Reagent Regeneration Operation

CCUS Innovation 2.0

Key Knowledge Deliverable 2.4

March 2025

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 the complete experimental plan for the remainder of this work package and intermediate results. The testing will include strength and durability results of magnesium carbonate products manufactured via the route(s) determined in D4.2 with various additions of filler and fibre materials to optimise performance.

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:
industry.innovation@energysecurity.gov.uk

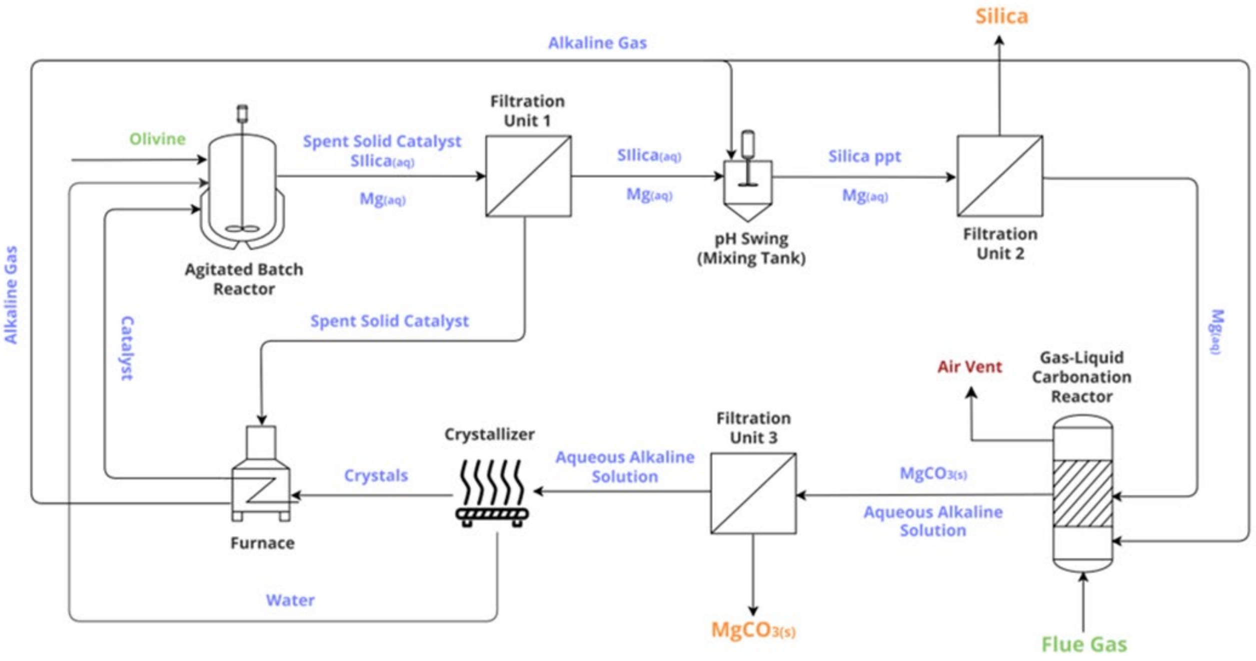
Contents

Introduction

Aims and Objectives

The aim of this report is to integrate the process stages optimized in the previous reports. These stages include dissolution, pH swing, carbonation, crystallization and finally regeneration. This is to provide a deeper understanding of process integration and operation and allow us to be better prepared for scaling up. This will mitigate potential setbacks during commercialization and pilot-scale operations, reducing risks and ensuring a smoother transition to larger-scale production. Figure 1 illustrates the integrated process flow diagram for the carbon mineralization technology.

Figure 1. Simplified process flow diagram of the carbon mineralisation process.



Methods

Experimental Setup and Steps

The operation of the full CCUS process conducted at lab scale requires approximately one week per cycle. This does not include additional time required for drying samples and analyzing the purity and yield of the products. As each cycle requires as full understanding of the purity of the products from the previous cycle, approximately 10 – 12 days are required per cycle. Over the 8 months of operation approximately half of the available time was dedicated to operating the process, with the remaining time spent collecting the required data for each of the intermediate and final products.

Dissolution Setup and Reaction Mechanism

The dissolution experiment is conducted using a 3 L beaker reactor on a hotplate inside a fume cupboard. Initially commercially sourced “catalyst” is dissolved in water filling the beaker up to 1.2 L. The extra 200ml of water was added because water is expected to evaporate during the reaction when samples are taken. The theoretical amount required to dissolve 78.5g of olivine to produce a 1M Mg2+ solution was used. The beaker was sealed with a cling film to reduce the amount of water loss during the dissolution reaction. A magnetic stirring was used, and the temperature of the beaker increased to roughly 80°C. This takes place for ~15 minutes to ensure all the catalyst is dissolved. Once all the catalyst is dissolved, 78.5g of olivine is added. A sample is taken before adding the olivine and at different time intervals during the reaction. The reaction is allowed to take place until the solution becomes clear, indicating reaction completion. When the reaction is complete, the hotplate is switched off, followed by filtering the mixture (solid spent catalyst from the solution) using a vacuum pump. The solid spent catalyst is placed in a 60°C oven to dry overnight. The sample is weighed to calculate the yield.

