IMPERIAL

Dissolution Operation

CCUS Innovation 2.0

Key Knowledge Deliverable 1.3

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

Report detailing production of silica from Dissolution stage over 5 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.

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

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Introduction

The following report details how the dissolution of olivine using acidic salts can be upscaled to increase the output of siliceous material. The upscaling of a chemical reaction requires a recalibration of operating conditions to ensure that the efficiencies are effectively managed. As such, this report will detail how temperature and reagent ratio impact the rate of the reaction and the final product yields.

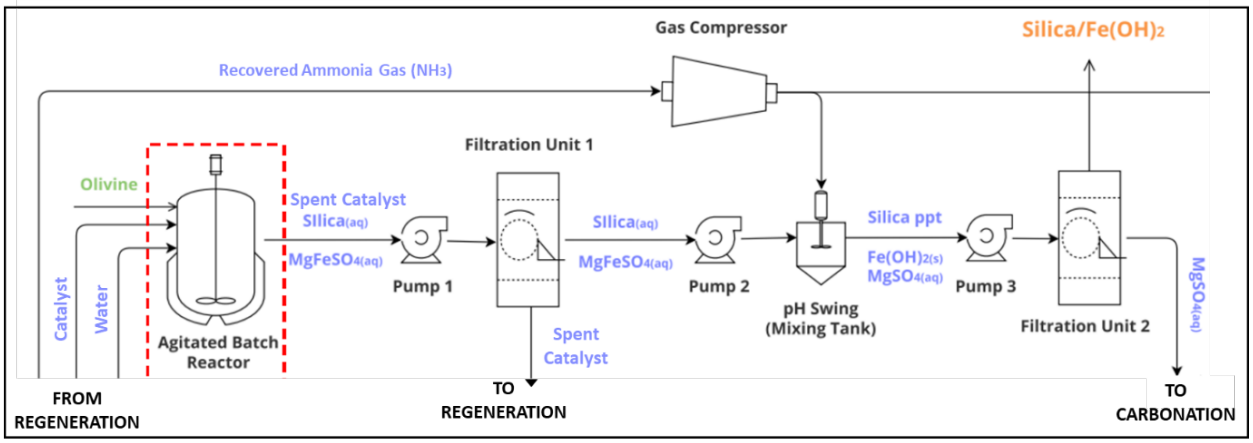
Dissolution Reaction

The dissolution stage of the CCS process in the present research uses catalytic digestion to process magnesium silicates, such as olivine. The complete reaction is:

Olivine + Catalyst $\rightarrow$ Spent Catalyst + Solution of Sulphates + Silica

This reaction relies on the formation of acidic components that subsequently attack the magnesium silicate raw material. The benefits of this processing method are 1) safety, the catalyst is a solid compound and considerably safer to handle than concentrated mineral acids; 2) cost, employing a catalyst removes the need for continual purchasing/shipping of chemical reagents; and 3) energy, recovering acidic and basic chemicals can be done but is energy intensive. The present research's innovative solution reduces the energy required in recovery.

Figure 1 Dissolution and separation stage of the CCS process



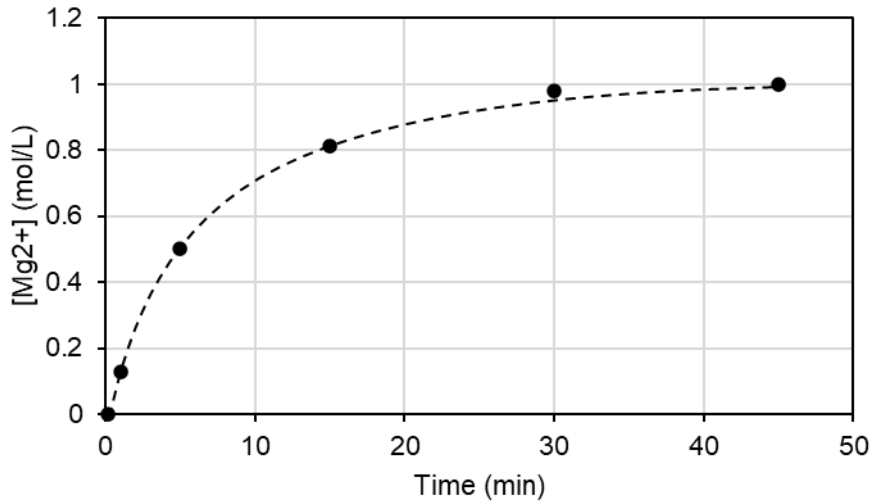
Mechanism

The reaction in Eq 1. occurs in two stages; 1) the catalyst produces sulphuric acid in the presence of water, and 2) the acidic species attack the magnesium silicate, splitting it into its constituent MgO and SiO2 elements, and producing spent catalyst . The reaction for the dissolution of magnesium silicate in a sulphuric acid environment is:

$Mg_2SiO_4 + 2H_2SO_4 \rightarrow 2MgSO_4 + H_4SiO_4$ Eq. 2

For a stoichiometric dissolution such as in Eq 2, the reaction is initially rapid. The is because there is a large amount of both acid and magnesium silicate. This effect diminishes as the reaction progresses and the reactants are consumed. As a result, the reaction slows (Figure 2).

