial activities such as mining and power generation. The gold mines in Gauteng are expected to decant 345 ML/day of acid mine drainage (AMD) when underground voids have 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 $Mg(HCO_3)_2$ 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 $Mg(HCO_3)_2$ 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 $BaSO_4$, respectively. The resultant, mixed $BaSO_4/Mg(OH)_2$ sludge is treated in a thermal stage to produce a mixture of BaS and MgO. To avoid this mixture it would be beneficial if $BaSO_4$ and $Mg(OH)_2$ could be separated prior to thermal treatment. This would allow pure $BaSO_4$ 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 $Mg(HCO_3)_2$ with CO_2 . By adding CO_2 to a $BaSO_4/Mg(OH)_2$ sludge, selective dissolution of $Mg(OH)_2$ occurs according to the following reaction:



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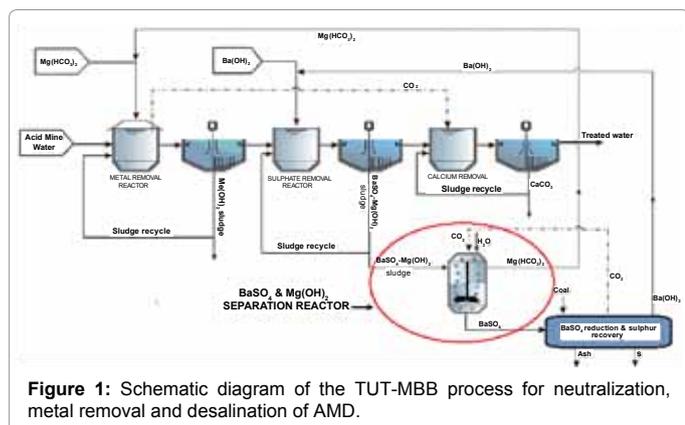


Figure 1: Schematic diagram of the TUT-MBB process for neutralization, metal removal and desalination of AMD.

As the system becomes enriched in CO_2 , the dissolution rate of $\text{Mg}(\text{OH})_2$ could be influenced by its saturation level, Ω .

$$\Omega = \frac{[\text{Mg}^{2+}][\text{OH}^-]}{K_{sp}} \quad (2)$$

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].

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-] \quad (3)$$

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 $\text{Mg}(\text{OH})_2$ (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 $\text{Mg}(\text{OH})_2$. 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), $\text{Mg}(\text{OH})_2$ 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 $\text{Mg}(\text{OH})_2$, 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 EriochromeBlack 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 $\text{Mg}(\text{OH})_2$ (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 $\text{Mg}(\text{OH})_2$ and BaSO_4

The mixture of $\text{Mg}(\text{OH})_2$ and BaSO_4 sludge produced by the TUT-MBO process cannot be separated by solubility differences due to the low solubility of both $\text{Mg}(\text{OH})_2$ (3.8 mg/LMg) and BaSO_4 (5.6 mg/L

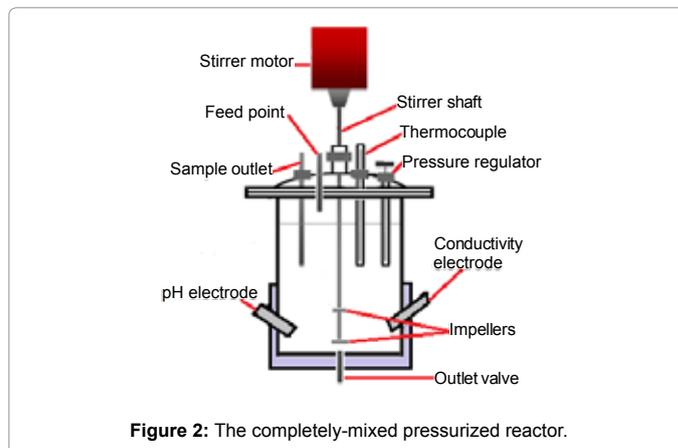


Figure 2: The completely-mixed pressurized reactor.

