IMPERIAL

Reagent Regeneration Procurement

CCUS Innovation 2.0

Key Knowledge Deliverable 2.3

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

Details of equipment procured for Reagent Regeneration 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

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Introduction

This deliverable will focus on the reagent regeneration section of the mineral carbonation process. It will demonstrate the equipment procured, experimental setup and procedure alongside some preliminary tests to give some direction for D2.4 (Reagent regeneration operation).

The reagent regeneration step is the step where the catalyst is regenerated and sent back to the batch reactor to react with olivine as shown in Figure 1. This step consists of two stages, firstly the crystallization part which separates the dissolved ammonium sulfate from the solution to form solid crystals. The second stage is reacting the ammonium sulfate crystals with spent catalyst. There are two methods for the crystallization process. The first is an evaporative crystallization process where the pressure of the solution is dropped to around 100 mbar which reduces the boiling temperature of water to around 50°C. The other method is using an anti-solvent crystallization, where an antisolvent is mixed with an ammonium sulfate solution which reduces its solubility, leading to supersaturation and subsequent crystallization of ammonium sulfate.

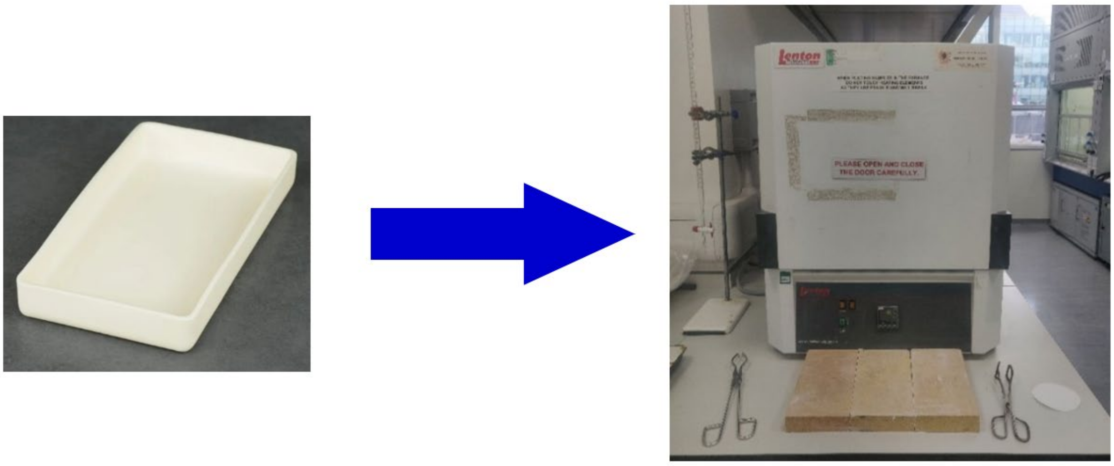
Method

Experimental Setup

Instead of ordering a vacuum rotary evaporator we used one that was already present in the department. The experimental setup is shown in Figures 1 & 2 below.

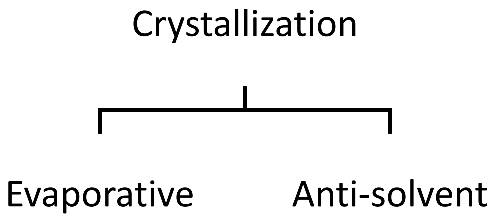
Figure 1. Bench scale rotary evaporator

Figure 2. Crucible (left) and furnace (right) for the reagent regeneration step



Reaction Mechanism

Crystallization



Evaporative Crystallization: The pressure is dropped to vacuum to reduce the boiling temperature of the water to separate the crystals in a vacuum rotary dryer (Figure 2).

Anti-solvent Crystallization: Organic solvent (methanol) is used to separate the ammonium sulfate from the water as crystals by reducing its solubility and reaching supersaturation which is then separated via filtration. The methanol-water mixture is separated using a vacuum rotary dryer (Figure 1).

Furnace

[Redacted]

Experimental Steps

A 1.4 M ammonium sulfate solution was made by completely dissolving a known mass of ammonium sulfate crystals in deionized water, mirroring that which exists within the process at the beginning of the regeneration step.

