IMPERIAL

Carbonation Operation

CCUS Innovation 2.0

Key Knowledge Deliverable 1.5

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Key Knowledge Deliverable Cover Sheet

This Key Knowledge Deliverable (KKD) has been produced by Imperial College London as part of the Department for Energy Security and Net Zero £1bn Net Zero Innovation Portfolio (NZIP) - CCUS Innovation 2.0 programme. The document is reflective of the status of the project at the time of writing. The material presented could have been subject to change as the project matured. These documents should not be considered a full representation of the final project.

Project Description

This project seeks to further develop and scale a new carbon sequestration process which transforms waste CO2 gas from industrial facilities into valuable construction products. Sequestered CO2 through this process is cheaper than conventional approaches that rely on purification, liquification and offshore or geological storage. The CO2 is stored in the form of a stable mineral which ensures they will be no leakage over time.

The patent-pending technology involves taking globally abundant magnesium silicate minerals and splitting this into magnesia and silica components. Through simple chemical processing two products of high purity are created: a) an amorphous silica that can be used as supplementary cementitious material (SCM) to facilitate low-carbon concrete and b) a concentrated magnesium solution in which CO2 from industrial flues can be sequestered to produce other construction materials.

This CCUS Innovation 2.0 award will be used to increase our technology and commercial readiness level by de-risking and facilitating the development of a pilot facility, in order to demonstrate that the technology is economically viable and deployable at scale.

Description of KKD

Report detailing production of silica from Dissolution stage and magnesium carbonate from Carbonation stage over 3 months of operation. Report to include production records containing batch sizes, reaction times and characterisation; as well as details of any changes to the process including reasoning and outcomes on reaction times and efficiencies etc.

KKDs to be released in full

- D3.4 – Concrete Trials 3
- D4.4 – Product Optimisation 2

KKDs to be released after redactions

- D1.1 – Flue Gas Recovery and Testing 1
- D1.2 – Dissolution Procurement
- D1.3 – Dissolution Operation
- D1.4 – Flue Gas Recovery and Testing 2 & Carbonation Procurement
- D1.5 – Carbonation Operation
- D2.3 – Reagent Regeneration Procurement
- D2.4 – Reagent Regeneration Operation
- D3.2 – Concrete Trials 1
- D3.3 – Concrete Trials 2
- D4.2 – Process Optimisation
- D4.3 – Product Optimisation 1
- D5.2 – Business Development 2 (Supply Chain)
- D5.3 – Business Development 3 (Business Planning)
- D5.4 - Business Development 4 (Commercial Readiness)
- D6.1 – Year 1 Report
- D6.2 – Year 2 Report

Any enquiries regarding this publication should be sent to us at:
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Contents

Introduction

Aims and Objectives

The aim of this deliverable is to optimise the carbonation reaction by maximizing the magnesium carbonation efficiency within one hour and gaining understanding of the rate of reaction. This will be done by changing different variables and identifying the effects they have on the process.

Background and Theory

Carbon capture utilization and storage (CCUS) will play a vital role in reducing global CO2 emissions. In order to overcome the disadvantages of traditional CCS for CO2 reduction, CO2 Capture and Utilization (CCU) has been proposed as a promising method. Unlike CCS, CO2 is utilized as a resource to be converted into thermodynamically stable materials by chemical reaction. The CCU process not only reduces CO2 emission, but also obtains high-value products. CO2 mineralization is one of the feasible CCU processes. There are several different elements that can be carbonated to produce water-insoluble carbonates, but alkaline earth metals, calcium and magnesium, have proven to be the most suitable ones since Ca/Mg-bearing compounds have a wide range of sources and huge reserves. Mg in particular is found in, the raw material, Olivine, used in carbon capture process discussed in the present research.

This report will focus on the operation of the carbonation of Mg-based solution. This is carbon capture section of the process, currently being actively researched. The CO2 is permanently sequestered in the form of nesquehonite mineral (MgCO3.3H2O) which can be used to replace various carbon intensive construction products, such as fired clay bricks, blocks, and gypsum boards. There have been several studies that looked at CO2 sequestration via carbonation by bubbling CO2 through Mg(OH)2 solutions, however literature is very limited in the carbonation in a solution of MgSO4 [1–3].

Reaction Mechanism

The overall reaction taking place in the carbonation process is:

$MgSO_4 + CO_2 + 2\ NH_4OH + 2\ H_2O \rightarrow MgCO_3.3H_2O + (NH_4)_2SO_4$ Eq.1

Step 1: Formation of Carbonate ions

1. Dissociation of Ammonium Hydroxide:

$NH_4OH \rightarrow NH_4^+ + OH^-$ Eq. 2

2. Reaction of CO_2 with Hydroxide Ions:

$CO_2 + OH^- \rightarrow HCO_3^-$ Eq. 3

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$ Eq.4

3. Formation of Ammonium Carbonate (in the presence of excess ammonia):

$2\ NH_4^+ + CO_3^{2-} \rightarrow (NH_4)_2CO_3$ Eq. 5

Step 2: Formation of Magnesium Carbonate

4. Dissociation of Magnesium Sulfate:

$MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$ Eq. 6

5. Reaction of Magnesium Ions with Ammonium Carbonate:

$Mg^{2+} + CO_3^{2-}\ MgSO_4 \rightarrow MgCO_3$ Eq. 7

6. Formation of Ammonium Sulfate:

$2\ NH_4^+ + SO_4^{2-} \rightarrow (NH_4)_2SO_4$ Eq. 8

Step 3: Hydration of Magnesium Carbonate

7. Hydration of Magnesium Carbonate:

$MgCO_3 + 3\ H_2O \rightarrow MgCO_3.3H_2O$ Eq. 9

8. Combined Ionic Equations

$Mg^{2+} + SO_4^{2-} + CO_2 + 2\ NH_4^+ + 2\ OH^- + 2\ H_2O \rightarrow MgCO_3.3H_2O + (NH_4)_2SO_4$ Eq. 10

Set of Experiments

Reaction variables have been selected in order to investigate their impact on the reaction:

1. pH
2. CO2 and NH3 injection period
3. Stoichiometric ammonia/MgSO4 ratio
4. Testing experimental MgSO4 solution

Table 1. Covers the set of experiments conducted in the report to optimize the process

