A new approach to capture and store CO$_2$ by mineral carbonation using recyclable ammonium salts was studied. This process integrates CO$_2$ capture with mineral carbonation by employing NH$_3$, NH$_4$HSO$_4$, and NH$_4$HCO$_3$ in the capture, mineral dissolution, and carbonation steps, respectively. NH$_4$HSO$_4$ and NH$_3$ can then be regenerated by thermal decomposition of (NH$_4$)$_2$SO$_4$. The use of NH$_4$HCO$_3$ as the source of CO$_2$ can avoid desorption and compression of CO$_2$. The mass ratio of Mg/NH$_4$HCO$_3$/NH$_3$ is the key factor controlling carbonation and the optimum ratio of 1:4:2 gives a conversion of Mg ions to hydromagnesite of 95.5%. Thermogravimetric analysis studies indicated that the regeneration efficiency of NH$_4$HSO$_4$ and NH$_3$ in this process is 95%. The mass balance of the process shows that about 2.63 tonnes of serpentine, 0.12 tonnes of NH$_4$HSO$_4$, 7.48 tonnes of NH$_4$HCO$_3$, and 0.04 tonnes of NH$_3$ are required to sequester 1 tonne of CO$_2$ as hydromagnesite.

Introduction

Carbon dioxide capture and storage (CCS) is considered to be one of the main solutions for reducing anthropogenic CO$_2$. CCS includes CO$_2$ capture from a point source, such as power plants, and transportation to a suitable site, where it is stored permanently and safely. Many projects for CO$_2$ storage are based on direct injection of CO$_2$ into underground formations (geologic sequestration) where it is stored by hydrodynamic, solubility, or mineral trapping.[1] However, the development of CO$_2$ geological storage has been slow with respect to potential environmental impact and regulation for CO$_2$ injection and monitoring.[2] Moreover, some countries, such as Finland and India, do not have sufficient storage capacity or lack suitable storage formations.[3] Therefore, there has been increasing interest in mineral carbonation.

The concept of CO$_2$ sequestration by mineral carbonation is based on accelerating the weathering of rocks. CO$_2$ reacts with alkaline earth oxide containing minerals to form insoluble carbonates. Magnesium and calcium silicate deposits, such as serpentinite and olivine, can be used for this process. Due to the availability and abundance of these minerals, the capacity for mineral carbonation to store CO$_2$ is estimated to be quite large.[4] Serpentine is an important source for this process due to its worldwide availability. For instance, a deposit of 30,000 km$^3$ of magnesium silicates found in Oman would be able to store all of the anthropogenic CO$_2$ generated from combustion of the world’s coal reserves.[5] Clearly, one of the main advantages of this process is the permanent safe storage of CO$_2$ due to the thermodynamically stable nature of the solid carbonates formed.[6][7][8] Moreover, carbonation is an exothermic process, which may reduce the overall energy consumption and costs.[5]

However, the slow reaction rate of mineral dissolution is the main barrier to this process.[5] Many researchers have focused on promoting the dissolution rate by using different solvents, such as H$_2$SO$_4$, HCl, HNO$_3$, organic acids, and inorganic salts.[3][6][8] For example, Maroto-Valer et al. have reported 70% dissolution of serpentine by using 2M H$_2$SO$_4$ in 2 h.[6] A multi-step aqueous carbonation process developed by Teir et al. used 4M HCl or HNO$_3$ to dissolve Mg ions from serpentinite, then NaOH was used to control the pH of the solution to precipitate high purity hydromagnesite.[9] This process achieved 79% carbonation efficiency at 80°C and ambient pressure. They also reported that electrolysis of the NaCl solution was used to regenerate HCl and NaOH.[9] However, this process suffered from a high energy penalty in the regeneration process, in which the energy consumption for electrolysis of NaCl is 3277 and 4361 kWh t$^{-1}$CO$_2$ sequestered using HCl and HNO$_3$, respectively.[9]

Therefore, there is a need to find low-cost, recyclable solvents that can provide high efficiency of mineral dissolution and carbonation. Recently, Krevor and Lackner tested NH$_4$Cl, NaCl, sodium citrate, sodium EDTA, sodium oxalate, and sodium acetate to dissolve serpentinite.[10] All experiments were carried out at 120°C and 20 bar (1 bar = 10$^5$ Pa) CO$_2$ in a batch autoclave. On using 0.1 M citrate, EDTA, and oxalate solutions, 60% dissolution efficiency of magnesium from serpentinite was achieved within 2 h, going up to 80% after 7 h and reaching nearly 100% between 10 and 20 h. Therefore, mineral dissolution with organic solvents is promising in terms of dissolution efficiency, but the dissolution rate is relatively slow. Pundsack

---

[a] X. Wang, Prof. M. M. Maroto-Valer
Centre for Innovation in Carbon Capture and Storage (CICCS)
Energy and Sustainability Research Division, Faculty of Engineering
University of Nottingham
University Park, NG7 2RD (UK)
Fax: (+44) 115-951-4115
E-mail: mercedes.maroto-valer@nottingham.ac.uk

Re-use of this article is permitted in accordance with the Terms and Conditions set out at http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1864-564X/homepage/2476_onlineopen.html.
reported the use of NH₄HSO₄ to dissolve serpentine and bubbled CO₂ directly into the high-concentration magnesium solution obtained with aqueous ammonia to precipitate magnesium carbonates. [11] The dissolution efficiency of magnesium for this process was 92.8%, but the carbonation efficiency was only 35%. Fagerlund et al. proposed a process for the production of Mg(OH)₂ from serpentine by using (NH₄)₂SO₄. [12] A solid-solid reaction of serpentine with (NH₄)₂SO₄ was carried out at > 440 °C to generate MgSO₄, which was added to aqueous ammonia to precipitate Mg(OH)₂ and regenerate (NH₄)₂SO₄. Mg(OH)₂ was then carbonated with CO₂ directly in a pressurised fluidised bed (PFB) reactor at 470–550 °C and 20 bar. However, only 20–60% extraction efficiency of magnesium from serpentine was reported, [13] and the carbonation efficiency of Mg(OH)₂ only achieved a maximum value of 50%. This was due to the conversion of Mg(OH)₂ into MgO at the temperature range used, at which the produced MgO cannot react with CO₂ to produce carbonates. [14] Therefore, work is needed to improve both dissolution and carbonation efficiencies.

