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Abstract: Carbon capture and storage by mineralisation aims to reduce carbon dioxide emissions (CO₂) by reacting CO₂ with rocks rich in magnesium or calcium oxide and producing solid mineral carbonates, which can provide safe storage capacity. Recently, indirect mineral carbonation by pH swing mineralisation processes that use recyclable ammonium salts has shown promising results, but the process needs to be optimised. For example, the feasibility of this process in the presence of a mixture of NH₃-salts has not been demonstrated. Accordingly, carbonation of rocks rich in magnesium and a mixture of NH₄HCO₃ and (NH₄)₂CO₃ under different temperatures was investigated to reproduce a real scenario from an ammonia capture process. The highest carbonation efficiency was 62.6% at 80°C and 1:4:3 as Mg:NH₄salts:NH₃ molar ratio, indicating that the process in presence of ammonium salts mixture is feasible.

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Carbon dioxide capture and storage by pH swing aqueous mineralisation using a mixture of ammonium salts and antigorite source

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Abstract

Carbon capture and storage by mineralisation aims to reduce carbon dioxide emissions (CO₂) by reacting CO₂ with rocks rich in magnesium or calcium oxide and producing solid mineral carbonates, which can provide safe storage capacity. Recently, indirect mineral carbonation by pH swing mineralisation processes that use recyclable ammonium salts has shown promising results, but the process needs to be optimised. For example, the feasibility of this process in the presence of a mixture of NH₃-salts has not been demonstrated. Accordingly, carbonation of rocks rich in magnesium and a mixture of NH₄HCO₃ and (NH₄)₂CO₃ under different temperatures was investigated to reproduce a real scenario from an ammonia capture process. The highest carbonation efficiency was 62.6% at 80°C and 1:4:3 as Mg:NH₄salts:NH₃ molar ratio, indicating that the process in presence of ammonium salts mixture is feasible.

Keywords: Mineral carbonation, CCS, ammonium salts, dissolution, serpentine

1. Introduction

Carbon Capture and Storage (CCS) in geological formations has the potential to sequester about 20% of the global CO₂ emissions per year by 2050 and can be applied mainly to emitters >1 Mt CO₂/year, while it is less appropriate for smaller emission sources [1,2,3].

CCS by mineralisation (CCSM) can sequester CO₂ by mixing the CO₂ from flue gases with industrial solid waste or rocks rich in magnesium or calcium oxides. The oxides react with CO₂ producing solid mineral carbonates, which are stable and can provide safe storage capacity on a geological scale. It is estimated that the global magnesium silicate rock deposits are enough to sequester the CO₂ generated

by all the fossil fuels resources [1,4,5]. CCSM can therefore contribute to decrease CO₂ emissions in areas (e.g. West coast of the USA, Canada, Japan, East Australia, Oman, Finland, Portugal) where there are large deposits of suitable rocks and where geological storage may result uneconomical or not feasible (e.g. Finland) [6,7]. Recently, interest in mineral carbonation is growing in many regions to provide additional large-scale carbon capture and storage capacity and last developments indicate that it should be possible to have a 1Mt CO₂/year plant running in ten years' time [8,9,10,11]. Indirect CCSM by pH swing using ammonium salts has been reported to enhance the efficiency of both dissolution of reactive minerals and carbonation resulting in 70-80% CO₂ sequestered [7,9,12]. The process shown in Figure 1 consists of (i) dissolving minerals rich in magnesium producing a MgSO₄ solution, (ii) removing the impurities (Fe, Al, Mn etc.) by increasing the pH from acid to basic; (iii) carbonating the MgSO₄ with ammonium carbonate as CO₂ carrier from the (iv) NH₃ capture stage and finally precipitating hydromagnesite. The main advantage of this process is that it can recycle most of the chemicals used overcoming the main issue of the indirect mineral carbonation processes.

Typical amines scrubbing have been commercially used to capture CO₂ from flue gases from small scale natural gas and coal power plants in the 1980s, but their main disadvantages include their high degradation rate and the high energy consumption of about 4 GJ/t CO₂ [13,14]. In contrast, ammonia-based wet scrubbing presents a heat of absorption of CO₂ by ammonia greatly lower than that for alkanolamines used for CO₂ capture (<2 GJ/t CO₂), degradation problems are not present and also, the ammonia process can be used to capture not only CO₂, but also SO₂, NO_x and HCl [15,16]. For all these reasons, the ammonia capture process presents reduced total cost and complexity of the overall emission control systems [13,17].

The NH₃ scrubbing process can precipitate several ammonium carbonate compounds in the absorber, including ammonium bicarbonate (NH₄HCO₃), ammonium carbonate ((NH₄)₂CO₃) and ammonium carbamate (NH₂COONH₄) where their molar ratio depends on the process conditions [18,19].

Previous research has been focused on CCSM in the presence of NH₄HCO₃ [9,12] while indications of the feasibility of this process in presence of a mixture of NH₃-salts are not available yet. Under CO₂ molar loadings higher than 0.5 both the ammonium carbonate and bicarbonate salts are present, while

when the CO₂ loadings is lower than 0.5 the only solid is ammonium carbonate [20]. Therefore, the ammonia process is likely to form a mixture of ammonium salts. Accordingly, this study aims to investigate the carbonation behaviour of silicate rocks in the presence of a mixture of ammonium salts at different temperatures to compare the results with previous experiments carried out using only ammonium bisulphate [9].