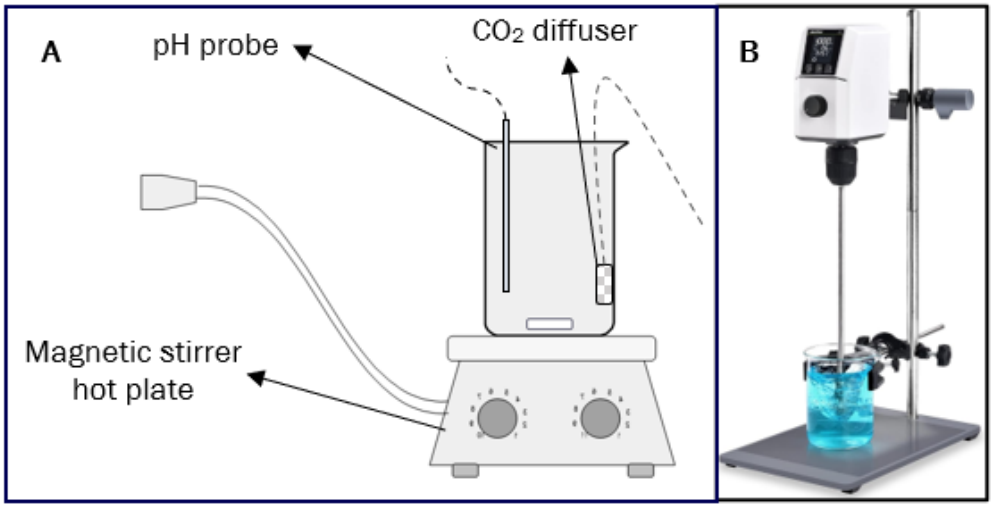
Testing Variable	MgSO4 concentration	pH	Injection Time	Stoichiometric ammonia/MgSO4 ratio	Testing Method
pH	0.2 M	7.5	30 min	x2	Titration
	0.2 M	8.9	30 min	x2	Titration
	0.2 M	9.5	30 min	x2	Titration
	0.2 M	10.0	30 min	x2	Titration
Injection Time	0.2 M	9.5	10 min	x2	Titration
	0.2 M	9.5	15 min	x2	Titration
	0.2 M	9.5	30 min	x2	Titration
	0.2 M	9.5	60 min	x2	Titration
	0.5 M	9.5	15 min	x2	Titration
	0.5 M	9.5	30 min	x2	Titration
	0.5 M	9.5	60 min	x2	Titration
Stoichiometric Ammonia/MgSO4 ratio	0.5 M	9.5	15 min	x1	Titration, XRD & SEM
	0.5 M	9.5	15 min	x1.5	Titration, XRD & SEM
	0.5 M	9.5	15 min	x2	Titration, XRD & SEM
Experimental Solution	0.4 M	9.5	15 min	x1.5	Titration, XRD & SEM

Method

Experimental Setup

The experiment was conducted in a semi-batch operation in a 5 L beaker (reactor). The reactor is connected to a peristaltic pump that allows for constant flow of ammonia solution into the reactor. A porous diffuser is also connected from a CO2 tank to the reactor set at 0.5 bar. A pH meter is inserted into the beaker throughout the experiment to ensure the reaction is taking place at the desired pH. The first set of experiments were conducted using the set up in Figure 2A using a magnetic stirrer, however as the thickness of the solution increased a better stirring mechanism was required hence set up in Figure 2B was used.

Figure 1. Lab based carbon mineralization experimental setup



Experimental Steps

- Preparation of MgSO4 Solution:

A 5 L beaker was filled with 3 L of the required amount of hydrated MgSO4 crystals and deionized water based on the target concentration:

- Solution Setup:

The beaker was appropriately positioned and secured as described in your setup section.

The initial pH of the $MgSO_4$ solution was measured.

- pH Adjustment:

Ammonia solution was gradually added dropwise while continuously stirring until the pH of the solution reaches 9.5.

The pH was closely monitored to avoid overshooting the desired pH.

- Sampling and Dilution:

Before starting the reaction, a 1.5 mL sample was taken of the solution.

The sample was diluted by a factor of 10 using deionized water.

- Setting Ammonia and CO_2 Flow Rates:

The ammonia peristaltic pump was set to the desired flow rate based on stoichiometric requirements (e.g., x1, x1.5, x2).

The CO_2 flowmeter was calibrated and set to maintain the desired pH during the reaction.

- Commencing the Reaction:

Simultaneously the ammonia peristaltic pump and the CO_2 flow were switched on

Continuous stirring was maintained to ensure uniform mixing throughout the reaction.

- Periodic Sampling:

Samples were collected at specified time intervals during the reaction (e.g., every 15 minutes).

Each sample was diluted by a factor of 10 using deionized water.

- Titration:

Titration was conducted on the diluted samples to measure the concentration of magnesium ions remaining in the solution [4].

The percentage completion of the reaction based on the titration results was calculated.

- Solid Extraction, Drying & Analysis

At the end of the reaction, the solution is filtered to separate the solid product.

The solid was washed with deionized water to remove any remaining soluble impurities.

The solid is dried in an oven at 60°C overnight to ensure complete removal of moisture.

The dried solid is analysed using X-Ray Diffraction (XRD) set at 7.5 degrees per min, Cu Ka radiation to determine its crystalline structure.

Scanning Electron Microscopy (SEM) test set at 15 kV back-scattered electron was conducted to study the morphology of the solid product.

- Specific method for each section:

Effect of pH

Using a 0.2 M $MgSO_4$ solution, several experiments were conducted at different pH levels ranging from 7.5 to 10. This was done by balancing the CO_2 and ammonia flowrate to achieve desired pH. The reaction was allowed to run for 30 minutes, with samples taken every 5 minutes.

Effect of Injection Period

This essentially required a constant flow of CO_2 and ammonia into the beaker for varied times ranging from 10 min to 60 minutes then it is stopped. The absolute amount of ammonia remained at 2x the stoichiometric required amount for each experiment. Samples were still taken after the feed flow of CO_2 and ammonia were stopped and the stirring was also allowed to carry on. This was initially conducted on a 0.2 M $MgSO_4$ then a 0.5 M $MgSO_4$ solution.

Effect of stoichiometric ammonia/$MgSO_4$ ratio

The effect of the different stoichiometric ratios of ammonia to $MgSO_4$ was conducted (x1, x1.5 and x2). In order to maintain a constant pH of 9.5 when the rate of ammonia addition is increased, the CO_2 flow rate must also be increased.

Magnetic stirrer vs overhead electric stirrer (OES)

It was observed that a higher $MgSO_4$ initial concentration solution resulted in a thicker $MgCO_3$ mixture which prevented the magnetic stirrer from mixing the solution as the reaction was taking place. Therefore, an overhead electric stirrer was purchased with a maximum RPM of 1800. Initially, an experiment was conducted at 1700 rpm at 0.5 M $MgSO_4$ using x1.5 ammonia and 15-minute injection time while maintaining pH at 9.5.

Two experiments were then conducted at different rpms of 900 and 1400 to see the effect of different mixing speeds. The experiments were conducted on a 0.5M $MgSO_4$ solution using x1.5 ammonia ratio. This was repeated for 1400 rpm agitation at different ammonia/$MgSO_4$ ratios (x1, x1.5 and x2).