Figure 2 Stoichiometric dissolution of magnesium silicate in H_2SO_4



Unlike a stoichiometric dissolution, the catalytic dissolution slowly releases the acidic components into a slurry that has an excess of magnesium silicate. To recreate these conditions and assess how quickly the acidic species attack the magnesium silicate, the rate of magnesium release in dilute sulphuric acid with an excess of olivine has been investigated.

Figure 3 Dissolution of excess magnesium silicate in dilute H2SO4

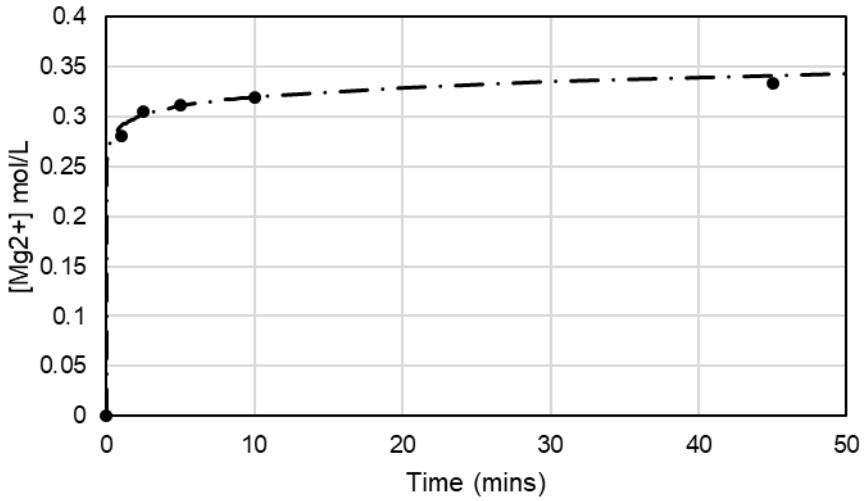


Figure 3 shows that given sufficient magnesium silicate the acidic attack is rapid. The rate is approximately 0.1 mol/L/min, which is 10x faster than the rate of catalytic digestion as a whole. This suggests that the formation of the acidic species by the catalyst is the rate limiting step (Figure 4). The acidic species are released slowly, and the relative concentration is consistent throughout the reaction, as can be confirmed with pH measurements. This may account for the linear release of magnesium ions seen in catalytic digestions.

Figure 4 [Redacted]

Methods

Materials

[Redacted]

Production of Initial Catalyst

[Redacted]

Dissolution Operation

Catalyst was placed in a 5 L beaker with 3 L of deionized water. The solution was placed on a heated magnetic stirrer with a Teflon coated stirrer bar. The temperature of the solution was increased to the working temperature of the experiment, 60, 70, 75 or 90 °C. The hot solution was then filtered to remove insoluble impurities. The filtrate was placed back on the magnetic stirrer set to the same temperature and olivine is added, either 1:1. 2:1 or 4:1 of the stoichiometrically required amount. The reaction was stopped once the filtrate was clear upon sampling. The resulting slurry was filtered, washed, and dried and used for regeneration of catalyst as before. 1M AH was added to the filtrate from the dissolution to achieve a pH of 7. The precipitate formed during the addition was filtered, washed, and dried. This precipitate is an iron-rich siliceous material, designated silica. This method was then cycled, with catalyst made from spent catalyst being used to digest more olivine, in order to acquire data on the repeatability of the dissolution.

Mg 2+ Concentration Measurements

Samples for magnesium concentration were collected by removing approximately 2 ml of solution from the dissolution with a syringe. The syringe was subsequently fitted with a 45 µm syringe filter that the sample was pressed through. Approximately 1.5 ml of sample was collected and weighed before gravimetrically diluting by a factor of 10.

Magnesium concentration was used to monitor the reaction progression over time. In mineral acid dissolutions, where iron concentration is negligible, the concentration of Mg2+ ions can be determined by volumetric EDTA-M2+ titration1.