We have developed a new pH-swing mineral carbonation process by using recyclable ammonium salts and the process route was presented in a previous paper. [15] The modified process diagram can be seen in Figure 1. In this process, aqueous NH₄HSO₄ was used to extract Mg from serpentine. The pH of the solution was then changed by adding aqueous ammonia, resulting in iron and silicon precipitating from solution. NH₄HCO₃ and NH₃ were then added to the solution to react with Mg and produce carbonates and (NH₄)₂SO₄, which was recycled from the solution by evaporation and then decomposed back into NH₃ and NH₄HSO₄. Dissolution experiments of serpentine with NH₄HSO₄ have been previously reported. [15] It was found that 1.4 mol NH₄HSO₄ could extract 100% Mg from serpentine, as well as 98% Fe and 17.6% Si in 3 h at 100 °C. In addition, the dissolution kinetics of the reaction were found to follow the model of constant size particles with a rate-limiting control step of the chemical reaction by using product layer diffusion control. [15]

It must be pointed out that this process is unique in using NH₄HCO₃ instead of direct CO₂ gas for mineral carbonation. The advantages of using NH₄HCO₃ include avoiding CO₂ desorption in the capture step and subsequent CO₂ compression for transportation, which are energy-intensive steps in the conventional CCS process. [15]

We have previously reported the dissolution of serpentine with NH₄HSO₄. [16] Herein, we investigated carbonation with NH₄HCO₃ and NH₄HSO₄ and NH₃ regeneration. The carbonation experiments were conducted at different molar ratios of Mg/NH₄HCO₃/NH₃. Finally, the mass balance of all streams in this process is presented.

**Experimental Section**

### Preparation of magnesium salt solutions from serpentine using NH₄HSO₄

Previous dissolution experiments conducted by us have shown that NH₄HSO₄ is suitable for extracting magnesium from serpentine. [17] The chemical equation for dissolution of magnesium from serpentine using NH₄HSO₄ is presented in Equation 1:

$$ \text{Mg}_3\text{Si}_2\text{O}_5\cdot(\text{OH})_4(\text{s}) + 6 \text{NH}_4\text{HSO}_4(\text{aq}) \rightarrow 3 \text{MgSO}_4(\text{aq}) + 2 \text{SiO}_2(\text{s}) + 5 \text{H}_2\text{O}(\text{l}) + 3(\text{NH}_4)^+\text{SO}_4(\text{aq}) $$

For the dissolution experiments, the same procedure and serpentine sample was used as in our previous paper. [15] Different temperatures (80, 90, and 100 °C) and reaction times (1, 2, and 3 h) were used for the preparation of solutions of MgSO₄. After dissolution, the solution was cooled to room temperature and filtered by using 0.45 μm Pall syringe filters. The filtrate is referred to as filtrate 1 (Figure 1) and was used for the pH regulation and removal of impurities. The solid residue was dried at 105 °C overnight and is referred to as product 1 (Figure 1). Filtrate 1 was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to measure the concentration of dissolved Mg, Fe, and Si. For the purpose of this analysis, filtrate 1 was acidified with 70 wt% HNO₃ to prevent precipitation of Mg and Fe. Product 1 was sampled and sent for X-ray fluorescence (XRF) analysis to determine the Mg, Fe, and Si con-

![Figure 1. Modified process route of pH-swing CO₂ mineral sequestration with recyclable ammonium salts.](image-url)
pH regulation and removal of impurities

About 40% excess NH₄HSO₄ was used for the dissolution of serpentinite to maximise magnesium extraction. After dissolution, the pH values of the solution were about 0.9–1.2. Because the carbonation reaction was favourable at high pH values, it was necessary to increase the pH of the solution to alkaline values. The chemical reaction of the pH regulation is presented in Equation (2):

\[
\text{NH}_4\text{HSO}_4 (aq) + \text{H}_2\text{O} (aq) \rightarrow (\text{NH}_4)_2\text{SO}_4 (aq) + \text{H}_2\text{O} (l)
\]

(2)

The reason for using aqueous ammonia is because the above reaction produces ammonium sulfate, which can be converted back into NH₃ and NH₄HSO₄ in the regeneration step to recycle the additives (Figure 1).

If a high-value product (pure magnesium carbonate) is desired, some impurities, such as Fe, Al, Cr, Zn, Cu, and Mn need to be precipitated from the system first by increasing the pH. To optimise the removal of impurities, extra aqueous ammonia was added to filtrate 1 after pH regulation, and the reactions for the removal of impurities are presented in Equations 3 and 4:

\[
(\text{Fe,Al,Cr})_2\text{SO}_4 (aq) + 6\text{NH}_4\cdot\text{H}_2\text{O} (aq) \rightarrow \\
2(\text{Fe,Al,Cr})(\text{OH})_2 (s) \downarrow + 3(\text{NH}_4)_2\text{SO}_4 (aq)
\]

(3)

\[
(\text{Zn,Cu,Mn,Fe})\text{SO}_4 (aq) + 2\text{NH}_4\cdot\text{H}_2\text{O} (aq) \rightarrow \\
(Zn,Cu,Mn,Fe)(\text{OH})_2 (aq) \downarrow + (\text{NH}_4)_2\text{SO}_4 (aq)
\]

(4)

During pH regulation and removal of impurities, aqueous ammonia (35 wt%) was added to filtrate 1 until the pH value was neutral. During this process, the solution was stirred and an in situ pH probe was used to measure the pH value. The solution was filtered with 0.7 μm Pall syringe filters. The filtrate is referred to as filtrate 2 (Figure 1) and was used for the carbonation experiments described in the section below on precipitation of hydromagnesite using NH₄HCO₃. The solid residue was dried at 105 °C overnight and is referred to as product 2 (Figure 1). Filtrate 2 was analysed by using ICP-AES to quantify its composition and identify the mineral phases present.