Experimental $MgSO_4$ solution

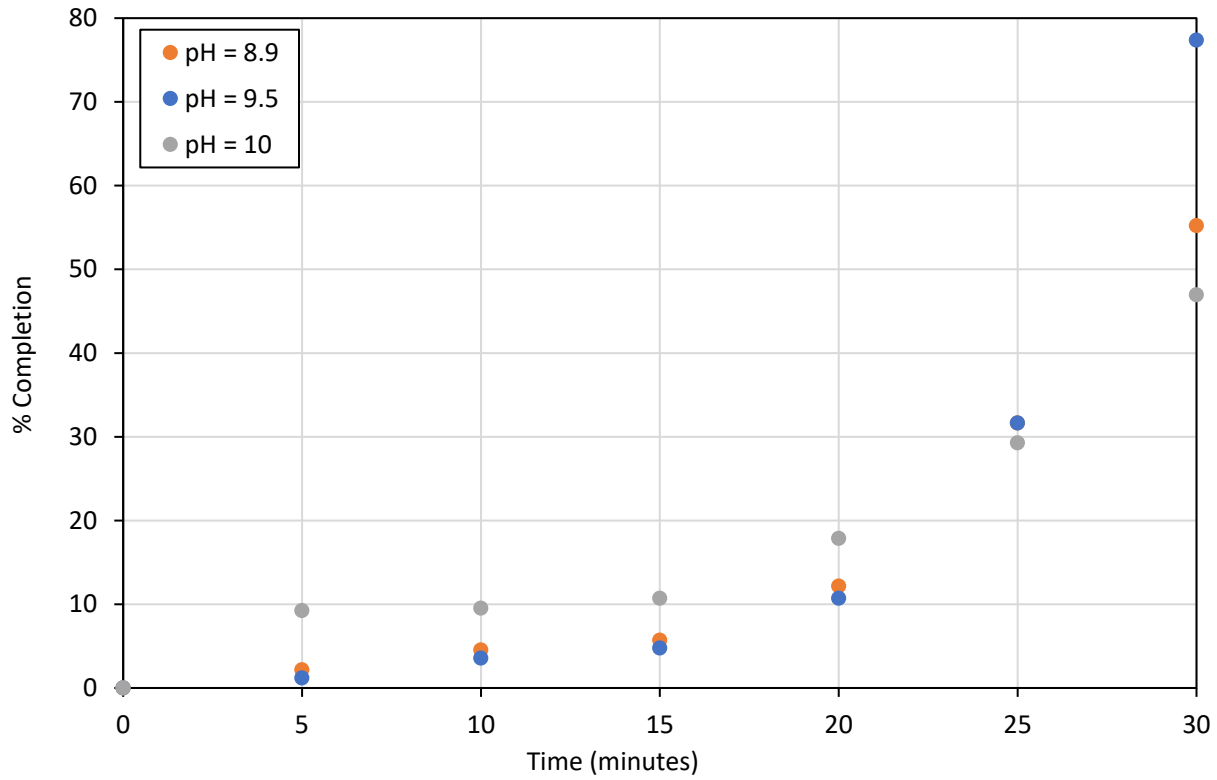
Experimental $MgSO_4$ solution from the previous steps within the whole process shown in Figure 1 is used instead of preparing a synthetic $MgSO_4$ solution. Titration was conducted to estimate the amount of Mg ions available in the solution. Based on that a 1.5x stoichiometric amount of ammonia was used injected with the first 15 minutes alongside CO_2 to maintain the pH at 9.5. A magnetic stirrer was used for the stirring.

Results and Discussion

Effect of pH

The first set of experiments aimed to determine the optimum pH for the reaction. The results in Figure 3 indicated that pH 9.5 was optimal, yielding the highest percentage completion after 30 minutes, consistent with the literature. At pH 7.5, no carbonation occurred as the solution remained clear; therefore, these samples were not tested or plotted, confirming that carbonation at pH 7.5 is unsuitable. At pH 8.9, the initial rate of carbonation was similar to that at pH 9.5. However, as time progressed, the reaction at pH 9.5 experienced an exponential increase, leading to a higher percentage completion. pH has a significant impact on the solubility of CO2 in water and the dissolved species it exists as (HCO3- or CO32-). The higher the pH, the more thermodynamically favourable CO32- ions become [5], resulting in greater conversion to MgCO3.3H2O. However, increasing the pH further to 10 did not enhance the final reaction completion, due to the competing effect of magnesium precipitation as brucite (Mg(OH)2), which is insoluble above pH 10.

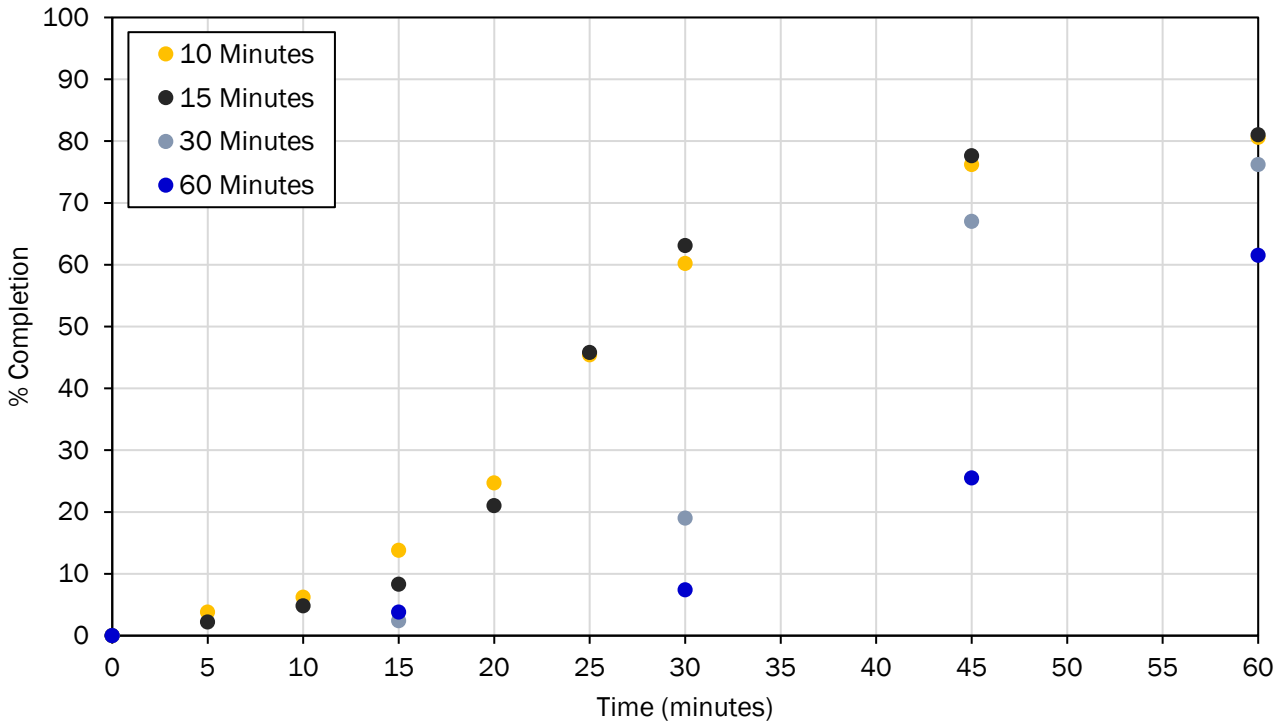
Figure 2. The effect of pH on the percentage completion of the reaction with time



