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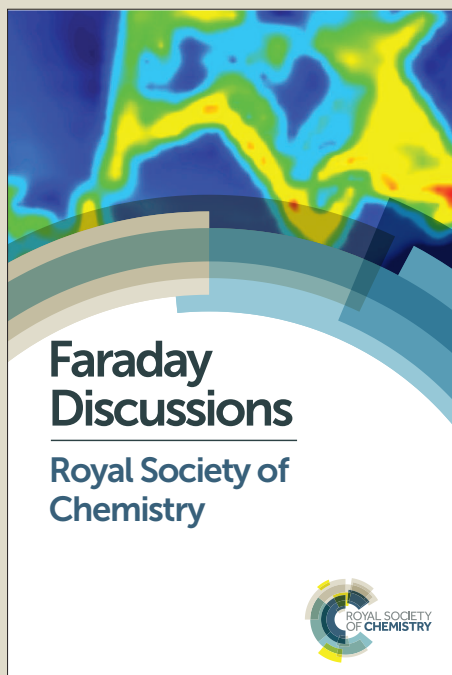
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## Extraction of Mg(OH)<sub>2</sub> from Mg silicate minerals with NaOH assisted with H<sub>2</sub>O: implications for CO<sub>2</sub> capture from exhaust flue gas

Silvia Madeddu<sup>1\*</sup>, Michael Priestnall<sup>2</sup>, Erik Godoy<sup>3</sup>, R. Vasant Kumar<sup>4</sup>, Sugat Raymahasay<sup>5</sup>, Michael Evans<sup>6</sup>, Ruofan Wang<sup>1</sup>, Seabelo Manenye<sup>1</sup> and Hajime Kinoshita<sup>1</sup>

<sup>1</sup> *Department of Materials Science and Engineering, The University of Sheffield, Sheffield, United Kingdom.*

<sup>2</sup> *Innovate UK, Swindon, United Kingdom (previously, Cambridge Carbon Capture Ltd)*

<sup>3</sup> *Polarcus DMCC, Dubai, U.A.E.*

<sup>4</sup> *Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom*

<sup>5</sup> *WRK Design & Engineering Ltd, Birmingham, United Kingdom.*

<sup>6</sup> *Cambridge Carbon Capture Ltd, Cambridge, United Kingdom.*

\*Corresponding author: [mtg11sm@sheffield.ac.uk](mailto:mtg11sm@sheffield.ac.uk)

### Abstract

The utilisation of Mg(OH)<sub>2</sub> to capture exhaust CO<sub>2</sub> has been hindered by the limited availability of brucite, Mg(OH)<sub>2</sub> mineral in natural deposits. Our previous study demonstrated that Mg(OH)<sub>2</sub> can be obtained from dunite, an ultramafic rock composed of Mg silicate minerals, in highly concentrated NaOH aqueous systems. However, the large quantity of NaOH consumed was considered an obstacle for the implementation of the technology. In the present study, Mg(OH)<sub>2</sub> was extracted from dunite reacted in solid systems with NaOH assisted with H<sub>2</sub>O. The consumption of NaOH was reduced by 97% respect to the NaOH aqueous systems, maintaining a comparable yield of Mg(OH)<sub>2</sub> extraction, i.e. 64.8 - 66%.

The capture of CO<sub>2</sub> from CO<sub>2</sub>-N<sub>2</sub> gas mixture was tested at ambient conditions using a Mg(OH)<sub>2</sub> aqueous slurry. Mg(OH)<sub>2</sub> almost fully dissolved and reacted with dissolved CO<sub>2</sub> by forming Mg(HCO<sub>3</sub>)<sub>2</sub> which remained in equilibrium storing the CO<sub>2</sub> in the aqueous solution.

The CO<sub>2</sub> balance of the process was assessed from the emission derived from the power consumption for NaOH production and Mg(OH)<sub>2</sub> extraction together with the CO<sub>2</sub> captured by Mg(OH)<sub>2</sub> derived from dunite. The process resulted carbon neutral when dunite is reacted at 250 °C for durations of 1 and 3 hours and CO<sub>2</sub> is captured as Mg(HCO<sub>3</sub>)<sub>2</sub>.

