IMPERIAL

Flue Gas Recovery 2 and Testing & Carbonation Procurement

CCUS Innovation 2.0

Key Knowledge Deliverable 1.4

October 2024

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 testing of subsequent flue gas(es). Report to include: source, composition, capture efficiency, reaction time, characterisation of magnesium carbonate product and residual solution. Details of equipment procured for Carbonation stage, with invoices. Report detailing the purpose of each part. Photos / videos demonstrating equipment in location and operational.

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:
nzip@energysecurity.gov.uk

Contents

Abstract

This study investigates the carbonation process of magnesium sulfate (MgSO4) in a cylindrical reactor to produce magnesium carbonate (MgCO3). A 0.2M MgSO4 solution and a 25% ammonia solution were used with CO2 gas to explore the influence of residence time on conversion efficiency and product characteristics. Initial experiments at a 30-minute residence time demonstrated significant agglomeration and blocking issues. Flow patterns within the reactor were analyzed using a dyed solution, revealing suboptimal lateral flow and stagnant regions. Subsequent experiments adjusted the flow rate to achieve a 10-minute residence time, resulting in a yield of 11.9%. To increase residence time without reducing flow, a recycle loop was implemented, effectively doubling the reactor's length and improving the yield to 19.8%. Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) were utilized to characterize the products. The results confirmed the presence of nesquehonite as the primary crystalline phase, with longer residence times favoring the formation of larger, well-defined crystals. This study highlights the importance of optimizing residence time and flow dynamics to enhance conversion efficiency and product quality in carbonation processes.

