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GHGT-12

## CO<sub>2</sub> sequestration using a novel Na-salts pH swing mineral carbonation process

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### Abstract

The main drawback of the indirect pH swing carbonation processes proposed so far is linked to the large amount of energy required to recycle the chemicals used to accelerate the reactions. The dissolution and carbonation steps of an alternative mineral carbonation pH swing process that employs sodium-based salts has been studied in order to minimize energy requirements typically associated to ammonium based mineral carbonation processes. The dissolution carried out at 70°C using NaHSO<sub>4</sub> gave Mg extraction efficiency comparable to that of NH<sub>4</sub>HSO<sub>4</sub> with about 50% of Mg brought into solution as MgSO<sub>4</sub>. In addition, the carbonation experiments (90% efficiency) demonstrate that NaHSO<sub>4</sub> and NaOH can be used in a combined process to mineralize CO<sub>2</sub>. The feasibility of the other process steps and optimization of the dissolution and carbonation are discussed.

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**Keywords:** CO<sub>2</sub>, Mineral carbonation, Carbon capture and storage, pH swing processes, serpentine.

### 1. Introduction

Carbon dioxide capture and storage by mineral carbonation is attracting major interests due to its permanent sequestration of CO<sub>2</sub>, but its costs are currently high for a widespread deployment of this technology, and therefore, new processes are being developed to lower its energy/costs requirements.

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The kinetic limitations of direct carbonation processes can be overcome in indirect processes by extracting the reactive Mg/Ca cations from silicate resources using chemical additives [1].

The commercial viability of indirect carbonation processes mainly depends upon the identification of recyclable solvents for efficient Ca and Mg cations extraction. Recyclable  $\text{NH}_4$ -salts by dry or aqueous approaches have recently attracted attention. For example, there is an indirect gas-solid dry process, where  $\text{Mg}(\text{OH})_2$  is extracted from minerals by their roasting at  $500^\circ\text{C}$  in presence of  $(\text{NH}_4)_2\text{SO}_4$  [4]. The resulting  $\text{MgSO}_4$  is dissolved in water and  $\text{Mg}(\text{OH})_2$  is precipitated by addition of ammonia water. The  $\text{Mg}(\text{OH})_2$  is then carbonated at 20bar and  $500\text{--}550^\circ\text{C}$  in a dry environment. However, a maximum Mg recovery of 50-52% and an regeneration of ammonium salt of only 72% were achieved [2,4,5]. Wang and Maroto-Valer have developed an aqueous multi-step process using serpentine with recyclable  $\text{NH}_4$ -salts [6], where an overall carbonation of 80% was achieved after 3 hours dissolution at  $100^\circ\text{C}$  in presence of  $\text{NH}_4\text{HSO}_4$  and 1 hour carbonation at  $80^\circ\text{C}$ . The main drawback of this technology was identified in the large amount of water (16t/ $\text{tCO}_2$  using a S/L ratio of 300g/L) which needs to be lower down to facilitate the deployment of this technology [7].

This work proposes a novel  $\text{CO}_2$  mineral carbonation process using bisulphates and NaOH in order to minimize energy requirements. A Na-bisulphate solution is used to leach cations from silicate rocks into sulphates and NaOH to capture the  $\text{CO}_2$  into  $\text{Na}_2\text{CO}_3$ . The integration of cations-rich silicates and Ca/Mg-rich industrial wastes with the purpose to recycle the  $\text{Na}_2\text{SO}_4$  remaining after the process and regenerate the required reagents, generating a range of Mg and Ca carbonates is considered. Similarly to the previously reported  $\text{NH}_4$ -salts processes, the proposed Na-salts process allows sequestering  $\text{CO}_2$  into benign and stable carbonates, generating valuable products, but in addition, there is a significant reduction in the energy required in the regenerations steps by exploiting the specific solubility trend of  $\text{Na}_2\text{SO}_4$  at different temperatures. The thermal-degradation step of the Na-based pH swing process only requires one third of the energy (400 kWh/ $\text{tCO}_2$ ) required by previous  $\text{NH}_4$ -based process (1300 kWh/ $\text{tCO}_2$ ).