### Introduction

Carbon Capture and Storage (CCS) is a portfolio of technologies developed for the abatement of anthropogenic CO<sub>2</sub> emissions via permanent isolation of CO<sub>2</sub> from the atmosphere<sup>1</sup>. CCS includes the separation of CO<sub>2</sub> from exhaust flue gases and its storage either underground, in seawater or through the fixation into stable mineral carbonates via mineral carbonation<sup>1</sup>.

Mg(OH)<sub>2</sub> can capture CO<sub>2</sub> in a wide range of conditions: it can permanently and safely store CO<sub>2</sub> into solid Mg carbonate minerals upon the exposure to gaseous or supercritical CO<sub>2</sub> or via dissolution in H<sub>2</sub>O with purged CO<sub>2</sub><sup>2,3,4</sup>. Mg(OH)<sub>2</sub> aqueous slurries have been successfully tested to separate CO<sub>2</sub> from gas mixtures via liquid-gas scrubbing, and the technology has been proposed to separate CO<sub>2</sub> from exhaust flue gases<sup>5</sup>. Mg(OH)<sub>2</sub> and CO<sub>2</sub> dissolved in H<sub>2</sub>O can react to form Mg(HCO<sub>3</sub>)<sub>2</sub> which remains in solution as soluble phase under controlled pH<sup>5,6</sup>. This chemistry is suited to

industrial applications such as coastal industry and power plants or ships, where CO<sub>2</sub> can be separated from exhaust flue gases using Mg(OH)<sub>2</sub> slurries and permanently stored in seawater as dissolved Mg(HCO<sub>3</sub>)<sub>2</sub><sup>7</sup>. This technology combines the separation and storage of CO<sub>2</sub> into a single stage, which is favourable because it avoids the capture and conversion of CO<sub>2</sub> into a pure CO<sub>2</sub> stream, as well as the compression and transport operations, all of which are expensive and energy demanding<sup>8,9</sup>. Despite the wide range of possible applications and potential advantages, Mg(OH)<sub>2</sub> utilisation for CO<sub>2</sub> capture has been hindered due to its rare occurrence in natural outcrops<sup>1,10</sup>.

Mg silicate minerals, on the other hand, in particular serpentine and forsterite have been the preferred feedstock materials for CO<sub>2</sub> sequestration due to their vast availability in natural deposits which provides large storage capacity<sup>1,11,12</sup>. The main challenge of Mg silicate minerals carbonation is the slow kinetic of the carbonation reaction which requires acceleration through mechanical and chemical pre-treatment of the materials and the application of high pressure and temperatures<sup>1,13</sup>.

The extraction of Mg(OH)<sub>2</sub> from Mg silicate minerals via chemical processing benefits from the large availability of Mg silicate minerals. The overall efficiency of the process is also improved as Mg(OH)<sub>2</sub> has a faster kinetic in carbonation than these Mg silicate minerals and allows greater flexibility in the design of the CCS technologies<sup>4</sup>. There are technologies currently available to obtain Mg(OH)<sub>2</sub> from Mg silicate minerals, e.g. a solid state reaction with ammonium salts at 400 - 500 °C or dissolution with HCl at 150 °C<sup>4,14</sup>. These technologies involve a second step where the pH of the system is increased by introducing another reactant to favour the precipitation of Mg(OH)<sub>2</sub> in alkaline condition<sup>4,14</sup>.

In a previous study we investigated the alkaline digestion of Mg silicate minerals to obtain Mg(OH)<sub>2</sub> using highly concentrated NaOH aqueous systems<sup>15</sup>. The alkali digestion of dunite, an ultramafic rock composed of Mg silicate minerals, at 180 °C for 6 hours, resulted in the near-complete digestion and formation of Mg(OH)<sub>2</sub>. The technology is advantageous because it is a one-step reaction and involves a single reactant, although the high consumption of NaOH was identified as a possible obstacle for the implementation<sup>15</sup>.