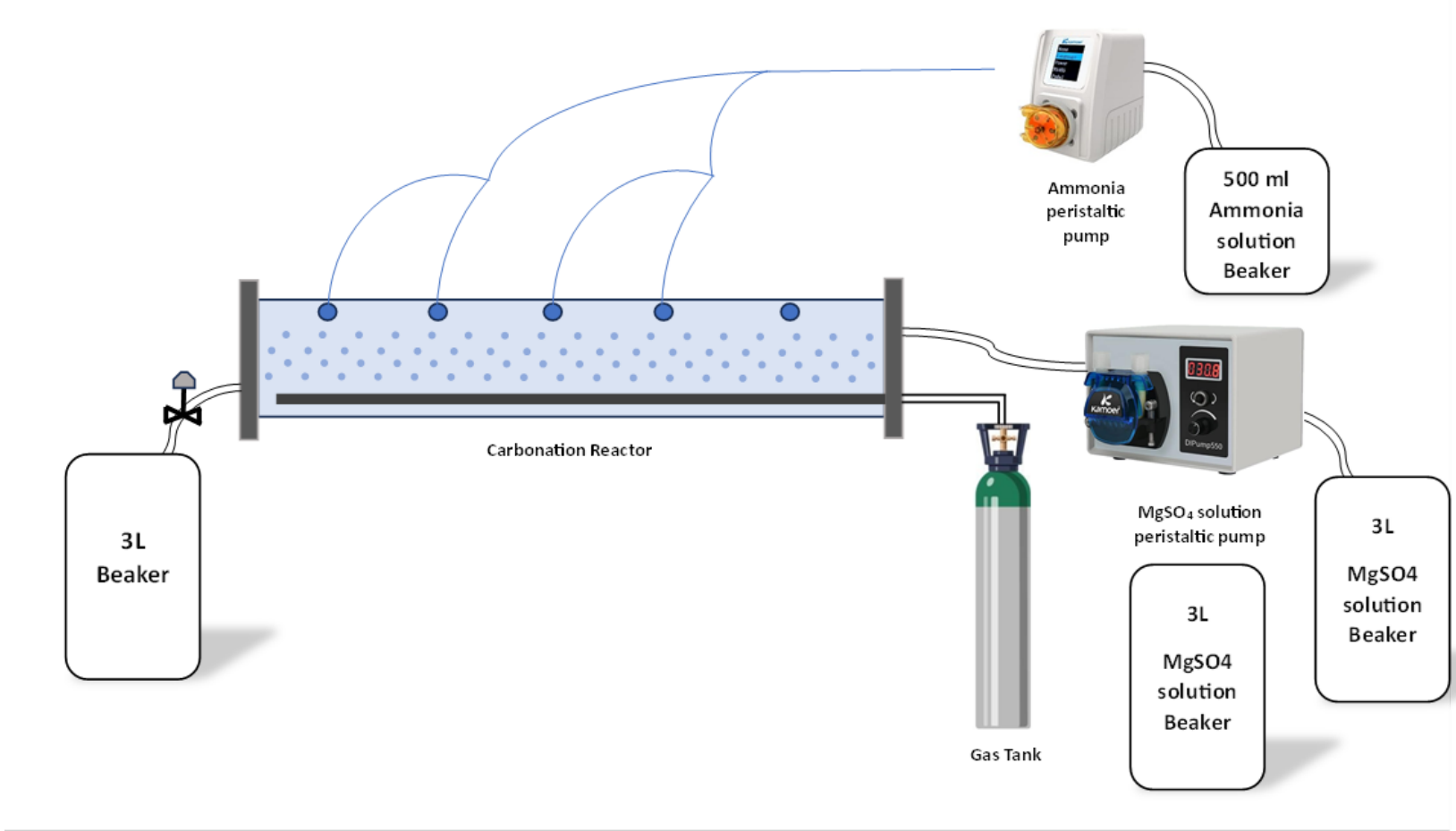
Methodology

Figure 1 demonstrates the experimental set up. A cylindrical carbonation reactor is connected to a 3L beaker at the inlet on the side of the reactor via a peristaltic pump. A 500 ml beaker is filled with 25% ammonia solution connected to the 4 holes on the top of the reactor using Y splitters via another peristaltic pump. A long tubular diffuser is placed across the cylindrical carbonation reactor and connected to a gas inlet. The outlet of the carbonation reactor is connected to a 3L beaker where the product is collected.

Initially a 0.2M $MgSO_4$ solution (made by mixing 148g of $MgSO_4.7H_2O$ crystals in 3 L deionized water) is prepared, filling 3L in the carbonation reactor and another 2x 3L in beakers. A 1.875x stoichiometric ratio of the ammonia solution was used which equates to 459 ml. This was chosen according to previous experiments conducted. The $MgSO_4$ solution in the beaker was set to pump at a specific flowrate to achieve the required residence time. The output valve was calibrated to ensure continuous steady state flow (flow in = flow out). The gas valve was an on and off switch which shows a maximum of 1 L/min flowrate.

To start the experiment the ammonia and $MgSO_4$ peristaltic pumps were switched on while simultaneously opening the solution exit valve and inlet gas flow valve and a timer was started. As the first residence time passes the solution collected in a beaker was disposed of since the exit stream had a variable output flow residence time. The first residence time batch was used to achieve a continuous equilibrium with all the exit flow having the same residence time. Samples were taken at different intervals during the first residence time to see the effect of residence time on conversion. After the first residence time the exit beaker was replaced with an empty one and outlet flow was collected. Samples were taken from the 5 holes on top of the reactor as shown in Figure 1 during the second residence time. The inlet and outlet flows were stopped after the second residence time. The samples collected were filtered using a syringe filter then diluted by a factor of 10. The solution collected in the beaker for the duration of the second residence time is then left for an hour in the beaker before being vacuum filtered and dried at 60°C in a furnace. The filter cake is then characterized using XRD, TG and SEM. Titration tests were conducted to estimate how much magnesium ion is in the samples to estimate the conversion at different residence times.

