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Optimization of carbon dioxide capture and storage with mineralisation using recyclable ammonium salts

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ABSTRACT

Optimization of CCSM (carbon dioxide capture and storage with mineralisation) using RAS (recyclable ammonium salts) was studied here in order to minimize the energy consumption of this process. Water evaporation is required for the recycling of ammonium salts in the process, however the water evaporation technologies normally impose high energy penalty. In the optimized process, solid to liquid (S/L) ratio was increased to reduce water usage, but this change impacts dissolution efficiency, where the dissolution efficiency decreased from 100% at S/L of 50 g/l to 71% at S/L of 300 g/l. However, a 6% increase of dissolution efficiency was reported when the S/L ratio increased from 200 g/l to 300 g/l, probably due to increasing mineral inter-collisions. Besides, the optimized process employed the pressurized reactor, this change resulted in the mineral phase of product changed from hydromagnesite to magnesite. The carbon fixation efficiency was significantly improved by using $(NH_4)_2CO_3$ compared to NH_4HCO_3, and the highest CO_2 fixation efficiency achieved was 46.6% at S/L of 300 g/l. The mass balance for the optimized process was 4.9 t of serpentine, 0.6 t of NH_4HSO_4, 4.7 t of $(NH_4)_2CO_3$ and 16 t of water required to sequester 1 t CO_2.

1. Introduction

CCSM (Carbon capture and storage by mineralisation) is a technology for CO_2 emission reduction, where CO_2 reacts with minerals to produce carbonates. It is an important technology due to its scalability for small/medium scale emitters, where geological storage may not be feasible [1]. Besides, CCSM offers a non-monitoring and leakage-free CO_2 storage option due to the thermodynamically stable nature of the solid carbonates formed [2]. However, CCSM also faces some barriers such as low efficiency of mineral dissolution, slow kinetics, and energy intensive pre-treatment processes [3]. The low efficiency and slow kinetics barriers have been overcome by using additives [4,5]. However, the addition of large amounts of chemicals used increases the costs significantly. Therefore, there is a need to find recyclable solvents.

Ammonium salts are receiving growing attention due to their feasibility of recovery with low energy requirements. Kodama et al. developed a pH-swing CCSM process using RAS (recyclable ammonium salts), where steel slags were firstly dissolved by NH_4Cl to leach Ca and produce ammonia gas [6]. The Ca-rich slurry with ammonia was then injected into the absorption tower to absorb CO_2 and produce ammonium carbonate. This is followed by the precipitation of calcium carbonate in another reactor and the recovery of ammonium chloride. In their experimental work, 72% dissolution efficiency was achieved at 80 °C for 60 min, and the precipitation was theoretically calculated to be 70% at 80 °C. Eloneva et al. studied mineral carbonation of steel slags using different ammonium salts, including ammonium chloride, ammonium nitrate and ammonium acetic [7]. These ammonium salts effectively dissolved 50–80% Ca at 30 °C and atmospheric pressure. Pure calcium carbonate was precipitated from the Ca-NH_4 salt solution by bubbling through CO_2 at 30 °C with conversion efficiencies of 50–70%. However, the ammonium losses need to be minimized. The previous work using RAS has focused on steel slags. However, it should be noted that steel slags present limited availability (350 Mt/y) [8]. In contrast, Mg-silicate minerals, such as serpentine, are abundant and worldwide availability feedstocks (100,000 Gt) [9]. Therefore, there is a need to investigate CCSM using RAS with serpentine minerals.

In the previous work, the authors developed a multi-step CCSM process using serpentine minerals with RAS [10]. The process was designed at S/L of 50 g/l, where 100% dissolution efficiency at 90 °C for 3 h, and 90% carbonation efficiency at 80 °C for 1 h were achieved

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[11,12]. Based on these results and the S/L used, 50–56 t of water was required to sequester 1 t CO_2. Since water evaporation is a high energy penalty process, water usage must be minimised in order to make this process economically feasible. However, the increase of S/L may impact both dissolution and carbonation efficiencies.

The previous reported multi-step CCSM process using RAS produced several products and required filtering facilities for products separation. A modified process is proposed here and it is presented in Fig. 1, where the filtering steps of silica and iron products are removed. This is a semi-continuous batch process using a pressurized reactor vessel (45–60 psi resulted from ammonia vapour), which can therefore prevent the loss of ammonia vapour.

Accordingly, in this work the modified CCSM process using RAS was investigated to understand the effects of S/L on both dissolution and carbonation efficiencies. The comparison of carbonation conversions using different ammonium salts, the amount of residual NH_4HSO_4 after dissolution and the pH increase were studied. Finally, the mass balance of all streams is reported.

2. Experimental methods

2.1. Dissolution of serpentine using recyclable ammonium salts at high solid/liquid ratio

In this study, the same serpentine sample with particle size fraction between 75 and 150 μm was used as in the previous work [11]. The dissolution experiments were carried out in a stirred 300 ml Parr T316 stainless steel autoclave reactor. The reactor system (shown in Fig. 2) includes a heating system, and a temperature control box (Parr 4843 controller) to accurately maintain a stable heating environment from ambient to 225 °C, mechanical stirring and a cooling water system. A pressure of 45 psi during the experiment was generated due to water evaporation.

