Carbon dioxide sequestration using $NaHSO_4$ and NaOH: A dissolution and carbonation optimisation study

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Abstract

The use of $NaHSO_4$ to leach out Mg fromlizardite-rich serpentinite (in form of $MgSO_4$) and the carbonation of CO_2 (captured in form of Na_2CO_3 using NaOH) to form $MgCO_3$ and Na_2SO_4 was investigated. Unlike ammonium sulphate, sodium sulphate can be separated via precipitation during the recycling step avoiding energy intensive evaporation process required in NH_4-based processes. To determine the effectiveness of the $NaHSO_4$/NaOH process when applied to lizardite, the optimisation of the dissolution and carbonation steps were performed using a UK lizardite-rich serpentine. Temperature, solid/liquid ratio, particle size, concentration and molar ratio were evaluated. An optimal dissolution efficiency of 69.6% was achieved over 3 hours at 100°C using 1.4M sodium bisulphate and 50g/l serpentine with particle size 75-150µm. An optimal carbonation efficiency of 95.4% was achieved over 30 minutes at 90°C and 1:1 magnesium:sodium carbonate molar ratio using non-synthesised solution. The CO_2 sequestration capacity was 223.6 g carbon dioxide / kg serpentine (66.4% in terms of Mg bonded to hydromagnesite), which is comparable with those obtained using ammonium based processes. Therefore, lizardite-rich serpentinites represent a valuable resource for the $NaHSO_4$/NaOH based pH swing mineralisation process.

Keywords: CO_2 fixation • CCS • mineral carbonation • clean energy • Sodium salts

1 Introduction

Carbon dioxide capture and storage by mineralization (CCSM) provides a permanent and safe way to store CO_2, since the dissociation of magnesite/hydromagnesite occurs at temperatures between 350-550°C (at ambient pressure) or at 1500°C at 115 GPa (Isshiki et al., 2004; Huijgen, et al., 2006). The process of silicate weathering, which involves cations such as Mg and Ca reacting with CO_2 to form solid, insoluble carbonates, takes place over geological time scales, so that a number of processes are being investigated to accelerate the CO_2 sequestration reactions.

In direct aqueous CCSM, high pressure and temperature are used to speed up the process by extracting the cations from Mg/Ca rich minerals/wastes and reacting the products with CO_2 to form solid carbonates (Goff & Lackner, 1998). The CO_2 storage capacity of the available raw materials for CCSM is believed to be approximately two orders of magnitude higher than that of geological storage, with Mg-silicate minerals such as serpentine providing available feedstock of approximately 100,000 Gt (Lackner, 2002). This means that there are theoretically enough raw materials to sequester all the CO_2 emitted by the burning of world's fossil fuel supplies. MC requires large volumes of rocks that may make such operations impractical for use with large emitters due to the large-scale mining of Mg silicates that would be required, but more suitable for small emitters closely located to rocks resources (Sanna et al., 2012). In addition, mining costs and potential environmental problems (e.g. wastewater treatment, environmentally protected areas) must be considered for a complete techno-economic assessment. For example, the costs of mining and milling (to fine sand) bulk rock in open pit mines are well known in the mining sector, being ~4€/t and 2€/t, respectively (Steen and Borg, 2002). Costs of lizardite mining for MC purpose was assessed to be $15/t (IPCC, 2007).

Direct CCSM of rocks and wastes is however subject to slow kinetics and low efficiencies. For example, the aqueous direct mineral carbon sequestration using industrial alkaline solid residues such as basic oxygen furnace slag from steel making and coal fly ash resulted in fixing up to 536 and 65 gCO_2/kg, respectively (Polettini et al., 2016; Muriithi, et al., 2013). Also, carbonation of inorganic wastes such as waste concrete and fly ash (FA) have been investigated for sequestration of CO_2 (Ghacham et al., 2015; Siriruang et al, 2016). Although inorganic wastes can be successfully used for cleaner industrial productions, with simultaneous reduction of CO_2 emissions and stabilization of wastes, their limited abundance and high variability limit the scale of their application for CCS purposes. Therefore, chemical additives are used in indirect aqueous processes to enhance the extraction of cations from Mg-rich rocks and the carbonation reaction with CO_2. A number of pH swing processes have been developed around the world (Azdarpour et al, 2015; Kodama et al, 2008; Teir et al, 2007; Park et al, 2004, Wang and Maroto-Valer, 2011). These processes use chemicals to leach out Mg from silicate rocks in acid environments and then carbonate the leached Mg with CO_2 forming magnesite or hydromagnesite at pH higher than 9. Therefore, a pH swing with addition of a base is required to raise the pH from the dissolution stage (pH ~0-2). The main advantage of the pH swing technologies is the fact that relatively pure products can be separated and their marketability reducing the costs involved in sequestering CO_2 (Sanna et al, 2014a). Yet, the use of these chemical additives significantly increases the energy requirements and cost of the process representing the bottleneck of the indirect CCSM technologies (Azdarpour et al, 2015). Also, since the carbonation reactions are favoured in water media, the regeneration of the chemicals must take into account the separation of the salts/acids form the aqueous solution remaining after the carbonation process, which is typical energy intensive due to the high water specific heat (Wang and Maroto-Valer, 2013). For example, ammonium sulphate in water is regenerated to ammonium bisulphate and ammonia by separating it from the water solution at the end of a pH swing CCSM process based on recyclable ammonium salts (AS). Then, the separated AS is thermally decomposed to produce the required reactants at 330°C (Wang & Maroto-Valer, 2011). Despite the fact that the thermal decomposition of the ammonium sulphate does not result in an energy intensive step, the recycling process requires a large amount of water evaporation, which results in high energy consumption. To address this problem, Wang and Maroto-Valer have developed a modified CCSM ammonium based process that increases the solid to liquid ratio from 50 to 200 g/L, resulting in a reduction in the amount of water evaporation needed (Wang & Maroto-Valer, 2013). The water evaporation step in the NH_4-based process required 3411.7 kWh for a 200g/l S/L ratio, with associated energy-cost ranging from £100/tCO_2 to £140/tCO_2 (considering 2.4 and 4.18 pence/kWh) (Sanna et al, 2016). Therefore, the process remains energy intensive and alternative pathways need to be developed.