The present study proposes a new technique for the extraction of Mg(OH)<sub>2</sub> from Mg silicate minerals, aiming to reduce the NaOH consumption by introducing NaOH into the system in solid state. After studying the basic reaction of the system at 180 °C with the aid of thermodynamic consideration, the investigation focused on the effect of H<sub>2</sub>O on the efficiency of Mg(OH)<sub>2</sub> extraction from the dunite-NaOH solid mixtures. The effects of temperature and duration of reaction were also studied for a dunite-NaOH-H<sub>2</sub>O system with fixed composition reacted at 130, 180 or 250 °C for 1, 3 and 6 hours. The obtained results are compared with those from the alkaline digestion of dunite with NaOH aqueous systems previously investigated. The feasibility of CO<sub>2</sub> sequestration using Mg(OH)<sub>2</sub> was also demonstrated using a Downflow Gas Contactor (DGC) reactor. CO<sub>2</sub> was separated from a flow of CO<sub>2</sub>-N<sub>2</sub> mixture at ambient conditions using an aqueous slurry of reagent grade Mg(OH)<sub>2</sub>, and the implications of using Mg(OH)<sub>2</sub> derived from dunite for CO<sub>2</sub> sequestration are discussed.

## Materials and Methods

### *Dunite*

The dunite mined in Åheim, Norway, was provided by Sibelco Ltd. The material analysed via X-ray Fluorescence (XRF) was composed of 48.3 wt% MgO, 45.35 wt% SiO<sub>2</sub>, and 6.16 wt% Fe<sub>2</sub>O<sub>3</sub>, while other oxides were present at < 1 wt%. The X-ray diffraction (XRD) analysis revealed that dunite was mainly composed of forsterite, Mg<sub>2</sub>SiO<sub>4</sub>, the Mg-rich member of the olivine group. The minor components were also Mg-bearing minerals, i.e. clinocllore, serpentine, enstatite, talc, hornblende and spinel. The Rietveld Refinement Quantitative Phase Analysis (QPA) conducted on the XRD pattern estimated the amount of forsterite to be 73 ± 2 wt%. Thermogravimetric analysis (TGA) detected the presence of Mg(OH)<sub>2</sub> at 0.42 wt% in the dunite.

The powdered dunite was sieved to < 63 µm and analysed by Laser Diffraction with dry dispersion, which showed an average distribution of the particles size around 25 µm, with 90% of the particles < 58 µm. These results were confirmed via SEM analysis.

### **Extraction of Mg(OH)<sub>2</sub>**

NaOH pearl, reagent grade provided by Fisher Chemical was mixed with powdered dunite, with or without addition of distilled H<sub>2</sub>O, in an agate mortar with a pestle. The mole ratio of the reactants in the samples used in the present study is summarised in Table 1. Three series were prepared at different dunite:NaOH mole ratio, i.e. 1:1, 1:1.5, and 1:2, which are referred to as Series 1, Series 1.5, and Series 2, respectively. The moles of dunite were estimated based on the chemical formula of forsterite, Mg<sub>2</sub>SiO<sub>4</sub>. For all series, the samples were prepared at different NaOH:H<sub>2</sub>O mole ratio of 4:1, 2:1, 1:1, and 1:2. Series 2 also includes a sample reacted without H<sub>2</sub>O addition.

When the reactants were well blended, the mixture was transferred in a steel vessel lined with Teflon which was sealed and heated at 180 °C for 6 hours in a Carbolite electric oven, series PF30. The system with dunite:NaOH:H<sub>2</sub>O mole ratio of 1:2:0.5 was replicated at different durations of reaction, i.e. 1 and 3 hours, and different temperatures, i.e. 130 and 250 °C.

After the reaction, the products were ground and washed with distilled water and the solid component was separated from the liquid phase via vacuum filtration. The solid filtrate was dried for 1 hour at 90 °C and then analysed via XRD and TGA.