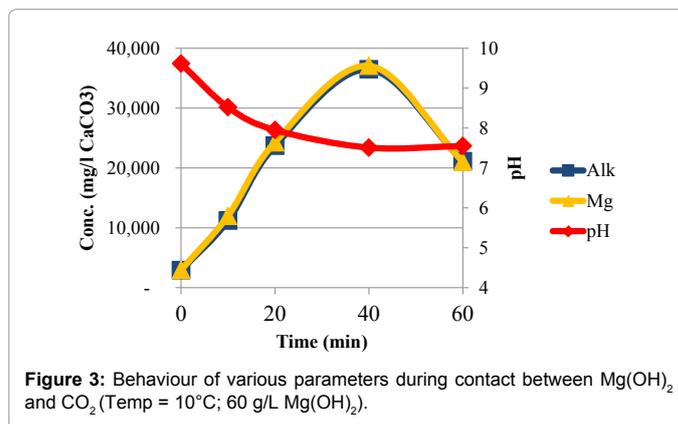


Figure 3: Behaviour of various parameters during contact between $\text{Mg}(\text{OH})_2$ and CO_2 (Temp = 10°C ; 60 g/L $\text{Mg}(\text{OH})_2$).

Exp No	Feedstock		Sulphate in treated water (mg/l)	pH		Temp	Alk (mg/l CaCO ₃) (aq)		Ba in solution (mg/l)
	Mg(OH) ₂ (s) (g/l)	BaSO ₄ (s) (g/l)		Predicted	Determined		Predicted	Determined	
Determined Predicted Behaviour of various parameters (see Figure 3)									
1.2	60	0	1		7.55	10	60,000	21,100	
Solubility of Mg (OH) ₂ and BaSO ₄ when in contact with CO ₂ ; pH and Mg measured and predicted (Figure 4)									
1.2	60	0	1		7.55	10	60,000	21,100	
3.2	0	20	1		6.81	10	-	50	
Effect of BaSO ₄ ; pH, Mg and Ba measured and predicted (Figure 5)									
1.1	60	0	1		7.44	0	60,000	21,000	
2.1	60	14	1	7.67	6.01	0	60,000	21,000	6.43
1.2	60	0	1		7.55	10	60,000	21,000	
2.2	60	14	1		7.55	10	60,000	19,796	
Effect of temperature on Mg(OH) ₂ ; pH and Mg predicted and measured (see Figure 6)									
1.1	60	0	1		7.44	0	60,000	21,000	
1.2	60	0	1		7.55	10	60,000	21,000	
1.3	60	0	1		7.45	25	60,000	17,600	
1.4	60	0	1		7.38	45	60,000	12,300	
Effect of temperature on Mg(OH) ₂ and BaSO ₄ ; pH, Mg and Ba predicted and measured (see Figure 7)									
2.1	60	14	1	7.67	6.01	0	60,000	22,700	6.43
2.2	60	14	1		7.55	10	60,000	19,796	9.17
2.3	60	14	1		7.47	25	60,000	20,000	14.67
2.4	60	14	1		7.48	45	60,000	8,000	24.29
Effect of sulphate on Mg(OH) ₂ ; pH, Ba and Mg(OH) ₂ predicted (Figure 8)									
4.1	60	0	0	7.67		0	60,000		6.43
4.2	60	0	9.6	7.67		0	60,000		2.75
4.3	60	0	48	7.67		0	60,000		0.66
4.4	60	0	96	7.67		0	60,000		0.34
4.5	60	0	192	7.67		0	60,000		0.17
Effect of sulphate on Mg(OH) ₂ ; pH, Ba and Mg(OH) ₂ predicted (Figure 8)									
5.1	60	14	0	7.76		25	60,000		14.67
5.2	60	14	9.6	7.75		25	60,000		9.75
5.3	60	14	48	7.76		25	60,000		3.32
5.4	60	14	96	7.76		25	60,000		1.72
5.5	60	14	192	7.76		25	60		0.87

Table 1: Effect of various parameters on the solubility of Mg(OH)₂ and BaSO₄ in a CO₂-rich solution.

Ba). 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 hydroxide, 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).

$$\text{Alk} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] + [\text{H}^+] \quad (4)$$

Figure 4 shows the contrast between the solubilities of Mg(OH)₂ (21100 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

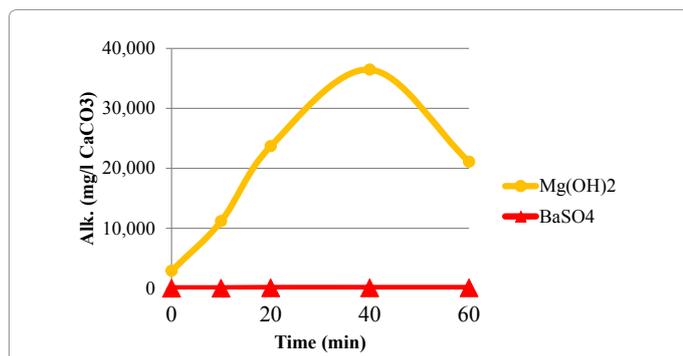


Figure 4: Comparison between dissolution of $Mg(OH)_2$ and $BaSO_4$ in a CO_2 -rich solution ($10^\circ C$; $60\text{ g/L } Mg(OH)_2$, $14\text{ g/L } BaSO_4$).