Figure 1. Carbonation Experimental Setup

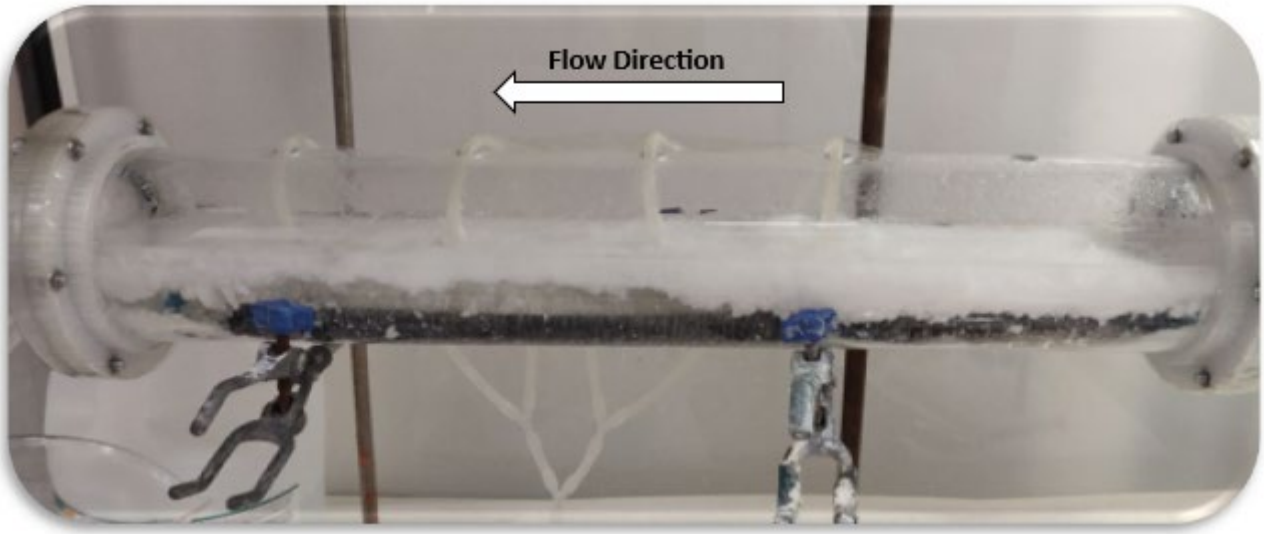


Results and Discussion

Reactor Operation

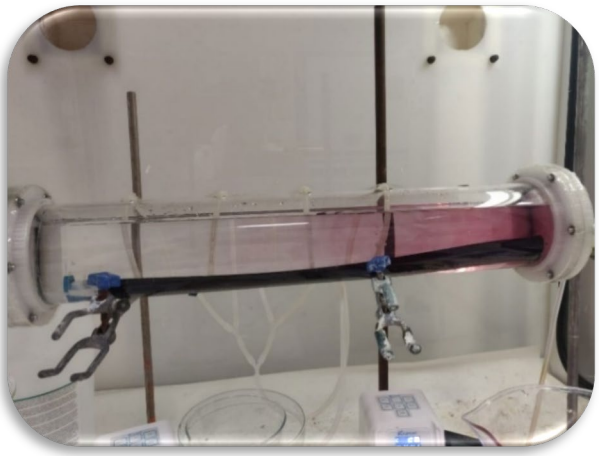
The first experiment was conducted at the following conditions. A residence time of 30 minutes, ~ 0.2 M $MgSO_4$ solution, a 1.875x stoichiometric ratio of ammonia solution (14.7 M), maximum CO_2 flow (0.85 L/min). It was observed that a long residence time allowed for the $MgCO_3$ produced to agglomerate into large particles which resulted in the outlet stream getting blocked. High residence time means decreasing the inlet and outlet flowrates requiring a decrease in outlet pipe diameter, resulting in higher possibility of clogging. Moreover Figure 2 show that some $MgCO_3$ floats and forms a layer on the surface which could be due to the small $MgCO_3$ particles formed being forced to the surface by the CO_2 bubbles allowing for the agglomeration of the $MgCO_3$ at the surface. A possible industrial design for the carbonation reactor can be a circular clarifier which is also used in wastewater treatment which removes the solids that float to the surface of the reactor. Moreover, the $MgCO_3$ formed accumulates in the first half of the reactor which could be due to the slow flowrate which doesn't drive the precipitate laterally to flow across the reactor.

Figure 2. Photograph of the first experiment with 30-minute residence time

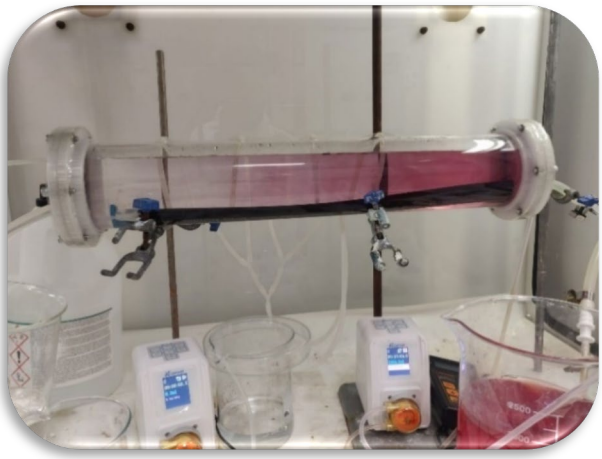


Therefore, before going ahead with another experiment at different conditions another test was conducted to understand the flow across the reactor by pumping in a dyed solution and tracking its flow across the reactor with a 30-minute residence time. The results with time are shown below in Figure 3. The results show that there is flow towards the left, however a higher concentration remains on the right-hand side that doesn't flow towards the exit which could suggest that there could be stagnant areas within the reactor or that the fluid diffusion is faster than the water flow across the reactor. Therefore, in the next test the inlet/outlet flowrates were increased to increase the axial flow across the reactor. We can also draw similarities between how the dye flows across the reactor in Figure 3 and the accumulation of the $MgCO_3$ in Figure2.