Material characterization is then conducted on the spent catalyst. The samples taken during the dissolution were diluted by 100x using 0.1M nitric acid solution so that the concentration of Mg is <50ppm and to prevent precipitation. The diluted samples are then tested using an Inductively Coupled Plasma Spectroscopy for elemental analysis.

The overall reaction taking place in the dissolution process is:

{redacted} [Eq. 1]

This reaction can be broken down into three sub-reactions.

The catalyst dissolves in water and creates an acidic solution

{redacted} [Eq. 2]

The acid in the solution reacts with the olivine, dissociating it to produce MgSO4 and Silica

{redacted} [Eq. 3]

The formation of spent catalyst

{redacted} [Eq. 4]

pH Swing Setup and Reaction Mechanism

The solution recovered from the previous filtration step is an acidic solution which contains aqueous silica, MgSO4 and an alkali sulfate. An alkaline solution is added to the solution while gently mixing and measuring the pH. The pH is increased to 8 to allow all the silica to precipitate while ensuring that the Mg does not precipitate. This is followed by a filtration step to separate the silica, and everything else that precipitated, from the rest of the solution. The silica is then placed in a 60°C oven to dry overnight. The silica is then weighed to calculate the yield.

Material characterization is then conducted on the silica which included XRD analysis using a Rigaku MiniFlex 600 and XRF using Malvern Pananlytical Zetium. A pressed pellet was used with cellulose as the binder to create the pellets for the XRF analysis. The reaction that takes place is:

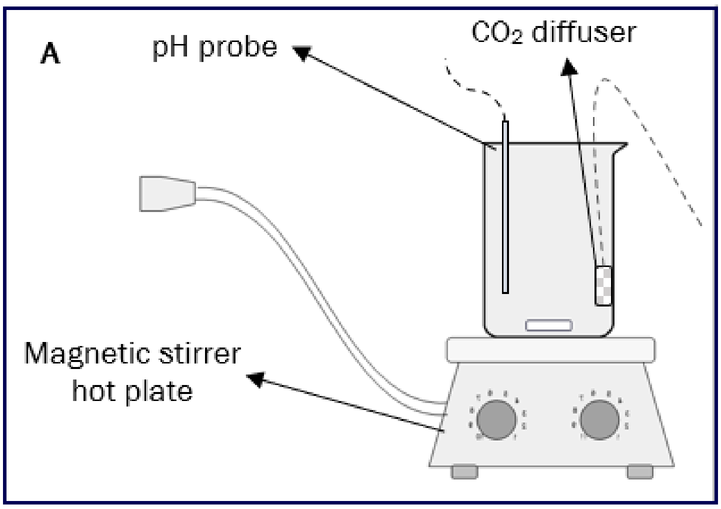
{redacted} [Eq. 5]

Carbonation Setup & Reaction Mechanism

The experiment was conducted as a semi-batch operation in a 3 L beaker (reactor). The reactor is connected to a peristaltic pump that allows for constant flow of an alkaline 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 required pH. The experiment was conducted as shown in Figure 2 using a magnetic stirrer. The pH of the solution was initially measured and then the alkaline solution gradually added dropwise while continuously stirring until the pH of the solution reached 9.5. The pH was closely monitored to avoid overshooting the desired pH. Before starting the reaction, a 1.5 mL sample was taken of the solution. The sample was diluted by a factor of 100 using 0.1M nitric acid solution. The alkaline solution peristaltic pump was set to the desired flow rate. The CO2 flowmeter was calibrated and set to maintain the desired pH during the reaction. Simultaneously the alkaline solution peristaltic pump and the CO2 flow were switched on. Continuous stirring was maintained to ensure uniform mixing throughout the reaction. Samples were collected at specified time intervals during the reaction. Each sample was diluted by a factor of 100 using 0.1M nitric acid. At the end of the reaction, the solution is filtered using a vacuum filter to separate the solid product. The solid is dried in an oven at 60°C overnight to ensure complete removal of moisture.

Material characterization is then conducted on the MgCO3 which included XRD analysis using Rigaku MiniFlex 600 and XRF elemental analysis using Malvern Pananlytical Zetium. A press pellet was used with cellulose as the binder to create the pellets for the XRF analysis.