We have recently proposed a similar process with one key alteration in that $NaHSO_4$ and NaOH are used in place of NH_4HSO_4/NH_3 (Sanna and Maroto-Valer, 2014b). In the sodium variant, sodium bisulphate is used instead of ammonium bisulphate in the dissolution stage, whereas CO_2 is captured by sodium hydroxide forming sodium carbonate. The advantage of using sodium salts is that their solubility in water decreases significantly at very low temperatures. Sodium sulphate's solubility in water for example is approximately 5g/100g H_2O at 0°C and 50g/100g H_2O at 40°C. In comparison, under the same conditions ammonium sulphate has a solubility of 70g/100g H_2O and 80g/100g H_2O respectively. Consequently, Na_2SO_4 can be successfully separated from water by using crystalline urea-functionalized capsules (90% separation obtained) or eutectic freeze crystallisation (100% separation) (Custelcean et al, 2015; Nathoo et al., 2009). For example, the cost saving of using eutectic freeze crystallisation over evaporative crystallisation resulted 85%, for separating $Na_2SO_4.10H_2O$ from ice and NaCl $2H_2O$ (Nathoo et al., 2009). When the temperature reaches 0°C ice crystallizes out, followed by $Na_2SO_4.10H_2O$ at -1°C and $NaCl.2H_2O$ at -23°C.

Previous work indicates that the feedstock has an important effect on the efficiency of the ammonium based processes (Styles et al, 2014). Ultramafic rocks, which globally could capture the emissions for 500 years are not uniformly distributed around the world and certain types of geological bodies and mineral combinations are far more abundant than others (Styles at al., 2014). However, this numbers do not take into account the feasibility of mining the rocks resources and the overall costs involved, which would need to be considered in a real scenario. Serpentine and serpentine-olivine mixtures are volumetrically dominant on a global scale. Using NH_4-salts, lizardite serpentinites resulted more efficient than serpentinized peridotites (olivine and lizardite with some pyroxene) with ca 80% Mg extraction. In the same work, the authors dismissed antigorite-rich serpentinites (40% Mg extraction) and pyroxene- and amphibole-rich rocks (only 25% dissolution) as potential resources for the NH_4-based pH swing MC processes (Styles at al., 2014).

In this work, lizardite-rich serpentinite (from the UK) has been studied to establish its behaviour in the dissolution and carbonation stages using a Na-based pH swing process and ascertain its potential as a CO_2 sequestration material.

2 Materials & Methods

2.1 Dissolution of serpentine using $NaHSO_4$

The serpentine used in this study came from the Ballantrae area in the West of Scotland where there is a large supply of the mineral. The serpentine was provided by the British Geological Survey (BGS) and selected from this area to emphasize the availability of the feedstock. There are two serpentinites belts in the Ballantrae area: a north belt (~8km x 1.5km) with an area of about 12 km^2. and a southern belt, which goes approximately from

Ballantrae to Millenderbale (~10km x ~2km), occupying about 20 km^2 for a total surface of 32 km^2 (BGS, 2016). Currently, serpentines are not mined in Ballantrae, but assuming a density of 2.6 t/m^3 (serpentine density) and open quarry of 30 m depth, it would result in a theoretical resource of 2,500 Mt, which would be able to sequester ~900 Mt CO_2 (in stoichiometric basis). Even assuming only 50% of it as usable (e.g. due to presence of sites of natural importance, farms etc.), it would represent an important feedstock for MC. Serpentinite from that Ballantrae is 92.3% lizardite and only 7.5% chrysotile plus minor contaminants, representing an ideal resource for MC (Styles et al, 2014).