Effect of Injection Period

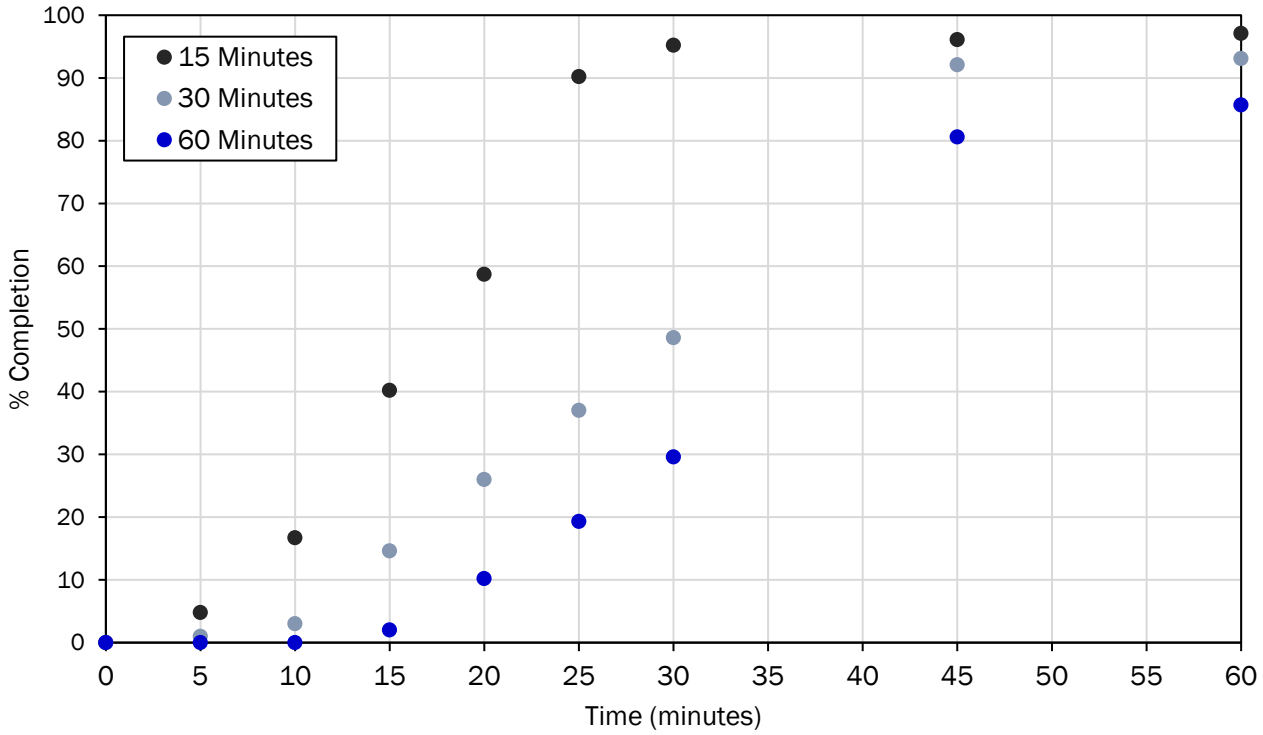
After concluding that pH 9.5 was the most optimum for a higher percentage completing, we investigated the effect of ammonia and CO2 feed period while maintaining the pH at 9.5. Figure 4 presents the results for a 0.2 M MgSO4 solution which shows a shorter induction time as the injection period is decreased. This is likely because a shorter injection period results in the solution reaching supersaturation conditions more quickly, allowing earlier nucleation and a greater nucleation rate. It was also observed that the shorter the injection time, the greater the rate of precipitation and therefore, faster overall reaction. Finally, after 1 hour, the final percentage completion of the reaction was highest for the 10-minute injection period test. This is likely because of greater availability of CO23- ions within the reaction solution at earlier times. It can be seen in the 1-hour graph that the crystal growth phase did not reach completion since the gradient is still increasing as it got to the 1-hour mark.

Figure 3. The effect of CO2 and ammonia injection period on the percentage completion of the reaction with time for a 0.2 M MgSO4 solution



The same experiment was repeated for the 15-minute, 30 minute and 60 minutes injection periods for 0.5 M MgSO4. The results were plotted on Figure 5. It was observed that there was an increase in final reaction percentage completion with the highest being 97.1% for the 15-minute injection period. It can also be seen that all experiments plateaued after 60 minutes. This shows that as you increase the concentration of MgSO4, the induction period decreases and overall rate of reaction increases. This is due to the greater availability of magnesium ions within the solution.

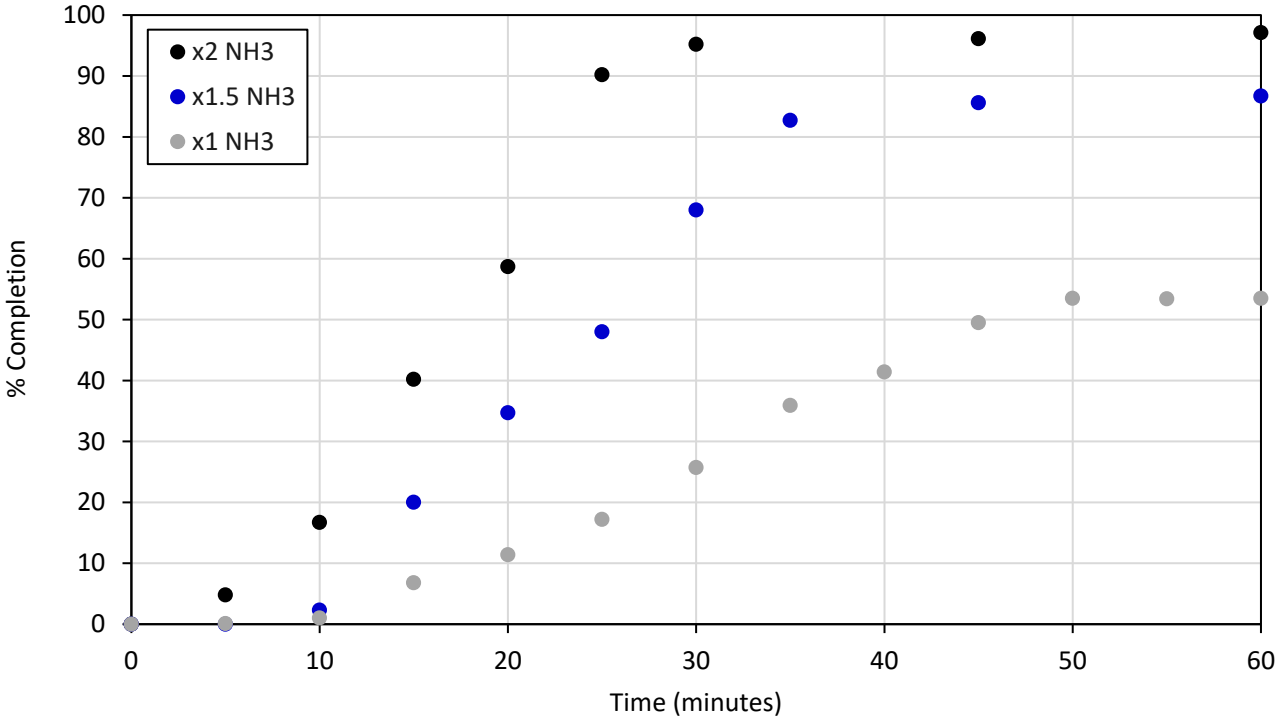
Figure 4. The effect of CO2 and ammonia injection period on the percentage completion of the reaction with time for a 0.5 M MgSO4 solution