## 2. Proposed process

Figure 1 shows the configuration of the proposed Na-based pH swing multi-steps mineral carbonation process.  $\text{CO}_2$  is separated from flue gas using sodium hydroxide forming sodium carbonate and/or sodium bicarbonate solution. Sodium bisulphate is then used to leach out magnesium from silicate rocks in form of magnesium sulphate.

Then, the  $\text{CO}_2$  in form of carbonate and the magnesium in form of sulphate are reacted in the carbonation step, where magnesite ( $\text{MgCO}_3$ ) or hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) is precipitated. A water solution of sodium sulphate remains after the carbonation step, which needs to be recycled into NaOH and  $\text{NaHSO}_4$ .

The regeneration of  $\text{Na}_2\text{SO}_4$  can be achieved via three stages employing  $\text{CO}_2$ , inorganic waste as source of CaO and acid environment. The regeneration of  $\text{Na}_2\text{SO}_4$  to NaOH and  $\text{NaHSO}_4$  is not covered in this work, which focuses on the mineral dissolution and carbonation steps. The regeneration steps involve the reaction of sodium sulphate with sulphuric acid to generate sodium bisulphate, the reaction of sodium sulphate with  $\text{CO}_2$  to generate sodium carbonate and sulphuric acid and finally the reaction of inorganic wastes rich in Ca with sodium carbonate to generate sodium hydroxide and calcium carbonate as by-product. Before the regeneration stages, the salt is separated from the water by decantation exploiting its very low solubility in water at temperature close to  $0^\circ\text{C}$ .

Table 1 shows the mass and energy balance for the capture of  $\text{CO}_2$  using NaOH, the dissolution of an Mg-rich silicate rock using  $\text{NaHSO}_4$  and for the carbonation reaction. The mass and heat balance were obtained using HSC chemistry 5.1, software for process simulation, reactions equations and equilibrium calculations.  $\text{CO}_2$  can be captured by NaOH at 1 bar and  $40^\circ\text{C}$  with the release of 1000 kWh/ $\text{tCO}_2$ . This heat could theoretically be recovered to run the dissolution step, but the low temperature employed in the capture step renders it very difficult. This reaction can also be used to remove other impurities, such as  $\text{SO}_2$  and  $\text{NO}_x$  from flue gas.

In the dissolution step, about 2.7t of serpentine rock (each t of  $\text{CO}_2$ ) are used. Dissolution is endothermic and requires about 490 kWh/ $\text{tCO}_2$ . Finally, Table 1 also shows that the carbonation step is exothermic and generates about 410 kWh/ $\text{tCO}_2$  captured. This heat may be used to reach the temperature required for the dissolution stage.

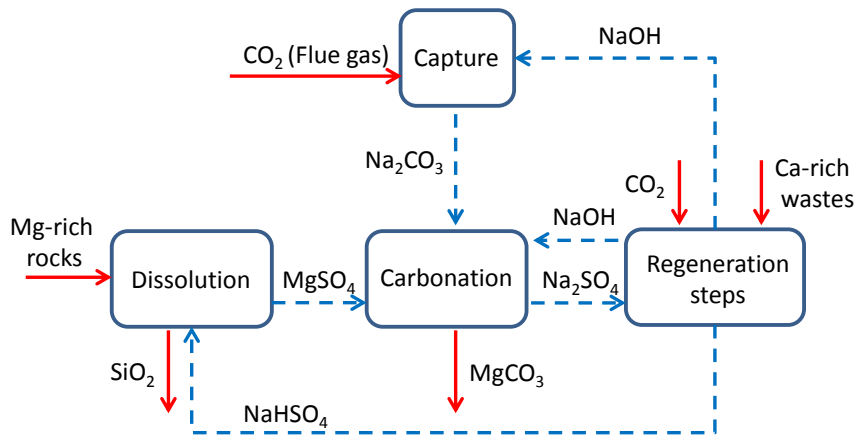


Figure 1. Na-salts based mineral carbonation process without pH swing step.

