Ex-situ mineral carbonation with regenerative ammonium salts

Xiaolong Wang, M. Mercedes Maroto-Valer Presenter: Anna Kaminska

Center for Innovation in Carbon Capture and Storage (CICCS), Fuels and Power Technology Research Division, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, United Kingdom

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Introduction

✓ Ex-situ mineral carbonation is a process which permanently and safely stores CO_2 in solid Mg- and/or Ca- carbonates.

✓ Mineral carbonation bears high cost due to the pre-treatment needed to increase reaction rate. The pre-treatment methods include heat or chemical (acid) treatment.

✓ Another barrier of ex-situ is a large demand for expensive chemicals for changing pH.

✓ Ammonium salts could reduce the cost as a regenerative catalyst to accelerate the reaction rate and swing pH. This have been applied to calcium silicates [1] but not magnesium silicates, which have higher capacity for CO_2 sequestration.

pH swing

$$6NH_4^+(a) + 3MgO \bullet 2SiO_2 \bullet 2H_2O(s) \rightarrow 3Mg^{2+} + 2SiO_2(s)\downarrow + 6NH_3(a) + 5H_2O$$

$$Mg^{2+} + 2NH_3(a) + H_2O + CO_2(a) \rightarrow MgCO_3\downarrow + 2NH_4^+$$

Regenerated Catalyst

Aim and objectives

Develop a new pH-swing process route for mineral carbonation with recyclable ammonium salts.

✓ Improve the dissolution rate of Mg-silicates with ammonium salts and investigate the carbonation of Mg-silicates with ammonia.

✓ Validate the pH swing cycle and prove the production of ammonia and the reproduction of ammonium salts during dissolution and carbonation.

Methodology

✓ Set up a high temperature and high pressure stirred reactor with Raman spectroscopy probe which can measure in-situ the concentration of molecules and ions in gas, solid and liquid phases (Fig.1).

✓ Compare the ammonium salts dissolution with traditional acid dissolution. The most efficient method to extract Mg/Ca cations from minerals is using sulfuric acid [2], but it brings high costs for chemicals and energy penalty in order to increase pH. Otherwise ammonium salts need heat pre-treatment to get high reaction rate, but it can swing pH without extra chemicals and can be reused.

✓ Investigate Mg/Ca-silicates carbonation with ammonia water at elevated conditions, measure the extent of carbonation conversion and identify the formation of magnesite precipitated.

Fig 1: High temperature and high pressure reactor system

Sample characterization

✓ Particle size: 75-150 μm used for this work (Grinding by Tema mill)

✓ Pre-treatment: heat activation up to 650 °C for an hour to produce heat-treated (HT) serpentine.

✓ The surface area (BET-N_2) increase after heat activation (Table 1)

Table 1: Surface area of serpentine, olivine and HT serpentine

Serpentine	8.09-10.13 m^2/g
HT-serpentine	10.15-15.71m^2/g
Olivine	2.74-4.22 m^2/g

✓ Mg weight content increase after heat activation (Table 2)

Table 2: SEM_EDX results of serpentine

Element	Parent Serpentine (wt%)	HT serpentine (wt%)
Mg	24.45	27.15
Ca	0.14	0.12
Fe	4.05	4.55
Si	17.92	19.57

Dissolution Studies

✓ There were 24 dissolution experiments carried out, the conditions are listed in Table 3.

Table 3: Conditions of dissolution studies

	Ammonium salts	Sulfuric acid
Samples	Serpentine, HT Serpentine	Serpentine
Chemicals	2 mol/L ammonium chloride (NH_4Cl), 1 mol/L ammonium sulfate ($(NH_4)_2SO_4$)	2 mol/L sulfuric acid (H_2SO_4)
Temperature (°C)	70, 120, 180, 220	30, 50, 70
Pressure (bar)	5-20	5-20
Solid/Liquid ratio (g/L)	25	25

✓ Ammonium salts extract Mg/Ca cations, and the extraction rate is around 15% (Fig. 2). By using HT-serpentine, the extraction rate increases significantly to 60% (Fig. 2).

✓ 44 % Mg extraction is achieved at 120 °C, compared to 12% reported by Lacker et al. (2007) [3] using ammonium salts but without heat pre-treatment.

✓ 52 % is achieved at 180 °C, compared to 70% in work by Gredemann and O'Connor's (2007) [4] using KOH and $NaHCO_3$ with heat pre-treatment, but the chemicals used were not regenerative.

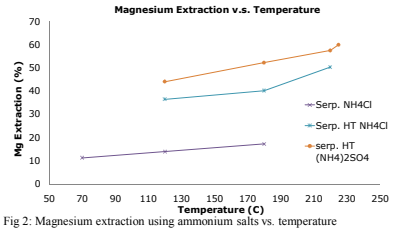

Fig 2: Magnesium extraction using ammonium salts vs. temperature

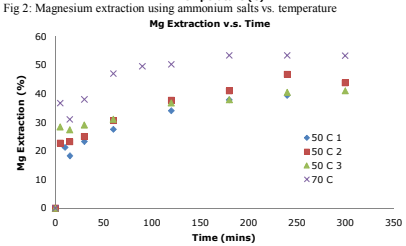

Fig 3: Magnesium extraction using sulfuric acid vs. time at different temperature

✓ The ammonium salts gave around 50% Mg^{2+} extraction rate at 120°C which was also seen with H_2SO_4 at 70°C (Fig 2 and 3).

✓ pH swing was observed from 5 to 7.5 for NH_4Cl, and 5.5 to 8.5 $(NH_4)_2SO_4$ (Table 4).

Table 4: pH change after dissolution experiment

	pH Start	pH Final
NH_4Cl	5.02	7.63
$(NH_4)_2SO_4$	5.55	8.50

✓ Ammonia was formed in reaction.

Conclusions

✓ HT serpentine shows much better performance than serpentine in terms of Mg extraction by ammonium salts.

✓ The Mg extraction efficiency of ammnium salts is similar to traditional acid. Moreover, ammonium salts can swing pH to favor carbonation and they can be regenerated after carboantion.

Future Plan

✓ Carbonation experiments are now being conducted (Table 5).

Table 5: Conditions of carbonation studies

	Ammonium salts
Samples	HT Serpentine
Chemicals	2 mol/L Ammonium chloride (NH_4Cl), 1 mol/L Ammonium sulfate ($(NH_4)_2SO_4$)
Temperature (°C)	120 °C, 180 °C, 220 °C
Pressure (bar)	10-150 bar
Solid/Liquid ratio (g/L)	25 g/L

✓ Measurement of ammonium salts concentration in solution (IC).

✓ Measurement of ammonia concentration in solution.

✓ Characterize the solids produced (TGA and Raman probe).

References

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Acknowledgements

The authors would like to thank the University of Nottingham and the Engineering and Physical Sciences Research Council (EPSRC) for financial support to carry out this work.

For further information please contact:
Prof. Mercedes Maroto-Valer
E-mail: Mercedess.maroto-valer@nottingham.ac.uk