Two methods of crystallization were trialled on identical solutions:

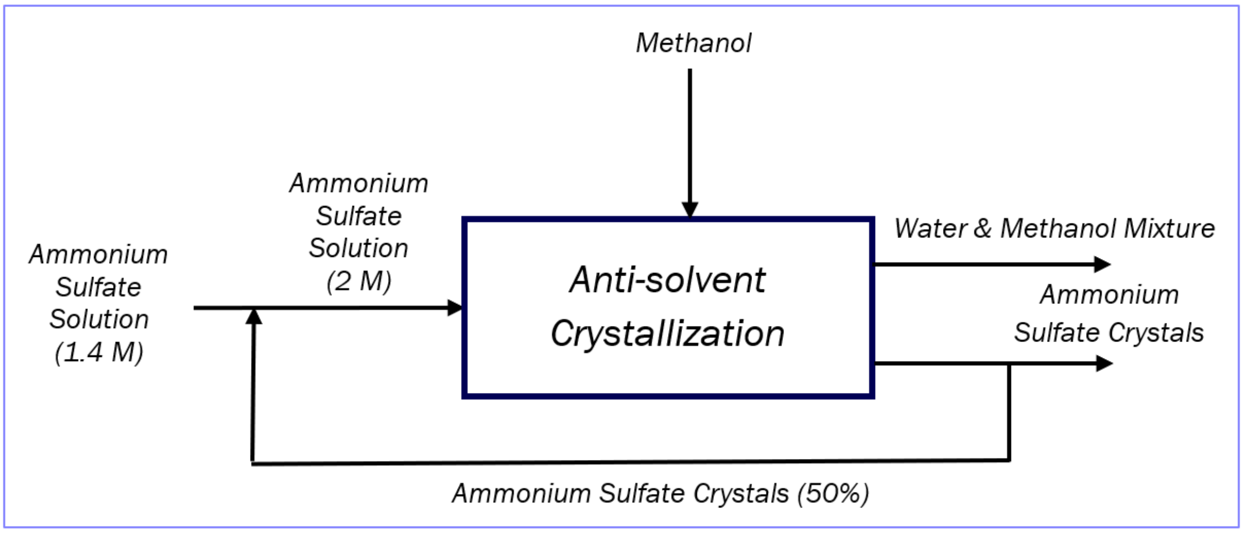
- Evaporative Crystallization

The solution was placed in the vacuum rotary evaporator with temperature and vacuum pressure set.

- Anti-Solvent Crystallization

The solution was combined with methanol in volumetric ratios of 1:1, 1:2, 1:3 and 1:4, in order to precipitate out ammonium sulfate from solution. The slurry was then filtered, and any ammonium sulfate crystals were dried and weighed to calculate percentage recovery. Additionally, another set of experiments with a recycle loop was conducted making the feed stream concentration of the ammonium sulfate solution equal to 2 M to assess whether a higher feed concentration would result in higher percentage recovery. To understand whether the manner in which the two solutions are combined may impact the recovery efficiency (Figure 3), solutions of 1.4 M and 2 M were also combined through slow, dropwise gradual addition over the course of 60 minutes (semi-batch) and instant batch addition. Both were consequently filtered 10 minutes after mixing.

Figure 3. Anti-solvent crystallization process with a recycle loop



Results and Discussion

In the evaporative crystallization the rotary evaporator was set up and the process was allowed to run for 6 hours, however very little water had evaporated. This could be due to the high solvation energy of the ammonium sulfate solution or due to the flask being set at a high RPM. This will be repeated with a lower flask rotation speed as well as altering other variables.

In the anti-solvent crystallization, Table 1 shows the results when using different methanol to solution volumetric ratios. The results showed that as you increase the amount of methanol more ammonium sulfate crystals can be recovered with the highest being 99% recovery using 4 times methanol to ammonia. However, the issue with using high amount of methanol is the increased energy required to recover the methanol as seen in Table 2, as well as incredibly large volumes required.