In catalytic dissolutions, volumetric titrations cannot be used and the magnesium concentration was determined by atomic adsorption spectroscopy (AAS). The magnesium samples were analysed on an MRC AAS220A instrument under an oxy-acetylene flame.

Solid Product Characterisation

Solid products from the dissolution, spent catalyst and silica, were analysed by scanning electron microscopy (SEM) and x-ray diffraction (XRD). In both cases, the solid powder samples were washed and dried at 105 °C before analysis.

SEM –Back scattered electron (BSE) images were captured on Hitachi TM4000 plus instrument with an accelerating voltage of 15 kV. The oxide composition of the solid samples was measured by area mapping energy dispersive spectroscopy (EDS) during SEM image capture.

XRD – XRD diffractograms of the samples were produced on a Rigaku MiniFlex benchtop XRD. The measured range was 5 – 80°2θ at a scanning rate of 3.0°/min using Cu Kα radiation.

Results and Discussion

Influence of Temperature on Rate

Three different temperatures have been investigated to determine the impact on dissolution rate. Figure 5 shows how magnesium is liberated into solution over time at the different temperatures investigated. Reactions are considered complete once the magnesium concentration reaches 1 mol/L, matching the acid concentration equivalence of the catalyst. Evidently, the dissolution reaction is incredibly temperature dependant. At 60 °C completion occurs after 5 hours, whereas at 90 °C, it is complete in under 1 hour.

With regards to operating the dissolution at an industrial scale, the results from this study suggest that operating at higher temperatures is more suitable, in order to increase rate. But as the entire process is continuous, the reaction times will need to be tailored in accordance with the other stages of the process. Therefore, understanding how temperature impacts rate is imperative.

Figure 5 Mg2+ concentration during olivine dissolutions at 60, 75 and 90 °C

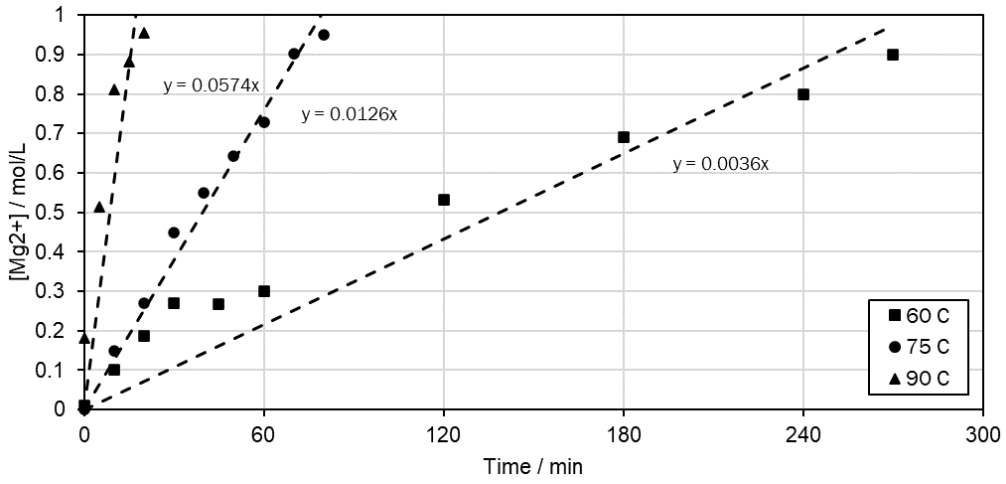


Figure 6 Arrhenius plot calculated from data in Figure 5

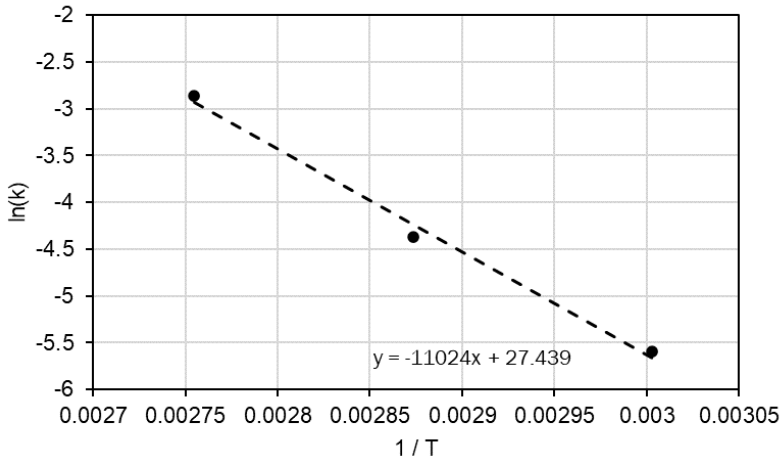


Table 1[Redacted]