Effect of stoichiometric ammonia/MgSO4 ratio

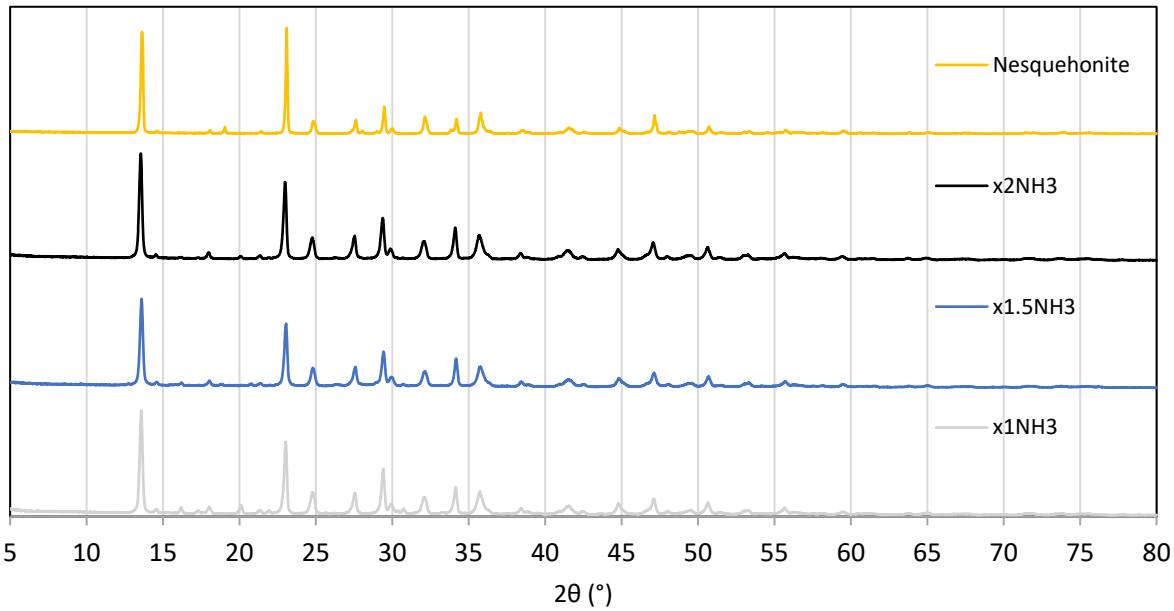
From the previous section we concluded that the highest percentage completion was when the injection period is within the first 15 minutes. This was done at x2 the stoichiometric requirement of ammonia solution. The use of excess ammonia in the carbonation reaction may be deleterious to the following stages in the overall process. There are only limited sulfate ions for the ammonia to associate with, therefore excess will likely associate with CO2. This ammonia can therefore not be recovered. Therefore, experiments at different ammonia/MgSO4 ratios were conducted to assess the impact of reducing the amount of ammonia on the reaction rate and percentage completion as shown in Figure 6. In order to maintain a constant pH of 9.5 when the rate of ammonia addition is greater, the CO2 flow rate must also be greater. This is due to the dissolution of CO2 producing H+ species which must associate with the OH- alleviated from the ammonia solution. It is observed that as we reduce the ammonia/MgSO4 ratio and therefore CO2 flow rate, the reaction rate and absolute reaction completion decrease. This is due to the lower availability of CO23- in solution, which is a rate determining variable.

Figure 5. The effect of ammonia ratio on the percentage completion of the reaction with time for a 0.5 M MgSO4 solution



Samples of the solid product were tested for different ammonia/MgSO4 ratio experiments to see the impact on the carbonate identity and its morphology. XRD diffractograms from each sample, given in Figure 7, shows that all magnesium carbonate products are nesquehonite. Some of the additional small peaks are magnesium sulfate hydrate, resulting from imperfect washing of the nesquehonite.

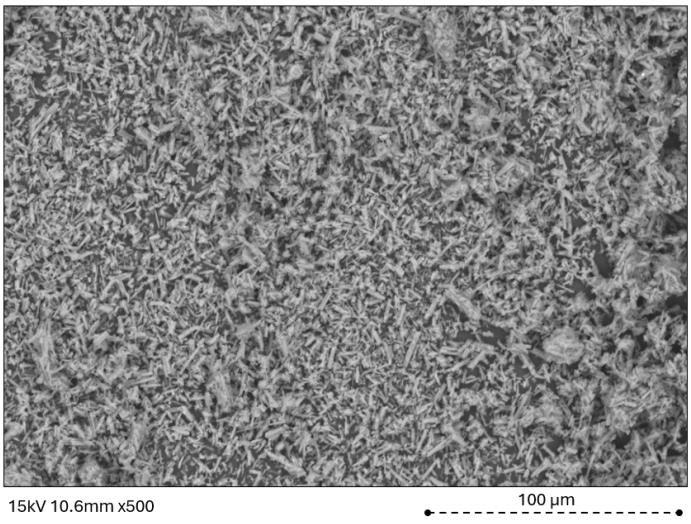
Figure 6. XRD data of the solid product from the carbonation reaction at different stoichiometric MgSO4 to ammonia ratios



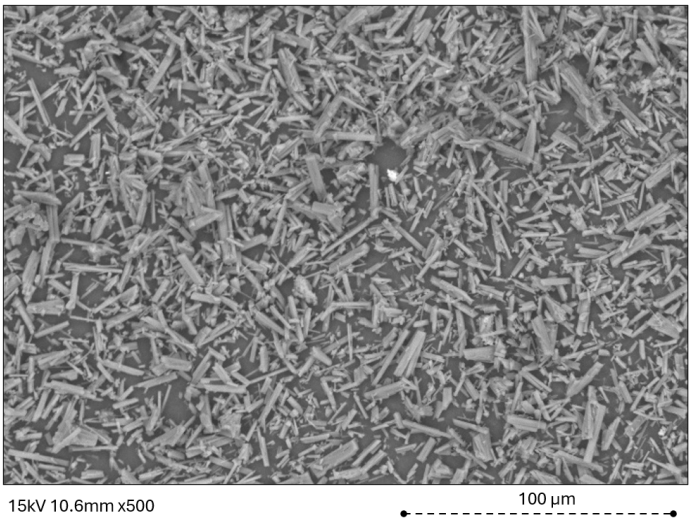
SEM was also conducted on the samples to see if the ammonia ratio has an impact on the morphology or particle size of the nesquehonite. Figure 8 shows the three solids resulting from using x1, x1,5 and x2 the stoichiometric amount of ammonia required. In all cases, the characteristic needle-like nesquehonite crystals were observed. It can be seen that the particle size increases as we increase the amount of ammonia used. This is likely due to the samples with greater ammonia addition also having more dissolved CO2, leading to earlier nucleation and more enhanced crystal growth.

Figure 7. SEM images of the solid product from the carbonation reaction at different stoichiometric MgSO4 to ammonia ratios (Magnification x500)