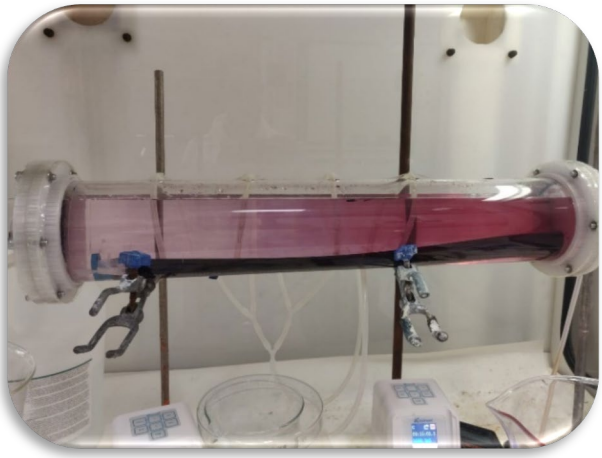
Figure 3. Experiment looking at the lateral flow within the reactor using dye



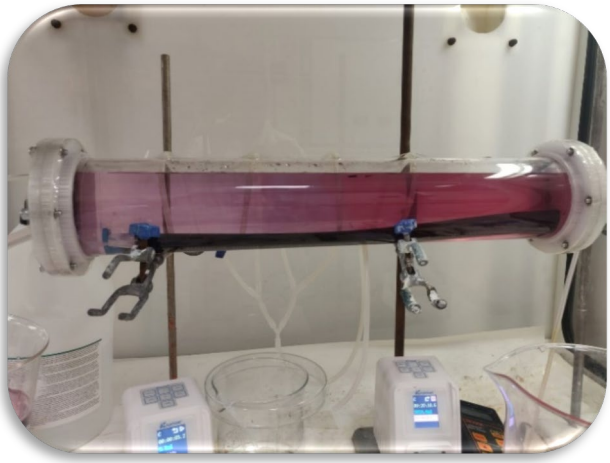
5 minutes



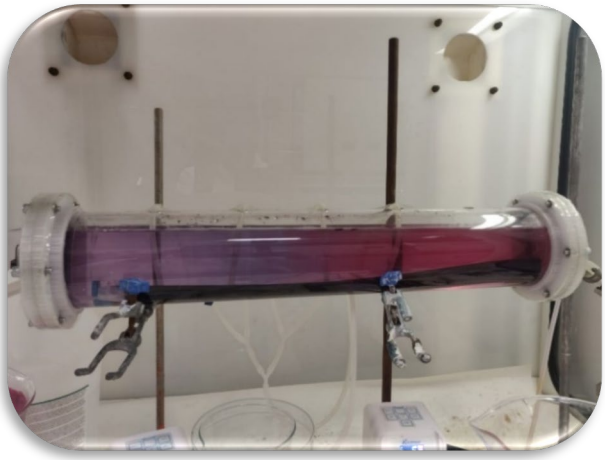
10 minutes



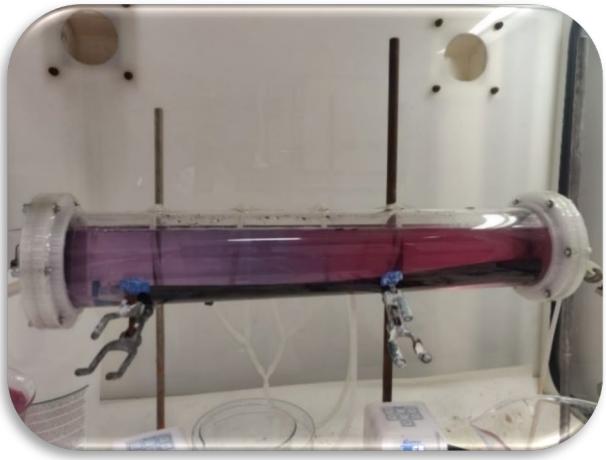
15 minutes



20 minutes



25 minutes

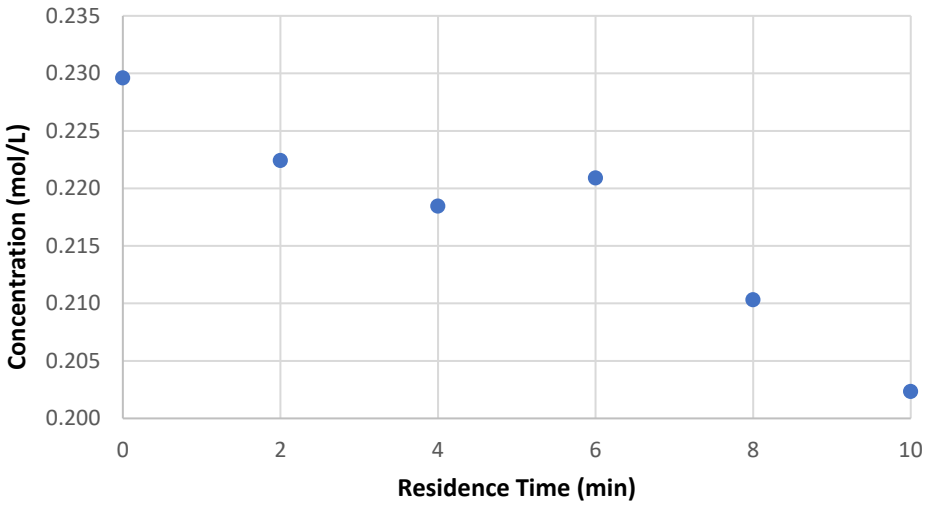


30 minutes

As a result of the person tests, the inlet/outlet flowrates were increased to reduce the residence time to 10 minutes in the hope to improve lateral flow. The all the other conditions were kept the same (~ 0.2 M $MgSO_4$ solution, a 1.875 x stoichiometric ratio of 25% ammonia solution (14.7 M), maximum CO_2 flow of 0.81 L/min). As can be seen in the video attached less $MgCO_3$ accumulating can be observed. Samples at the outlet were collected and tested via titration to measure the concentration of Mg ions at different residence times. Figure 4 below shows the effect of residence time of the carbonation reaction on the concentration of Mg ions in the outlet solution. It can be seen that the Mg concentration decreases as expected with an increase in residence time, with the 6-minute value being an anomaly. The results show that a 10-minute residence time resulted in a yield of 11.9%. The low yield is firstly due to the short residence time which gives less time for the $MgCO_3$ particles to form. The second reason is that a 10-minute residence time requires a stoichiometric flowrate of ~1.54 L/min of CO_2 for a 0.2M $MgSO_4$ solution assuming that all the CO_2 is consumed. However, some of the CO_2 does not dissolve in the solution and escapes at the top of the reactor. It was estimated that the CO_2 capture efficiency was equal to 23%.