Table 1 includes data on the mineral composition of the serpentine sample, which indicate that this material is an ideal feedstock for mineral carbonation due to the abundance of Mg (Styles et al., 2014).

Table 1: Wt% of Minerals in Serpentine (modified from Styles et al. 2014).

Na (wt%)	**Mg (wt%)**	**K (wt%)**	**Ca (wt%)**	**Al (wt%)**	**Si (wt%)**
0.01855	23.25	0.004141	0.02144	0.3707	17.63
Mn (wt%)	**Fe (wt%)**	**Ni (wt%)**	**Cu (wt%)**	**Zn (wt%)**	
0.03125	2.623	0.2043	0.00799	0.00803	

Table 2 presents the matrix of the dissolution experiments conducted under different conditions. The sodium salt used for the dissolution experiments was sodium bisulphate which leaches the Mg cations from the serpentine to form magnesium sulphate ($MgSO_4$) through the following reaction:

$$Mg_3Si_2O_5(OH)_4 + 6NaHSO_4 \rightarrow 2SiO_2 + 3MgSO_4 + 3Na_2SO_4 + 5H_2O \qquad (1)$$

The $NaHSO_4$ solution was prepared in 200ml of distilled water. The molecular weight (mw) of the salt is 120.06g/l and so the amount needed was calculated depending on the concentration required for the experiment. Once the salt had been dissolved in the water it was then transferred to a 250ml three neck flask which was then placed in a silicon oil bath.

The silicon oil is used due to its effective heat transfer characteristics and temperature stability. Once the flask had been placed in the bath, a cooling apparatus and thermocouple were connected to the top of the flask. The flask was then sealed, the cooling apparatus was switched on and the solution was heated and stirred at rates of 0.310°C/min and 900rpm respectively. The apparatus setup is shown in Figure 1. The solution was then left to reach the desired temperature and then, the serpentine was added. At this point, the timer was started and after 5 minutes the sampling began. For each sample, approximately 2ml of solution was taken and filtered into a vial. Exactly 1ml of solution was then acidified with 2ml of nitric acid in 97ml of distilled water. The digested solutions were then sent off for ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analysis. Nitric acid was added so as to prevent reactions between the ions. This process was repeated after 5, 10, 15, 30, 60, 120 and 180 minutes. Samples are taken at these time intervals so that the different dissolution efficiencies can be measured and the dissolution rate observed. At the end of the experiment, the solution was filtered using a vacuum pump so that the dissolution residue, which consists of namely SiO_2 and unreacted serpentine, could be removed and the remaining solution could be used in the carbonation experiments. The samples, along with the solution, were refrigerated and the dissolution residue was placed inside an oven so that any excess liquid could be evaporated. Upon completion, the residue was collected and placed in a sampling bag for FTIR (Fourier Transform Infrared Spectroscopy) and XRD (X-ray Diffraction) analysis.

Figure 1: Experimental set-up used for low temperature dissolution/carbonation experiments.

The dissolution efficiency was calculated by determining the percentage of Mg present in solution. This was done by first converting the units from mg/l to g/l and then by using the following equation:

$$\%Mg = \frac{Mg\ present\ in\ solution}{Mg\ present\ in\ serpentine} \times 0.2 \times 100 \tag{2}$$

The Mg present in solution relates to the value provide by the ICP-MS. The Mg present in serpentine corresponds to how much Mg was present in the original serpentine sample that was added to the $NaHSO_4$ solution. The wt% of Mg in serpentine was 23.25 and therefore there was approximately 2.325g of Mg present in 10g of serpentine. This value was multiplied accordingly for higher solid/liquid ratios. The 0.2 value is due to the fact that 200ml of solution was used and the 100 value is merely used to convert the result into a percentage.

Table 2: Matrix of dissolution experiments under different conditions

Experiment	**Temperature**	**Concentration**	**Solid/Liquid**	**Particle Size**
2	70°C	1.4M	50g/l	<250μm
3	100°C	1.4M	50g/l	<250μm
4	100°C	0.7M	100g/l	<250μm
5	100°C	0.47M	150g/l	<250μm
6	100°C	0.35M	200g/l	<250μm
7	100°C	1.4M	100g/l	<250μm
8	100°C	1.4M	150g/l	<250μm
10	140°C	1.4M	50g/l	<250μm
12	100°C	1.4M	50g/l	75-150μm

2.2 Mineral carbonation experiments

The carbonation experiments involved reacting sodium carbonate with magnesium sulphate to form a solid carbonate by the following reaction:

$$Na_2CO_3 + MgSO_4 \rightarrow MgCO_3 + Na_2SO_4 \quad (3)$$

Table 3 presents the matrix of the mineral carbonation experiments conducted under different conditions. For the carbonation experiments, the Na_2CO_3 was used as a source of CO_2. Na_2CO_3 is produced in the capture step, where 2 moles NaOH are reacted with CO_2, forming Na_2CO_3 and H_2O. This process has been investigated in previous work and for this reason was not tested (Nikulshina et al., 2008). There were two different methods of preparing the $MgSO_4$ solution for the carbonation experiments; the first involved using a solution obtained from the previous experiments, whereas the second method involved synthesising a solution using hydrated $MgSO_4$.