A series of dissolution (at 100°C) and carbonation experiments (50, 70, 100°C) were performed at ambient pressure in a batch reactor and using different Mg:NH₄HCO₃/(NH₄)₂CO₃:NH₃ ratios, to evaluate their effect on the dissolution of an antigorite rich serpentine from Cedar Hills (USA). The overall CO₂ sequestration efficiency was compared with previous work [7,9,12].

2. Experimental section

2.1 Dissolution experiments

The dissolution experiments were carried out in triplicates considering the optimal dissolution conditions indicated in previous work [7]. Therefore, 200g of serpentine from Cedar Hills with particle size ranging from 75 to 150µm were added into 4000mL 1.4M NH₄HSO₄ solution for a 50g/L solid liquid ratio. The solution was placed into a three neck flask glass reactor under a constant stirring rate of 800rpm and heated using a silicon bath at the desired temperature of 100°C.

An aliquot of 1mL was extracted after 5, 10, 15, 30, 60, 120 and 180 minutes to determine the content of Mg and other ions in the solution. After 3 hours of dissolution, the flask content was cooled down to ambient temperature and filtered with a 0.7µm Pall syringe filter.

2.2 pH swing experiments

After the dissolution experiments, the impurities were removed by adding ammonia-water to rise the initial acid pH of the solution from 0.2 to a pH value of 8.5 to precipitate all the impurities such as iron, manganese and aluminium. A different volume of NH₃ was necessary for this step depending on the temperature used, where 10vol%, 12vol% and 25vol% NH₃ was added to 200mL dissolution solution during the experiments at 50, 70 and 100°C, respectively, probably due to loss of NH₃ by evaporation.

2.3 Carbonation experiments

The carbonation experiments were carried out at 50, 70, 80 and 100°C. 200mL of the solution produced after the pH swing experiments was poured into a 250mL 3-necks flask and heated up at the required temperature by using a silicon-oil bath under continuous stirring at 800rpm. As soon as the desired temperature was reached and stayed constant for 20 minutes, the amount of NH₃ required to raise the pH to 8.5 was added to the solution and then, the mixture of 50% (NH₄)₂CO₃ and 50% NH₄HCO₃ was added to start the carbonation reaction. Different Mg:NH₄HCO₃:NH₃ molar ratios were also investigated (1:2:7, 1:2:2, 1:2:4). An aliquot of 1mL was extracted after 5, 10, 15, 30 and 60 minutes to measure the concentration of Mg by ICP-MS.

2.4 Products analysis

1mL of sample was acidified with 2mL of HNO₃ and then diluted to 100mL with deionised water to be analysed by ICP-MS. The liquid acidified samples for the ICP-MS were prepared following the same method indicated in the dissolution experiments. Inductively coupled plasma mass spectroscopy (ICP-MS) Thermo-Fisher Scientific X Series Instrument, was used to measure the concentrations of the dissolved Mg, Fe and others elements of the samples. For instrument calibration, scandium (100 µg/L), rhodium (20 µg/L) and iridium (10 µg/L) in 2% trace analysis grade (Fisher Scientific, TAG) HNO₃ were used as internal standards. Also for calibration, external standards for elements were prepared in the range 0-100 µg/L (ppb). An autosampler (Cetac ASX-520) and a concentric glass venture nebuliser (ThermoFisher Scientific) were used and the data processing was undertaken using a Plasmalab software (version 2.5.4, Thermo-Fisher Scientific, UK).

After each experiment, the solids were dried for 24 hours at 90°C and then characterised by ICP-ES and TGA. The carbonate content in the starting serpentine and final products was investigated by TGA analyses performed using a thermal TGA Q500, TA Instrument. Representative samples (10-20mg) were heated in alumina cups under nitrogen atmosphere at 10°C/min from ambient to 900°C. The temperature was hold for 10, 15 and 20 minutes at 105°C, 500°C and 950°C, respectively. The weight loss in the temperature region of 350°C to 500°C was determined to be carbonates. Total abundances of the major oxides and several minor elements of the serpentine (from Ceder Hills) used

in this work was obtained from ICP-optical emission spectroscopy (Thermo Scientific iCAP 6500). Data were reported on a 0.2g sample analysed following a lithium metaborate/ tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) was determined by weight difference after ignition at 1000°C. The elemental composition of the starting serpentine, dissolution residue and carbonation product at 100°C was also analysed using a Flash EA 1112 Series elemental analyser. The mineral phases of the samples were determined by X-ray diffraction (XRD). For qualification of mineral phases, 1 gram sample was analyzed using a Philips Analytical 1050 X-ray Diffraction (XRD) at scan speed 3°2θ/minute from 5°2θ to 65°2θ under 40 kV/40 mA and peaks were identified using the ICDD Powder Diffraction Files. A laser diffraction Malvern LS 15 320 series was used to determine the particles size distribution of the investigated materials. About 1g of sample was dispersed in water for the analysis.