Precipitation of hydromagnesite using NH₄HCO₃

The reaction of precipitation of hydromagnesite by treating MgSO₄ with NH₄HCO₃ and NH₃ is presented in Equation 5:

\[
\text{MgSO}_4 (aq) + \text{NH}_4\text{HCO}_3 (aq) + \text{NH}_3 \cdot \text{H}_2\text{O} (aq) + 2\text{H}_2\text{O} (l) \rightarrow \\
\text{MgCO}_3 \cdot 3\text{H}_2\text{O} (s) \downarrow + (\text{NH}_4)_2\text{SO}_4 (aq)
\]

(5a)

\[
5\text{MgCO}_3 \cdot 3\text{H}_2\text{O} (s) \rightarrow 4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O} (s) \downarrow \\
+ 10\text{H}_2\text{O} (l) + \text{CO}_2 (g) \uparrow
\]

(5b)

The formation of magnesium carbonate species depends on temperature and pressure.136 Nesquehonite (MgCO₃·3H₂O) can precipitate from aqueous solutions at ambient temperatures as described in Equation 5a, whereas at higher temperatures (50 and 100 °C), nesquehonite is transformed into hydromagnesite (4MgCO₃·Mg(OH)₂·5H₂O), as presented in Equation 5b. For temperatures above 100 °C, hydromagnesite is transformed into magnesite (MgCO₃). In this study, hydromagnesite was produced because the experiments were conducted at 85 °C.

For the carbonation experiments, filtrate 2 was added to a 500 mL three-necked glass vessel and heated to 60 °C by using a silicon oil bath. The experimental setup was the same as that previously reported.137 The time, temperature, and pH values were recorded every 5 min. Before heating, aqueous ammonia (35 wt%) was added to filtrate 2. When the temperature reached 60 °C, NH₄HCO₃ (as the CO₂ source) was added and the solution was heated to 90 °C. After the solution was stabilised at 90 °C, the solution was kept at that temperature for 30 min. Aliquots (2 mL) were sampled by using a needle syringe at 5, 10, 15, 30, 45, and 60 min. The liquid samples were filtered by using a mini filter unit and acidified with HNO₃ for subsequent ICP-AES analysis to measure the Mg concentration. At the end of the experiment, the solution was cooled and filtered by using 0.7 μm Pall syringe filters and the filtrate is referred to as filtrate 3 (Figure 1). The solid residue was dried at 105 °C overnight and is referred to as product 3 (Figure 1).

The composition of product 3 was analysed by using XRF, and the mineral phases were identified by using XRD. Experiments were conducted at different mass ratios of Mg/NH₄/NH₄HCO₃, in which Mg is the mass of Mg in filtrate 2; and NH₃ and NH₄HCO₃ represent the mass of aqueous ammonia and the mass of NH₄HCO₃ added, respectively. In addition, a preliminary experiment was conducted in which no NH₃ was added. The matrix of the experiments conducted at different mass ratios is listed in Table 1.

| Experiment | Mg | Ratio NH₄HCO₃ | NH₃ | Carbonation [%] |
|------------|----|-------------|-----|----------------|
| preliminary | 1  | 1  | 3     | 25.5           |
| 1          | 1  | 1  | 3     | 71.6           |
| 2          | 1  | 1  | 3     | 53.0           |
| 3          | 1  | 1  | 3.5   | 46.5           |
| 4          | 1  | 1  | 4     | 53.4           |
| 5          | 1  | 1  | 2     | 41.5           |
| 6          | 1  | 1  | 4     | 77.9           |
| 7          | 1  | 1  | 5     | 89.9           |
| 8          | 1  | 1  | 4     | 95.9           |
| 9          | 1  | 1  | 4     | 91.5           |
| 10         | 1  | 1  | 4     | 91.3           |

The carbon content of product 3 was measured by using a thermogravimetric analysis (TGA) Q500 analyzer. The temperature programme was from 30 to 950 °C at 20 °C min⁻¹ under a nitrogen atmosphere. The carbonation efficiency from soluble magnesium sulfate to hydromagnesite is defined by Equation 6:

\[
\text{Carbonation efficiency (\%)} = \frac{\text{CO}_2 \text{ content (wt \%)} \times 24m_1}{44c_1V_2} \times 100
\]

in which CO₂ content (wt%) is the weight loss of product 3 during the temperature range from 300 to 500 °C, corresponding to the carbonate decomposition found in TGA studies;137 m₁ is the mass (g) of product 3 from carbonation experiment; c₁ is the magnesium concentration in filtrate 2 from ICP-AES and V₂ is the volume of...
filtrate 2, whereas 24 and 44 are the total molecular weights of Mg and CO₂ in hydromagnesite, respectively.

Thermal decomposition of (NH₄)₂SO₄

Filtrate 3 was evaporated by using a rotary evaporator at 60 °C for 15 min. The solid collected from the rotary evaporator is referred to as product 4 (Figure 1). The regeneration of NH₄HSO₄ and NH₃ was conducted by thermal decomposition of product 4 in an oven at 330 °C, and the reaction is presented in Equation 7:

\[(\text{NH}_4\text{)}_2\text{SO}_4 (s) \rightarrow \text{NH}_4\text{HSO}_4 (s) + \text{NH}_3 (g) \uparrow\]  

The thermal decomposition of product 4 was characterised by performing TGA studies by using a TGA Q500 instrument in the temperature range of 30–530 °C under nitrogen atmosphere. The temperature programme was as follows: from 30 to 230 °C at 10 °C min⁻¹, hold for 10 min at 230 °C, up to 330 °C at 10 °C min⁻¹, hold for 10 min at 330 °C, and finally up to 530 °C at 10 °C min⁻¹. The choice of these three heating steps was to avoid decomposition of the mixture of products. To ascertain the decomposition from the TGA of product 4, pure (NH₄)₂SO₄ and NH₄HSO₄ were also characterised by using TGA using the same heating procedure.