2.2.1 Mineral carbonation experiments using non-synthesised solutions

For experiments using non-synthesised solutions, the amount of Mg present in the solution had to first be determined. This was done using the results of ICP-MS analysis which are provided in section 3. The amount of solution obtained from the previous experiments was slightly over 100ml. Due to this limitation, only 100ml of $MgSO_4$ solution was used for these carbonation experiments. Once the amount of Mg present in the 100ml solution had been determined and knowing the mw of $MgSO_4$ and Mg, equation (3) can be used to determine how much Na_2CO_3 is required.

Example: 10g serpentine = 2.32g Mg

60% dissolution efficiency = 2.23g x 60% = 1.392g in 200ml or 0.696g in 100ml.

Need (120.366/24.305) x 0.696 = 3.447g $MgSO_4$

and (3.447/120.366) x 105.99 = 3.3035g Na_2CO_3

Similar to the dissolution experiments, the $MgSO_4$ solution was added into a 250ml three neck flask containing a stirring bar and set up was done identically as described in Section 2.1.1.. This was done for all experiments taking place at a pressure of 1 bar. Once the solution had been added, the distilling device was switched on and set to a heating rate of 0.310°C/min and stirring rate of 900rpm. The solution was then left to reach the desired temperature. Upon reaching said temperature, the pH of the solution was measured.

The non-synthesised solutions contained impurities such as iron, nickel and manganese as well as unreacted $NaHSO_4$ and Na_2SO_4. Therefore the pH of these solutions was very low (<1). To promote mineral carbonation the pH needs to be greater than 8 so that CO_3^{2-} ions are present in the solution which can then react with the Mg^{2+} ions to form solid, insoluble carbonates (Soong, et al., 2004). To remove the impurities and increase the pH a pH-swing was required. The pH swing process involved adding a base (NaOH) to the solution until the pH was approximately 7 as the addition of the Na_2CO_3 would further bring the pH up to the desired 8. Once the pH had reached approximately 7, the Na_2CO_3 was added and the carbonation experiments began.

The sampling for the carbonation experiments was done in the exact same way as for the dissolution experiments. Each experiment lasted 30 minutes with samples being taken after 5, 10, 15 and 30 minutes. The samples were collected from the flask and prepared with nitric acid and distilled water as described in the section 2.1. Once all the samples had been taken the remaining solution was filtered, leaving the solid $MgCO_3$ behind, which was placed in the oven to dry. Upon drying, the solid carbonate was placed in a sampling bag for FTIR and TGA Analyses.

2.2.2 Mineral carbonation experiments using synthesised solutions

Synthesised $MgSO_4$ solutions were also used for the carbonation experiments to evaluate the effect of impurities on the process efficiency. Each experiment was run in the exact same way as described in section 2.2.1. However, the preparation was different and no pH-swing was required as the synthesised $MgSO_4$ did not have any impurities and so the pH was already at the desired level. To prepare the solution, hydrated magnesium sulphate ($MgSO_4 \cdot 7H_2O$) was used. The amount needed was calculated in the following way by assuming that 100% dissolution efficiency was achieved and using equation (3):

Example: 10g serpentine = 2.32g Mg, so 2.32g in 200ml.

$MgSO_4 \cdot 7H_2O$: (256.48/24.305) x 2.32 = 23.578g

Na_2CO_3: (23.578/120.366) x 105.99 = 20.762g

The measured $MgSO_4 \cdot 7H_2O$ was then placed in a 200ml flask and 200ml of distilled water was added, at which point the solution was placed in the distilling flask. Once the desired temperature had been reached, the Na_2CO_3 was added and the experiment was performed just as before.

Two methods were used to calculate the mineral carbonation efficiency, depending on whether the solution used in the experiments was synthesised or one resulting from the dissolution experiments. If the solution was synthesised, then it has been assumed that there was 100% dissolution efficiency and hence all the Mg from the serpentine was extracted and is present in the solution. As a result equation (2) can be used to calculate the percentage of Mg present in the final solution. The result of which is then subtracted from 100 to determine the carbonation efficiency.

Two alterations to the calculation have to be made if the solution was not synthesised. The first is that the value for the Mg present in serpentine has to be multiplied by the final dissolution efficiency of said solution as there will be less Mg present. In addition since the solution used was only 100ml instead of 200ml, the 0.2 value is replaced with 0.1. As before the value obtained from the modified equation (2) is subtracted from 100 to determine the carbonation efficiency.