Since we are limited by the CO_2 flowrate and want a longer residence time while maintaining/improving the lateral flow across the reactor, the following test conducted was to recycle the outlet stream once. This would theoretically double the length of the reactor hence increasing the residence time while maintaining flow.

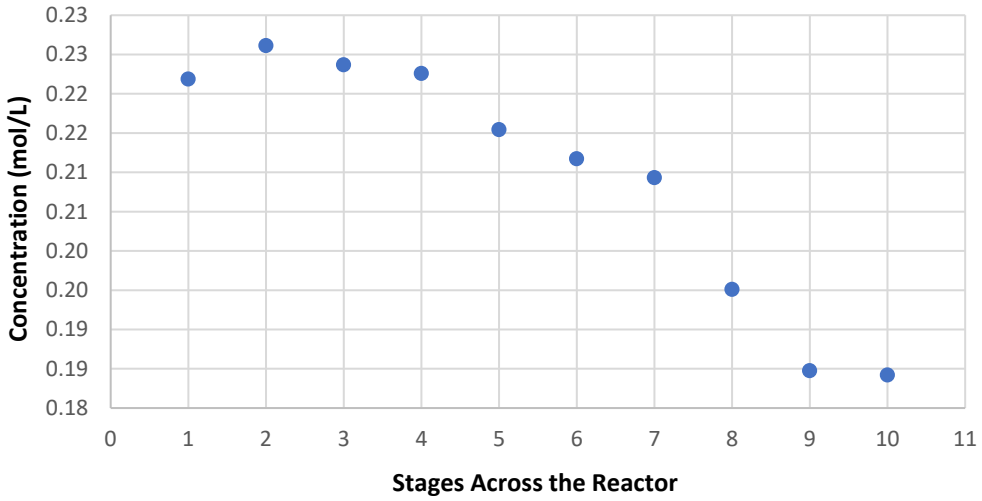
Figure 4. Illustrates the change in Mg concentration of the solution exiting the reactor during the first 10 minutes



The following experiment was conducted with the exact same conditions as the one conducted previously (A residence time of 10 minutes, ~ 0.2 M $MgSO_4$ solution, a 1.875 x stoichiometric ratio of ammonia solution (14.7 M), maximum CO_2 flow 0.81 L/min) with the addition of a recycle stream. The increases the theoretical residence time across the reactor to 20 minutes. The results below show that a 20-minute residence time with a recycle loop resulted in a yield of 19.8%, which is an increase to the 10-minute residence time. Figure 5 shows a decrease in Mg ions concentration across the reactor. The stages across the reactor 1 – 5 represent that

sample were taken from the 5 holes across the reactor in the first cycle, 6 – 10 represent the same respective holes for the second cycle.