Results and Discussion

Preparation of magnesium salts solutions from serpentine using NH₄HSO₄

The results from the ICP-AES analyses (Table 2) of the filtrate 1 solutions from all experiments show that high concentrations of Mg and Fe were dissolved, whereas most of the Si remained in the serpentine. The dissolution efficiency is calculated as the percentage of dissolved elements in filtrate 1 solution over elements in parent serpentine. The values for serpentine are also reported in Table 2. Taking experiment 3 as an example, using the data in Table 2, the dissolution efficiency of Mg from serpentine was 91% for 1.4 M NH₄HSO₄ at 100 °C for 2 h. The dissolution efficiency of other elements for experiment 3 is presented in Figure 2. It was found that 96% Fe, 17% Si, 100% Ni and Mn, and some Ca, Zn, Cu, and Al were also extracted from serpentine. This result is consistent with previous dissolution studies, in which the dissolution efficiencies of Mg, Fe, and Si from serpentine were 95, 83, and 17%, respectively, under the same experimental conditions. For Ni, Mn, Ca, Zn, Cu, and Al were very similar for all experiments conducted. Because high purity MgCO₃ is desired, all other cations are considered to be impurities; Fe and Si are identified as the main impurities and are reported in Table 2. In conclusion, Mg was removed from serpentine, leaving behind amorphous silica. This could be explained by incongruent dissolution of Mg and Si, as previously discussed, for which a chemical reaction with product-layer diffusion control was found to be the rate-limiting step of serpentine dissolution in NH₄HSO₄.

| Sample | Filtrate | Mg [mg L⁻¹] | Si [mg L⁻¹] | Fe [mg L⁻¹] | Dissolution [%] | Carbonation [%] |
|--------|---------|-------------|-------------|-------------|----------------|----------------|
| serpentine | filtrate 1 | 11970.0 | 3680.0 | 2050.0 | 73.8 | 71.56 |
| 1 | 2 | 8252.0 | 74.1 | 600.0 | 73.8 | 71.56 |
| 3 | 8247.0 | 11.2 | 1.0 | 73.8 | 71.56 |
| 1 | 9052.0 | 447.0 | 1284.0 | 73.8 | 71.56 |
| 2 | 2 | 8290.0 | 110.0 | 244.0 | 75.4 | 53.0 |
| 3 | 3 | 3219.0 | 20.2 | 0.5 | 75.4 | 53.0 |
| 1 | 10957 | 621.0 | 1964.0 | 75.4 | 53.0 |
| 3 | 2 | 9629.0 | 98.0 | 337.0 | 91.3 | 46.5 |
| 3 | 2983.0 | 5.2 | 0.3 | 91.3 | 46.5 |
| 1 | 8497.0 | 399.0 | 1131.0 | 91.3 | 46.5 |
| 4 | 2 | 7840.0 | 105.0 | 187.0 | 70.8 | 53.4 |
| 3 | 2914.0 | 21.0 | 0.2 | 70.8 | 53.4 |
| 1 | 9550.0 | 411.0 | 1133.0 | 70.8 | 53.4 |
| 5 | 2 | 8690.0 | 154.0 | 145.0 | 79.6 | 41.5 |
| 3 | 4097.0 | 35.2 | 0.9 | 79.6 | 41.5 |
| 1 | 8261.0 | 478.0 | 1175.0 | 79.6 | 41.5 |
| 6 | 2 | 7866.0 | 132.0 | 206.0 | 68.8 | 77.9 |
| 3 | 1625.0 | 19.4 | 0.2 | 68.8 | 77.9 |
| 1 | 8960.0 | 463.0 | 1084.0 | 68.8 | 77.9 |
| 7 | 2 | 8123.0 | 98.0 | 133.1 | 74.7 | 89.9 |
| 3 | 865.0 | 15.2 | 0.4 | 74.7 | 89.9 |
| 1 | 8487.0 | 422.0 | 1064.0 | 74.7 | 89.9 |
| 8 | 2 | 7679.0 | 68.5 | 97.0 | 70.7 | 95.9 |
| 3 | 889.2 | 6.9 | 0.6 | 70.7 | 95.9 |
| 1 | 6311.0 | 289.5 | 738.3 | 70.7 | 95.9 |
| 9 | 2 | 5784.0 | 58.5 | 80.0 | 52.6 | 91.5 |
| 3 | 589.8 | 12.5 | 0.3 | 52.6 | 91.5 |
| 1 | 8264.0 | 311.0 | 1135.0 | 52.6 | 91.5 |
| 10 | 2 | 7794.0 | 82.5 | 98.0 | 68.9 | 91.3 |
| 3 | 780.6 | 8.5 | 0.7 | 68.9 | 91.3 |

Figure 2. Dissolution efficiency of different elements after serpentine dissolution by using NH₄HSO₄ (experiment 3, 100 °C, 2 h).
Finally, to compare our work with that of Pundsack, carboxination experiments were carried out by following his procedure. CO₂ was bubbled into the prepared high-magnesium concentration solution from serpentine and excess aqueous ammonia was added to adjust the pH to a value of 9. Only 35% carbonation efficiency was obtained. In comparison, the carbonation efficiency from this work can achieve a maximum of 95.9% (experiment 8) due to the faster reaction rate between NH₄HCO₃ and Mg.