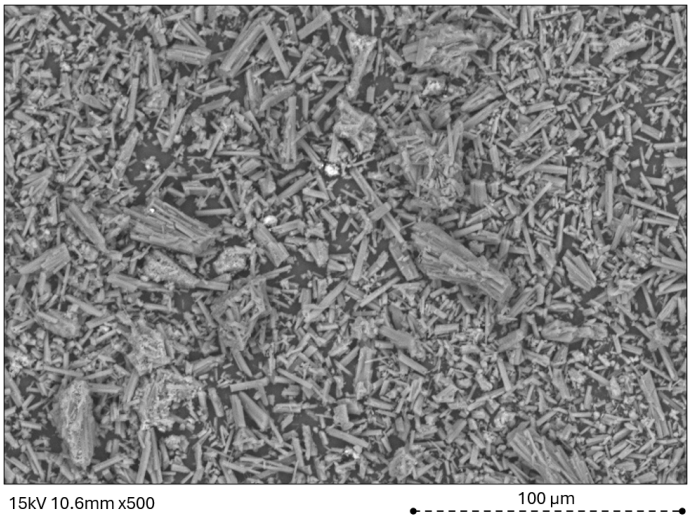
x1 NH3



x1.5 NH3



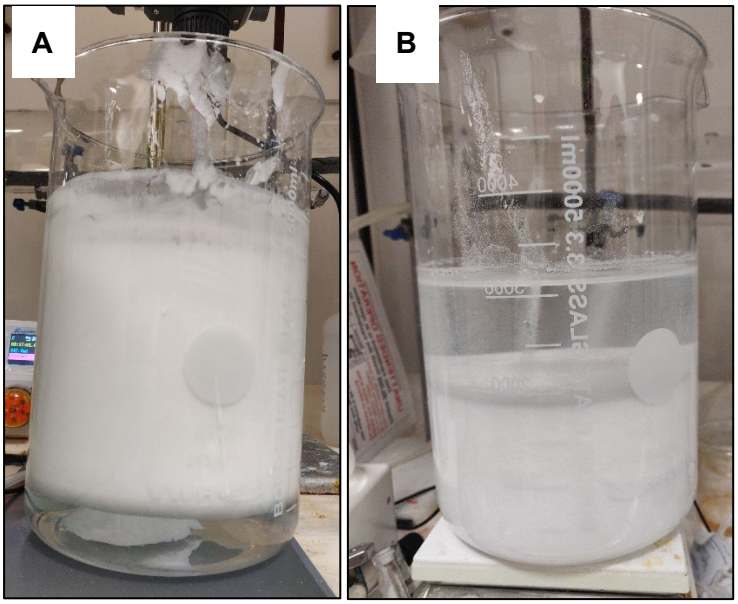
x2 NH3



Magnetic stirrer vs overhead electric stirrer (OES)

When the overheard electric stirrer was used, due to the high shear mixing, the solution became frothy due to improved mixing between the gas (air from surrounding and bubbled CO2) and liquid. As shown in Figure 9A, the final carbonate produced was floating instead of settling as typically observed (Figure 9B), likely due to increased air entrainment in the precipitated solid network.

Figure 8. Picture of the final solid product when using an overheard electric stirrer (A) and a magnetic stirrer (B)



According to the XRD diffractogram in Figure 10 we can conclude that both are nesquehonite and that the mixing rate has no impact on the phase identity of the product. However, SEM analysis (Figure 11) of the nesquehonite formed in both cases revealed that when using the OES at high 1600 rpm, the mean crystal size is much smaller than when using a magnetic stirrer. The high shear mixing associated with the OES is widely reported as likely limiting the particle size through two complementary impacts [6]:

- Disrupting crystal growth – As the precipitation of nesquehonite is a bulk diffusion-controlled growth process, it relies greatly on concentration gradients within the solution. The high sheer mixing disrupts these, favouring nucleation overgrowth [7].
- Facilitating increased nucleation rates as air bubbles generated with strong agitation may act as heterogeneous nucleation sites.

Figure 9. XRD data of the solid product from the carbonation reaction when using an OES vs a magnetic stirrer

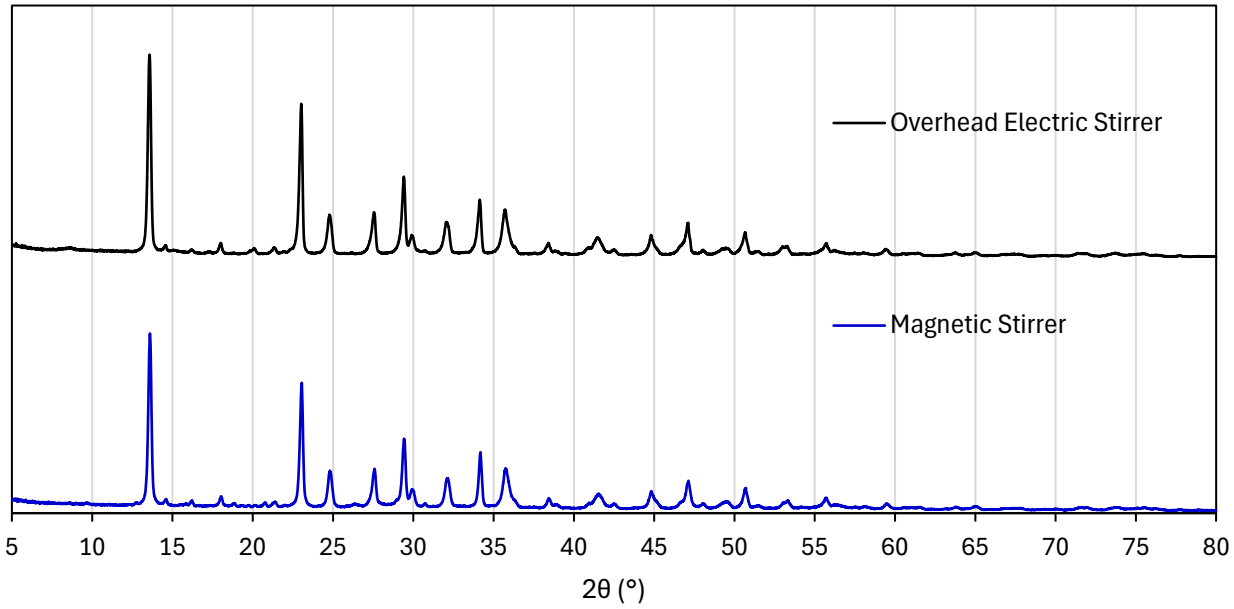


Figure 10. SEM images of the nesquehonite from the carbonation reaction when using an OES vs a magnetic stirrer