Figure 1. Lab based carbon mineralization experimental setup



The overall reaction taking place in the carbonation process is:

MgSO4 + CO2 + alkaline solution + 2 H2O → MgCO3.3H2O + alkali sulfate [Eq. 6]

Step 1: Formation of Carbonate ions

Dissociation of alkali in solution:

alkali → alkali+ + OH– [Eq. 7]

Reaction of CO2 with Hydroxide Ions:

CO2 + OH– → HCO3– [Eq. 8]

HCO3– + OH– → CO32– + H2O [Eq. 9]

Formation of alkali carbonate (in the presence of excess alkaline solution):

alkali+ + CO32– → alkali carbonate [Eq. 10]

Step 2: Formation of Magnesium Carbonate

Dissociation of Magnesium Sulfate:

MgSO4 → Mg2+ + SO42– [Eq. 11]

Reaction of Magnesium Ions with alkali carbonate:

Mg2+ + CO32– MgSO4 → MgCO3 [Eq. 12]

Formation of alkali Sulfate:

alkali+ + SO42– → alkali sulfate [Eq. 13]

Step 3: Hydration of Magnesium Carbonate

Hydration of Magnesium Carbonate:

MgCO3 + 3 H2O ® MgCO3.3H2O [Eq. 14]

Crystallization Setup and Reaction Mechanism

The remaining solution after the filtration during the carbonation step is then placed in a beaker and placed on a hot plate at maximum temperature. This evaporates the water in the solution until it reaches saturation point. The solution is then transferred into a cylindrical container and placed in a 105°C oven. When the crystals are formed and dried, they are weighed to calculate/measure the yield.

Material characterization is then conducted on the crystals which included XRD analysis using Rigaku MiniFlex 600 and XRF elemental analysis using Malvern Pananlytical Zetium. A press pellet was used with cellulose as the binder to create the pellets for the XRF analysis.

Regeneration Setup and Reaction Mechanism

The spent catalyst produced from the dissolution process and the alkali sulfate crystals from the crystallization process are mixed, crushed using a pestle and mortar and placed in a crucible. The crucible is placed inside a furnace at 380°C for 2 hours (Carbolite furnace).

Material characterization is then conducted on the catalyst via XRF elemental analysis using Malvern Pananlytical Zetium. A press pellet was used with cellulose as the binder to create the pellets for the XRF analysis.

Below is the reaction that takes place in the furnace.

{redacted} [Eq. 15]

Results and Discussion

In the course of optimizing and testing the entire process, the work was divided into two sets of cycles. The first set of cycles (round 1) involved 6 cycles where several learning outcomes were gained. These learning outcomes were then applied in the second set of cycles (round 2) which involved 4 cycles.

Round 1

The feed values for each cycle as well as the percentage yield of the products and intermediates for the first 6 cycles is presented in Table 1.

Table 1. Feed values for each cycle as well as the percentage yield of the products and intermediates

Regeneration	1	2	3	4	5	6	7
Raw Materials							
Olivine (g)	78.5	78.5	78.5	78.5	78.5	78.5	78.5
Catalyst (g)	507	280	280	280	280	280	280
Water (ml)	1200	1200	1200	1200	1200	1200	1200
Alkaline solution (ml) - pH swing	57	43.5	12	8	13	14	NA
Alkaline solution (ml) - Carbonation	1x stoic	1.5x stoic	2x stoic	2x stoic	2x stoic	2x stoic	NA
Products							
Spent catalyst (g)	120.4	93.4	107.4	115.7	82.9	90.2	NA

Regeneration	1	2	3	4	5	6	7
Silica (inc. Fe(OH)3)	179.0	254.3	98	47.6	48.3	46.7	NA
MgCO3	26.3	19.3	26	36.9	37.4	40.3	NA
Alkali sulfate	74.5	/*	74.8	91.8	75.1	76.3	NA

*Mishandling led to loss of material, hence commercial alkali sulfate was used instead

Dissolution Step 1.0

Figures 3A and 3B illustrate the ICP results for the effect of Mg concentration with time during the dissolution reaction for 7 cycles, respectively. The time to stop the reaction was when the solution became clear. However, for cycle 1 the solution took longer than expected, ~ 2 hours, to become clear. This is due to the hydrated commercial catalyst which was used for the first cycle reducing the rate of reaction. Hence, for cycle 1 the reaction was stopped after three hours (the solution was not completely clear). Figure 3A shows that the initial concentration decreases every cycle, which indicates that the amount of catlayst regenerated decreases every cycle. However, top-up precursor was added at the start of cycles 6 and 7 to increase the concentration, resulting in more olivine dissociating which increased product yield.

Figure 3B shows that the amount of Mg in the solution reaches a maximum of 0.67M whereas in theory the amount of olivine added should allow the concentration to reach 1M. However, since it did not, this suggests that not all the olivine was reacted (dissociated). It can also be seen that the initial amount of Mg every cycle increases gradually. This could be due to some Mg being recycled with the catalyst which as a result increases the initial concentration of the Mg in the solution. The rate of Mg increases in the solution, although final concentration is different due to the reaction being stopped at different times.

