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

Aimaro Sanna [a,b,*], Marco Dri [a,b], Mercedes Maroto-Valer [a]

[a] School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK
[b] Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK

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ABSTRACT

Carbon Capture and Storage by mineralisation aims to reduce carbon dioxide emissions (CO_2) by reacting CO_2 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 NH_3-salts has not been demonstrated. Accordingly, carbonation of rocks rich in magnesium and a mixture of NH_4HCO_3 and $(NH_4)_2CO_3$ under different temperatures was investigated to reproduce a real scenario from an ammonia capture process. The highest 'carbonation efficiency' (expressed as the conversion of Mg ions to hydromagnesite) was 93.5% at 80 °C and 1:4:3 as Mg:NH_4 salts:NH_3 molar ratio, while the 'total CO_2 captured' was 62.6% under the same conditions, indicating that the process in presence of ammonium salts mixture is feasible.

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1. Introduction

Carbon Capture and Storage (CCS) in geological formations has the potential to sequester about 20% of the global CO_2 emissions per year by 2050 and can be applied mainly to emitters >1 Mt CO_2/year, while it is less appropriate for smaller emission sources [1–3]. Alternative approaches such as carbon dioxide capture and storage by mineral carbonation (CCSM) have also been proposed and presents a theoretical carbon capture potential two orders of magnitude higher than geological storage [4].

CCSM can sequester CO_2 by mixing the CO_2 from flue gases with industrial solid waste or rocks rich in magnesium or calcium oxides [5]. The oxides react with CO_2 producing solid mineral carbonates, which are stable and can provide safe storage capacity on a geological time scale. It is estimated that the global magnesium silicate rock deposits are enough to sequester the CO_2 generated by all the fossil fuels resources [1,6,7]. CCSM can therefore contribute to decrease CO_2 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 is uneconomical or not feasible (e.g. Finland) [8,9]. 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 1 Mt CO_2/year plant running in ten years' time [10–13]. 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% CO_2 sequestered [9,11,14]. The process shown in Fig. 1 consists of (i) dissolving minerals rich in magnesium producing a $MgSO_4$ solution, (ii) removing the impurities (Fe, Al, Mn etc.) by increasing the pH from acid to basic; (iii) carbonating the $MgSO_4$ with ammonium carbonate as CO_2 carrier from the (iv) NH_3 capture stage precipitating hydromagnesite and finally (v), regenerating the chemicals required for stages (i) and (iv). 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 [11].

Typical amines scrubbing have been commercially used to capture CO_2 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 CO_2 [15,16]. In contrast, ammonia-based wet scrubbing presents a heat of absorption of CO_2 by ammonia greatly lower than that for alkanolamines used for CO_2 capture (<2 GJ/t CO_2), degradation problems are not present and also, the ammonia process can be used to capture not only CO_2, but also SO_2, NOx and HCl [17,18]. For all these reasons, the ammonia capture process presents reduced total cost and complexity of the overall emission control systems [15,19].

The NH_3 scrubbing process can precipitate several ammonium carbonate compounds in the absorber, including ammonium bicarbonate (NH_4HCO_3), ammonium carbonate ($(NH_4)_2CO_3$) and

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[*] Corresponding author at: Room 3.23, Mountbatten Building, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK.
E-mail address: a.sanna@hw.ac.uk (A. Sanna).

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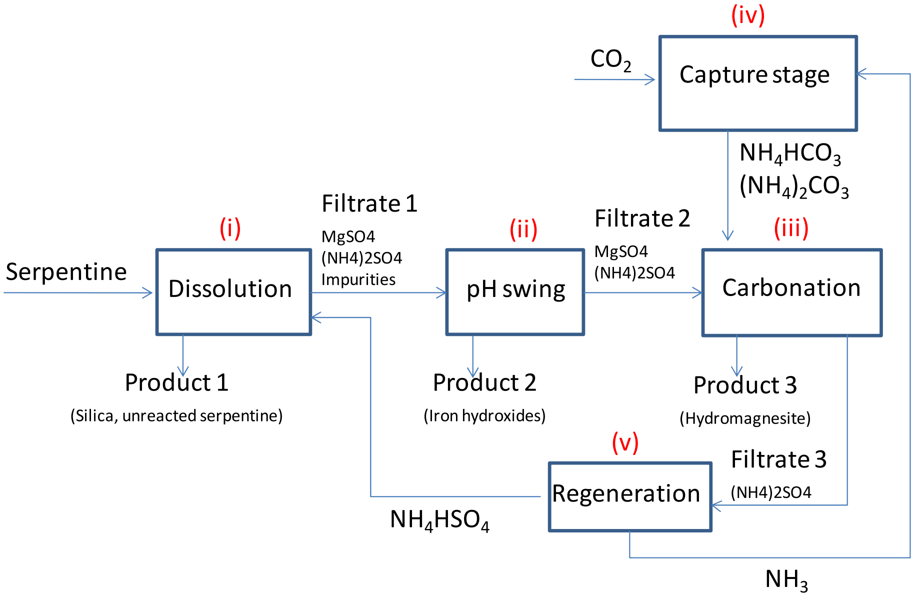