**pH regulation and removal of impurities**

It was found that after adding aqueous ammonia (35 wt %) to filtrate 1 solution, some particles precipitated. After filtering and drying overnight at 105°C, the resulting solid and filtrate were labelled product 2 and filtrate 2 (Figure 1), respectively. Aqueous ammonia (35 wt %) was then added to filtrate 2 until the pH value reached 8.5. Table 3 presents the XRF results of the products and the mass balance for Mg, Si, and Fe will be discussed in the section below on mass balance (Figure 9). Taking experiment 7 as an example, it can be seen that product 2 consists of 19.3% Fe, 8.2% Si, and 2.8% Mg. The XRD pattern of product 2 for experiment 7 (Figure 3) allowed the identification of double ammonium salts, (NH₄)₂Fe₂(SO₄)₂·6H₂O, (NH₄)₂Mg₂(SO₄)₂·6H₂O and (NH₄)₂Zn₂(SO₄)₂·6H₂O, as the major phases. The presence of these double ammonium salts resulted from excess aqueous ammonia. Hot water flashing can decompose these double ammonium salts into ammonium sulfate and insoluble hydroxide salts. Table 2 clearly shows that the concentration of Fe in filtrate 2 decreased significantly relative to filtrate 1. This decrease in Fe concentration indicates that Fe precipitates. The results of XRF, ICP-AES, and XRD analysis in Tables 1 and 2 and Figure 3 are consistent with this observation, indicating that a high iron-content precipitate was produced. Some magnesium also pre-

| Sample | Product | Mg [wt %] | Mass ratio [%] | Si [wt %] | Mass ratio [%] | Fe [wt %] | Mass ratio [%] | CO₂ [wt %] |
|--------|---------|-----------|----------------|-----------|----------------|-----------|----------------|------------|
| 1      | 1       | 10.5      | 26.2           | 42.3      | 86.3           | 5.6       | 42.5           | N/A        |
| 2      | 1       | 2.7       | 5.0            | 6.3       | 11.7           | 20.4      | 28.2           | N/A        |
| 3      | 1       | 21.5      | 49.2           | 0.2       | 1.7            | 2.2       | 29.2           | 38.8       |
| 1      | 2       | 9.8       | 24.6           | 43.6      | 87.9           | 5.3       | 37.4           | N/A        |
| 2      | 2       | 2.0       | 6.6            | 6.4       | 9.2            | 21.2      | 50.7           | N/A        |
| 3      | 2       | 16.5      | 42.3           | 0.3       | 2.4            | 0.8       | 11.9           | 30.1       |
| 1      | 3       | 3.5       | 8.7            | 45.7      | 83.1           | 3.0       | 4.2            | N/A        |
| 2      | 3       | 5.4       | 11.1           | 11.0      | 14.2           | 27.5      | 79.2           | N/A        |
| 3      | 3       | 21.9      | 55.4           | 0.2       | 2.5            | 1.1       | 16.4           | 39.5       |
| 1      | 4       | 11.8      | 29.2           | 42.4      | 89.2           | 5.8       | 44.8           | N/A        |
| 2      | 4       | 2.5       | 5.5            | 8.8       | 8.0            | 18.5      | 46.0           | N/A        |
| 3      | 4       | 20.1      | 41.1           | 0.3       | 2.3            | 0.8       | 9.1            | 37.5       |
| 1      | 5       | 8.2       | 20.4           | 42.8      | 88.8           | 5.8       | 44.7           | N/A        |
| 2      | 5       | 3.4       | 7.2            | 5.8       | 7.0            | 20.1      | 48.2           | N/A        |
| 3      | 5       | 23.8      | 38.3           | 0.4       | 3.2            | 0.8       | 7.0            | 40.9       |
| 1      | 6       | 12.5      | 31.2           | 42.2      | 87.0           | 5.6       | 42.7           | N/A        |
| 2      | 6       | 3.9       | 3.3            | 6.4       | 9.4            | 21.3      | 47.3           | N/A        |
| 3      | 6       | 19.8      | 52.0           | 0.4       | 3.1            | 0.7       | 1.0            | 35.5       |
| 1      | 7       | 10.1      | 25.3           | 40.7      | 87.4           | 5.9       | 47.1           | N/A        |
| 2      | 7       | 2.8       | 7.0            | 8.2       | 9.9            | 19.3      | 46.4           | N/A        |
| 3      | 7       | 20.5      | 60.5           | 0.3       | 2.3            | 0.4       | 6.2            | 36.7       |
| 1      | 8       | 11.7      | 29.3           | 42.0      | 88.5           | 6.0       | 48.1           | N/A        |
| 2      | 8       | 4.6       | 16.7           | 9.6       | 9.6            | 19.8      | 47.2           | N/A        |
| 3      | 8       | 17.7      | 56.6           | 0.2       | 1.7            | 0.3       | 4.7            | 26.5       |
| 1      | 9       | 18.7      | 47.4           | 35.4      | 92.1           | 7.1       | 64.0           | N/A        |
| 2      | 9       | 4.8       | 4.4            | 13.9      | 6.3            | 20.2      | 32.1           | N/A        |
| 3      | 9       | 18.2      | 43.3           | 0.1       | 1.3            | 0.3       | 3.9            | 27.0       |
| 1      | 10      | 12.5      | 31.1           | 43.4      | 91.5           | 5.8       | 44.6           | N/A        |
| 2      | 10      | 4.6       | 3.9            | 4.7       | 6.2            | 16.3      | 50.6           | N/A        |
| 3      | 10      | 21.3      | 58.5           | 0.1       | 2.0            | 0.3       | 4.7            | 38.5       |

[a] N/A = not applicable.

![Figure 3. XRD pattern of product 2 from experiment 7.](image-url)
Precipitation studies

Ten precipitation experiments were carried out at different mass ratios of Mg/NH₃/NH₄HCO₃, as shown in Table 1. The observations and findings from these ten experiments were similar in terms of carbonation and morphology of the products. Taking product 3 of experiment 7 as an example, Figure 4 shows the presence of magnesium carbonate. This corresponds to the decrease in magnesium concentration in solution for ICP-AES results presented in Table 2.

Figure 4 shows the magnesium concentration variation with time and temperature for experiment 7. The starting time was recorded as heating started. It can be seen that the pH of filtrate 2 decreased from 8.5 to 7.3 as the temperature increased during the first 20 min. As the temperature reached 60 °C, NH₄HCO₃ was added, and the pH increased slightly to 7.6. No precipitate was formed before adding NH₄HCO₃. The concentration of magnesium started to drop as the temperature went up to 70 °C at 25 min. In the following 5 min, half of the Mg ions precipitated at a very high rate of 33.3 mmol min⁻¹. As the temperature stabilised at 85 °C after 40 min, the pH became stable, and Mg precipitated at a constant rate of 7.9 mmol min⁻¹. 25 min after the addition of NH₄HCO₃, the concentration of Mg in solution became constant and finally fell below 1000 mg L⁻¹.