The activation energy of this reaction has been calculated by the Arrhenius method shown in Figure 6. The temperature studies in this report show results that are concordant with literature data (shown in Table 1) for the activation energy of spent catalyst precipitation. In literature studies, the base used in spent catalyst precipitation is ammonium hydroxide, whereas, in the present study, the base used is olivine. This is most likely the reason for the marginally higher activation energy observed for this reaction as magnesium silicates have significantly lower basic properties than either a strong or weak base, such as ammonium or sodium hydroxide.

Influence of Olivine Ratio on Rate

Three different ratios of olivine to catalyst have been investigated to assess the impact this has on the rate of dissolution.

Figure 7 Mg2+ concentration during olivine dissolutions at 4:1, 2:1, and 1:1 olivine:catalyst ratios

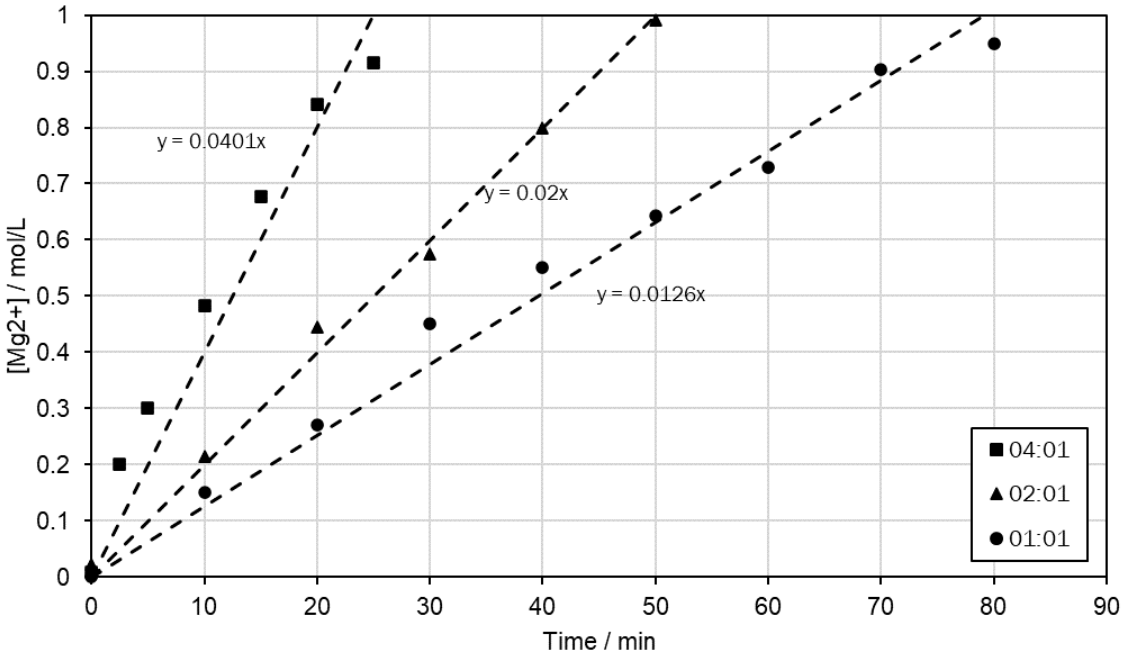


Figure 8 Relationship between olivine amounts and reaction rate

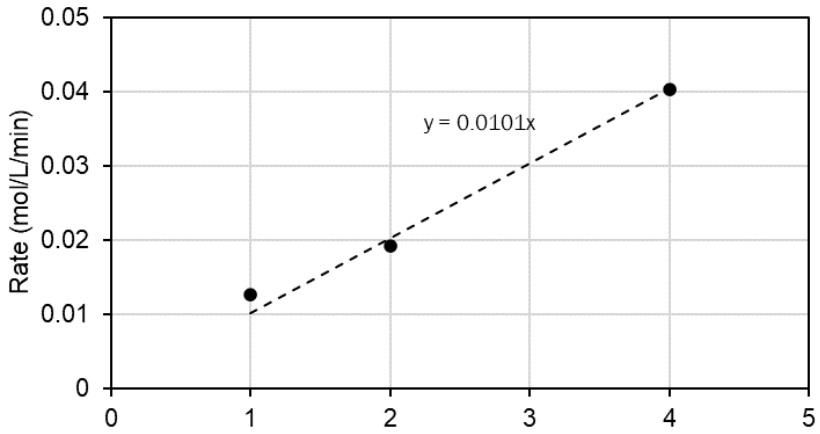


Figure 7 shows that the addition of excess olivine in the dissolution reaction had a significant impact on the rate of magnesium liberation from the olivine. Figure 8 shows a linear relationship between olivine excess and the reaction rate during dissolution. The proposed mechanism for the dissolution, and explanation as to the role of olivine in determining rate, is outlined below.