Table 1 Mass balance and total heat requirement for the capture, dissolution and carbonation process using Na-based salts.

Capture step		temp, C	k mole	kg	Latent H, kWh	Tot H, kWh
IN	NaOH	40	45.4	1817.5	11.4	-5363.1
	CO <sub>2</sub> (g)	40	22.7	1000.0	3.6	-2480.2
OUT	Na <sub>2</sub> CO <sub>3</sub>	40	22.7	2408.3	10.6	-7126.4
	H <sub>2</sub> O(1bar)	40	22.7	409.3	7.1	-1796.8
Balance	IN1		68.2	2817.5	15.0	-7843.3
	OUT1		45.4	2817.6	17.7	-8923.2
	BALANCE		-22.7	0.1	2.8	<b>-1079.9</b>

Dissolution step		temp, C	k mole	kg	Latent H, kWh	Tot H, kWh
IN	NaHSO <sub>4</sub>	90	22.7	2727.9	0.0	-7108.8
	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	90	7.6	2098.8	40.6	-9138.6
OUT	MgSO <sub>4</sub>	90	22.7	2734.9	41.5	-8093.0
	SiO <sub>2</sub>	90	15.1	910.2	13.1	-3819.6
	NaOH	90	22.7	908.8	25.3	-2662.2
	H <sub>2</sub> O	90	15.1	272.9	20.7	-1182.1
Balance	IN1		30.3	4826.7	40.6	-16247.5
	OUT1		75.7	4826.7	100.6	-15756.8
	BALANCE		45.4	0.0	60.0	<b>490.7</b>

Carbonation step		temp, C	k mole	kg	Latent H, kWh	Tot H, kWh
IN	Na <sub>2</sub> CO <sub>3</sub>	80	22.7	2408.3	39.8	-7097.3
	MgSO <sub>4</sub>	80	22.7	2734.9	34.9	-8099.6
OUT	Na <sub>2</sub> SO <sub>4</sub>	80	22.7	3227.4	46.0	-8714.0
	MgCO <sub>3</sub>	80	22.7	1915.8	27.9	-6889.7
Balance	IN1		45.4	5143.2	74.6	-15196.9
	OUT1		45.4	5143.2	73.9	-15603.7
	BALANCE		0.0	0.0	-0.7	<b>-406.8</b>

In the carbonation step, an aqueous solution of sodium sulphate is left behind after the precipitation of the magnesite. The unusual solubility properties of sodium sulphate in water can be used to separate the salt without the need of thermal evaporation, which requires large amount of energy. In fact, as shown in Figure 2, the solubility of  $\text{Na}_2\text{SO}_4$  dramatically decreases at temperatures lower than  $32^\circ\text{C}$ , reaching a minimum of only 7 g/100 mL at  $0^\circ\text{C}$ . In comparison,  $(\text{NH}_4)_2\text{SO}_4$  solubility is between 70.6 g/100 mL ( $0^\circ\text{C}$ ) and 103.8 g/100 mL ( $100^\circ\text{C}$ ).