This explains why the catalyst regeneration yield (120.4%) as shown in Table 1 is above 100% which is due to the unreacted olivine that adds to the weight of the filtered spent catalyst after the dissolution stage. Additionally some insoluble solid impurities may build up in the spent catalyst. A way to get rid of the solid impurities is by adding a filtration step after dissolving the catalyst and before adding the olivine. This allows all the soluble catalyst to dissolve while the solid insoluble impurities can be filtered. This was done at the start of cycle 2 which resulted in the catalyst regeneration yield dropping and below 100%. However, for the following cycles the yield increased since the filtration step was not done. This coupled with a decrease in the amount of catalyst, resulted in a less acidic solution hence less olivine dissociation. The build up of unreacted olivine is what contributed to the yield going over 100%. Another filtration was done at the start of cycle 5 (post catalyst dissolution and pre olivine mixing) which brought the yield back down. Additionally, since it was observed that the amount of precursor decreased via the decrease in concentration from Figure 3A, 40g top-up catalyst was added to ensure more olivine was being dissolved. The following cycle (cycle 6) 60g of top-up catalyst and 80g for cycle 7 was added to try and push the initial concentration in the solution, which corresponds to more H+ ions to dissolve the Olivine.

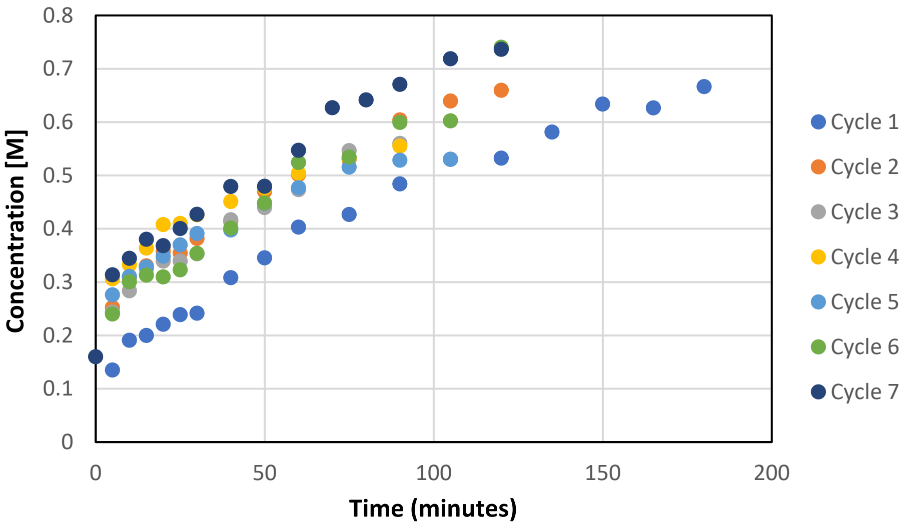
Cycle 7 was allowed to run for as long as possible to produce the spent catalyst while dissociating all the olivine. However, the longer the reaction takes place and the more H+ ions are consumed to dissociate the olivine. This resulted in the pH of the solution increasing to the point where the silica started gelling within the solution and mixing with the spent catalyst making separation difficult. This made it a lot harder to separate the spent catalyst from the silica, hence the cycles were stopped. Another factor that could have induced gelling of the silica is the solubility of the silica, since some water might have evaporated, resulting in its precipitation. The samples collected from cycle 7 was also analysed using ICP and plotted on Figures 3A and 3B. The concentration of Mg reached 0.74 M at the end of the reaction, which is after allowing the reaction to run to for 2.5 hours, resulting in the gelling of the silica, forming a silica-spent catalyst mix. The higher concentration could be due to loss of some water via evaporation.

Due to the gelation that occurred during the operation of cycle 7, only the data collected during the dissolution could be used. This data, as with previous dissolutions, is provided in figure 3. The cross contamination of silica, residual olivine, and spent catalystmeant that accurately determining the yields of these products was not possible. Because of this, only the initial conditions of cycle 7 are outlined in Table 1. Additional data such as the XRF composition of solid products and XRD characterization does not include data for cycle 7, as the solid products were deemed unsuitable for further testing.

Figure 3. ICP results of the concentration of {redacted} (A) and Mg (B) from cycles 1 to 7 (round 1) at different intervals.

A) {redacted}

B) Magnesium Concentration



According to the XRD diffractogram in Figure 4 we can see peaks matching the spent catalyst which proves that that we are producing spent catalyst, however we can also see some Forsterite, Chabazite, Vermiculite and Lizardite peaks in the spent catalyst sample, which is impurities from the unreacted olivine.

Table 2 presents the XRF elemental analysis of the spent catalyst. We can see that the amount of SiO2 which partially gels and mixes with the spent catalyst during the dissolution decreases during the cycles when insoluble solid impurities are separated. A better way to calculate the yield would be to estimate the amount of spent catalyst there is in the sample by estimating the amount of a specific element in the spent catalyst. This will also help in the regeneration step allowing for a more accurate stoichiometric balance between spent catalyst and alkali sulfate. However, since the XRF data in Table 2 disregards the mass of water molecules in the spent catalyst sample, a loss on ignition test is helpful to estimate how much spent catalyst there is in the sample.

Table 2. XRF data of the spent catalyst produced from cycles 1 to 6.