The ICP-ES data presented in Table 2 were used to calculate the quantity of NH₄-salt needed in the process. The Mg content present in the samples was calculated on the basis of the MgO content of the mineral sample, by using the following formula:

$$\text{Mg\%} = \text{MgO\%} * (\text{MW Mg} / \text{MW MgO}) \quad (\text{i})$$

Where, MW is the molecular weight of Mg and MgO. The extraction efficiency of dissolution of a specific element X (e.g. Mg) at a given time y (at 5, 15, 30mins etc.) was calculated as follows:

$$\text{X extraction\%} = (\text{C}_y * \text{V}) / (\text{M batch} * \text{W}_x) * 100 \quad (\text{ii})$$

Where, C_y is the concentration of element X in the solution sampled at y time, V is the volume of the solution in the reactor, M batch is the mass of serpentine sample added and W_x is the initial weight percentage of mass of element X over the total mass of solid present in the patent sample [6].

The inherent carbonate content of the raw mineral samples, residues after dissolution and carbonated powders were characterized by a thermal gravimetric analyzer. The CO₂ content in the carbonation products (iii) was calculated considering the weight lost by the carbonation product between 300 and 500°C (Δm 300-500°C), while the degree of carbonation, from Mg (ξMg%) and the CO₂ uptake in the

hydromagnesite (CO₂ (wt%) hydromag.) were calculated as shown below in equations iv and v, respectively:

$$\text{CO}_2 \text{ (wt\%)} = \Delta m_{300-500^\circ\text{C}} / m_{105^\circ\text{C}} * 100 \quad (\text{iii})$$

$$\xi \text{Mg\%} = \text{Mg in hydromag. (after carb)} - \text{Mg in hydromag. (before carb)} / \text{Mg in serpentine} * 100 \quad (\text{iv})$$

$$\text{CO}_2 \text{ (wt\%)} \text{ hydromag.} = \text{mass carbon. residue} * (\text{CO}_2 \text{ hydromag. (after carb.)} - \text{CO}_2 \text{ MgCO}_3 \text{ (before carb.)}) \quad (\text{v})$$

Where, (befor carb) and (after carb) stand for before and after the carbonation step.

3. Results and Discussion

3.1 Dissolution experiments

The main reaction involved in the dissolution step is as follows:

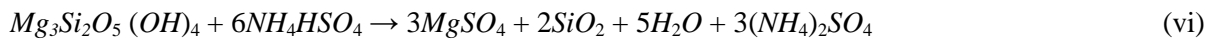


Figure 2 shows the extraction of Mg and Fe, Al and Ni. The higher magnesium extraction was obtained after 3hrs with 70% of the Mg removed from the serpentine particles. The triplicate runs present the same dissolution trend indicating that a fast extraction indeed occurs in the first 30 minutes, where 55% of the Mg is extracted and only 15% more is extracted after 2 hours. Less than 10% of Al was removed from the mineral lattice after 5 minutes extraction and this value was not increased ever after 3 hrs extraction time. About 40-45% of Fe was extracted in the first 30 minutes and similarly to the Al extraction trend, no further Fe was removed from the mineral lattice after the next 2.5 hours. Finally, Ni was extracted (above 60%) after only 30 minutes and 70% after 3hrs dissolution. Overall, the first 5-10 minutes present a fast dissolution of metals from the mineral structure, while after 30 minutes the extraction is very slow and a long reaction time (3 hrs) is required to enhance a further 10-15% the final extraction. This indicates that while 2 hours is the optimal dissolution time in terms of higher Mg extraction, 30 minutes might be preferred considering the lower capital costs associated with fast processes in presence of large volumes to be treated [12].

The dissolution trends observed with the initial fast removal of cations followed by a much slower step can be associated with the low extraction of silica oxide that creates a passive layer on the serpentine particles surface [21]. The formation of a silica-rich passive layer could inhibit the continuous leaching of magnesium and iron from the inside of the particles and this probably explains why the dissolution rate slows down over time [22].

Interestingly, the dissolution experiments resulted in 30% less Mg extracted after 3 hours compared to previous work carried out using serpentine rock from the same location [7], indicating mineral phase variability of the resources that need to be taken into account during the process' planning and design operations.

3.2 pH swing experiments

The second stage of the overall process was the pH swing from acidic (pH 0.2) to neutral (pH 7) and then basic (pH ≥ 8) by addition of ammonia water to remove all the impurities (Fe, Al, Zn, Ni, Cu, Mn etc.) from the solution by precipitating them as hydroxides and oxides, as shown below:

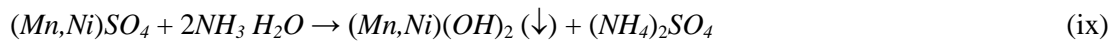


Figure 3 shows the concentration of Fe, Al, Ni and Mn in function of the pH change at two different temperatures (25 and 60°C). At ambient temperature, 90% of Al and Mn are removed from the solution with pH changing from 0.2 to 2.5, while only 40% and 60% of Ni and Fe, respectively, precipitated under the same conditions. The Fe concentration (most abundant element after Mg) remained stable until the pH value approached 8. Then, at pH higher than 8 the remaining Fe, Al, Ni and Mn precipitated as hydroxides, leaving the solution of MgSO₄ ready for the carbonation reaction. The pH swing process at 60°C was better in terms of hydroxides precipitation compared to the ambient temperature process, as shown in Figure 3, where the amount of iron removed at pH 6 and 7 was 8% and 20% larger at 60°C compared to ambient temperature; probably because precipitation rate is dependent on seeding temperature [23]. The increase of pH and temperature enhanced the solubility

of the Fe species and increased the precipitation reactions explaining the higher removal of Fe from the solution [24]. Generally, the removal of metals from the mineral structure is considered a metal-proton exchange reaction and at acidic conditions (pH 0-3), monovalent metal-oxygen bonds break more rapidly than divalent metal-oxygen bonds, which break faster than trivalent bonds [25].

The raise of the pH from 7 to about 8.5 requires a large volume of $\text{NH}_3 \cdot \text{H}_2\text{O}$ leading to the unwanted removal of about 7-10% of the free Mg in solution.

3.3 Carbonation experiments

The last step of the process was the carbonation of the MgSO_4 solution using a 50/50 mixture of NH_4HCO_3 and $(\text{NH}_4)_2\text{CO}_3$, as shown below:

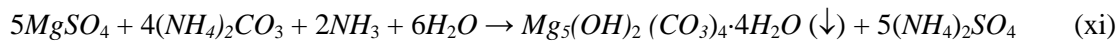
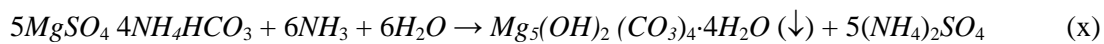


Figure 4 shows that the concentration of magnesium in solution decreases during the carbonation experiments due to the precipitation of the final product ($\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$). Only 10%, 30% and 60% of the total Mg precipitated in the first 5 minutes of the reaction in the experiments at 50, 70 and 80°C, respectively. In contrast, just after 5 minutes 80% of the total Mg in solution was precipitated at 100°C. The carbonation at 100°C presents much faster kinetics than the carbonation at the lower temperatures and finally, 90% of the Mg in solution precipitates after 60 minutes.

Carbonation is affected by species concentration in solution and their dissociation which is temperature-dependent. Therefore, dissociation of NH_4HCO_3 ($\text{NH}_4\text{HCO}_3 \leftrightarrow \text{NH}_4^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$) and $(\text{NH}_4)_2\text{CO}_3$ ($(\text{NH}_4)_2\text{CO}_3 \leftrightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-}$) can influence the precipitation of Mg carbonates. The CO_3^{2-} activity increases with temperature reaching its maximum at 90-100°C and promoting precipitation of Mg carbonate species [26]. Also, the high activation energy for the desolvation of the strongly hydrated Mg^{2+} ions at low temperature affects carbonation as indicated in Figure 4 [27]. Temperature also affects the size and morphology of the resultant carbonated species,

due to a combination of factors that include an increased nucleation rate at higher temperatures resulting in the growth of nuclei into smaller particles [28]. This is correlated to the lower viscosity of the solution at higher temperature, which accelerates the collision rate of the nuclei, and in consequence, enlarges the number of nucleated particles, so it will produce smaller particles [29].

Also, the effect of the Mg:NH₄ salts:NH₃ ratio was investigated to establish its influence on carbonation efficiency. Figure 4 indicates that the best ratio in terms of carbonation efficiency is 1:4:3 with a final carbonation of 93.5%. If NH₃ is not used in the carbonation process, the maximum stoichiometric conversion of Mg(HCO₃)₂ in solution into precipitated MgCO₃·3H₂O is calculated to be only 50%, while the use of NH₃ improves the conversion to 90-95% by converting NH₄HCO₃ into (NH₄)₂CO₃ which can directly produce MgCO₃ [9]. The high efficiency reached with the ratio 1:4:3 can be explained by the evaporation of NH₃ in the set-up used, so that 3 moles of ammonia water were required to reach the higher efficiency.

The Mg content in the solution was also used to calculate the carbonation efficiency at the different temperatures. A carbonation efficiency of 69%, 71%, 88% and 91% was calculated considering the precipitated magnesium at 50, 70, 80 and 100°C, respectively. Table 1 reports the masses of CO₂ before and after carbonation reaction, the degree of carbonation, the total CO₂ capture considering both dissolution and carbonation steps and the final amount of serpentine required to sequester 1 tonne of CO₂ based on the CO₂ uptake. The total CO₂ capture efficiency is low at 50°C and 70°C (46-47%) and was higher at 80°C and 100°C with 62.6% and 61.5%, respectively. Therefore, the mineral carbonation at 80 and 100°C would require the lower amount of starting serpentine (4.6-4.8t/tCO₂). However, the carbonation efficiency using different mineral phases from the same location and only NH₄HCO₃ under the same conditions was found higher (70-80%) [2,7,20], indicating that the resource type and the dissolution efficiency represent the limiting step for a widespread deployment of this technology.