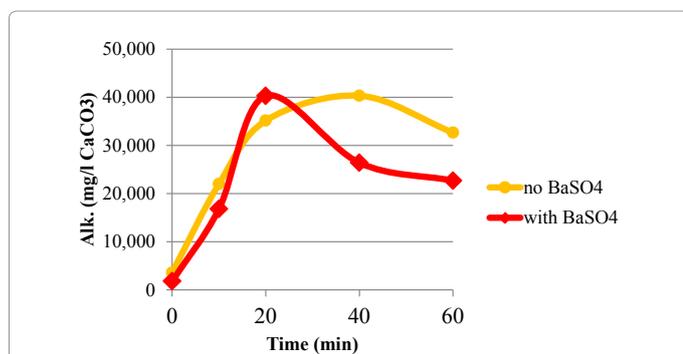


Figure 5: Effect of $BaSO_4$ on the rate of formation and solubility of $Mg(HCO_3)_2$ ($0^\circ C$, $60\text{ g/L } Mg(OH)_2$, no $BaSO_4$; $60\text{ g/L } Mg(OH)_2$ and $14\text{ g/L } BaSO_4$).

the solubility of $Mg(HCO_3)_2$. This was because $BaSO_4$ does not react with CO_2 . The known low solubility of $BaSO_4$ was also reflected by the low predicted values for Ba^{2+} in solution, when $BaSO_4$ is contacted with CO_2 (Table 1).

Effect of temperature on solubility

In the previous section it was shown that $Mg(OH)_2$ can be dissolved by the formation of $Mg(HCO_3)_2$, 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 $Mg(HCO_3)_2$. Therefore, it was decided to determine the effect of temperature on the solubilisation of $Mg(OH)_2$ as $Mg(HCO_3)_2$. 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, $BaSO_4$ was also present. As in the previous case, it was found that $BaSO_4$ had no effect on the solubilisation of $Mg(OH)_2$ when contacted with CO_2 . These figures also showed that the concentration of Mg^{2+} 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 $Mg(HCO_3)_2$.

$$P_{\text{gas}} = kC \quad (\text{at constant } T) \quad (5)$$

Where, P = gas partial pressure (Pa)

k = Henry's law constant ($\text{Pa m}^3/\text{mol}$)

C = concentration of the gas (mol/L)

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.

$$K = \frac{P_i}{C_w} \quad (6)$$

Where, K is in $\text{Pa.m}^3/\text{mol}$; P , is partial pressure (Pa) and C , is aqueous concentration (mol/L).

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

$$\ln K = K = \frac{P_i}{C_w} \quad (7)$$

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, $\Delta H_v/R$ in K^{-1} , and A is the ratio of the entropy of volatilization to the gas constant $\Delta S_v/R$, 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 $BaSO_4$ in a CO_2 -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 $Mg(HCO_3)_2$ at $1\text{ atm } CO_2$ when no $BaSO_4$ and $14\text{ g/L } BaSO_4$, respectively, were present over the temperature range $0-45^\circ C$. 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 CO_2 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 Ba^{2+} at $0^\circ C$ in the treated water. The Ba^{2+} concentration increased from 6.4 to 24.3 mg/L for a temperature change of $45^\circ C$. It is preferred to have Ba^{2+} 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 $25^\circ C$, a Ba^{2+} concentration of less than 2 mg/L at a

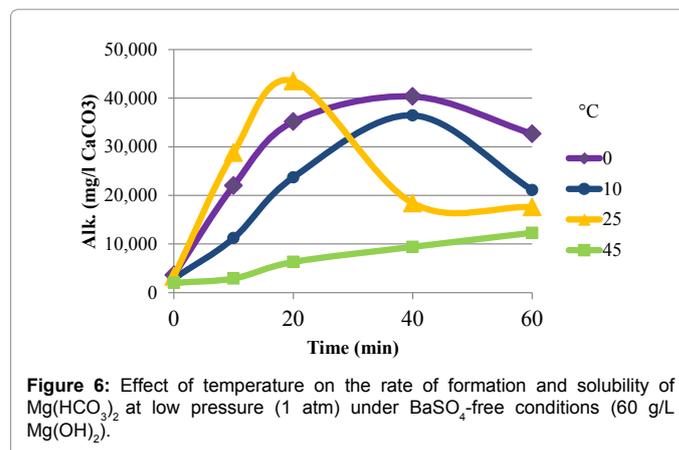


Figure 6: Effect of temperature on the rate of formation and solubility of $Mg(HCO_3)_2$ at low pressure (1 atm) under $BaSO_4$ -free conditions ($60\text{ g/L } Mg(OH)_2$).