During an olivine dissolution, there is a large pool of dissolved catalyst ions in solution that are able to react to produce spent catalyst and H+. However, only a small portion of the ions can do this due to the self-limiting nature of the reaction, whereby below a certain pH the reaction

stops. There is a maximum concentration for H+ in the solution, and the existing H+ ions need to come into contact with olivine before more can be produced. As such, an equilibrium is established where the concentration of H+ ions in solution is constant throughout the reaction.

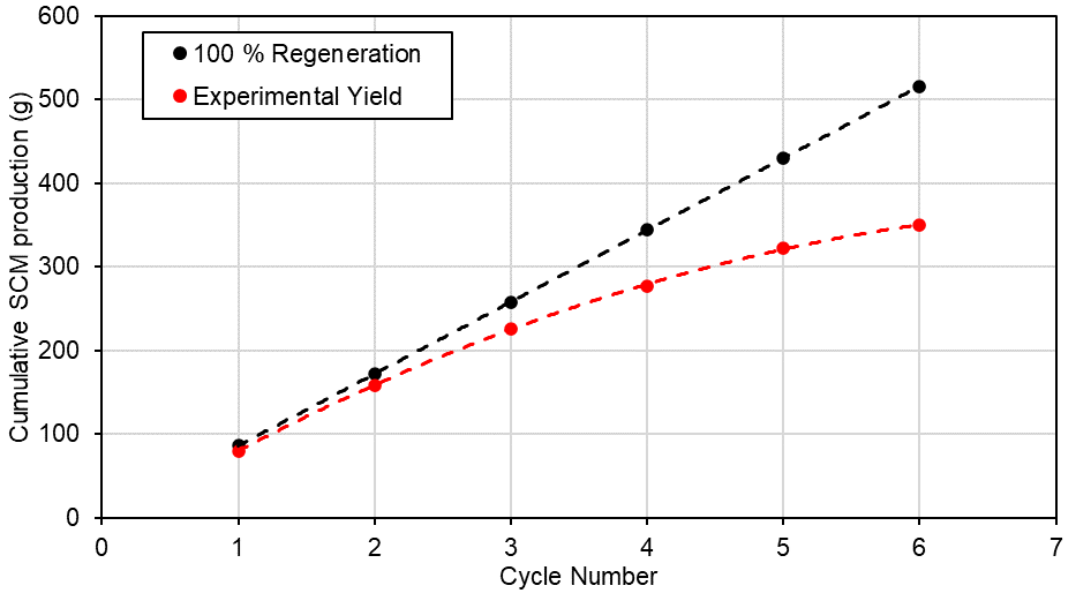
In a stoichiometric dissolution of olivine, all of the olivine that is required is present, but the vast majority of it exists in the unexposed interiors of the particles. At equilibrium, there is a finite amount of exposed olivine, an excess of H+ ions relative to this exposed olivine, and the large pool of catalyst. As the H+ ions are consumed by the surface of the olivine, more spent catalyst is produced to replace them, fresh olivine is exposed, and more H+ are consumed, etc. As the effective acid concentration is constant for a set temperature and the rate of olivine dissolution is constant as the particle is consumed, one would expect a pseudo-zero order reaction.

In doubling the amount of olivine present, again almost all of the olivine required for the reaction is not yet exposed, but there is twice as much surface area at which H+ can be consumed, and Mg2+ leached. In this case, again the large pool of dissolved catalyst ions are in a significant excess to the exposed olivine and another equilibrium is established such that one would expect another zero-order reaction. However, in this case, you would expect the rate to be twice as fast, which is what we see. The same is true again for the 4:1 dissolution.

Catalyst Looping

Figure 9 shows how the experimental yields of silica decline over time compared to those expected from a 100% efficient process.

Figure 9 SEM image of silica produced from large dissolution.