{redacted}

Figure 4. XRD diffractogram of the spent catalyst produced from the dissolution for cycles 1 to 6. Green dot (Chabazite), Blue diamond (Vermiculite), Cyan star (Forsterite), Yellow triangle (spent catalyst).

{redacted}

pH Swing 1.0

During the pH swing we can see that more alkaline solution was required for cycles 1 and 2 to increase the pH to 8 (Table 2). This is required to ensure all the silica has precipitated while the Mg remains in the solution.

According to the XRF data (Table 3) high percentage of Mg and SO3 residues can be seen on the silica in cycles 1, 2 and 3 compared to cycles 4, 5 and 6. This is because the silica from the first 3 cycles was not washed, whereas for Cycle 4 the silica has been dried, milled and washed hence no sulfates remained due to it being thoroughly washed whereas cycle 5 silica was not milled properly before being washing which allowed for some sulfates and Mg trapped within the silica to remain, hence was not washed thoroughly. This suggests that the silica will require a milling stage before washing. It can also be observed that the percentage of silica within the sample increases.

The silica produced during the process should be amorphous. However according to the XRD diffractogram of the samples from Cycle 1 – 6 (Figure 5), we can see that the cycles 1 – 3 do not demonstrate a broad hump which would alludes to the amorphous nature of the silica, rather it shows sharp diffraction peaks. This is due to the high amount of crystalline alkali sulfates which overshadows the amorphous nature of the silica in the XRD diffractogram. Cycles 1 and 3 have a slight hump which shows that there is amorphous silica, whereas cycle 2 shows a very insignificant hump which is due to only 18% of the sample being silica according to the XRF.

Cycles 4, 5 and 6 have a broad hump with no sharp peaks due to the silica being washed which removes the soluble residual impurities. The broad hump represents the amorphous silica. Cycles 5 and 6 have a very tiny peak around 21° which corresponds to alkali sulfate. This is expected due to the higher SO3 value in cycles 4 and 5 compared to cycle 3 as shown in Table 3.

Table 3. XRF data of the silica produced from cycles 1 to 6.

{redacted}

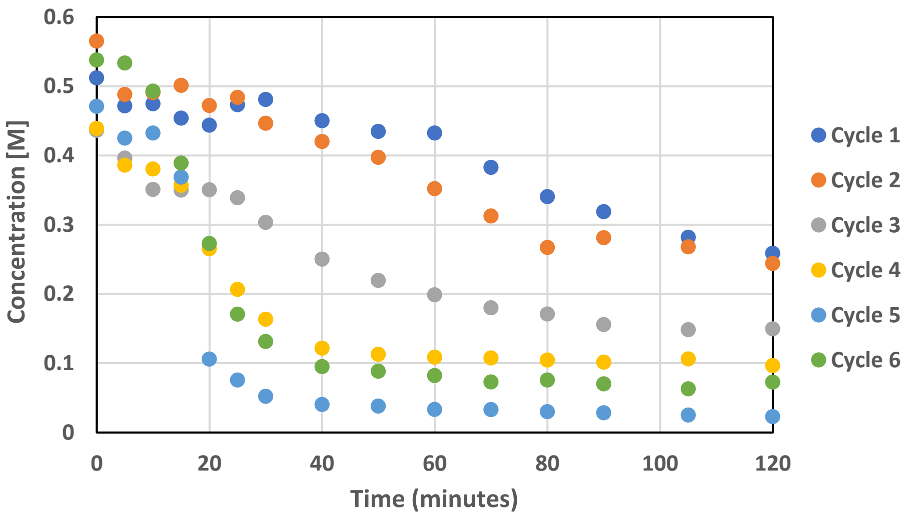
Figure 5. XRD diffractogram of the silica from the pH swing for cycles 1 to 6.

{redacted}

Carbonation 1.0

The carbonation results from the ICP in Figure 6 show a decrease in Mg concentration with time. This is due to the Mg in the solution being carbonated to form MgCO3. Cycles 1 and 2 had a lower rate of consumption of Mg and a higher final concentration of Mg after 2 hours compared to cycle 3, while cycle 3 had a lower rate of Mg consumption and a higher Mg final concentration compared to cycles 4,5 and 6. This is because x2 the stoichiometric requirement of alkaline solution was used in cycles 4,5 and 6 which resulted in higher yields whereas cycle 3 used x1.5 amount of stoichiometric amount of alkaline solution while cycles 1 and 2 used x1. The higher amount of alkaline solution requires a higher flowrate of CO2 to maintain the pH around 9.5, hence increasing the concentration of CO2 in the solution resulting in a shift to increase the amount of Mg consumed to produce MgCO3. It can also be seen in Table 1 that the yield increases with an increase in the amount of alkaline solution added during the reaction. A dip in the yield during cycle 2 was observed, this corresponds to the silica from cycle 2 containing highest percentage of MgO (16.18%), showing that some Mg was lost in the silica which resulted in the yield dropping. Since washing water used to wash the silica is added back into the process, the MgCO3 yield increased in cycle 4, 5 and 6.

Figure 6. ICP results of the concentration of Mg during the carbonation at different intervals for cycles 1 to 6.