**Table 1:** Normalised mole of reactants in samples

	Dunite* (mole)	NaOH (mole)		H <sub>2</sub> O** (mole)			
Series 1	1	1	-	0.25	0.5	1	2
Series 1.5	1	1.5	-	0.375	0.75	1.5	3
Series 2	1	2	0	0.5	1	2	4

\* Approximate mole of dunite was estimated based on the chemical formula of forsterite, Mg<sub>2</sub>SiO<sub>4</sub>.

\*\* Different amounts of H<sub>2</sub>O were tested at NaOH:H<sub>2</sub>O mole ratio of 4:1, 2:1, 1:1 or 1:2 for each series. Series 2 also includes a *dry* system without H<sub>2</sub>O.

### **CO<sub>2</sub> capture with Mg(OH)<sub>2</sub> suspension**

A Downflow Gas Contactor (DGC) reactor, designed by WRK Design & Engineering Ltd, with a liquid volume of 10 litre capacity was used as the liquid-gas reactor to capture CO<sub>2</sub> from a flowing gas-mixture. In this reactor, the gas-mixture at atmospheric

pressure enters at the top of the bubble column, entrained (at 0.8 atm) in the downward circulating liquid flow, and exits at 1atm from the bottom of the column after reaction and separation from the recirculating liquid phase. The DGC reactor provides a large interfacial area between the gas bubbles and liquid which enhances the reactivity of the phases involved. The rate of liquid recirculation was typically 10 L/minute to maintain a stable bubble-liquid interface.

A gas-mixture of N<sub>2</sub> and 4 – 5% CO<sub>2</sub> was injected at the top of the column at a fixed flow-rate of 2.25 ± 0.07 L/minute and bubbled through the column at approximately 10 °C and under ambient pressure. When the solution was saturated with CO<sub>2</sub>, i.e. the concentration of CO<sub>2</sub> in the outlet gas became the same in the inlet gas, 50.8 g of powdered Mg(OH)<sub>2</sub> was added to the circulating H<sub>2</sub>O.

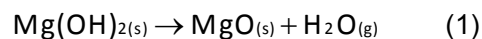
The Mg(OH)<sub>2</sub> with 98% purity used in the study was provided by Lehmann & Voss & Co. The material had average particle size of 7 µm, and also contained 0.5% CaO and smaller amounts of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> as impurities.

The CO<sub>2</sub> concentration in the inlet and outlet gas was periodically monitored using a calibrated inline infrared data logger, and the monitoring continued until the concentration of CO<sub>2</sub> in the outlet gas had increased and become equal to that in the inlet gas, indicating that no further reaction was occurring. The experiment took approximately 12 hours to complete and it was run over the course of two days with an overnight shut-down. Samples of the circulating liquid were also taken periodically to monitor the change in pH.

### ***Products and data analysis***

The XRD was conducted for the phase analysis on the reaction products using a Siemens D5000 with Cu Kα X-ray source, λ = 1.54 Å. The powdered samples were placed in a plastic sample holder, and the scans were run from 10° to 70° 2θ with a step size of 0.05° 2θ.

TGA was also conducted on the reaction products using the PerkinElmer Pyris 1. The samples were placed in an alumina crucible and heated at a rate of 10 °C/minute from room temperature to 1000 °C under N<sub>2</sub> flow. The first derivative of the TG curve, DTG, was also determined to assist the analysis. The amount of Mg(OH)<sub>2</sub> was calculated based on the dehydroxylation of Mg(OH)<sub>2</sub> (Reaction 1) taking place at 350 – 450 °C<sup>16</sup>.



The analysis was also assisted with the thermodynamic consideration. The change in the Gibbs free energy and enthalpy for the possible reactions were calculated using SGTE Substances Database (SSUB5) in Thermo-Calc<sup>17</sup>. The calculation was also performed for the minor mineral phases in the dunite. The calculation was not performed for clinocllore and hornblende due to the lack of available data in SSUB5.