In the present study, a total of three catalyst looping experiments were conducted, with between 4 – 6 cycles in each trial. A similar drop in production was seen in all of the experiments. The most significant mass losses were observed in the regeneration stage of the process. This is because the regeneration ideally produces one phase, catalyst, which is responsible for producing acidic species in solution. However, during the study it was clear that the regeneration was also producing phases that are insoluble and therefore, do not dissociate to produce acidic species. This impurity phase produced is likely an iron oxide such as hematite or goethite, due to inefficient gas transfer and temperature gradients in the furnace. Further analysis of the regeneration stage is required to fully understand how to optimise this stage of the process. The decrease in yield with each cycle is deemed an acceptable amount for a process of this scale, and are expected to increase with further scaling and regeneration optimisation.

Solid Product Characterisation

The solid products, silica material and spent catalyst, have been characterised with XRD and SEM in order to understand how temperature, olivine ratio and cycling the process impact their phase identity, impurity levels and particle morphology.

Impact of Olivine Ratio on Solid Products

The spent catalyst resulting from each dissolution has been characterised by XRD, with Figure 10, showing how excess olivine present in the dissolution can result in residual olivine being present in the spent catalyst. A 1:1 dissolution produces a spent catalyst sample that shows only a few, weak peaks that can be assigned to forsterite (Mg2SiO4). Forsterite is the primary phase in olivine, that being targeted for acidic digestion in the dissolutions. At a 2:1 or 4:1 dissolution, a greater number of forsterite peaks are observed. Additionally, the olivine sample used in this study contains impurities that are insoluble in the acidic salt solution. These phases, including vermiculite and talc, are present at the end of the dissolution and observed in all samples. The peaks assigned to olivine impurities are significantly stronger in the 4:1 dissolution sample than either the 2:1 or the 1:1 dissolution samples. To prevent these soluble impurities from building up throughout cyclic operation, we have added a filtration stage in the process to aid their removal.

Figure 10 [Redacted]

These findings are supported by SEM and EDS data, presented in Figure 11 and Table 2. Figure 11 highlights how excess olivine present during a dissolution will contaminate the spent catalyst sample produced after filtration. In addition to olivine being observed in the BSE images, Figure 11d and 11e show significant spent catalyst agglomerations which are not present in the 4:1 sample (Figure 11f).

MgO and SiO2 are assumed to be present as residual olivine and not as any other phase as the reaction pH is too low for silica polymerisation or the formation of insoluble magnesium

oxide. The molar ratio expected for olivine is 2:1 (Mg:Si). The Molar ratio of Mg and Si observed in these samples are consistently lower than expected, suggesting that there may have been some incongruent dissolution on the residual olivine particles (ie. Mg has been removed from the surface without SiO2). An alternative mechanism proposed by Johnson, N.C. et al. (2014)1 suggests a re-deposition of dissolved silica on residual olivine particles. Either mechanism could account for the observed increased in SiO2 molar ratio.[1]

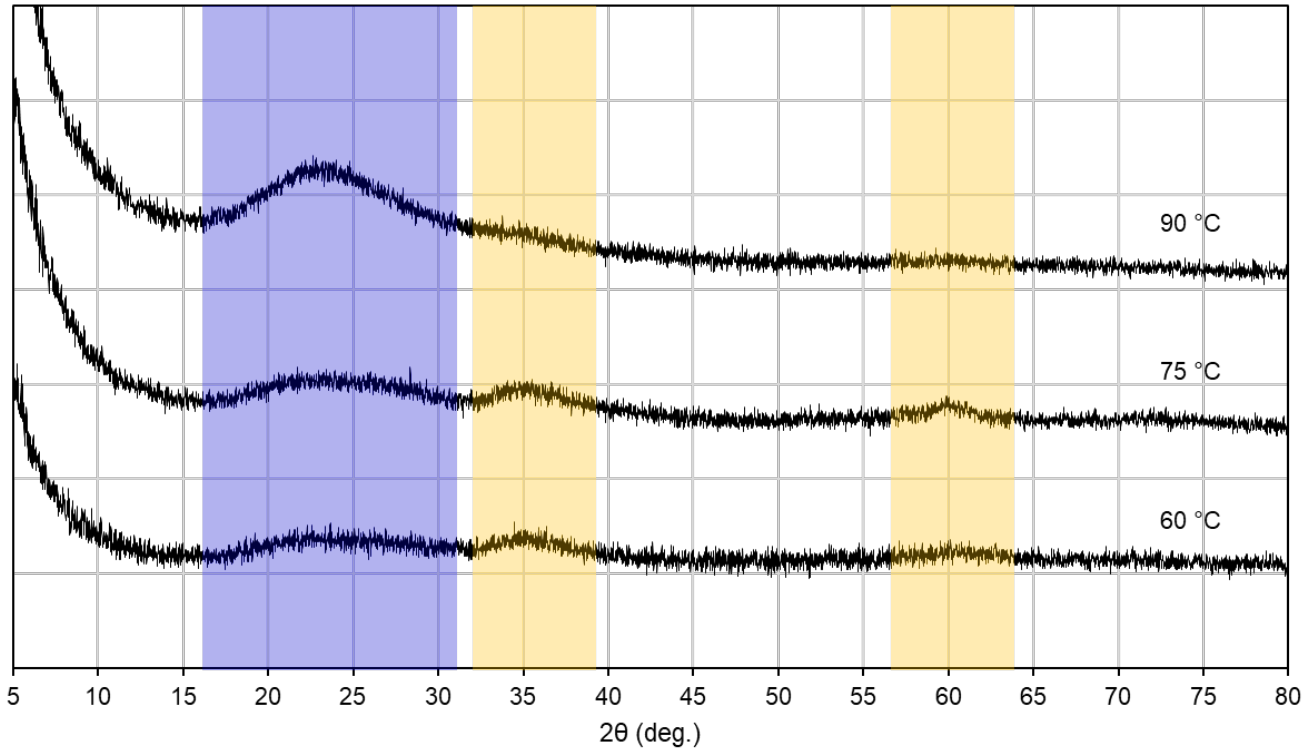
Figure 11 [Redacted]