Table 3: Matrix of mineral carbonation experiments at different conditions

Experiment	**Temperature**	**Pressure**	**Solid/Liquid**	**Molar Ratio ($Mg:Na_2CO_3$)**	**Synthesised (Yes/No)**
11	90°C	1bar	50g/l	1:1	Yes
13	90°C	1bar	50g/l	1:1	No
14	90°C	1bar	100g/l	1:1	No
15	60°C	1bar	50g/l	1:1	Yes
16	90°C	1bar	50g/l	1:1.5	Yes

1kg serpentine contains 232.5g Mg (23.25 wt%)

CO_2 sequestration efficiency based on Mg conversion is 66.4%

Mg = 232.5g * 66.4% = 154.38g present in hydromagnesite

Hydromagnesite = 154.38/25.99% = 593.99g

CO_2 in hydromagnesite = 593.99 * 37.64% = 223.58g

Therefore 223.58gCO_2/kg serpentine

To compare the study with previous mineral carbonation experiments, the values of CO_2 sequestered in terms of Mg conversion were converted in grams CO_2 sequestered per kg of serpentine used. To do that, the Mg content in the starting serpentine (Table 1) and the wt% of Mg (25.99%) and CO_2 (37.64%) in hydromagnesite were considered.

3 Results and Discussion

3.1 Dissolution Studies

The objective of the dissolution experiments was to achieve the optimum conditions to extract Mg cations from serpentine. There were four different parameters investigated, namely concentration of $NaHSO_4$ used, solid/liquid ratio, temperature and particle size. Table

4 depicts the dissolution efficiency obtained under different condition. The effect of temperature, pressure, S/L ratio and particle size on the dissolution efficiency, is discussed in the following sections.

Table 4: Dissolution efficiencies under varying experimental conditions

Experiment	**Temperature**	**Concentration**	**Solid/Liquid**	**Particle Size**	**Dissolution Efficiency**
2	70°C	1.4M	50g/l	<250μm	56.43%
3	100°C	1.4M	50g/l	<250μm	61.47%
4	100°C	0.7M	100g/l	<250μm	42.02%
5	100°C	0.47M	150g/l	<250μm	34.88%
6	100°C	0.35M	200g/l	<250μm	24.36%
7	100°C	1.4M	100g/l	<250μm	60.44%
8	100°C	1.4M	150g/l	<250μm	57.52%
10	140°C	1.4M	50g/l	<250μm	60.09%
12	100°C	1.4M	50g/l	75-150μm	69.63%
17	140°C	1.4M	50g/l	75-150μm	67.60%

3.1.1 Concentration of $NaHSO_4$

For the dissolution experiments, serpentine was reacted with $NaHSO_4$, which in an industrial process would be regenerated after carbonation to reduce costs. The standard concentration used for these experiments was 1.4M of $NaHSO_4$, with the 40% excess, allowing all the serpentine to react with the sodium salt which would result in the highest possible dissolution efficiency. However, higher concentrations of $NaHSO_4$ mean more regeneration is needed. Therefore it would be desirable to reduce the concentration but only if the dissolution efficiency was not greatly affected. To ascertain the effect that lowering the concentration of $NaHSO_4$ has on the dissolution efficiency, experiments 3-6 (shown in Table 2) were undertaken. The calculated dissolution efficiencies from the ICP-MS analysis indicate that salt concentration has an important impact on the Mg leached out from the serpentine, with the amount-removed passing from only 24% using 0.35M solution to 61% using 1.4M solution.

The same lizardite was previously dissolved using 1.4M NH_4HSO_4 salt at 100°C. A larger amount of Mg was extracted (87% after 3h using 75–150 μm particles (Styles at al, 2014). This result was higher than the Mg extracted using $NaHSO_4$ under the same conditions (exp 12, 70%). Therefore, $NaHSO_4$ seems to be less effective at the dissolution of this particular lizardite-rich serpentine. However, the dissolution result is comparable when another lizardite-rich serpentine (serpentinised lherzolite from the Lizard peninsula, Cornwall, UK) was used at 70°C (Sanna and Maroto-Valer, 2014b). These differences can be ascribed to a wide variation in the rock composition as shown in our previous work and the necessity for accurate mineralogical characterization of potential resources and for technologists to be aware of the impact of feed material variations on process efficiency and development (Styles at al., 2014). As shown in this work, Lizardite serpentinites, with ca 69% extraction are suitable feed material for aqueous leaching with sodium bisulphate. This efficiency resulted similar to that (65% extraction in presence of NH_4-salts) obtained using serpentinized peridotites (olivine and lizardite with some pyroxene), which is probably the largest resource worldwide (65% extraction) (Styles et al., 2014).