3.4 Products characterisation

The characterization of the starting serpentine, dissolution residues and carbonation products was carried out by analysing their chemical content (ICP-ES and EA) and their mineral composition (XRD). Also, the particle size was analysed to give some useful indication of the potential technologies required for the post-processing of the produced powders. Table 2 shows that the composition of the starting serpentine is richer in silica, alumina and magnesium oxide compared to that used previously [7], indicating a different mineralogical composition that can explain the different dissolution behaviour. In fact, the higher concentration of Mg in the parent serpentine does not result in a higher extraction of Mg in solution. The composition of the dissolution residue also indicates a preferential extraction of Mg from the mineral lattice that remains rich in silica, alumina and iron oxide. The carbonation product consists mainly of MgO and has a high LOI (66%) as expected in the precipitation of hydromagnesite during the reactions. The presence of iron (3.7%) is detrimental in terms of using this carbonate material as filler in the paper industry because of the low brightness related to Fe presence and further investigations are required to establish other potential uses and post-processing required to enhance the purity of these materials. Moreover, the Mg mass balance (4.98g of Mg in the starting material, 1.72g in the dissolution residue and 3.12g in the carbonation product) indicates that about 62% (68% from ICP-MS of liquids) of Mg is removed from the serpentine sample after 3hrs dissolution.

The elemental analysis of the material used in this work and the reactions products are presented in Table 3. The presence of S and N at the lower carbonation temperatures indicates precipitation of NH_4 and SO_4 salts together with hydromagnesite. These salts are unwanted in terms of post-processing application in constructions because of the potential formation of thaumasite ($\text{Ca}_3\text{SiSO}_4\text{CO}_3(\text{OH})_6 \cdot 12\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) in concrete [30]. In fact, considering that Mg, H, C and O contents in pure hydromagnesite are 26%, 2.1%, 10.2% and 61.6%, the elemental analysis indicate that small amount of another mineral phase was also precipitated. Small amounts of ammonium magnesium sulphate salt namely boussingaultite $(\text{NH}_4)_2(\text{Mg}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ which were

found among the carbonation products in previous work due to some liquid solution remaining into the filtrate before the drying step, were not detected in the products [9].

The starting serpentine, solid residues after the leaching process and carbonation product at 100°C were characterized using XRD. The XRD pattern of the serpentine leaching residue presented in Figure 5 (a) indicates that the main phase in the starting serpentine is antigorite and the secondary phases are lizardite and possible small traces of chrysotile. In contrast, the dissolved residue is mainly leached residual antigorite (Figure 5 (b)) that seems to be more resistant to dissolution compared to lizardite under these process conditions. It has been reported that antigorite presents tri dimensional chemical bonds among the corrugated octahedral and tetrahedral sheets, while lizardite presents flat not bonded layers that can explain the different dissolution behaviour [31]. This may be the reason of the different dissolution efficiency found with rocks from the same locations but different mineral phase (see Section 3.1). The XRD pattern of the precipitated carbonation products shown in Figure 18 (c) indicates that hydromagnesite is the main phase.

Particles size distribution is an important parameter in terms of process plant design and product materials utilisation. Figure 6 shows the particles size distribution of the starting serpentine, the dissolution residue and the carbonation product at 100°C. The D50 of the dissolved particles was 81µm (86 µm for the starting serpentine particles) while the D90 was 157µm (162µm for the starting serpentine). Therefore, the size of the particles after the dissolution decreased by about 5µm compared to those feed into the reactor, and this is consistent with the shrinking core dissolution model [32,33]. The preferential leaching of Mg from the serpentine surface leaves behind a porous layer of amorphous silica as indicated by the dissolution residue composition in Table 2 that limit the further extraction of mg and explains the little difference between the stating serpentine and dissolution particles. Instead, the hydromagnesite particles present a small diameter with D50 of 60µm and D90 of 141µm. The wide range of distribution for the carbonation product can be due to agglomeration of particles during the drying process.

4. Conclusions

In this study, the carbonation behaviour of antigorite-rich serpentine using a mixture of ammonium salts at different temperatures was investigated. The dissolution trends observed with the initial fast removal of magnesium (55% in 30 minutes extraction) was then slowed down by diffusion limitations due to the formation of a silica product layer. The pH swing process at pH 8 virtually removed all the impurities (Al, Ni, Fe, Mn) from the dissolution liquid leaving a pure MgSO_4 solution ready for the carbonation step. The carbonation at 100°C presents much faster kinetics than the carbonation at the lower temperatures investigated because of enhanced ions dissociations, lower desolvation activation energy and faster particles nucleation during precipitation. The carbonation in presence of the NH_4 salts mixture requires a temperature of 80°C to give efficiencies greater than 90%. The CO_2 captured in the overall capture and storage process (62%) using the antigorite rich sample and salts mixture can be further optimised to reach higher CO_2 capture efficiencies. The resource used in this process plays a primary role because it can limit the amount of Mg available for carbonation. In particular, antigorite seems to be less reactive than lizardite and further investigations are needed to enhance the efficiency of the overall process and in particular to establish the optimal resources to use with this CCS technology.