The concentration of NH_4HSO_4 in this study was established based on the stoichiometric amount, where 2 mol of NH_4HSO_4 are consumed to dissolve 1 mol of Mg from serpentine. For example, 40 g of serpentine (containing 24 wt% of magnesium) for a 200 ml solution required ammonium bisulfate as follows:

$$C_{NH_4HSO_4} = \frac{2 \times 40(\mathrm{g}) \times 24\%}{24(\mathrm{g/mol}) \times 0.2(\mathrm{l})} = 4(\mathrm{mol/l}) \quad (1)$$

4 and 6 mol/l NH_4HSO_4 were used for experiments where the S/L ratio was 200 and 300 g/l, respectively.

The matrix of dissolution experiments conducted at different conditions is presented in Table 1. In order to compare the dissolution efficiency when using different types of reactors (unpressurized and pressurized), two experiments were conducted using the un-pressurized reactor (open glass vessel) for the two S/L ratios. The same procedure was used as presented in previous work for these two experiments [11]. Typical dissolution experiments in the pressurized reactor were performed as follows. A serpentine sample was placed into a vessel with 200 ml NH_4HSO_4 solution at the corresponding concentration depending on the S/L ratio used. The reactor was then sealed and the stirring was started at 800 rpm. Once reaching 100 °C, the dissolution experiments were conducted for 3 h. At the end of experiment, the vessel was cooled down quickly to room temperature by immersing the vessel in an ice bath. Once the reactor was opened, the slurry was washed and transferred into a 1500 ml glass beaker, where Millipore water was used to dissolve the precipitated $MgSO_4$. After 30 min, the slurry was filtered using a 0.45 μm syringe filter unit. The filtrate was prepared in a 10% HNO_3 solution for ICP–AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) analyser for determining the concentrations of Mg, Ca, Fe, Al and Si. The solid residues were tested by SEM–EDX.

For the carbonation experiments, the same dissolution experiment procedure as described above was followed to prepare Mg-rich slurry. The reactor vessel was moved to a fume cupboard for pH-regulation after dissolution (see Section 2.2).

2.2. Measuring the amount of residual NH_4HSO_4 and pH-regulation

After the dissolution, the pH values of the solution were acidic (0.9–1.2) due to the presence of residual NH_4HSO_4. Because the carbonation reaction is favourable at pH values above 9, it was necessary to increase the pH of the solution to alkaline values by adding ammonia water (see Eq. (3)). The reason for using ammonia water is that the acid/base reaction produces ammonium sulphate, which can be converted back to NH_3 and NH_4HSO_4 in the regeneration step in order to realize the recycling of the additives [12]. Some impurities, such as Fe, Al, Cr, Zn, Cu and Mn leached from serpentine minerals, can also react with the added ammonia water to produce some solid products [12].

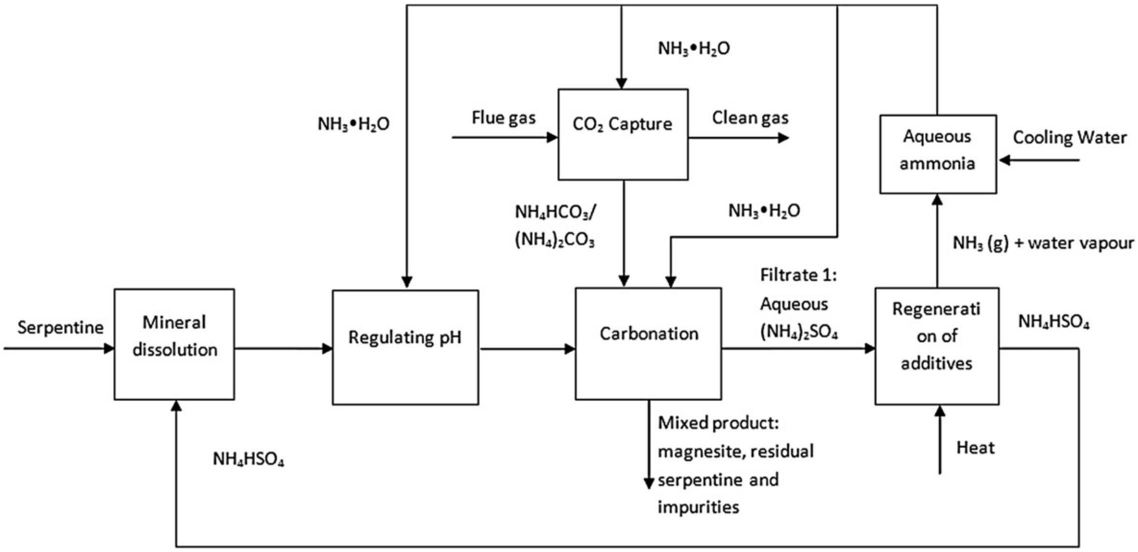

Fig. 1. The schematic of a single step CCSM process using RAS.