For product 3 of experiment 7, the XRD pattern of product 3 (Figure 5) showed that the Mg precipitated as hydromagnesite, Mg₅(CO₃)₄(OH)₂·4H₂O. Combining the results from XRF of product 3 (Table 3) and the ICP-AES results from filtrate 3 (Table 2), it can be concluded that product 3 is 80% pure hydromagnesite with only 0.79 wt% of Fe and 0.29 wt% Si.

The carbon content of product 3 can be calculated from the TGA profiles (Figure 6a), as described in the Experimental Section. All samples presented one carbonate phase, according to the XRD studies. Therefore, the mass of the identified carbonate phase was estimated based on the corresponding weight loss from the TGA studies. As an example, Figure 6a shows two peaks: the first peak below 250 °C is about 12 wt% and corresponds to the release of crystal water,[17] the second peak, located between 250 and 500 °C, accounts for 37 wt% and is due to the decomposition of hydromagnesite.[16] Finally, based on the CO₂ content (Table 3) and the Mg concentration in filtrate 2, the precipitation of Mg in solution became constant and finally fell below 1000 mg L⁻¹.
trate 2 (Table 2), it can be calculated that the carbonation efficiency of experiment 7 is 90%.

### Improving carbonation by adding NH₂

During the carbonation step, the Mg ions first react with HCO₃⁻ to form Mg(HCO₃)₂ [Eq. 8a], which then thermally decomposes into insoluble nesquehonite at above 70°C, and then molecular MgCO₃ is hydrated to form nesquehonite, followed by the transformation of nesquehonite into hydromagnesite [Eq. 5b]. It must be pointed out that in the thermal decomposition reaction of Mg(HCO₃)₂ into MgCO₃·3H₂O [Eq. 8b], 1 mol of Mg(HCO₃)₂ is converted into 1 mol of insoluble MgCO₃·3H₂O and 1 mol of CO₂. This means that the maximum stoichiometric carbonation efficiency from soluble Mg(HCO₃)₂ into precipitated MgCO₃·3H₂O is only 50%. As an example, in the preliminary experiment in which no NH₃ was used (Table 1), the carbonation efficiency was only 25.5%. However, the joint use of aqueous ammonia and NH₄HCO₃ can improve the carbonation, as described by the reactions presented in Equations 9–14:

\[
\text{MgSO₄ (aq) + NH₄HCO₃ (aq) → Mg(HCO₃)₂ (aq) + NH₄SO₄ (aq)}
\]

(8a)

\[
\text{Mg(HCO₃)₂ (aq) + 2H₂O (l) → MgCO₃·3H₂O (s) } \downarrow + \text{CO₂ (g)}
\]

(8b)

\[
\text{NH₃ (g) + CO₂ (g) + H₂O (l) → NH₄HCO₃ (aq)}
\]

(9)

\[
\text{NH₃ (g) + NH₄HCO₃ (aq) → (NH₄)₂CO₃ (aq)}
\]

(10)

\[
\text{MgSO₄ (aq) + (NH₄)₂CO₃ (aq) + 3H₂O (l) → MgCO₃·3H₂O (s) } \downarrow + (NH₄)₂SO₄ (aq)
\]

(11)

\[
\text{MgSO₄ (aq) + 2NH₃·H₂O (aq) → Mg(OH)₂ (s) } \downarrow + (NH₄)₂SO₄ (aq)
\]

(12)

\[
\text{Mg(OH)₂ (s) + 2CO₂ (g) → Mg(HCO₃)₂}
\]

(13)

\[
\text{Mg(OH)₂ (s) + Mg(HCO₃)₂ (aq) + 4H₂O (l) → 2MgCO₃·3H₂O (s) } \downarrow
\]

(14)

Ammonia captures CO₂ to regenerate NH₄HCO₃ [Eq. 9]; this reaction is already used in CO₂ capture technology.²⁹,³⁰ Ammonia can convert NH₄HCO₃ into (NH₄)₂CO₃ [Eq. 10], which can directly produce MgCO₃ [Eq. 11]. Ammonia can also react with MgSO₄ to form insoluble Mg(OH)₂ if the pH value is above 10, as shown in Equation 12.²¹ Once the CO₂ is released from the decomposition of Mg(HCO₃)₂ [Eq. 8b], Mg(OH)₂ can react with CO₂ to form MgCO₃·3H₂O [Eq. 13]. Moreover, Mg(OH)₂ can also react with Mg(HCO₃)₂ directly to precipitate MgCO₃ [Eq. 14]. Therefore, the carbonation efficiency was improved by the addition of aqueous ammonia to the high-magnesium concentration solution. In experiments 1–10, in which aqueous ammonia was added, the carbonation efficiency could reach up to 95.9% (Table 1, experiment 8).

#### Prevention of precipitation of magnesium ammonium carbonate

The precipitation of magnesium ammonium carbonate (MgCO₃·(NH₄)₂CO₃·4H₂O) can reduce carbonation efficiency because MgCO₃·(NH₄)₂CO₃·4H₂O is generated from the reaction of NH₃ and NH₄HCO₃ with Mg ions at temperatures below 60°C [Eq. 15].²² It can be seen from Figure 7 that the magnesium concentration decreased until the temperature reached 60°C during the first 15 min. However, MgCO₃·(NH₄)₂CO₃·4H₂O decomposes quickly to produce Mg(HCO₃)₂ and NH₃ gas if the temperature goes above 60°C [Eq. 16].

\[
\text{MgSO₄ (aq) + NH₄HCO₃ (aq) + NH₃·H₂O + 3H₂O → MgCO₃·(NH₄)₂CO₃·4H₂O (s) } \downarrow
\]