According to the XRD diffractogram in Figure 7 it can be concluded that in all the cycles, the MgCO3 product was in the form of nesquehonite with some showing additional peaks which represent silica and other phases. According to the XRF data in Table 4 it seems that these other phases are formed when there is a high amount of silica within the carbonation product. It can also be seen from the XRF data that the carbonation product from cycle 1 had a large amount of sulfate. This is due to low amount of alkaline solution feed during the reaction, hence some of the magnesium remained as MgSO4 and other magnesium sulfates as shown in Figure 7.

Table 4. XRF data of the carbonation product from cycles 1 to 6

{redacted}

Figure 7. XRD diffractogram of the carbonation product for cycles 1 to 6.

{redacted}

Crystallization 1.0

Table 5 illustrates the XRF elemental analysis data of the crystallization process product. There was no sample for cycle 2 due to mishandling of the process, hence commercial alkali sulfate was used during the regeneration step. Both cycles 1 and 3 have increased amounts of Mg compared to cycles 4, 5 and 6. This is due to less carbonation taking place, as seen in Figure 6, resulting in higher Mg concentration remaining in the solution post-carbonation. The presence of high Mg content results in the crystallization product forming other sulfates, including those with bound water which increases the weight of the product. The presence of hydrated sulfates can be detected from the XRD diffractogram as shown in Figure 8. The presence of Mg in the crystallized product results in higher initial Mg concentration at the dissolution stage as can be seen in cycles 2 onwards in Figure 3B (ICP). The higher the percentage completion of the carbonation reaction, the fewer hydrated sulfate crystals will form within the alkali sulfate crystals. When topping up the alkali sulfate to achieve the required mass for the following step, the bound water crystals within the hydrated sulfates was not accounted for.

Table 5. XRF data for the crystallization product from cycles 1 to 6.

{redacted}

Figure 8. XRD diffractogram of the crystallization product for cycles 1 to 6.

{redacted}

Regeneration 1.0

The regeneration stage depends on the yield and purity of the spent catalyst and alkali sulfates from the previous steps. Table 6 presents the XRF elemental analysis of a commercial catalyst, which is compared to the catalyst produced from the regeneration step. We can see that the SO3 content is higher in the catalyst from cycle 1 compared to the commercial catalyst. The excess SO3 could be in the form of a stable salt which is expected since all the Mg was not consumed during the carbonation step.

During the reaction, some catalyst decomposes and forms a solid and acidic gases if the reaction was allowed to go for longer than required. This is observed by a change of colour in the products. This reduces the yield of the regeneration step and therefore top up reagents are required. This was done for cycles 4, 5 and 6, where additional catalyst was added. This resulted in the content of SO3 coming closer to the commercial ratio.

Moreover, the build-up of silica during the first 4 cycles can be noticed, which is reduced in cycles 5 and 6 due to the insoluble impurities being removed before the dissolution.

Table 6. XRF data of the catalyst (regeneration product) from cycles 1 to 6

{redacted}

Point to conclude from dissolution after the first 7 cycles.

- Adding a filtration step after dissolving the catalyst and before adding the olivine is essential to get rid of the solid impurities
- The dissolution reaction should be allowed to keep running for as long as possible to ensure minimum amount of olivine build up in the catalyst
- The reaction shouldn’t be kept for too long otherwise the silica gels with the spent catalyst
- The hydrated catalyst should be given longer time for the dissolution to take place and spent catalyst to be formed
- Conduct loss on ignition tests to better estimate the yield

Point to conclude from the pH swing after the first 6 cycles.

- Running the dissolution until solution is clear ensures that the majority of spent catalyst is generated
- The silica should be washed so that we do not lose residual Mg and sulfate ions

Point to conclude from the carbonation after the first 6 cycles.

- Carbonation should take place with x2 stoichiometric need of alkaline solution
- Washing the silica increases the amount of MgCO3 produced

Point to conclude from the crystallization after the first 6 cycles.

- When topping up the alkali sulfate to achieve the required mass for the following step, the bound water crystals within the hydrated sulfates was not accounted for
- The more efficient the carbonation, the less hydrated sulfates there is within the crystals

Round 2

Based on the learning outcomes from round 1, improvements have been implemented for the second set of cycles.

Dissolution Step 2.0

The first cycle was conducted twice during the second round. The first time the reaction was allowed to carry on taking place for as long as possible without taking samples it identify the longest possible time the reaction can run for without the silica gelling. It was observed that the silica-spent catalyst gelling starts taking place after 5 hours and 45 minutes. Therefore, the repeat of cycle 1 was stopped after 5 hours and 30 minutes with a clear solution, indicating very little to no iron was in the solution. This showed better drop in concentration as shown in Figure 9A compared to cycle 1 in the first set of cycles (Figure 3A). Cycles 2, 3 and 4 were allowed to run for at least 2 hour or more to ensure maximum spent catalyst recovery and olivine dissolution. To prevent buildup of solid insoluble impurities in the catalyst, a filtration step was added after every cycle. Figure 9A shows that the initial concentration increased from cycle 2 to cycle 4, this is due to the quality of the improved catalyst from the regeneration step. This will be further elaborated on later in the regeneration section.