The results obtained from the ICP-MS are backed up by FTIR and XRD analysis. Figure 2 shows the results of the FTIR analysis of the four dissolution products as well as the original serpentine and standard SiO_2. The spectrum assigned to the original Serpentinite peaks around 940 cm^{-1}, which corresponds to the Si–O basal vibration, while the lower intensity peak at about 1050 cm^{-1} is characteristic of the Si–O apical vibrations> In addition, the small sharp peak at 3680 cm^{-1} (not visible in Figure 2) is associated to OH bonded to Mg cations in the octahedral position (Sanna et al., 2013a). As shown in Figure 2, the dissolved materials present the triple degenerate asymmetric stretch of SiO_4 centred at about 1080 cm^{-1}, characteristic for highly condensed silicate species, which corresponds well with the spectra of the standard silica. Silica and the dissolved materials also present an absorption band at 797 cm^{-1} as can be seen in Figure 3 (Balan et al, 2002). Although the dissolved materials partially retain the original structure (core of the particles), they suffer a morphological and structural rearrangement with formation of porous (due to selective removal of Mg) silica-type structure in the shell of the particles. The dissolution effect of the different $NaHSO_4$ solutions can be extrapolated by the transmittance, which decreases accordingly to the rising solution molarity. A concentration of 1.4M resulted in the majority of the Mg cations being removed from the serpentine and a large amount of amorphous SiO_2 being formed, which is in agreement with the ICP-MS results. The gap between the peaks for the experiment using 0.7M is relatively small in comparison to that for 1.4M, and for the experiments using 0.47M and 0.35M it appears that most of the serpentine is still intact.

High dissolution efficiency is represented by a large gap of the most intense (100%) XRD pattern of the lizardite (2θ, 12.40; D1 Å, 7.12) represented in Figure 3, which shows the reduction in intensity of the lizardite phase, due to the Mg cations leached from the serpentine. The XRD analysis shows that very little serpentine has been left intact after experiment 3, whereas in experiments 5 and 6 the majority of the serpentine remains. Once again this confirms the ICP-MS results. The Mg depletion in the leached serpentine particles is also supported by the elemental analysis of the particles surface shown in Figure 4, with the Mg that dropped from 23% (Table 1) to ~ 11%.

The results of all three types of analysis are in agreement and conclude that reducing the concentration of $NaHSO_4$ results in a significant drop in dissolution efficiency. It is therefore likely that a substantial reduction in the concentration of $NaHSO_4$ would lead to a large increase of the size of the MC plant, since a larger quantity of serpentine would be required to sequester the same amount of CO_2.

Figure 2: FTIR spectra of samples with varying concentrations of $NaHSO_4$, SiO_2 and serpentine.

Figure 3: XRD analysis of samples with varying concentrations of $NaHSO_4$. (Only XRD patters between 11 and 14 2-Theta are shown)

Figure 4. SEM-EDX of dissolved serpentine (100°C, 1.4M $NaHSO_4$).

3.1.2 Solid/Liquid Ratio

In an industrial plant, large volumes of slurry will be required in the mineralisation process. The amount of slurry that needs to be treated can be reduced by increasing the solid/liquid ratio of the solution. However, increasing the ratio can have a detrimental effect on the dissolution efficiency as the liquid can become saturated. To investigate this parameter, experiments 3, 7 and 8 were carried out, as described in Table 2. The results of the ICP-MS analysis (Table 4) and FTIR (Figure 5) clearly show that by increasing the solid/liquid ratio there is a decrease of the dissolution efficiency, especially when increasing the ratio from 50 to 100g/l. The results obtained from the ICP-MS are once again supported by XRD analysis (Figure 6), which suggests that a S/L ratio of 150g/l sample is less effective than the other two samples.

Figure 5: FTIR analysis of samples with varying solid/liquid ratios.

Figure 6: XRD analysis of samples with varying solid/liquid ratios.

3.1.3 Temperature

To measure the effect of temperature on dissolution efficiency experiments 2, 3 and 10 were conducted. The FTIR analysis (Figure 7) alone suggests that performing the dissolution experiment at 140°C will provide a slightly better efficiency than at 100°C and both experiments have far superior dissolution efficiencies than the experiment taking place at 70°C. It was expected that the final dissolution efficiency for the experiment taking place at 140°C would be much higher than that of the 100°C experiment (Sanna et al., 2013a); this expectation was not reflected by the results in Table 4. Although, the FTIR analysis reported in Figure 7, show that the structure of the serpentine has suffer stronger modification at 140 °C, which do not corresponds to higher MG extracted (Table 4). This can be assessed by the ratio between the FTIR peak assigned to the original serpentine (960cm^{-1}) and those formed by its dissolution (1000-1150 cm^{-1}). A possible explanation for this is that an Mg precipitate has formed at 140°C. If most of the Mg cations have been removed from the serpentine and are not contained within the solution then they must have formed Mg precipitate.

Figure 7: FTIR analysis of samples with varying temperature.

The XRD results are in agreement with the FTIR analysis and the hypothesis that an Mg precipitate has formed. Figure 8 clearly shows that experiments 3 and 10 are far more effective at extracting Mg cations than experiment 2. It has to be noted that the Mg present in the precipitated salts is still available for carbonation, however it would require further treatment which would add cost. Therefore, it is clear from these results that increasing the temperature to 140°C would not be ideal.

Figure 8: XRD analysis of samples with varying temperature.