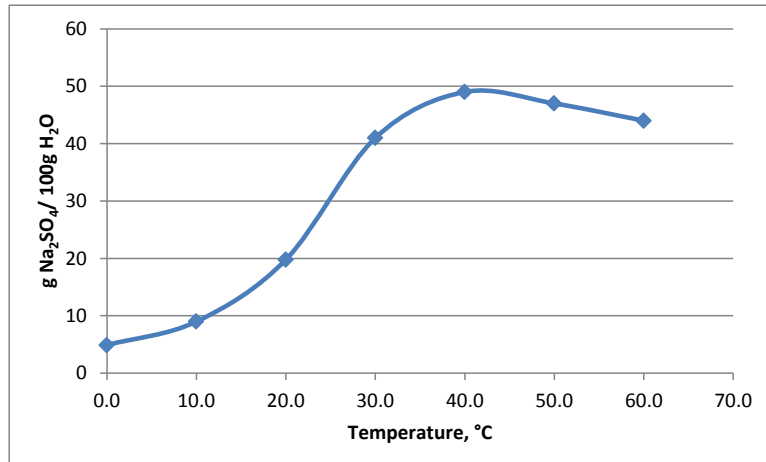


Figure 2. Solubility of  $\text{Na}_2\text{SO}_4$  in function of temperature.

Therefore,  $\text{Na}_2\text{SO}_4$  is separated by precipitation from water solution at  $0^\circ\text{C}$ , and thus, saving large amount of energy by removing the evaporation step, which is instead required in the processes based on ammonium salts. When the water is absorbed into the inorganic compound, the salt retains its solid state and can be removed by decanting or gravity filtration.

### 3. Method

A serpentinised lherzolite from the Lizard peninsula, Cornwall, UK was selected for this work. The dissolution of serpentine rich in lizardite was carried out with the purpose of comparing the efficiency of  $\text{NaHSO}_4$  with that of  $\text{NH}_4\text{HSO}_4$ . For this reason, the experimental conditions and the material used were similar to those previously reported by the authors with  $\text{NH}_4\text{HSO}_4$  [8].

Dissolution experiment was run at  $70^\circ\text{C}$  for 3 hours using the same serpentine with particle size between 75 and  $150\mu\text{m}$ , stirring at 800rpm and a solid/liquid ratio of 50g/L in a 0.5 L stainless steel Parr reactor (model No. 4575A). Aliquots of 1 ml were extracted between 5 min and 180 min to determine the content of Mg and other ions in the solution. After 3 h of dissolution, the flask content was cooled down to ambient temperature and filtered with a 0.7  $\mu\text{m}$  Pall syringe filter. Then, 1 ml of solution was acidified with 2 ml of 70%  $\text{HNO}_3$  (Fisher Scientific) and diluted to 100 ml with deionized water to be analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) using a Thermo-Fisher Scientific X Series Instrument [8].

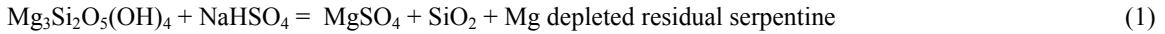
Sodium hydroxide was used to raise the pH of the dissolution solution to 8.5 prior to carbonation experiments.

Carbonation was run at  $80^\circ\text{C}$  and a qualitative analysis of the products was done by XRD and SEM techniques. The morphology and elemental composition of the serpentine before and after chemical dissolution was analysed by SEM-EDS, using an Oxford Instruments INCA 200 energy dispersive X-ray microanalysis (EDS) system. Also, XRD was used to confirm the production of carbonate. For qualification of mineral phases, 1 gram sample was analysed using a Philips Analytical 1050 X-ray Diffraction (XRD) at scan speed  $3^\circ/2\theta/\text{minute}$  from  $5^\circ 2\theta$  to  $65^\circ 2\theta$  under 40 kV/40 mA.

4. Results and Discussion

4.1. Rock dissolution

Figure 3 compares the Mg extraction trend in presence of NH<sub>4</sub>HSO<sub>4</sub> and NaHSO<sub>4</sub>. The higher magnesium extraction was obtained after 3hrs with 50% of the Mg removed from the serpentine particles. The extraction of Mg is similar to those obtained in presence of NH<sub>4</sub>HSO<sub>4</sub> [8]. A representing particle of the residue remaining after the dissolution is shown in Figure 4. The particle has been depleted in Mg, which is now ~11% and is mainly made of Si (22%) and O<sub>2</sub> (63%). The dissolution reaction is as follows:



It can be seen that if the dissolution reaction is not complete, as in this work, residual serpentine with less Mg should remain after the dissolution stage. This is confirmed by the SEM-EDS image presented in Figure 4. A silica framework remains behind due to the selective removal of Mg.