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List of Captions

Table 1 Carbonation efficiency at 50, 70, 80 and 100°C and mass of serpentine required for each tonne of CO₂ sequestered. (1:2:2 and 1:4:3 stand for Mg:NH₄HCO₃:NH₃ molar ratio).

Table 2 ICP-ES analysis of starting serpentine, residue after dissolution and carbonation product.

Table 3 Elemental analysis of starting serpentine, residue after dissolution and carbonation product.

Figure 1 Scheme of the UoN pH swing process used in this work [modified from 6].

Figure 2 Magnesium, iron, aluminium and nickel extraction during the 3hrs experiment. Triplicate of magnesium and iron are reported.

Figure 3 Precipitation of iron, aluminium, manganese and nickel in function of the pH.

Figure 4 Variation of the magnesium concentration in carbonation solutions at different temperatures. (1:4:3 and 1:2:2 stand for Mg:NH₄HCO₃:NH₃ molar ration). A ratio 1:2:7 was used in the experiments at 50-70-100°C.

Figure 5 XDR spectra of (a) original serpentine rock, (b) dissolution residue, (c) carbonation product.

Figure 6 Size distributions of the starting serpentine particles and residue after dissolution and carbonation.

Table 1 Carbonation efficiency at 50, 70, 80 and 100°C and mass of serpentine required for each tonne of CO₂ sequestered. (1:2:2 and 1:4:3 stand for Mg:NH₄HCO₃:NH₃ molar ratio).

Experiment	CO₂ (wt%) after carbonation (TGA)	Carbonation efficiency, % (ICP-MS)	Total CO₂ captured, % (TGA)	Total CO₂ captured, % (ICP-MS)	Rock resource (t_{Serpentine}/t_{CO2})
50°C	16.5	69.5	38.5	46.5	7.7
70°C	17.5	71.3	41	47.7	7.2
100°C	20.1	91.3	61.5	61.5	4.8
80°C (1:2:2)	24.7	88	60	58.9	4.9
80°C (1:4:3)	28.8	93.5	62	62.6	4.6

Table 2 ICP-ES analysis of starting serpentine, residue after dissolution and carbonation product.

Sample	SiO₂	Al₂O₃	Fe₂O₃	MgO	CaO	TiO₂	P₂O₅	MnO	Cr₂O₃	Ni	Sr	Sc	LOI
	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	%
Serpentine	35.42	0.51	7.06	41.29	0.24	0.03	<0.01	0.11	0.303	2189	7	4	14.0
Dissol. residue	57.51	0.81	6.14	14.25	0.09	0.05	<0.01	0.03	0.639	919	9	2	19.8
Carb. product (100°C)	1.40	0.10	3.67	28.89	0.10	<0.01	<0.01	0.09	0.006	251	<2	3	66.2

Table 3 Elemental analysis of starting serpentine, residue after dissolution and carbonation product.

	Element, wt%							
	N	C	H	S	Mg*	Fe*	Si*	O**
Serpentine	0.00	0.52	1.32	0.00	24.90	2.47	16.58	54.22
Dissolution residue	0.20	0.00	0.92	0.36	8.59	2.14	26.90	59.68
Carbonation product 50°C	6.21	5.78	3.69	7.23	na	na	na	na
Carbonation product 70°C	6.04	6.24	3.25	7.45	na	na	na	na
<u>Carbonation product 100°C</u>	<u>4.08</u>	<u>9.91</u>	<u>2.87</u>	<u>4.02</u>	<u>15.61</u>	<u>1.28</u>	<u>0.65</u>	<u>59.79</u>

* from ICP-ES, ** by difference, na not available

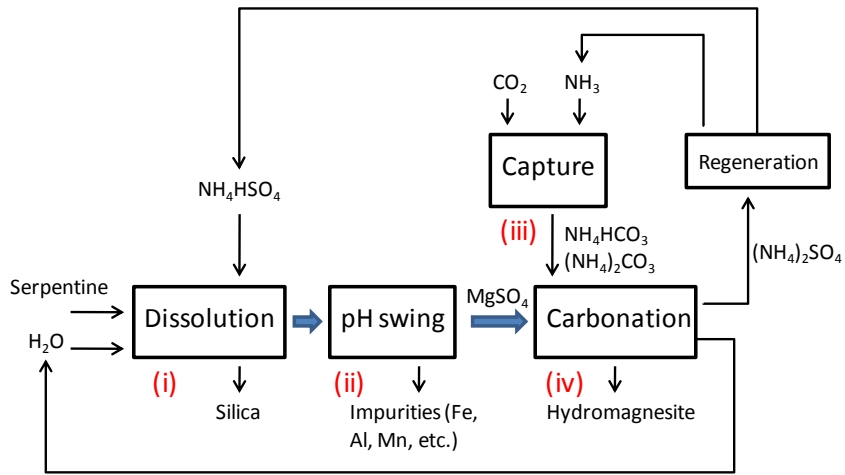


Figure 1 Scheme of the UoN pH swing process used in this work [modified from 6].