OES Nesquehonite

Magnetic Stirrer Nesquehonite

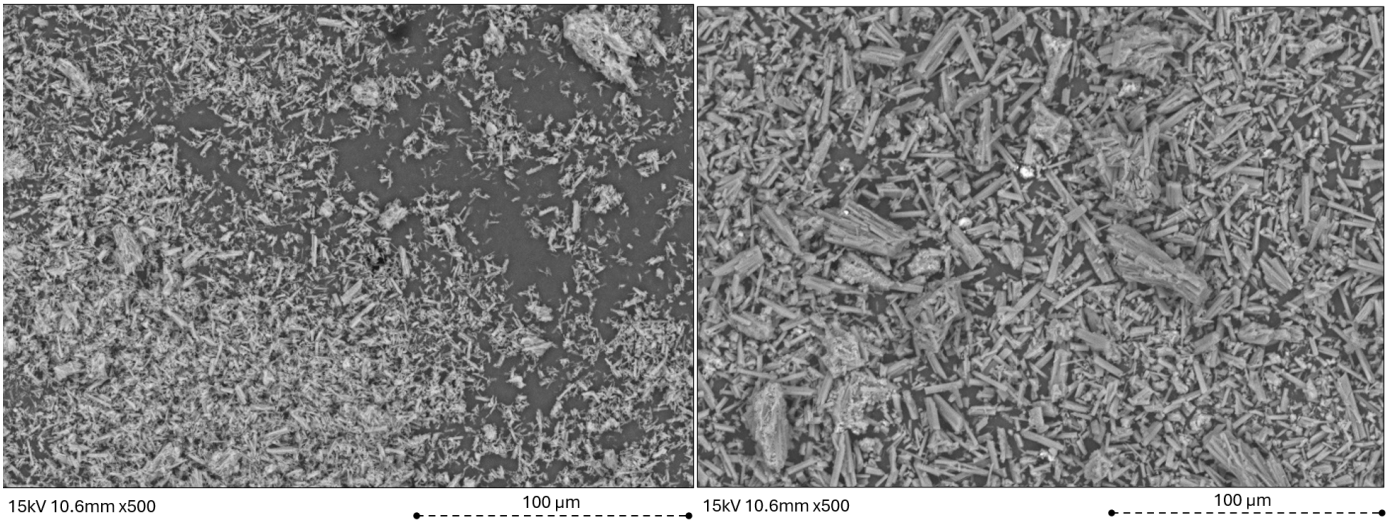
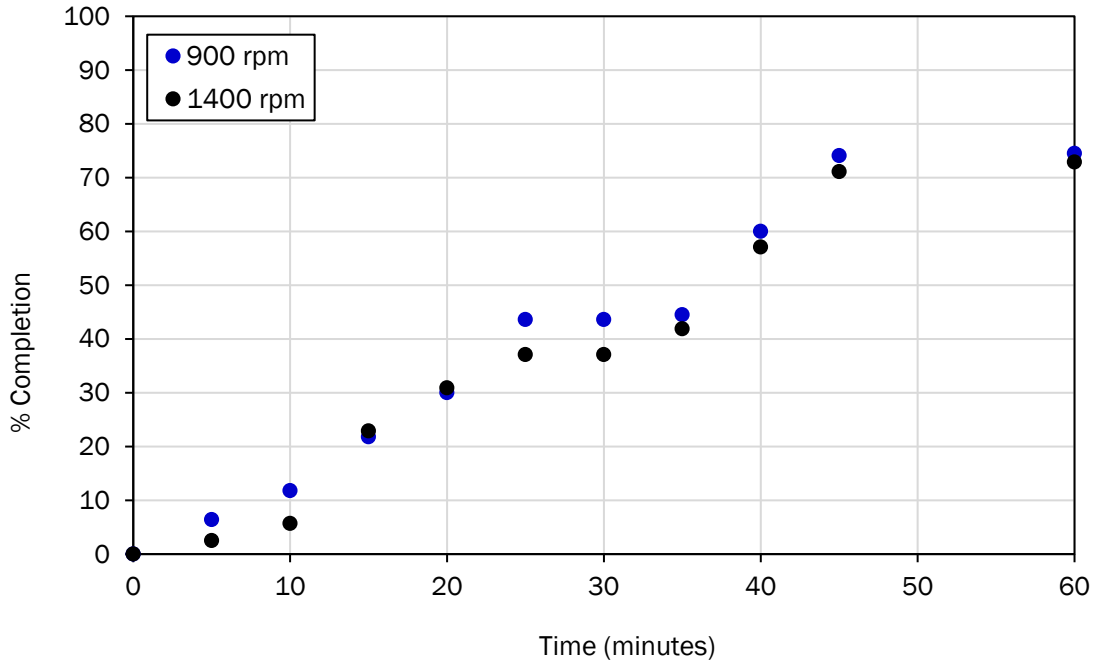


Figure 12 shows a temporary plateau between 25 - 35 minutes which does not happen when using a magnetic stirrer. When comparing between both rpm speeds, it can be concluded that there is little difference between agitating at 900 or 1400 rpm. However, the final nesquehonite produced did not float in either case.

Figure 11. Compares the effect of agitation speeds (900 rpm and 1400 rpm) on the % completion of the reaction



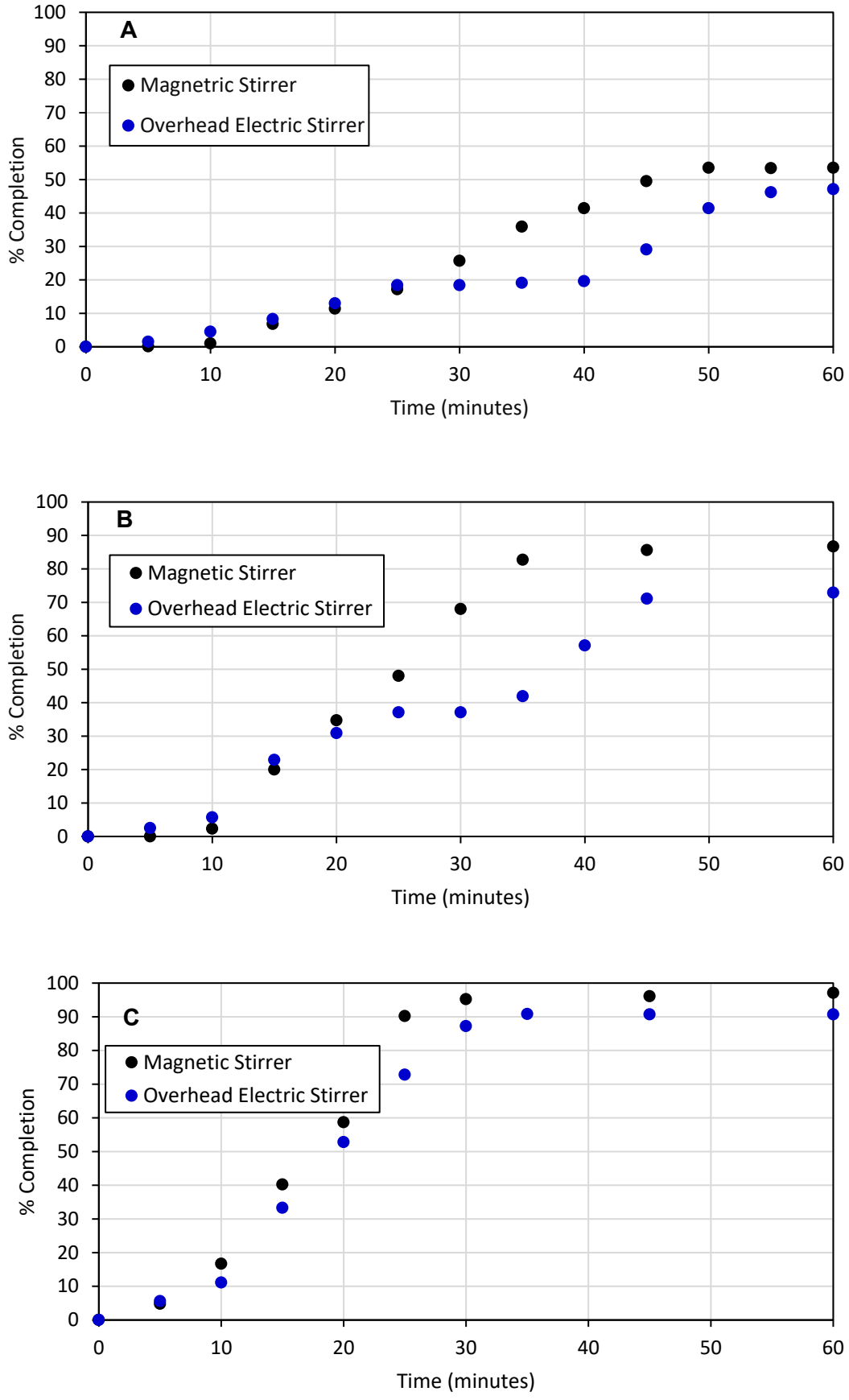
To further understand the plateau in Figure 12, the test was repeated at 1400 rpm at different ammonia ratios (x1, x1.5 and x2) and results were compared to when using a magnetic stirrer. It was assumed that better mixing would result in faster rates and a higher percentage completion after the 1-hour mark. However, as shown in Figures 13A, 13B & 13C it can be seen otherwise.

Results presented in Figure 13A show the reaction has almost no progression between 25 and 40 minutes of reaction. A similar effect can be seen in Figure 13B, but for a shorter time period. As previously discussed, increased agitation is characteristic of facilitating nucleation and inhibiting growth rates. As the reaction progression rate at early times is similar for both magnetic and electrical stirring, it can be inferred that the increase in nucleation rates is being counterbalanced by the decrease in growth rate leading to the same rate of magnesium removal from the solution. This is supported by the smaller and more abundant crystals from OES observed in Figure 11.