With regards to the concentration of Mg, the dissolution of the olivine can never be 100% complete due to the gelling between the silica and spent catalyst if the reaction is left for too long. The maximum olivine concentration is calculated to be 0.7M from Figure 9B assuming the theoretical max is 1M. We can also see in Figure 9B that the initial concentration of Mg keeps increasing due to some of the Mg cycling back into the process due to incomplete carbonation.

Table 7. Data of the catalyst from each cycle used to calculate the yield.

{redacted}

The yield of spent catalyst has been calculated more accurately be conducting a loss on ignition test. Based on the amount of an element in the sample after LoI, the amount of spent catalyst was calculated, which was used to calculate the yield. According to this, in this cycle top-up spent catalyst was added to the process before the regeneration step instead of added top-up catalyst. Table 7 shows that the yield initially drops then gradually increases which is inline with the ICP results shown in Figure 9A.

Table 8 illustrates the XRF data of the spent catalyst samples for the 4 cycles. The spent catalyst was washed during cycles 3 and 4 which reduced the amount of sulfates. Moreover, since the regeneration step is improved there will be less unreacted soluble sulfate salts recycling back into the process. It can also be seen that the silica does not build up after the insoluble solid impurities separation step has taken place which removes unreacted olivine from the process. The XRD diffractogram (Figure 10) shows that some unreacted olivine is present on the spent catalyst produced. Some of the impurities are (Chabazite, Vermiculite and Forsterite.

Figure 9. ICP results of the concentration of {redacted} (A) and Mg (B) from cycles 1 to 4 (round 2) at different intervals.

A) {redacted}

B) Magnesium Concentration

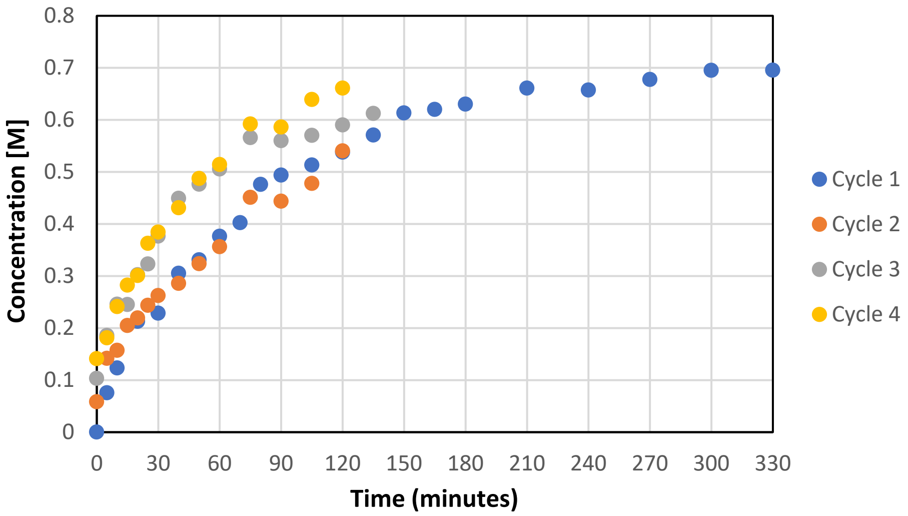


Table 8. XRF data of the spent catalyst from cycles 1 to 4.

{redacted}

Figure 10. XRD diffractogram of the spent catalyst from the dissolution for cycles 1 to 4.

{redacted}

pH Swing 2.0

In this set of cycles, the dissolution was allowed to run for as long as possible to maximize the yield of silica. The yield was calculated by estimating the amount of silica in the sample excluding the mass of bound water. Therefore, a loss on ignition test was conducted followed by XRF analysis on the sample to calculate the mass of silica without the water. Similar to what has been seen with the catalyst percentage yield, the silica as shown in Table 9 followed the same trend, a high yield for cycle 1 (79.4%) followed by a drop then gradual increase. This can be explained in the improved regeneration step.

The silica has been washed thoroughly in this set of cycles as shown from the XRD diffractogram (Figure 11) which shows no residual peaks, rather shows the broad hump which represents amorphous silica.

Table 9. Data of the silica from each cycle used to calculate the yield.

{redacted}

Figure 11. XRD diffractogram of the silica from the pH swing for cycles 1 to 4.

{redacted}

Carbonation 2.0

The yields during these set of cycles were a lot higher compared to round 1. This is because the silica was always washed, therefore no residual MgSO4 was lost during the process, but also because the dissolution reactions were allowed to run for at least 2 hours, hence dissolving more olivine. There was a reduction in yield during cycle 2 which could be due to the dissolution step not dissolving as much olivine, hence low initial concentration of Mg in the solution as shown in Figure 12. The yield then increases in the following two cycles. This can be linked to the improved catalyst regeneration step.