The carbon content in the solid residue recovered from the CO<sub>2</sub> capture test was determined using the Perkin Elmer 2400 CHNS/O Series II Elemental Analyser. The sample was combusted at 975 °C under oxygen environment. The gases released were reduced by copper and separated through a chromatographic column. The amount of carbon was obtained from the gases eluting off the column based on their

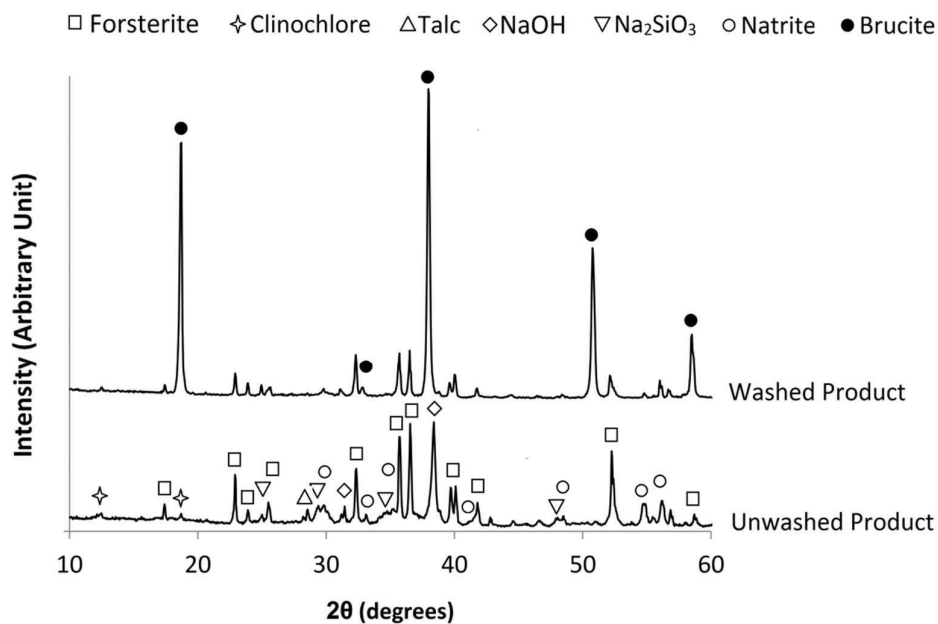


thermal conductivity, which were converted into CO<sub>2</sub> wt% to assess the CO<sub>2</sub> captured in the solid phase.

## Results and Discussion

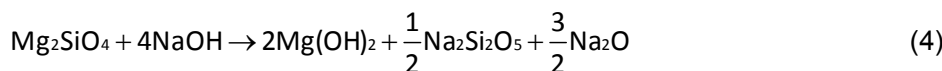
### Extraction of Mg(OH)<sub>2</sub>

The reaction of dunite with NaOH usually resulted in formation of brucite, Na<sub>2</sub>SiO<sub>3</sub> and natrite, i.e. Na<sub>2</sub>CO<sub>3</sub>, together with the mineral components from unreacted dunite and remaining NaOH. Figure 1 shows the XRD patterns of selected reaction products from solid systems with dunite:NaOH mole ratio of 1:2 and dunite:NaOH:H<sub>2</sub>O mole ratio of 1:2:0.5, before and after being washed with distilled H<sub>2</sub>O, respectively. The by-products, Na<sub>2</sub>SiO<sub>3</sub> and natrite are usually detected before washing the reaction products as demonstrated in Figure 1. These by-products are soluble in water and can be removed together with the remaining NaOH by washing the reaction products. After the washing and successive filtration, the samples are typically left with a solid fraction composed of Mg(OH)<sub>2</sub> and remaining dunite components (Figure 1).

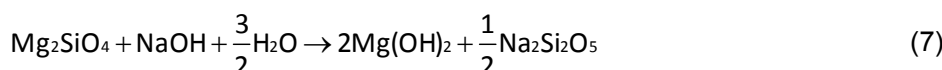
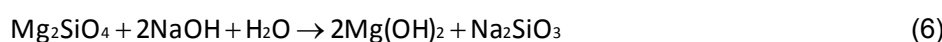
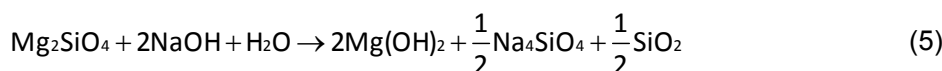


**Figure 1:** XRD patterns of selected reaction products from solid systems with dunite:NaOH mole ratio of 1:2 and dunite:NaOH:H<sub>2</sub>O mole ratio of 1:2:0.5 before and after washing, respectively.