The pause in reaction progression could be explained by the inhibition of growth rates overshadowing the increased facilitation of nucleation. For example, many nuclei may be forming but not able to grow to reach equilibrium crystal size so redissolve into solution, preventing any reaction progression from occurring.

In the case of Figure 13C, reaction progressions of magnetic stirring and OES are comparable. This is likely due to the thickness of the solution preventing high shear mixing of the OES.

Figure 12. Compares between OES and magnetic stirring in their effect on percentage completion of the reaction with time for a x1 ammonia/MgSO4 ratio (A), x1.5 ammonia/MgSO4 ratio (B) and x2 ammonia/MgSO4 ratio (C)



Experimental MgSO4 Solution

Figure 13. SEM data of the solid product from the carbonation reaction when using the experimental MgSO4 solution

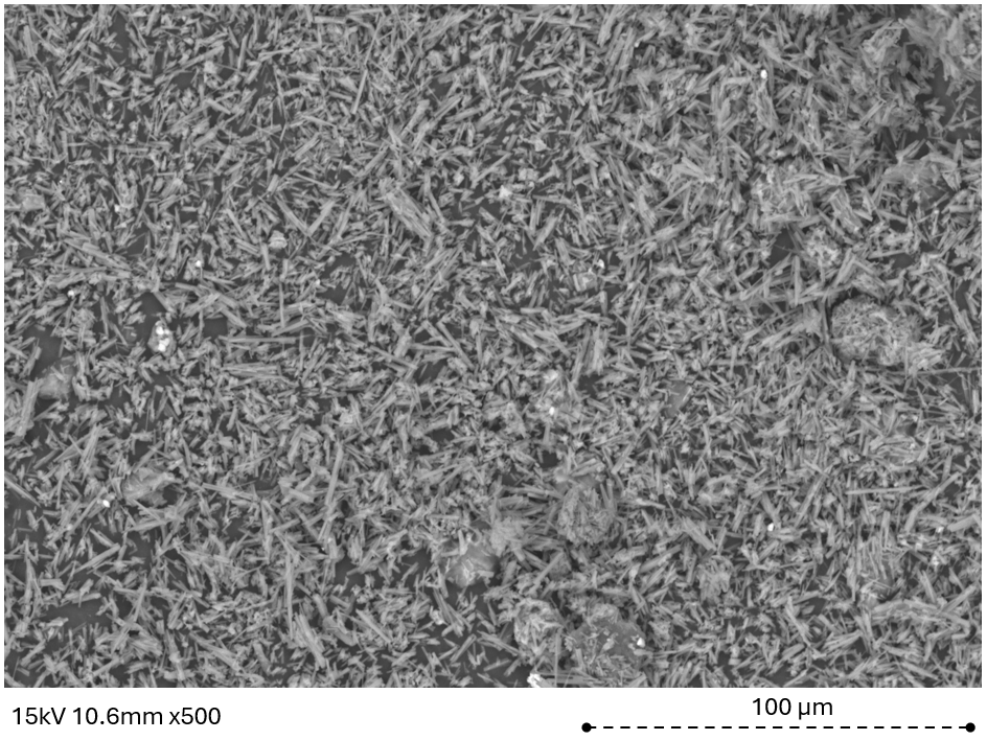
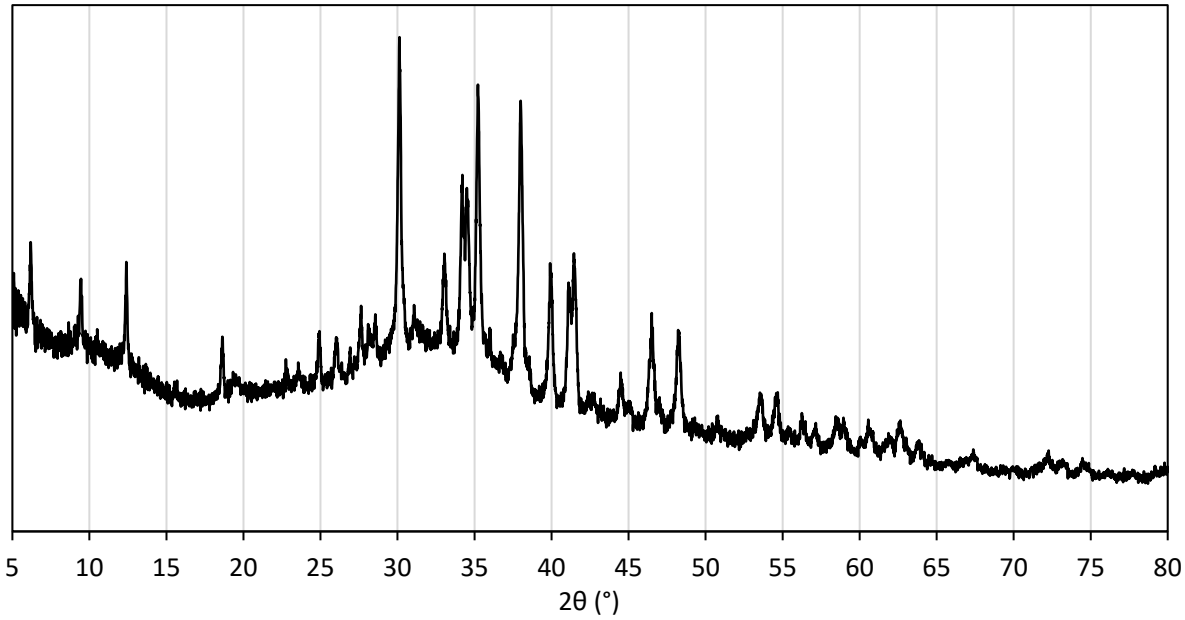


Figure 14. XRD data of the solid product from the carbonation reaction when using the experimental MgSO4 solution



Conclusion

This study focused on optimizing the carbonation reaction of magnesium sulfate (MgSO4) to sequester CO2 in the form of nesquehonite (MgCO3·3H2O). The optimal pH for the reaction was found to be 9.5, as this condition yielded the highest reaction percentage completion. The injection period of ammonia and CO2 significantly influenced the reaction rate, with shorter injection times while maintaining the same absolute amount of ammonia and CO2 leading to faster reactions and higher completion rates. A 15-minute injection period for a 0.2 M MgSO4 solution resulted in rapid supersaturation and efficient nucleation. Moreover, an increase in MgSO4 concentration from 0.2 M to 0.5 M increased the percentage completion of the reaction.

Adjusting the ammonia/MgSO4 ratio impacted both the reaction rate and product morphology. Using excess ammonia (up to twice the stoichiometric requirement) facilitated higher reaction completion but introduced challenges for subsequent process stages with the highest percentage completion being 97.1%. The study showed that an overhead electric stirrer (OES) enhanced mixing but resulted in smaller particle sizes and increased frothiness due to high shear mixing, which disrupted crystal growth and consequently reduced percentage completion of the reaction.

Experiments using the experimental MgSO4 solution demonstrated lower carbonation efficiency, suggesting interference from other ions present in the solution. XRD and SEM analyses confirmed the formation of sodium carbonate rather than nesquehonite, indicating that impurities can significantly affect the carbonation process. Therefore, previous steps within the process should be optimized to prevent disruption of the process.

Overall, the findings emphasize the importance of controlling pH, injection periods, and reactant ratios to optimize the carbonation process for effective CO2 sequestration using MgSO4 solutions.

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