Table 2 [Redacted]

Impact of Temperature on Solid Products

The XRD patterns of the silica solid product from dissolutions run at 60, 75 and 90 °C are compiled in Figure 12.

Figure 12 XRD diffractograms of silica produced from dissolutions run at 60, 70 and 95 °C. Highlighted blue regions denote an amorphous hump associated with SiO2; yellow regions denote amorphous iron species



The siliceous material product by increasing the pH of the dissolution filtrate contains SiO2 and Fe2O3/FeO species. This study found that operating the dissolution at a higher temperature

[1] Johnson, N.C. et al. (2014) 'Olivine dissolution and carbonation under conditions relevant for in situ carbon storage', Chemical Geology, 373, pp. 93–105. doi:10.1016/j.chemgeo.2014.02.026.

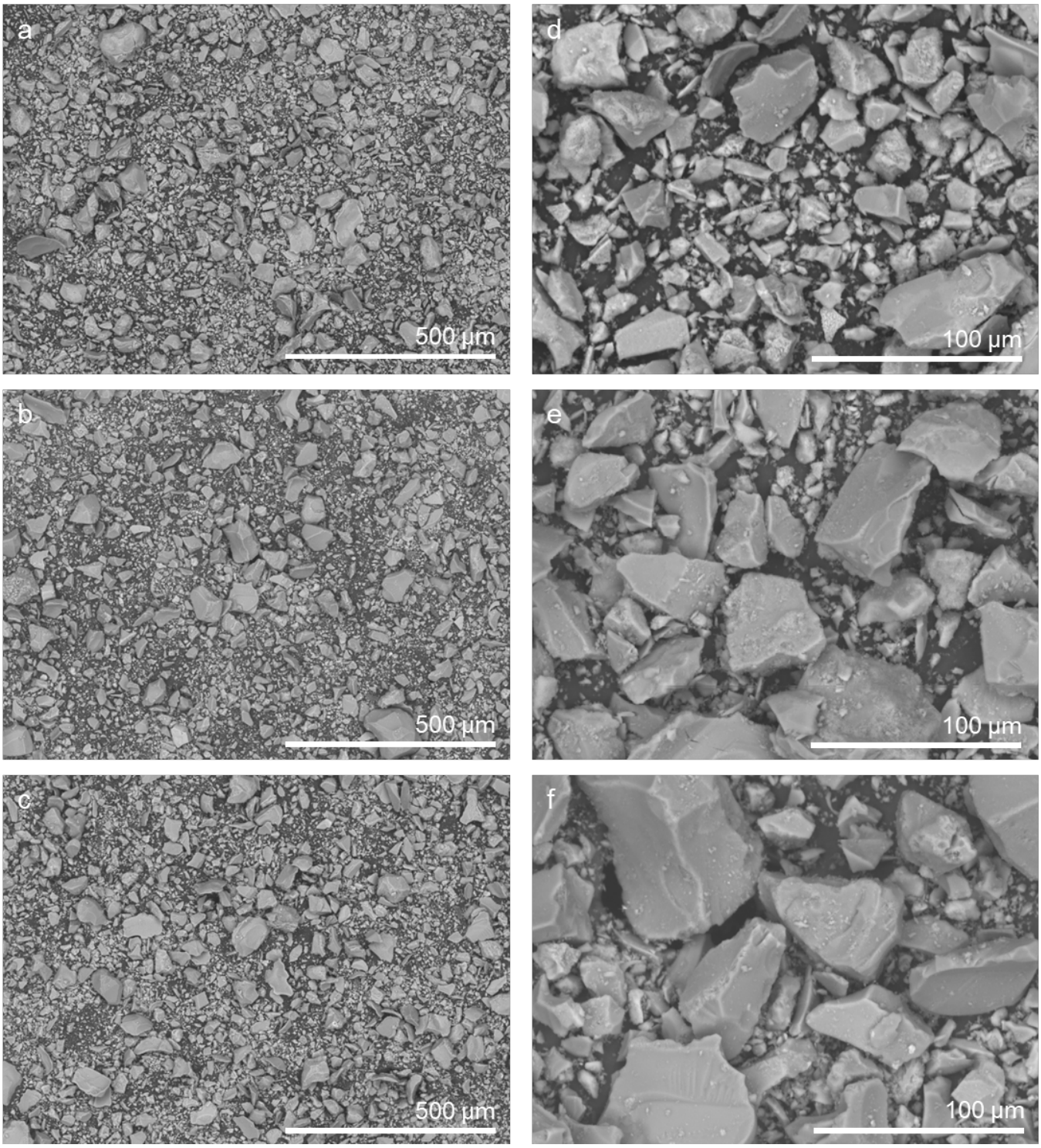
did have an impact on the composition of the siliceous material, with the 60 and 70 °C samples showing amorphous humps around 30 – 40 °2θand 55 – 65 °2θ, in addition to the silica hump. These areas are associated with amorphous iron species, or a modified amorphous silica network. Further work is required to identify whether these additional areas in the diffractogram are indicative of a separate phase or of a modified silica. The difference in the samples is likely due any residual dissolved catalyst in the solution resulting from incomplete reaction, which is potentially lower in the 90 °C dissolution. An additional factor may be the form the dissolved silica takes during a dissolution. Dissolved silica may be in the form of silicic acid (H_4SiO_4) or partially condensed in dimers and oligomers. If these oligomers form in the presence of Fe ions, they may be taken up into the network. Increasing the temperature of the dissolution may favour a monomeric form of silica until more of the iron has been consumed to produce spent catalyst.