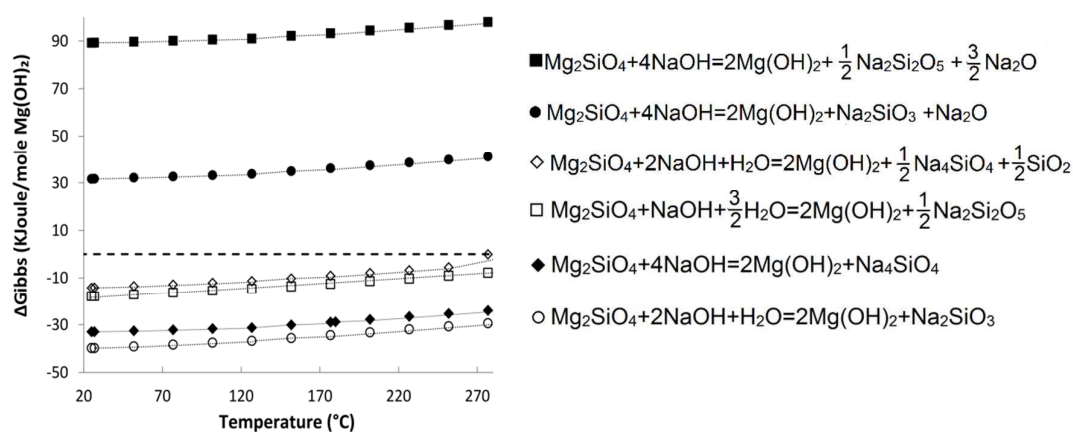
It is expected to be difficult to obtain Na<sub>2</sub>SiO<sub>3</sub> from the reaction of dunite and NaOH. Reactions 2, 3 and 4 are examples of reactions for Mg<sub>2</sub>SiO<sub>4</sub> and NaOH which assume Na<sub>4</sub>SiO<sub>4</sub>, Na<sub>2</sub>SiO<sub>3</sub> and Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> as reaction products, respectively. Mg<sub>2</sub>SiO<sub>4</sub> was chosen as representative of dunite because it is the main mineral component. The calculation of the Gibbs energy change, ( $\Delta G^\circ$ ), for Reactions 2, 3 and 4 showed that only the formation of Na<sub>4</sub>SiO<sub>4</sub> is thermodynamically favoured, as indicated by the negative  $\Delta G^\circ$  of reaction in Figure 2, whereas, the formation of Na<sub>2</sub>SiO<sub>3</sub> or Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> is not possible because of  $\Delta G^\circ > 0$ .



However, when H<sub>2</sub>O is involved in the reactions (Reactions 5, 6 and 7), the formation of these Na silicate species becomes possible because their  $\Delta G^\circ$  are all negative, as shown in Figure 2.