(15)

\[
\text{MgCO₃·(NH₄)₂CO₃·4H₂O (s) → Mg(HCO₃)₂ (aq) + 2NH₃ (g) } \uparrow + 5H₂O (l)
\]

(16)

According to Equation 16, NH₃ is produced, which would decrease the carbonation efficiency due to a shortage of NH₃. Therefore, the precipitation of MgCO₃·(NH₄)₂CO₃·4H₂O should be prevented to maintain high carbonation efficiency. Taking experiment 4 as an example, the precipitation of MgCO₃·(NH₄)₂CO₃·4H₂O is indicated on the top left corner of Figure 7. If the temperature increased above 60°C, the Mg concentration increased, indicating the decomposition of MgCO₃·(NH₄)₂CO₃·4H₂O. The subsequent decrease of magnesium ions after 30 min indicates the precipitation of hydromagnesite. The carbonation efficiency of experiment 4 is as low as 53.4% due to the shortage of NH₃ gas, which escaped from the reaction system during the thermal decomposition of MgCO₃·(NH₄)₂CO₃·4H₂O. Comparing experiments 4 and 9 by using the same mass ratio of Mg/NH₃/HCO₃/NH₃ and same experimental conditions, the carbonation efficiency decreased from 91.5 to 53.4% if there was precipitation of MgCO₃·(NH₄)₂CO₃·4H₂O (Table 1). Therefore, to prevent low carbonation efficiency caused by precipitation of magnesium ammonium carbonate,
NH₄HCO₃ should preferably be added into the solution above 60 °C.

**Thermal decomposition of (NH₄)₂SO₄**

Product 4 is obtained from the carbonation step by evaporating filtrate 3 (Figure 1). Product 4 was used to generate NH₃ and NH₄HSO₄ by thermal decomposition in an oven at 330 °C for 20 min. The released gas (NH₃) was collected by using water to produce aqueous ammonia. The solid residue obtained after heating was NH₄HSO₄. These results were verified by conducting TGA studies, as described herein. Studies of the thermal conversion of ammonium sulfate into ammonium bisulfate can be found in several patents.[23–25] As an example in this work, the thermal decomposition of product 4 from experiment 7, as studied by TGA, is shown in Figure 6b. The TGA profile shows two peaks, where the first weight loss below 330 °C is about 21.7 wt%, corresponding to the release of NH₃ and the formation of NH₄HSO₄.[23–25] The second weight loss between 350 and 500 °C is 75.8 wt% and is due to further decomposition of NH₄HSO₄.[23–25] In total, the weight loss of product 4 is 97.5 wt% and the residual 2.5 wt% is due to the presence of MgSO₄ that did not react during carbonation. The TGA profile of pure (NH₄)₂SO₄ (purchased from Fisher Scientific) is presented in Figure 6c, where two peaks appear at the same temperature range as those for the TGA profile of product 4 (Figure 6b). The TGA curve of NH₄HSO₄ is presented in Figure 6d and shows only one peak between 330 °C and 500 °C due to decomposition into NH₃, H₂O and SO₃. The NH₄HSO₄ and NH₃ regeneration efficiency from (NH₄)₂SO₄ has been reported to be nearly 97%.[23–25] Herein, the regeneration efficiency of NH₄HSO₄ and NH₃ from product 4 is 95%. These TGA results indicate that the reaction of thermal decomposition of (NH₄)₂SO₄ should not be conducted above 330 °C to avoid further decomposition, because NH₄HSO₄ can decompose into NH₃, SO₃ and H₂O above 330 °C.

**The effect of the mass ratio of Mg/NH₄HCO₃/NH₃ on carbonation**

The mass ratio of Mg/NH₄HCO₃/NH₃ is the key factor controlling carbonation efficiency, as discussed herein. The stoichiometric mass ratio of Mg/NH₄HCO₃ is 1:2, but experiment 5 shows that if a stoichiometric ratio of 1:2 is used, the carbonation efficiency is only 41.5% (Table 1). Increasing the Mg/NH₄HCO₃ ratio can improve the carbonation efficiency, as presented in Table 1, whereby the carbonation efficiency increases to 71.6, 77.9, and 89.9%, if the ratio of Mg/NH₄HCO₃ is 1:3, 1:4, and 1:5, respectively. This can be explained by the thermal decomposition of NH₄HCO₃ [Eq. 17], and reported by Zhang et al.[19] NH₄HCO₃ can regenerate NH₃ and release CO₂ if the temperature is above 70 °C. The two reactions [Eq. 5 and Eq. 17] compete for NH₄HCO₃, and this may cause low carbonation efficiency due to the shortage of NH₄HCO₃.

\[
\text{NH}_4\text{HCO}_3 \text{(aq)} \rightarrow \text{NH}_3 \text{(g)} \uparrow + \text{CO}_2 \text{(g)} \uparrow + \text{H}_2\text{O} \text{(l)} \quad (17)
\]

Moreover, adding aqueous ammonia can increase the carbonation efficiency, as discussed in the section above on precipitation studies. In comparison to the preliminary experiment, experiments 1 and 2 show that carbonation efficiencies increase from 25.5% to 53 (experiment 2) and then 71.6% (experiment 1) if the mass ratio of Mg/NH₄HCO₃/NH₃ increases from 1:3:0 to 1:3:0.5 and then 1:3:1, respectively. This trend was also found in experiments 6, 8, and 9; however, if the ratio increases to 1:4:3, the carbonation efficiency does not increase any further.

Herein, the optimum mass ratio of Mg/NH₄HCO₃/NH₃ was determined. A 3D graph (Figure 8) is used to show the relationship of the four variables, including mass of Mg, mass of NH₄HCO₃, mass of NH₃, and carbonation efficiency. Figure 8 clearly shows that a low summit of 71.6% carbonation efficiency appears if the mass ratio of Mg/NH₄HCO₃/NH₃ is 1:3:1 and a high summit of 95.9% carbonation efficiency appears if the mass ratio of Mg/NH₄HCO₃/NH₃ is 1:4:2. Continuously increasing both NH₄HCO₃ and NH₃ does not result in a further significant rise of the carbonation efficiency. However, an optimum amount of NH₄HCO₃ and NH₃ are needed to achieve the highest carbonation efficiency due to the loss of CO₂ and NH₃ in an open system.