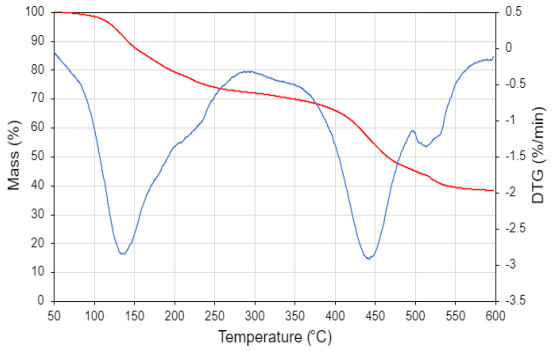
Figure 5. Illustrates the change in Mg concentration within the solution across the reactor for the 20 minutes resident time (10 minutes recycle) experiment



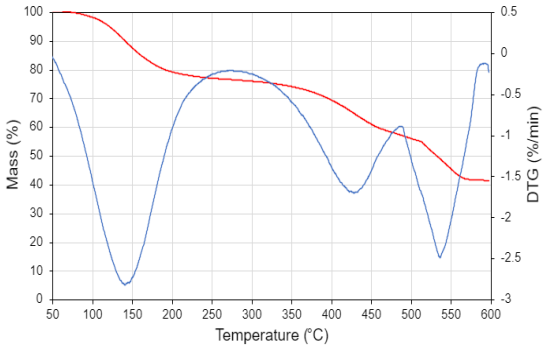
Thermogravimetric Analysis

Figure 6. TGA (red) and DTG (blue) analysis of 10-minutes sample (top left), 10-minutes recycle sample (top right), and 20-minutes recycle sample (bottom left)

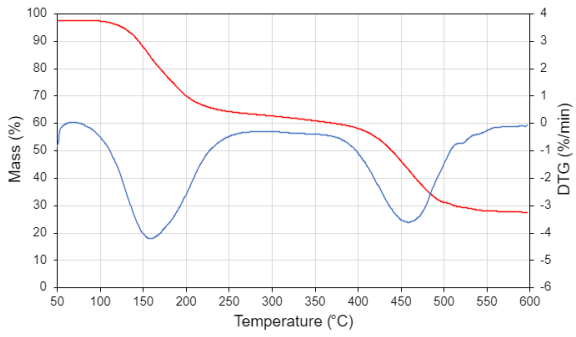
10 Minutes



10 Minutes Recycle



20 Minutes Recycle



The TGA graphs for the samples in Figure 6 exhibit distinct mass losses in the 400°C – 500°C range, suggesting the formation of carbonate species in all three reactions. This temperature range is indicative of the decomposition of carbonate compounds. Among the analyzed samples, the 20-minute recycle TGA shows the closest alignment with the literature data for nesquehonite. The primary discrepancy between this sample and the literature is a lack of resolution between the three individual water peaks occurring between 100 °C and 200 °C. This difference is likely due to the experimental conditions, specifically the use of a 10 K/min heating rate rather than the 5 K/min rate commonly used in literature, which can affect the thermal resolution.

The initial dehydration mass loss of nesquehonite, based on literature, is approximately 40%. However, both the 10-minute and the 10-minute recycle samples exhibit less mass loss than anticipated. This reduced mass loss may be attributed to under hydration, resulting in a lower amount of coordinated water within the samples. Consequently, the hydrated carbonate formula for these samples can be considered as $MgCO_3.xH_2O$, where x is less than 3. Calculations reveal that for the 10-minute sample, x equals 2, and for the 10-minute recycled sample, x equals 1.3. This reduced hydration level indicates that these samples are in the relatively early stages of carbonate formation.

An anomalous sharp triangular peak observed at 530 °C in the 10-minute recycle sample is likely due to an experimental error, necessitating a re-analysis of the sample to confirm its thermal behavior. Despite this error, the mass loss observed up to this point remains lower than expected, suggesting incomplete carbonate decomposition or other experimental anomalies.

Additionally, both the 10-minute and 10-minute recycled samples exhibit a significant shoulder peak around 525 °C. This feature may indicate the formation of a different form of carbonate, potentially an amorphous phase. Such phases can form prior to the crystallization of nesquehonite and are sometimes observed in carbonate systems. This interpretation is supported by XRD (X-ray Diffraction) analysis of the 10-minute recycle samples, which suggests the presence of an amorphous carbonate phase. The appearance of these features and phases underscores the complexity of carbonate formation and the potential influence of experimental conditions on the thermal and structural properties of the samples.