3.1.4 Particle Size

All of the previous experiments were run using serpentine with particle size <250µm as using larger particles means less pre-treatment of the serpentine and hence cuts down on both operational and capital expenses. Prior experiments using NH_4HSO_4 had shown that similar dissolution efficiencies could be achieved by using larger particles (Sanna, et al., 2013b). Particles with size 75-150µm were tested to see the effect that decreasing the particle size had on Mg-extraction rate and to see if $NaHSO_4$ was more susceptible to increased particle size than NH_4HSO_4.

The results in Table 4 show that decreasing the particle size results in an increase in dissolution efficiency, of approximately 7-8% due to larger surface area contact. The FTIR analysis shown in Figure 9 also indicates, considering the peaks ratios, a slight increase in dissolution efficiency for the experiments taking place using 75-150µm particles at 100°C.

Figure 9: FTIR analysis of samples with varying particle size at 100°C.

The results show that the amount of energy used in the dissolution process may be reduced by altering several of the parameters. For instance, increasing the solid/liquid ratio from 50g/l to 100g/l has a negligible effect on the dissolution efficiency (Experiments 3 and 7, Table 4). In addition reducing the temperature from 100°C to 70°C lead to only a 5% reduction in efficiency (Exps. 2 and 3, Table 4), while temperature of 140°C had a negative effect even at smaller particle size, so it would be recommended to run the process at 100°C regardless of particle size. This increases efficiency, albeit by a small amount, but more importantly can reduce the energy consumption associated with higher temperatures.

Increasing the particle size to <250µm results in an approximately 8% drop (Exps. 3 and 12, Table 4). This means that similar dissolution efficiency can be achieved while reducing the amount of pre-treatment required to reduce the particles size of the feedstock. Changing these parameters may result in a more feasible process if the reduction in energy consumption can justify the loss in efficiency.

3.2 Mineral Carbonation Studies

The objective of the carbonation experiments was to identify the optimum conditions to form solid hydrated magnesium carbonate, towards the minimisation of the energy consumption in the process. As described in section 2.2, experiments took place using both synthesised and non-synthesised solutions. Table 5 provides a summary of the reaction condition tested and the resulting carbonation efficiencies obtained after 30 minutes, while the single parameters are discussed in the following sections.

Table 5: Carbonation efficiencies under varying experimental conditions.

Experiment	**Temperature**	**Pressure**	**Solid/Liquid**	**Molar Ratio ($Mg:Na_2CO_3$)**	**Synthesised (Yes/No)**	**Carbonation Efficiency**
11	90°C	1bar	50g/l	1:1	Yes	98.89%
13	90°C	1bar	50g/l	1:1	No	95.43%
14	90°C	1bar	100g/l	1:1	No	83.08%
15	60°C	1bar	50g/l	1:1	Yes	98.07%
16	90°C	1bar	50g/l	1:1.5	Yes	99.35%

3.2.1 Non-Synthesis Solutions

These experiments were undertaken to show the effect of increasing the solid/liquid ratio on carbonation efficiency, as well as to show how the pH-swing process works. The experiments were run using the parameters shown in Table 3.

The solutions from experiments 3 and 7 had to undergo pH-swing before the carbonation experiments could take place so as to remove the impurities such as Ni, Fe and Al as hydroxides. Figure 10 shows the effect that the pH-swing process had on the solution obtained from experiment 7. The majority of Fe, Ni and Al was precipitated from the solution as hydroxides by the addition of NaOH. Same trend was shown in presence of NH_4HSO_4, with 95% Fe precipitated out form the solution previous carbonation (Azdarpour A, 2015). However, the behaviour of trace elements such as Mn (0.03 wt%), Cu and Zn (0.008 wt%) will also need to assessed in future, to evaluate the potential risks in terms of water contamination and the wastewater treatment costs. Mining acid wastewater treatment is an established technique. For an indication on potential costs, the average estimated cost for mining waste-water treatment using a Successive Alkalinity Producing Systems (SAPS) ranges from $0.003 to 0.03 per gallon of acid mine drainage, with CAPEX between $72k (2013 USD) per year for a 5-gallons per minute (gpm) system to $151k (2013 USD) per year for a 100-gpm system (EPA, 2014).

Figure 2: Effect of pH swing process on solution from Exp 7.

Table 5 shows the carbonation efficiency after 30 minutes. Unlike with the dissolution experiments, increasing the solid/liquid ratio from 50g/l to 100g/l resulted in a drop in carbonation efficiency of approximately 12%. The FTIR analysis for the carbonation experiments does not give an indication to the carbonation efficiency, but it is used to confirm the formation of hydromagnesite. The bands appeared at 1123 cm^{-1} and 1172 cm^{1} (Na_2SO_4) are assigned to asymmetric stretching of SO_4 groups (Periasamy et al, 2009). The absorption bands between 695 and 857 cm^{-1} are attributed to the in-plane bending and out-of-plane bending modes of CO_3^{2-}; the band at 1106 cm^{-1} is attributed to the symmetric C–O stretching vibration; the bands at 1433 and 1485 cm^{-1} are linked with asymmetric C–O stretching vibration and finally, the 1691 cm^{-1} band is ascribed to an OH-bending mode of H_2O (Wu et al., 2011). The formation of the solid hydromagnesite is confirmed for both experiments, as shown in Figure 11, along with the existence of un-reacted Na_2SO_4, which would be left in the solution from the dissolution experiments.