These results are mirrored in SEM and EDS analysis, shown in Figure 14 and Table 2, respectively. Figure 13 shows the BSE images of silica produced through catalytic dissolution at 60, 75, and 90 °C. Table 3 shows the average oxide compositions of the silica images captured at 500 x magnification. Figure 13 shows that the dissolution temperature does not have a significant impact on silica particle morphology. All dissolutions produced silica with a maximum size of approximately 100 µm. Figure 13d shows a significant and uniform shift in image brightness of the particles. The oxide composition of the image confirmed that this is due to an increase in Fe within the sample. The uniformity of the grey scale increase across the particles suggests that the increased iron is in silica gel network and not present as a distinct phase.

Table 3 Oxide composition of silicas

Oxide (wt.%)	60 °C Silica	75 °C Silica	90 °C Silica
SiO_2	57.5	75.5	91.0
Fe_2O_3	28.5	20.1	6.0
MgO	10.2	3.3	2.6
Al_2O_3	2.3	0.0	0.0
SO_3	0.8	0.3	0.3

Figure 13 BSE images of silica produced in dissolutions operated at 60, 75 and 90 °C at 100 x magnification (images a, b, and c, respectively). And at 500 x magnification (images d, e, and f, respectively)



Conclusions

The dissolution behaviour of olivine in an acidic salt solution has been reported. The present study has discussed the practicalities of the cyclic acidic salt mechanism and the efficiency of continued operation. The work has also discussed the influence that temperature and excess olivine have on the rate of the dissolution reaction and on the nature of the solid products produced.

- When operating cyclic dissolutions using the acidic salts in this study the biggest mass losses - and therefore greatest source of inefficiency - arose from the regeneration stage. Incorrectly regenerating the catalyst produces insoluble impurities that cannot easily be recovered.
- The activation energy of the acidic salt dissolution of olivine has been calculated to be 88 kJ/mol. While this is the first time this value has been reported, literature values for the same reaction using aqueous alkalis suggest that this is reasonable.
- The impact of olivine ratio on the rate of dissolution showed a linear relationship. The mechanism of the dissolution has been investigated and a tentative explanation for the mechanism has been proposed. The dissolution appears to be a zeroth order reaction, with rate dependent on initial olivine surface area and dissolution temperature.

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