X -Ray Diffraction Analysis

Figure 7. SEM imagery of 10-minutes sample (top left), 10-minutes recycle sample (top right), and 20-minutes recycle sample (bottom left)

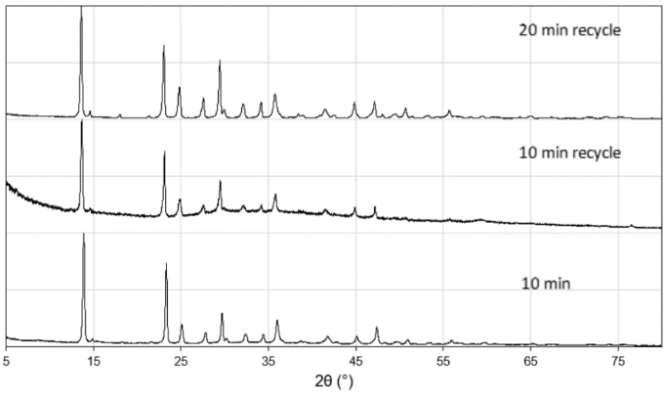
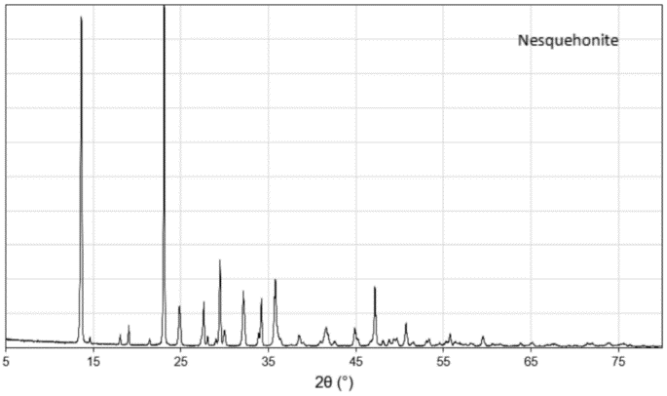


Figure 8. SEM imagery of 10-minutes sample (top left), 10-minutes recycle sample (top right), and 20-minutes recycle sample (bottom left)



XRD analysis (Figure 7) of all the samples tested indicates that the only crystalline phase present is nesquehonite, a hydrated magnesium carbonate. This suggests that the primary crystalline product of the reactions is consistently nesquehonite across different sample conditions. Notably, no significant quantities of other salts were detected in the XRD patterns. However, Scanning Electron Microscopy (SEM) imagery of the 10-minute sample reveals the presence of some salts. The salts observed via SEM are not prevalent enough to be detected by XRD, which implies that their concentration is below the detection threshold of the XRD technique.

Furthermore, the XRD diffractogram of the 10-minute recycle sample displays a prominent hump in the 20 – 50 2θ° range. This broad feature is indicative of an amorphous fraction within the sample, suggesting that not all of the material has crystallized into nesquehonite. The presence of this amorphous phase could be due to incomplete crystallization or the presence of other non-crystalline materials.

To fully assess the amorphous content of the 10-minute recycle sample, Quantitative X-ray Diffraction (QXRD) will be employed. QXRD is a more refined analytical technique that allows for the quantification of both crystalline and amorphous phases within a sample. By using

QXRD, it will be possible to obtain a more accurate and detailed understanding of the composition of the sample, particularly the proportion of amorphous material relative to the crystalline nesquehonite. This detailed analysis is crucial for understanding the formation processes and stability of the carbonate phases within the sample.

Scanning Electron Microscope Analysis

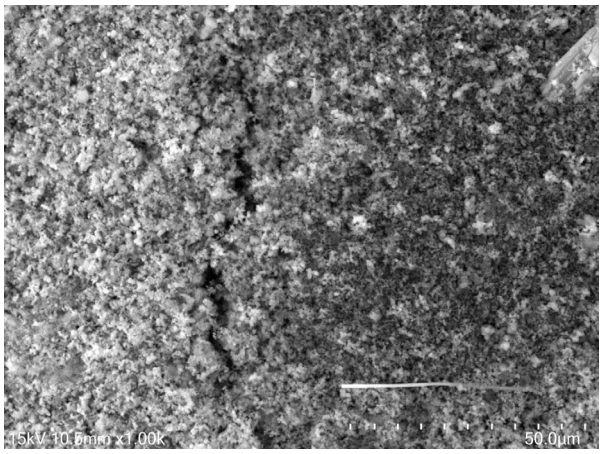
SEM analysis of the 10-minute sample reveals it is under-washed, which complicates the proper assessment of the image. Despite this, nesquehonite crystals are clearly present and are approximately 100 μm in length. These findings suggest that the sample, although not thoroughly washed, still contains a significant amount of crystalline nesquehonite. This incomplete washing likely leaves behind residues that obscure a clearer view of the sample's morphology and purity.

In contrast, the SEM analysis of the 10-minute recycle sample does not show the characteristic needle-shaped crystals typically associated with nesquehonite. Instead, the particles in this sample are small and ill-defined. This observation is consistent with the presence of an amorphous phase, as suggested by the XRD data, which showed a significant hump in the diffractogram between 20 – 50 2θ°. The amorphous nature of the particles indicates that the carbonate formation process is incomplete or that the sample includes non-crystalline materials.