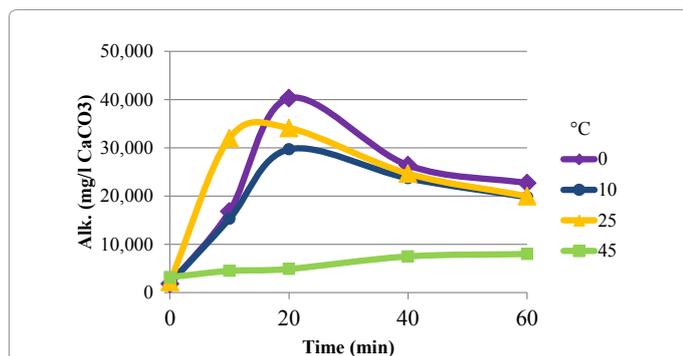


Figure 7: Effect of temperature on the rate of formation and solubility of $Mg(HCO_3)_2$ in the presence of $BaSO_4$ (60 g/L $Mg(OH)_2$, 14 g/L $BaSO_4$).

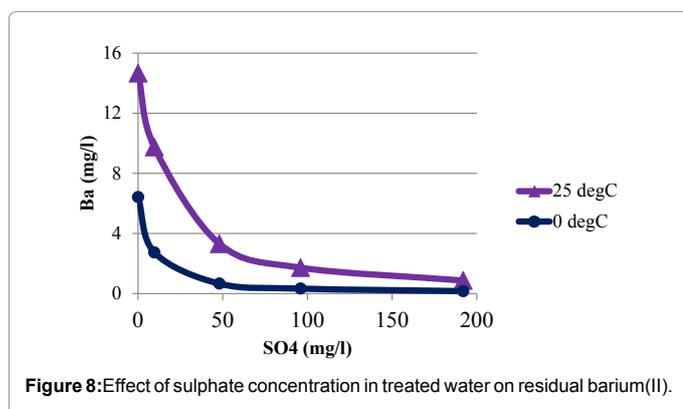


Figure 8: Effect of sulphate concentration in treated water on residual barium(II).

sulphate concentration of 100 mg/L. At 0°C a sulphate concentration of 25 mg/L sulphate was sufficient to keep the Ba^{2+} concentration at less than 2 mg/L.

Pressure: Rukuni et al. [12] showed that the solubility of $Ca(HCO_3)_2$ is influenced by pressure. It was also planned to investigate the effect of pressure on $Mg(HCO_3)_2$ solubility. Due to the high solubility of $Mg(HCO_3)_2$ at ambient pressure and temperature this was seen as less practical in the context of the process being developed. The high concentration also does not allow the use of the *Visual Minteq* [8,9] model to predict the solubility at various pressures.

Cost

The process cost for this process is low because all the process raw materials (CO_2 and the $Mg(OH)_2$ - $BaSO_4$ sludge) are waste products of the TUT-MBO process (Figure 1). It is also foreseen that the cost can also be kept low in other applications by producing CO_2 on-site by burning coal and scrubbing in water than the purchase of pure CO_2 .

Conclusions

It was found that:

- $Mg(OH)_2$ can be separated from $BaSO_4$ and $Mg(OH)_2$ in a mixed sludge by carbonating it to $Mg(HCO_3)_2$ using CO_2 .
- The dissolution rate of $Mg(OH)_2$ in the presence of CO_2 is fast in the initial 20 minutes of the reaction.

- $Mg(OH)_2$ had a high solubility of about 22 700 mg/l when in contact with CO_2 at 1 atm, while $BaSO_4$ is almost completely insoluble.
- The solubility of $Mg(OH)_2$ increases with decreasing temperature and increasing pressure.
- The *Visual Minteq* model was a powerful tool to predict the “solubility” of $Mg(OH)_2$ and $BaSO_4$ when contacted with CO_2 .

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 $Mg(HCO_3)_2$ 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 than those at atmospheric pressure conditions.

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