Table 1. The amount of ammonium sulfate recovered from the solution

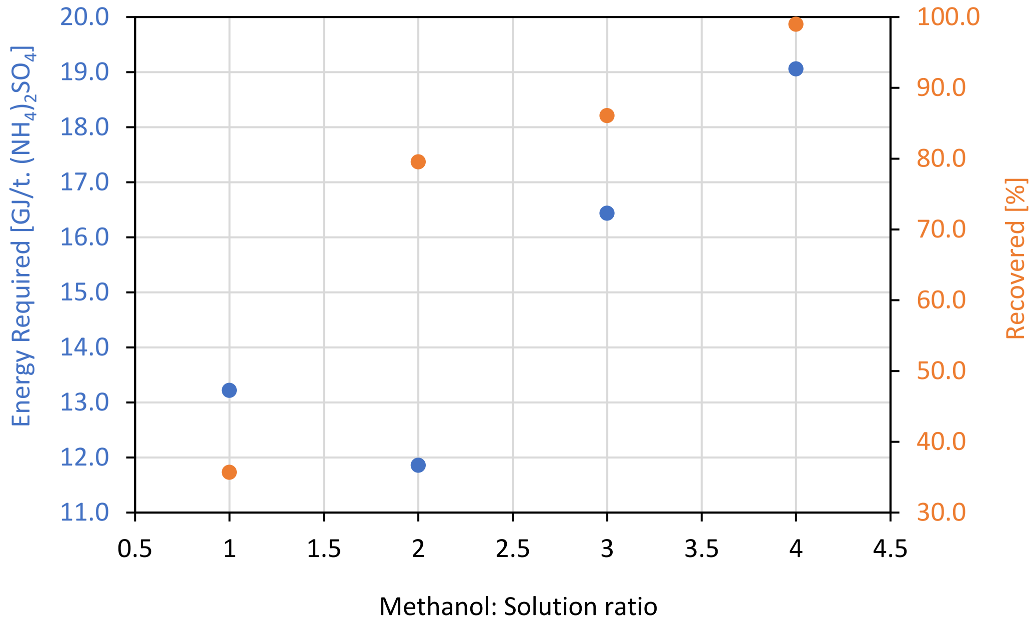
Methanol: Solution ratio	Mass recovered (g)	Column 3	Recovery increase factor based on 1: 1 ratio
1: 1	8.24	35.7	1.0
2: 1	18.37	79.5	2.2
3: 1	19.88	86.1	2.4
4: 1	22.86	99.0	2.8

Table 2. The amount of energy required per tonne of ammonium sulfate recovered

Methanol: Solution ratio	Energy Required (MJ/t)	Energy increase factor based on 1: 1 ratio	Methanol: Solution ratio
1: 1	13.2	1	1: 1
2: 1	11.9	2	2: 1
3: 1	16.4	3	3: 1
4: 1	19.1	4	4: 1

This can also be seen in Figure 4 doubling the amount of methanol from a 1: 1 ratio reduces the amount of energy required per tonne of ammonium sulfate, however further increase in methanol to solution ratio does not yield more ammonium sulfate crystal recovery relative to the amount of energy required to separate the methanol.

Figure 4. Plot showing the energy required and percentage recovery as a function of methanol: solution ratio



The results in Table 3 show how the use of dropwise addition over 60 minutes impact the percentage recovery. The percentage recovery of ammonium sulfate increased from 79.5% to 86%. This increase in percentage recovery could be associated with gradual addition of the anti-solvent giving more time to allow for larger crystals to form, which could result in higher yields. Another experiment was conducted assessing the effect of a recycle ammonium sulfate crystals stream as shown in Figure 4 would affect the percentage recovered. Table 3 also gives information on how increasing the concentration of the ammonium sulfate solution by recycling 50% of the ammonium sulfate can impact the percentage recovered. It was observed that having a recycle stream would increase the feed ammonium concentration stream to 2 M and would increase the percentage recovery to 93.3% if the addition of methanol was direct batch and 96.5% of semi-batch addition of continuous addition for 60 minutes.

Table 3. The ammonium sulfate recovery for a 1 M and 1.4 M solution via drop-wise gradual addition (semi-batch) and instant addition (batch) of methanol

Addition Method	Ammonium Sulfate Concentration (M)	Initial Ammonium Sulfate Mass	Mass Recovered	% Recovery
Batch addition	1.4	23.1	18.37	79.5
Semi-batch addition	1.4	23.1	19.88	86.0
Batch addition	2.0	33.0	29.5	93.3
Semi-batch addition	2.0	33.0	31.9	96.5