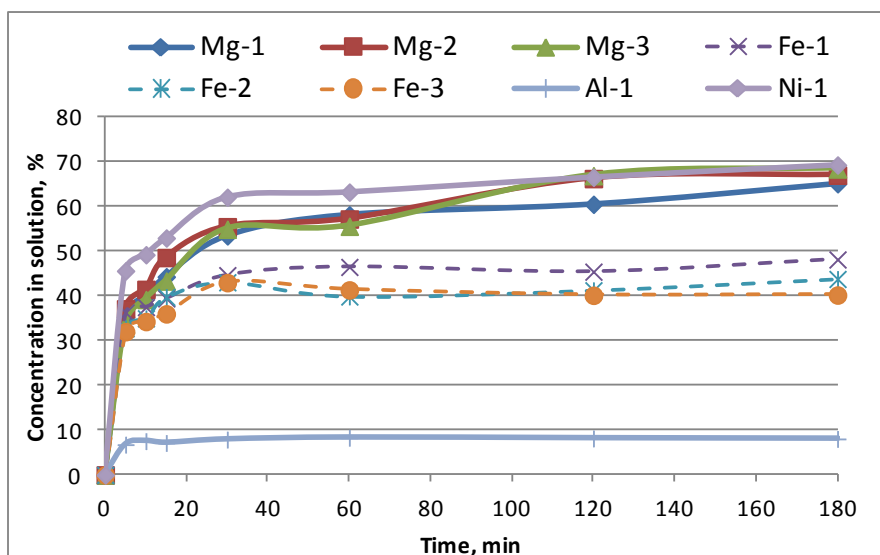


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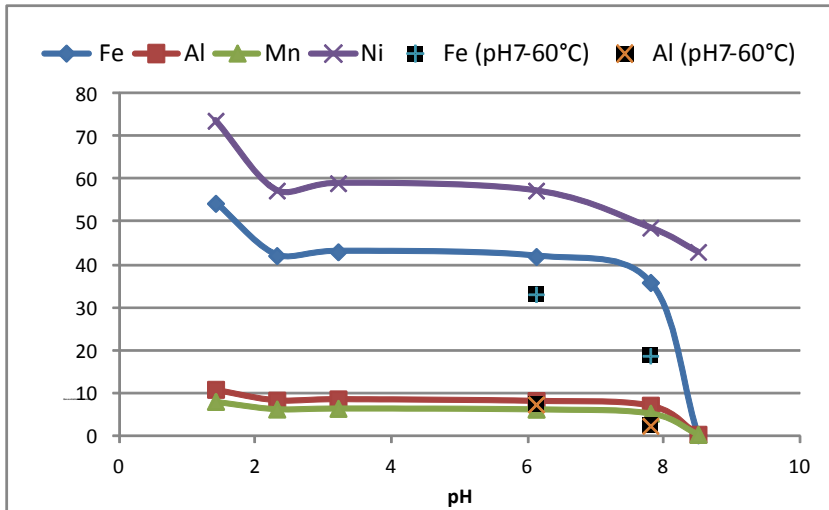


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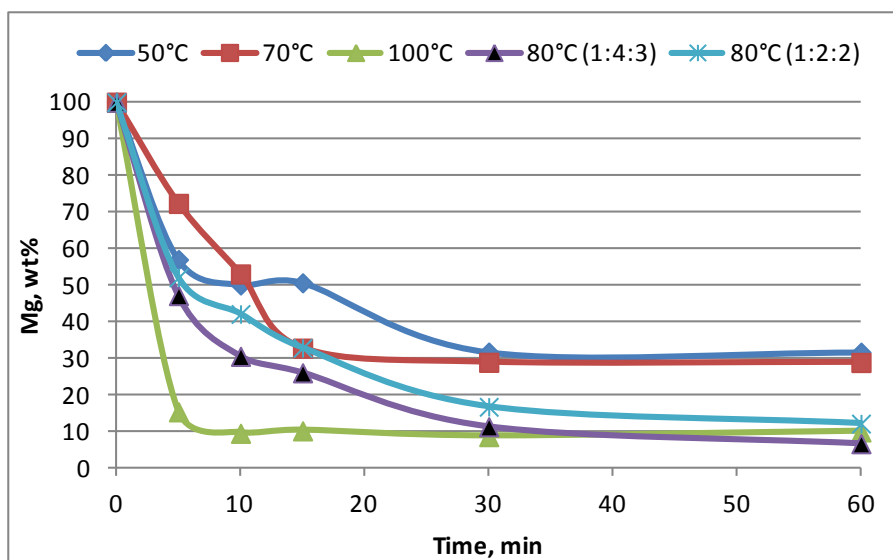