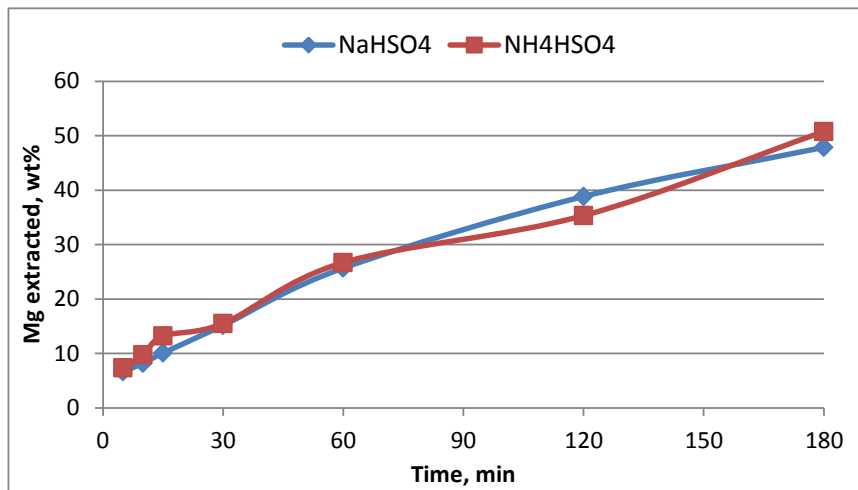


Figure 3 Mg extraction from serpentine at 70°C, 1 bar, 800 rpm and S/L ratio of 50g/l using Na-based and NH<sub>4</sub>-based processes [8].

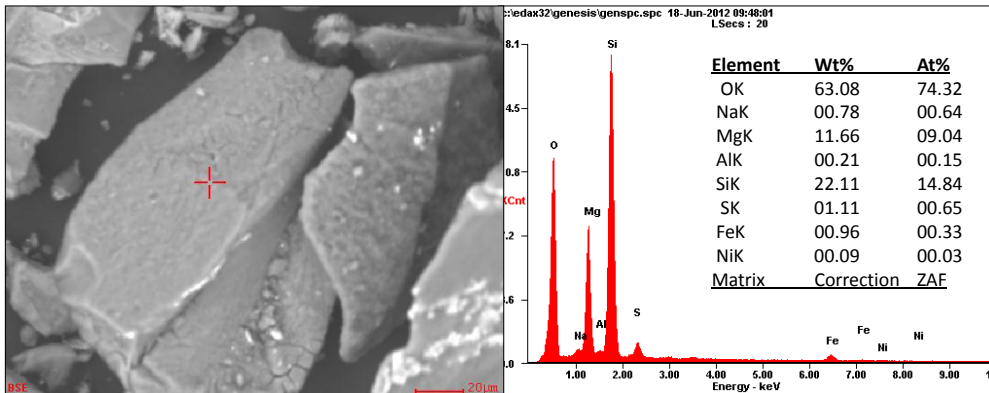


Figure 4. SEM-EDS of dissolved serpentine after 3 hours.

#### 4.2. Carbonation step

The carbonation step was carried out at 80°C. Figure 5 shows that the carbonation product, at the investigated conditions, is pure hydromagnesite. Carbonation in presence of excess  $\text{Na}_2\text{CO}_3$  was very effective (90% Mg in solution was carbonated). This is confirmed by the SEM image in Figure 6, where the formation of small hydromagnesite particles with spherical shape and size between 4-8  $\mu\text{m}$  is visible.

The presence of Mg, C, and O compatible to that of hydromagnesite (Mg=26%, C=11%, O= 61%) is also confirmed by SEM-EDS analysis (Figure 6). The higher content in carbon (compared to that expected for hydromagnesite) can be related to the incomplete coverage of the surface, which leaves the below carbon coating exposed.