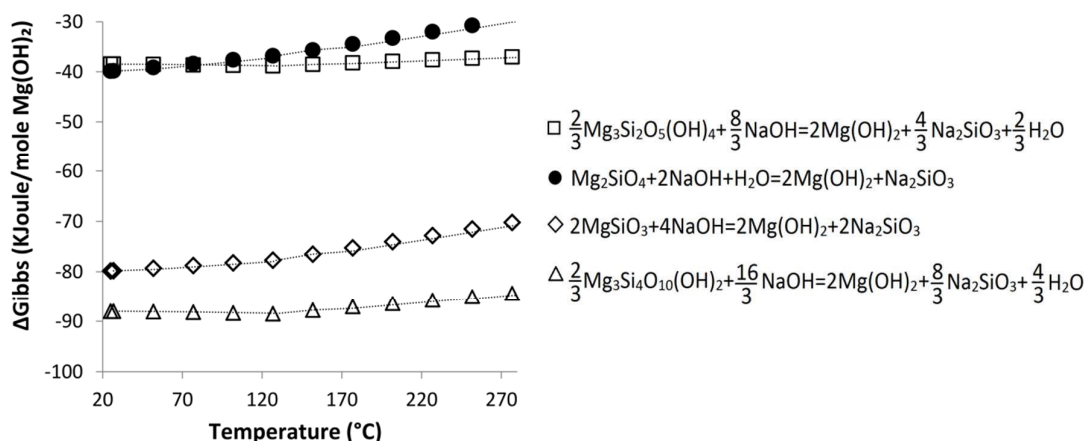
It should be noted that the formation of Na<sub>2</sub>SiO<sub>3</sub> in the presence of H<sub>2</sub>O becomes thermodynamically more favourable than that of Na<sub>4</sub>SiO<sub>4</sub> in *dry* reaction. These data suggest the involvement of H<sub>2</sub>O in the studied reaction and its thermodynamical advantage over the *dry* reaction. The carbonation of NaOH could also aid the involvement of H<sub>2</sub>O in the reaction. As seen in the XRD data in Figure 1, natrite has been formed in the system. Because the samples are in contact with air during the preparation and the reaction (in the closed vessel with trapped air), a part of NaOH in the system can be carbonated, and this reaction releases H<sub>2</sub>O through the following reaction.



**Figure 2:**  $\Delta G^\circ$  per 1 mole of  $\text{Mg}(\text{OH})_2$  produced calculated for possible reactions for  $\text{Mg}_2\text{SiO}_4$  and  $\text{NaOH}$ . Closed data points are for the *dry* reactions, and open data points for those involving  $\text{H}_2\text{O}$ .



The  $\Delta G^\circ$  for the reactions of NaOH and minor phases in the dunite i.e., serpentine ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), and enstatite ( $\text{MgSiO}_3$ ) are shown in Figure 3 and suggests that the formation of  $\text{Mg}(\text{OH})_2$  and  $\text{Na}_2\text{SiO}_3$  from these Mg silicate minerals is also thermodynamically possible ( $\Delta G^\circ < 0$ ). The thermodynamical feasibility of  $\text{Mg}(\text{OH})_2$  extraction from serpentine with NaOH is particularly relevant because serpentine is widely available in natural deposits and contain high wt% of Mg which makes it a suitable alternative feedstock material to dunite<sup>4</sup>.



**Figure 3:**  $\Delta G^\circ$  per 1 mole  $\text{Mg}(\text{OH})_2$  produced calculated for possible reactions for serpentine ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), and enstatite ( $\text{MgSiO}_3$ ) with NaOH in comparison with that for forsterite ( $\text{Mg}_2\text{SiO}_4$ ).