The XRD diffractogram (Figure 13) shows that the product is nesquehonite, however as observed in the first set of cycles there are additional peaks which represent silica and other phases in cycles 2, 3 and 4 which correspond with high amount of silica in the sample as shown in Table 10.

Figure 12. ICP results of the concentration of Mg during the carbonation at different intervals for cycles 1 to 3.

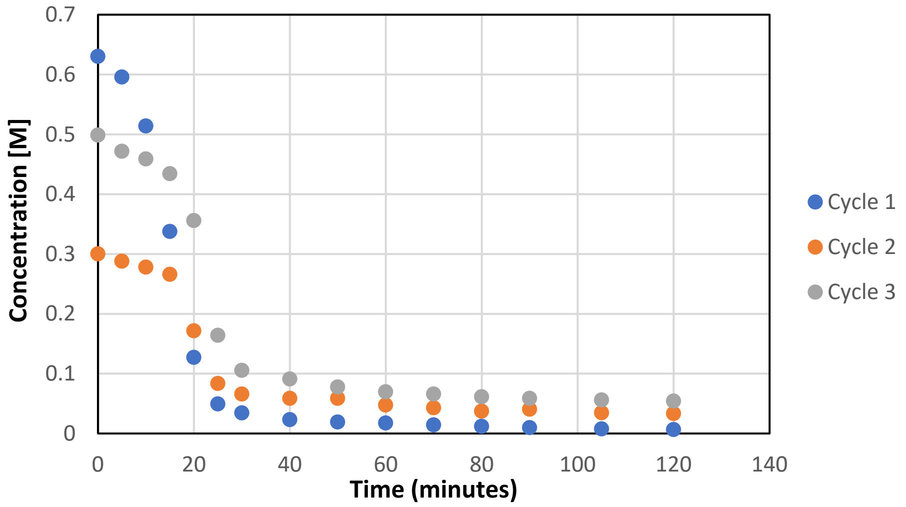


Table 10. XRF data of the MgCO3 from each cycle used to calculate the yield

{redacted}

Figure 13. XRD diffractogram of the carbonation product for cycles 1 to 4.

{redacted}

Crystallization 2.0

Table 11 illustrates the XRF percentages of SO3, MgO and SiO2 in the crystallization product. It can be seen that the percentage of magnesium remains relatively low, which is due to the carbonation step reacting most of the magnesium. The presence of some magnesium resulted in the formation of hydrated sulfates as shown in the XRD diffractogram (Figure 14) as expected. To completely get rid of all the hydrated sulfates within the crystallization product, the carbonation step should reach 100% completion which is challenging. The presence of Mg does not have any impact on the regeneration step and will be recycled back into the process to be carbonated in the following cycle. However, the additional weight of the bound water from hydrated sulfates should be taken into consideration when estimating the amount of alkali sulfate required when topping up to reach the required feed amount into the regeneration step.

Table 11. XRF data of the crystallization product used to calculate the yield

Compound Name	Cycle 1 Concentration (%)	Cycle 2 Concentration (%)	Cycle 3 Concentration (%)	Cycle 4 Concentration (%)
SO3 (XRF)	94.54	95.49	93.53	96.17
MgO (XRF)	3.42	3.10	5.21	2.00
SiO2 (XRF)	0.74	0.31	0.21	0.56
%Yield	87.9	89.9	84.8	86.5

Figure 14. XRD diffractogram of the crystallization product for cycles 1 to 4.

{redacted}

Regeneration 2.0

The regeneration step has been optimized during this set of cycles. The catalyst product from cycle 1 came out as {redacted} (Figure 15) which suggests that the reaction in the furnace did not take place as required to produce the catalyst, due to incomplete regeneration or the catalyst being over cooked. This could have been due to non-uniform mixing between the spent catalyst and alkali sulfate, or due to the alkali sulfate particle sizes being slightly larger than the spent catalyst (fine power). Therefore, for the following cycle, instead of manually milling the alkali sulfate and spent catalyst mix using a pestle and mortar, a ball mill was used to ensure more effective mixing and uniform particle sizes. This appeared to slightly improve the catalyst product, however, as can be seen in Figure 15, the cake appeared to have two layers of differing colours. This is a result of the bottom layer being over cooked in the furnace, therefore for the following cycle the weight of the sample in each batch was halved to prevent over-cooking of the bottom layer. As a result, the product from the third cycle came out as a homogeneous cake suggesting more catalyst was formed. Practically in industry this would be translated into a rotary kiln furnace to prevent overcooking of one layer and to allow alkaline gas and steam formed during the reaction to escape.

According to the XRF results in Table 12, the SO3 content is converging each step to get closer to the SO3 content of the commercial precursor, which suggests that a purer catalyst is produced during regeneration.

Table 12. XRF data of the catalyst from cycles 1 to 4.

{redacted}

Figure 15. Illustration of the colour of the catalyst from cycles 1, 2 and 3.

{redacted}

Conclusions

[Redacted]