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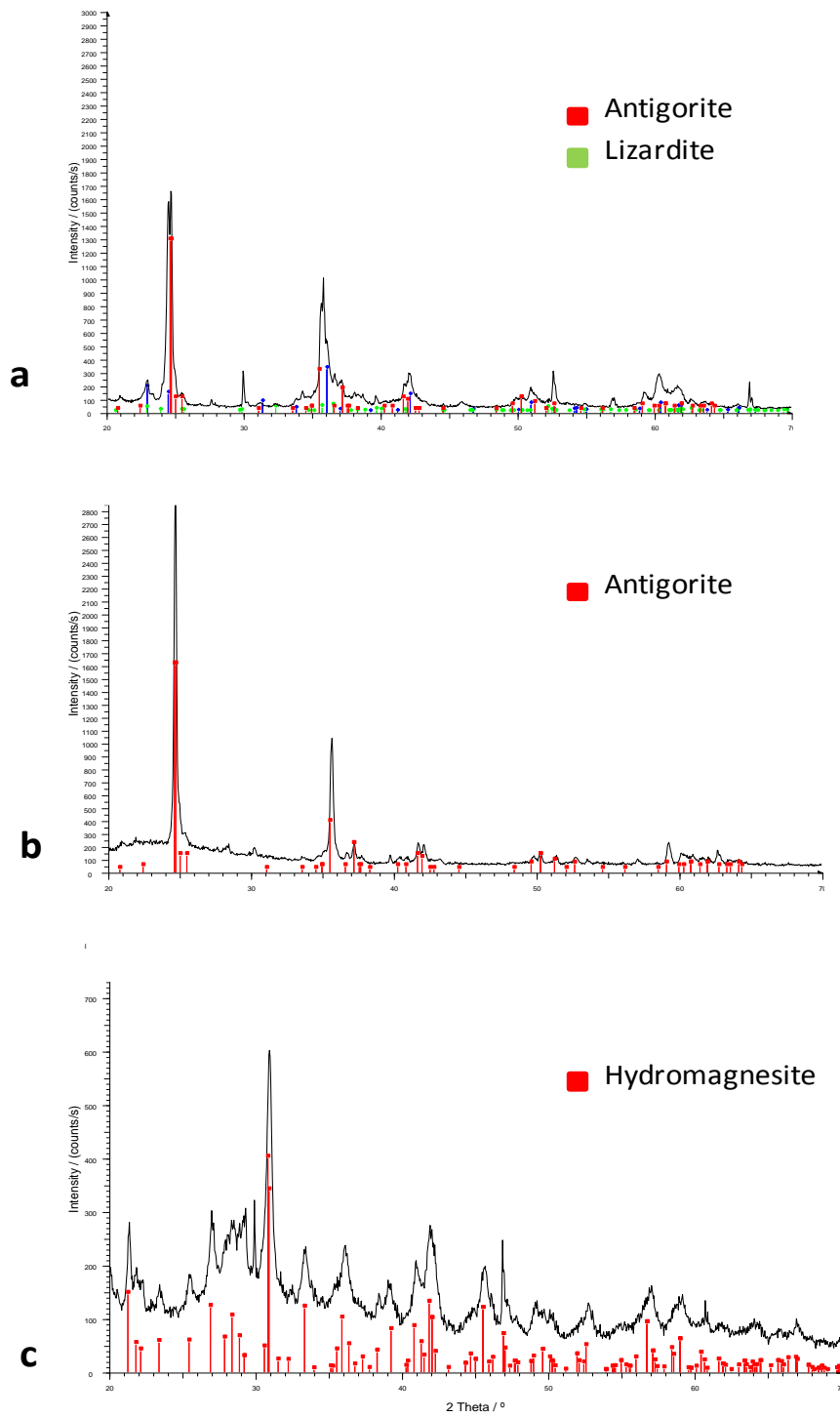


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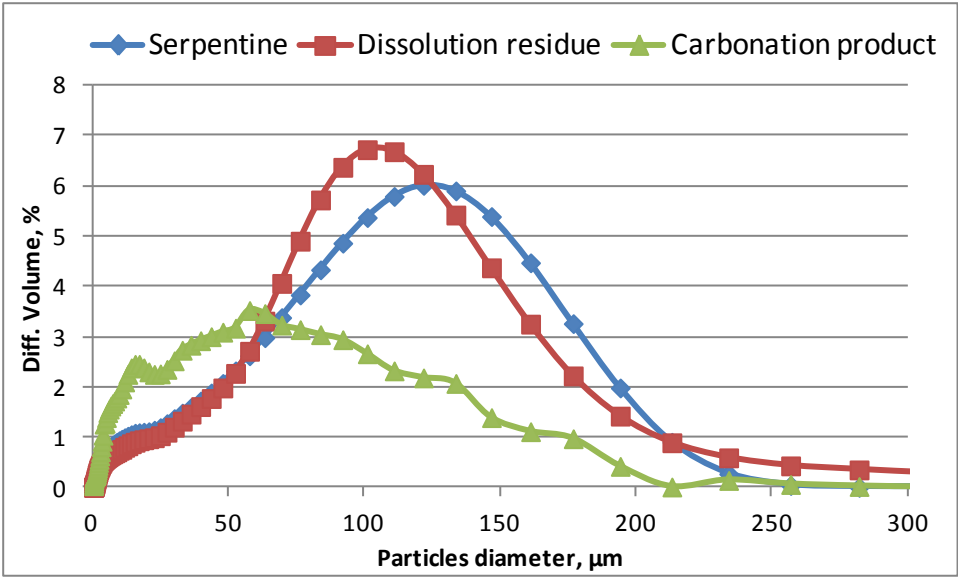


Figure 6 Size distributions of the starting serpentine particles and residue after dissolution and carbonation.