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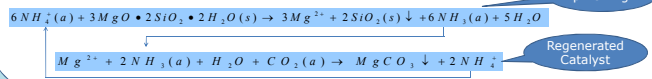
# Ex-situ mineral carbonation with regenerative ammonium salts

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## Introduction

- Ex-situ mineral carbonation is a process which permanently and safely stores CO<sub>2</sub> 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 has been applied to calcium silicates [1] but not magnesium silicates, which have higher capacity for CO<sub>2</sub> sequestration.



## 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.

## 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
<b>Samples</b>	Serpentine, HT Serpentine	Serpentine
<b>Chemicals</b>	2 mol/L ammonium chloride (NH <sub>4</sub> Cl), 1 mol/L ammonium sulfate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	2 mol/L sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )
<b>Temperature (°C)</b>	70, 120, 180, 220	30, 50, 70
<b>Pressure (bar)</b>	5-20	5-20
<b>Solid/Liquid ratio (g/L)</b>	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 Lackner 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<sub>3</sub> with heat pre-treatment, but the chemicals used were not regenerative.

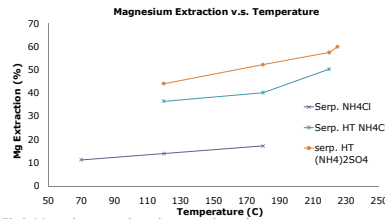


Fig 2: Magnesium extraction using ammonium salts vs. temperature

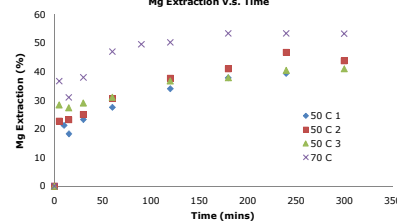


Fig 3: Magnesium extraction using sulfuric acid vs. time at different temperature

## 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<sub>2</sub>) increase after heat activation (Table 1)

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

Sample	Surface area (m <sup>2</sup> /g)
Serpentine	8.09-10.13
HT-serpentine	10.15-15.71
Olivine	2.74-4.22

- 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

## Future Plan

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

Table 5: Conditions of carbonation studies

	Ammonium salts
<b>Samples</b>	HT Serpentine
<b>Chemicals</b>	2 mol/L Ammonium chloride (NH <sub>4</sub> Cl), 1 mol/L Ammonium sulfate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )
<b>Temperature (°C)</b>	120 °C, 180 °C, 220 °C
<b>Pressure (bar)</b>	10-150 bar
<b>Solid/Liquid ratio (g/L)</b>	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).

- The ammonium salts gave around 50% Mg<sup>2+</sup> extraction rate at 120°C which was also seen with H<sub>2</sub>SO<sub>4</sub> at 70°C (Fig 2 and 3).
- pH swing was observed from 5 to 7.5 for NH<sub>4</sub>Cl, and 5.5 to 8.5 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Table 4).

Table 4: pH change after dissolution experiment

	pH Start	pH Final
NH <sub>4</sub> Cl	5.02	7.63
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	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 ammonium salts is similar to traditional acid. Moreover, ammonium salts can swing pH to favor carbonation and they can be regenerated after carbonation.

## References

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