Figure 3: FTIR analysis for varying solid/liquid ratios.

Before testing the other parameters using synthesised solutions, experiment 13 was rerun using a synthesised solution to compare the two methods. As stated in section 2.2.2, synthesised solutions were used to compensate for solutions with low amounts of Mg present or where not enough solution was obtained to perform the carbonation experiment. The results displayed in Table 5 are as expected. The synthesised solution presents higher carbonation efficiency than the non-synthesised solution and this is due to the fact that even though the pH-swing process removes most of the impurities there are still some remaining, while the synthesised solution contains only $MgSO_4$.

3.2.2 Synthesised Solutions

There were three parameters investigated using the synthesised solutions, namely temperature and molar ratio. Decreasing the temperature from 90°C to 60°C will reduce the amount of energy required but decrease the carbonation efficiency. The highest carbonation efficiency should be achieved by increasing the molar ratio i.e. using more Na_2CO_3. This would lead to larger extent of reaction, but would increase the amount of chemicals required. Experiments 15-17 were run using the conditions shown in Table 3 and the results compared with experiment 11. As expected, increasing the molar ratio resulted in the highest efficiency;

however, this increase is negligible compared with the amount of additional chemicals that would be required. Decreasing the temperature to 60°C appears to be the most effective method of reducing energy consumption while maintaining a high efficiency as the results are almost on par with those from experiment 11. As expected, the FTIR analysis (Figure 12) shows the presence of hydromagnesite for experiments 11 and 15. For experiment 16, the FTIR analysis (Figure 13) shows residual Na_2CO_3 which is due to an excess of the additive being used.

Figure 4: FTIR analysis of experiments 11 & 15.

Figure 5: FTIR analysis for experiment 16 showing residual Na_2CO_3.

Previous work found a dissolution and carbonation efficiency of 77% and 87.7%, respectively using ammonium salts and lizardite from the Lizard peninsula, UK (dissolution at 100°C, 75-150µm, 1.4M NH_4HSO_4; carbonation at 80°C and 1:4:3 as Mg:NH_4 salts:NH_3 molar ratio, 30 minutes), which resulted in a CO_2 sequestration of 67.5%, based on Mg conversion (Sanna, et al., 2013a). In addition, Styles et al. (2014) found a CO_2 sequestration of 75.7% using ammonium salts and Lizardite from Ballantre same as in this work (Styles et al., 2014). For comparison, the CO_2 sequestration was found to be 66.4% in this work using non-synthetic solutions (dissolution 69.6%, carbonation 95.4%), which corresponds to 223.6 gCO2/kg serpentine. Therefore, the sodium process is able to sequester comparable amount of CO_2 (-12% at the worst) as using the ammonium salts based process. This small loss in sequestration efficiency would be acceptable considering the potential large energy saving achievable using the sodium based mineral carbonation process due to the potential separation of the Na-salt from the water solution without thermal-treatment (Sanna and Maroto-Valer, 2014b). Moreover, the experiments indicate that the carbonation temperature could be decreased to 60°C and the S/L ratio in the dissolution could be increased to 100g/l without losing efficiency in the process.

4 Conclusions

The purpose of this work was to ascertain whether or not $NaHSO_4$ can effectively dissolve lizardite-rich serpentinites and the resulting $MgSO_4$ used to carbonate CO_2 in a pH swing MC process and evaluating the best conditions to do so. It was found that the use of the sodium salts based process was able to sequester 223.6 gCO_2/kg serpentine using lizardite-rich serpentinite from Ballantrae, UK, which is comparable to the CO_2 sequestration achieved using ammonium based processes and other pH swing processes. Moreover, this work indicate that $NaHSO_4$presents good dissolution efficiencies under solid/liquid ratios of 50g/l - 100g/l, temperatures close to 100°C and particles smaller than 150 µm and a 0.4 molar excess of NH_4HSO_4, since the reduction of the $NaHSO_4$ concentration resulted in a significant drop in dissolution efficiency.

On the other hand, the carbonation step was very efficient under all the conditions used, with almost complete (99%) conversion at 60 and 90 °C, ambient pressure and 50 g/l. S/L ration is the parameter that most affected the carbonation, with the efficiency dropping to 83% at 100 g/l.

Overall, this work indicate that the investigated process can be employed to convert CO_2 from industrial/power emitters into stable carbonates. However, whether the $NaHSO_4$/NaOH process can be effectively deployed for the sequestration of CO_2 will require further investigation and complete techno-economic and life cycle assessments.

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