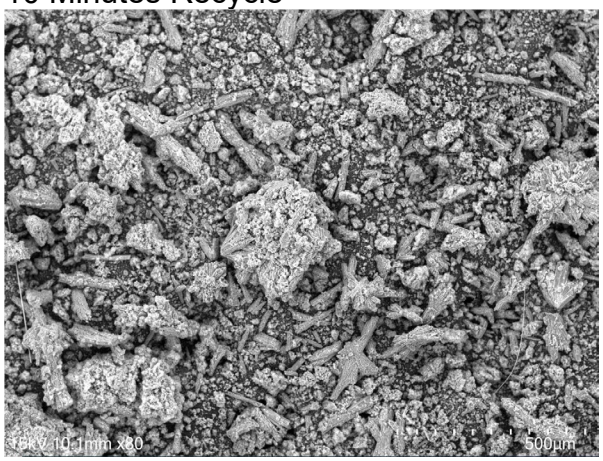
The SEM imagery of the 20-minute recycled sample presents a starkly different picture. This sample shows well-defined nesquehonite crystals that exceed 150 μm in length. In addition to their size, some of these crystals exhibit dumbbell-shaped and spherical growth patterns. These morphological features are commonly observed when carbonation occurs with pure CO2 over longer periods, leading to more extensive crystal growth. The large and well-formed crystals in this sample indicate a more complete and efficient carbonation process compared to the 10-minute samples.

Figure 9. SEM imagery of 10-minutes sample (top left), 10-minutes recycle sample (top right), and 20-minutes recycle sample (bottom left)

10 Minutes



10 Minutes Recycle



20 Minutes Recycle

The presence of large particles, as seen in the SEM image of the 20-minute recycled sample, has practical advantages for material workability and water demand. Larger particles are generally easier to handle and mix, which is beneficial for industrial applications. Additionally, materials with larger particle sizes tend to require less water to achieve a workable consistency, which can be advantageous in various processing and application contexts. Therefore, targeting the conditions that produce these larger, well-defined nesquehonite crystals is a desirable goal for future experiments and applications.

Conclusion

The experimental investigation into the carbonation of magnesium sulfate has highlighted key factors influencing the process efficiency and product characteristics. Initial experiments with a 30-minute residence time indicated significant agglomeration and blockage issues due to prolonged exposure. Adjusting the residence time to 10 minutes improved lateral flow and reduced clogging but yielded a lower conversion efficiency of 11.9%. Implementing a recycle loop to extend the residence time to 20 minutes proved effective, increasing the yield to 19.8% and producing larger nesquehonite crystals. Characterization techniques confirmed the formation of nesquehonite across different conditions, with longer residence times and recycling enhancing crystal growth and quality. The study demonstrates that optimizing flow dynamics and residence time is crucial for efficient carbonation processes, providing valuable insights for industrial applications aiming to produce high-quality magnesium carbonate.

Invoices/Receipts

Reactor (from Plastic Oline Ltd.) Receipt

Items	Qty	Price
100mm Diameter Clear Acrylic Tube SKU: TUBE-100 ***Length*** 550	1	exc VAT: £16.98 inc VAT: £20.38
Amber Orange Tint 300 Acrylic Shapes SKU: L-TI-AMB5L ***Shape*** Circle With Hanging Hole ***Thickness*** 5mm ***A (Overall Diameter)*** 100mm ***B (Diameter of Hanging Hole)*** 5mm ***C (Distance Of Hole From Edge)*** 13mm ***Edge Finishing*** included	2	exc VAT: £5.22 inc VAT: £6.26
750mm x 1000mm SKU: 75X100-5S-CA-CLR ***Thickness*** 5mm	1	exc VAT: £33.83 inc VAT: £40.60
Dichloromethane Acrylic Adhesive SKU: PO3-500 ***Size (ml)*** 500ml	1	exc VAT: £9.80 inc VAT: £11.76
	Subtotal (Excl. VAT)	£65.83
	Subtotal (Incl. VAT)	£79.00

Ammonia Pump Receipt

Invoice details

Description	Qty	Unit price (excl. VAT)	VAT rate	Unit price (incl. VAT)	Item subtotal (incl. VAT)
Stepper peristaltic Pump 24V Small Intelligent Variable Speed high Flow lab Liquid dosing Pump Kamoer DIP 3 rotors 0-452 ml/min BPT Tube 4.8 mm ID x 8 mm OD | B07H3NFSSD ASIN: B07H3NFSSD	1	£112.50	20%	£135.00	£135.00
Shipping Charges		£1.66		£1.99	£1.99
Promotions		-£1.66		-£1.99	-£1.99
		Invoice total			£135.00

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