Fig. 1. Scheme of the UoN pH swing process used in this work (modified from [9]).

ammonium carbamate (NH_2COONH_4) where their molar ratio depends on the process conditions [20,21]. Previous research has been focused on CCSM in the presence of NH_4HCO_3 [11,14] while indications of the feasibility of this process in presence of a mixture of NH_3-salts are not available yet. Under CO_2 molar loadings higher than 0.5 (expressed as the ratio of the number of mole of CO_2 and NH_3 in their various aqueous forms) both the ammonium carbonate and bicarbonate salts are present, while when the CO_2 loadings is lower than 0.5 the only solid is ammonium carbonate [22]. 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 [11].

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:NH_4HCO_3/$(NH_4)_2CO_3$:NH_3 ratios, to evaluate their effect on the dissolution of an antigorite rich serpentine from Cedar Hills (USA). The overall CO_2 sequestration efficiency was compared with previous work [9,11,14].

2. Experimental section

The overall experimental work (see Fig. 1) consisted in: (1) the dissolution of a serpentine sample with the production of a $MgSO_4$ and iron impurities (Filtrate 1) and a solid residue of amorphous silica (Product 1); (2) the removal of the impurities from Filtrate 1 by a ph swing step producing a solution rich in $MgSO_4$ (Filtrate 2) and a precipitate of iron hydroxides (Product 2); and finally; (3) the carbonation of Filtrate 2 with NH_4salts and the production of hydromagnesite (Product 3) and a solution rich in $(NH_4)_2SO_4$ namely Filtrate 3. The summary of the analyses carried out on parent material and reactions products is summarised in Table 1.

2.1. Dissolution experiments

The dissolution experiments were carried out in triplicates considering the optimal dissolution conditions indicated in previous work [9]. Therefore, 200 g of serpentine from Cedar Hills with particle size ranging from 75 to 150 μm were added into 4000 mL 1.4 M NH_4HSO_4 solution for a 50 g/L solid liquid ratio. The solution was placed into a three neck flask glass reactor under a constant stirring rate of 800 rpm and heated using a silicon bath at the desired temperature of 100 °C. A condensation apparatus was used to prevent vapour losses of NH_3.

The determination of the content of Mg and other ions in the dissolution solution was carried out by sampling an aliquot of 1 mL from Filtrate 1 (Fig. 1) after 5, 10, 15, 30, 60, 120 and 180 min. The 1 mL liquid samples of Filtrate 1 were then acidified with 2 mL of 70 wt% HNO_3 and then diluted to 100 mL with deionised water to be analysed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). A Thermo-Fisher Scientific X Series ICP-MS instrument was used to measure the concentrations of the dissolved Mg, Fe and others elements. For instrument calibration, scandium (100 μg/L), rhodium (20 μg/L) and iridium (10 μg/L) in 2% trace analysis grade (Fisher Scientific, TAG) HNO_3 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 3 h of dissolution, the remnant Filtrate 1 was cooled down to ambient temperature and filtered with a 0.7 μm Pall syringe filter. The solid residue remaining after the filtration was namely Product 1 and consisted in residual unreacted serpentine and amorphous silica.

2.2. pH swing experiments

After the dissolution experiments, Filtrate 1 was used for the impurities removal study by adding ammonia–water to rise the initial acid pH of Filtrate 1 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 NH_3 was necessary for this step depending on the temperature used, where 10 vol%, 12 vol% and 25 vol% of NH_4OH was added to 200 mL dissolution solution during the experiments at 50, 70 and 100 °C, respectively, probably due to loss of NH_3 by evaporation. The solution was then filtered with a 0.7 μm Pall syringe filter and namely Filtrate 2. The precipitated impurities (Product 2) mainly contain Fe–hydroxides.

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