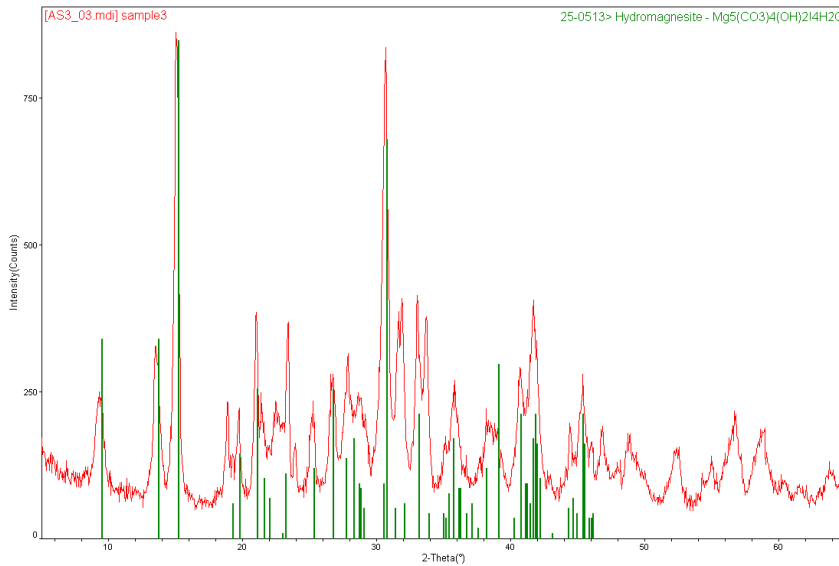


Figure 5. XRD of carbonation product.

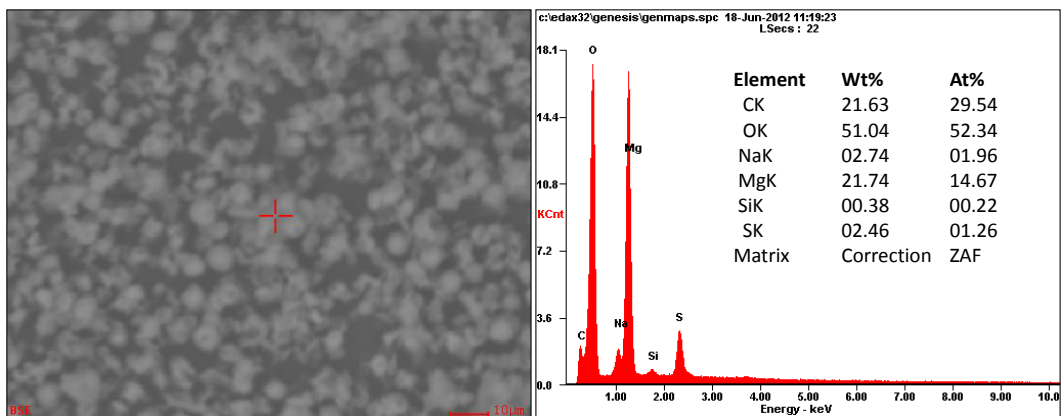


Figure 6. SEM-EDS of carbonation product.

## 5. Conclusions

The technical feasibility of the dissolution and carbonation steps of an alternative mineral carbonation that employs sodium-based salts has been conducted. The dissolution carried out at 70°C using NaHSO<sub>4</sub> gave Mg extraction efficiency comparable to that of NH<sub>4</sub>HSO<sub>4</sub> with about 50% of Mg brought into solution as MgSO<sub>4</sub>. In addition, the carbonation experiments demonstrate that NaHSO<sub>4</sub> and NaOH can be used in a combined process to mineralize CO<sub>2</sub>. Further work is being conducted on the regeneration steps proposed here to determine the technical feasibility of this process.

## Acknowledgements

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