The process studied herein presents higher carbonation efficiency than that reported previously.[8,21] For example, in a work by Gerdemann et al.[6] 64% carbonation efficiency was achieved in direct carbonation of heat-treated serpentine at 155 °C and 115 bar CO₂ in 0.64 m NaHCO₃ and 1 m NaCl solution. In a work by Teir et al.[21] the conversion of Mg ions into hydromagnesite was 94% using HNO₃ and 79% using HCl at pH 9 with the addition of NaOH (1.1 g NaOH/g precipitate). Herein, the highest carbonation efficiency is 95.9% at 85 °C and ambient pressure within 30 min by using NH₄HCO₃ and NH₃.
Mass balance

To examine the distribution of magnesium released from serpentine in the solids formed in the process (products 1, 2, and 3) and filtrate 3, a mass balance was constructed based on the XRF and ICP-AES and the results are presented in Figure 9. It can be seen that most of the magnesium from the parent serpentine ends up in the precipitated hydromagnesite (product 3). The use of additives at the optimised ratio to improve carbonation conversion results in less magnesium remaining in the final solution after carbonation (filtrate 3, experiments 6–10). Longer dissolution times may leach more magnesium from the serpentine and therefore reduce the amount present in product 3. [1] In addition, the presence of magnesium in relation to serpentine. From top to bottom: filtrate 3/serpentine (black), product 3/serpentine (white), product 2/serpentine (dark grey), and product 1/serpentine (light grey).

Figure 9. Mass balance of magnesium in products 1, 2, and 3 and filtrate 3 in relation to serpentine. From top to bottom: filtrate 3/serpentine (black), product 3/serpentine (white), product 2/serpentine (dark grey), and product 1/serpentine (light grey).

Conclusions

We have studied the precipitation of hydromagnesite from prepared high-magnesium concentration solutions by using NH₃ and NH₄HCO₃. The regeneration of NH₃ and NH₄HSO₄ was also investigated. Pure hydromagnesite can be produced from serpentine by using regenerated ammonium salts with a net conversion of 86.3%. Amorphous silica can be obtained from the dissolution step. Byproducts with a maximum 27.5 wt% iron content were obtained from the pH regulation and removal of impurities step. The additives used, NH₄HSO₄ and NH₃, can be regenerated by thermal decomposition of (NH₄)₂SO₄ at 330 °C. The addition of aqueous ammonia before carbonation could significantly improve the carbonation efficiency. It must be pointed out that NH₄HCO₃ should be added to the solution after 60 °C to prevent the production of magnesium ammonium carbonate. The mass ratio of Mg/NH₄HCO₃/NH₃ was 1:4:2, a carbonation efficiency of 95.9% was achieved. From the TGA studies, the regeneration efficiency of NH₄HSO₄ in this process was found to be 95%. According to mass balance, about 2.63 tonnes of serpentine, 0.12 tonnes of NH₄HSO₄, and 0.04 tonnes of NH₃ are required to sequester 1 tonne CO₂, and 2.95 tonnes of hydromagnesite is produced.

Acknowledgements

The work presented within this paper was funded by the Centre for Innovation in Carbon Capture and Storage (Engineering and Physical Sciences Research Council grant EP/F012098/1).

Keywords: ammonium salts · carbon dioxide fixation · carbon storage · green chemistry · mineral carbonation

[1] Working Group III of the Intergovernmental Panel on Climate Change (Eds.: B. Metz, H. C. d. C. O. Davidson, M. Loos, L. A. Meyer), IPCC Special Report on Carbon Dioxide Capture and Storage, Cambridge University Press, Cambridge, 2005.
[2] For a benchmark study on problems related to CO₂ storage in geologic formations, see: H. Class, A. Ebigbo, R. Helmig, H. K. Dahle, J. M. Nordbotten, M. A. Celia, P. Thomas, L. Trenty, L. L. Wei, Comput. Geosci. 2009, 13, 409 – 434.

[3] S. Teir, H. Revitzer, S. Eloneva, C. Fogelholm, R. Zevenhoven, Int. J. Miner. Process. 2007, 83, 36 – 46.

[4] F. Goff, K. S. Lackner, Environ. Geosci. 1998, 5, 89 – 101.

[5] K. S. Lackner, H. J. Ziock, Modern Power Systems 2000, 20, 31 – 32.

[6] M. M. Maroto-Valer, D. J. Fauth, Y. Zhang, J. M. Andresen, Fuel Process. Technol. 2005, 86, 1627 – 1645.

[7] A.-H. A. Park, L.-S. Fan, Chem. Eng. Sci. 2004, 59, 5241 – 5247.

[8] S. G. Thomas, L. Trenty, L. L. Wei, Comput. Geosci. 2009, 13, 409 – 434.

[9] S. Teir, S. Eloneva, C. Fogelholm, R. Zevenhoven, Appl. Energy 2009, 86, 214 – 218.

[10] S. C. Krevor, K. S. Lackner, Energy Procedia 2009, 1, 4867 – 4871.

[11] F. L. Pundsack, US Patent 3338667, 1967.

[12] J. Fagerlund, S. Teir, E. Nduagu, R. Zevenhoven, Energy Procedia 2009, 1, 4097 – 4914.

[13] E. Nduagu, R. Zevenhoven, Production of Magnesium Hydroxide from Magnesium Silicate for the Purpose of CO₂ Mineralisation and Increasing Ocean Alkalinity: Effect of Reaction Parameters, in ACEME 10, Proceedings 31 – 40, 2010, Turku.

[14] R. Zevenhoven, T. Björklöf, J. Fagerlund, I. Romao, J. Highfield, B. Jie, Assessment & Improvement of a Stepwise Magnesium Silicate Carbonation Route via MgSO₄ & Mg(OH)₂, in ACEME 10, Proceedings 41 – 50, 2011, Turku.