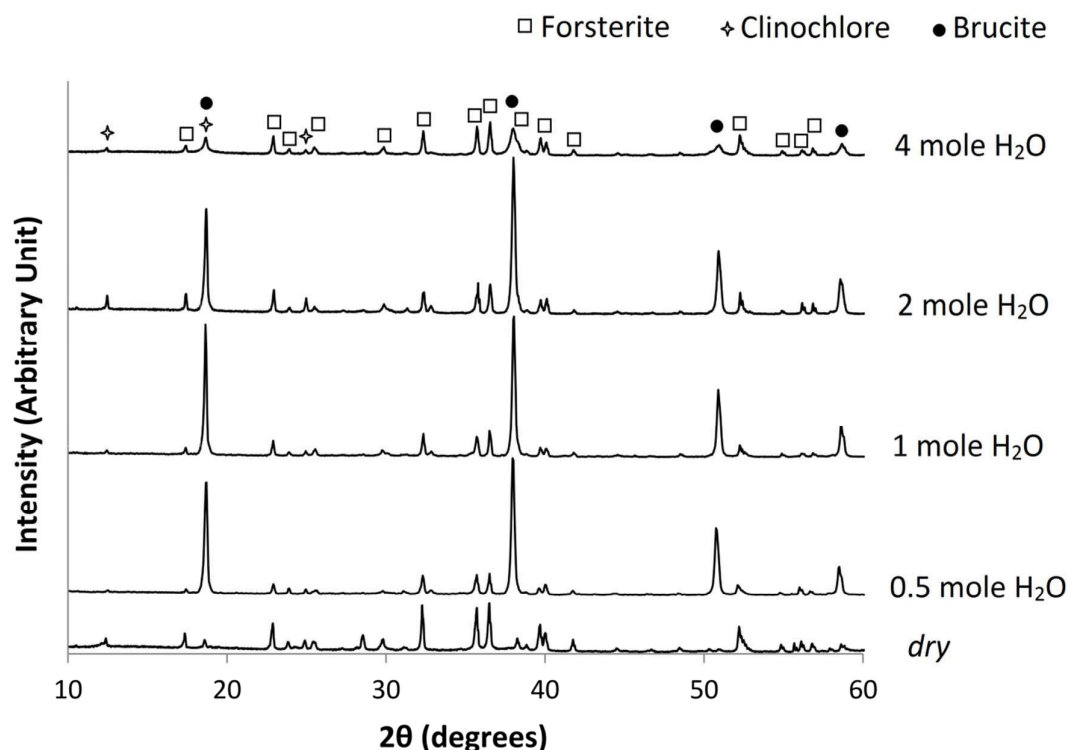
The enthalpy change ( $\Delta H^\circ$ ) for the possible reactions occurring in the dunite-NaOH system was also calculated at the temperatures of reaction investigated in this study, i.e. 130, 180 and 250 °C. All the reactions showed negative  $\Delta H^\circ$  in the temperature range of interest and the lowest was found at 250 °C. The values of  $\Delta H^\circ$  at this temperature are shown for each reaction in Table 2. These reactions are all exothermic and although their balance is not known, overall the extraction of  $\text{Mg}(\text{OH})_2$  from dunite should be energetically favoured.

**Table 2:** Standard Enthalpy change per 1 mole of  $\text{Mg}(\text{OH})_2$  produced at 250 °C

Reactions	$\Delta H^\circ$ (KJ)*
$\text{Mg}_2\text{SiO}_4 + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow 2\text{Mg}(\text{OH})_2 + \text{Na}_2\text{SiO}_3$	-58
$\frac{2}{3}\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \frac{8}{3}\text{NaOH} \rightarrow 2\text{Mg}(\text{OH})_2 + \frac{4}{3}\text{Na}_2\text{SiO}_3 + \frac{2}{3}\text{H}_2\text{O}$	-44
$2\text{MgSiO}_3 + 4\text{NaOH} \rightarrow 2\text{Mg}(\text{OH})_2 + 2\text{Na}_2\text{SiO}_3$	-98
$\frac{2}{3}\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + \frac{16}{3}\text{NaOH} \rightarrow 2\text{Mg}(\text{OH})_2 + \frac{8}{3}\text{Na}_2\text{SiO}_3 + \frac{4}{3}\text{H}_2\text{O}$	-99
$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	-176

### Effect of added H<sub>2</sub>O

The introduction of H<sub>2</sub>O into the system had a significant effect on the extraction of Mg(OH)<sub>2</sub>. Figure 4 compares the XRD patterns of the reaction products from the *dry* reaction and reaction with added H<sub>2</sub>O in Series 2. These samples were washed with distilled water and Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> had been removed. The extraction of brucite (Mg(OH)<sub>2</sub>), in the *dry* dunite-NaOH system appeared to be limited. The only reflection peaks identified are for the mineral components present in the dunite, while the reflection peaks for brucite were not observed. On the other hand, the systems with added H<sub>2</sub>O all indicated the presence of brucite. The two main reflection peaks for the brucite, are detected at 18.6 ° and 38 ° 2θ. These peaks partially overlap with those for clinocllore and forsterite, respectively, but are distinguishable based on the proportion of the other peaks intensity. The introduction of H<sub>2</sub>O is beneficial and the intensity of the reflection peaks for brucite considerably increases in systems with 0.5, 1 and 2 moles of H<sub>2</sub>O, although, the intensity significantly decreases in the system with 4 moles of H<sub>2</sub>O. A similar trend was observed also in Series 1.5 and 1.

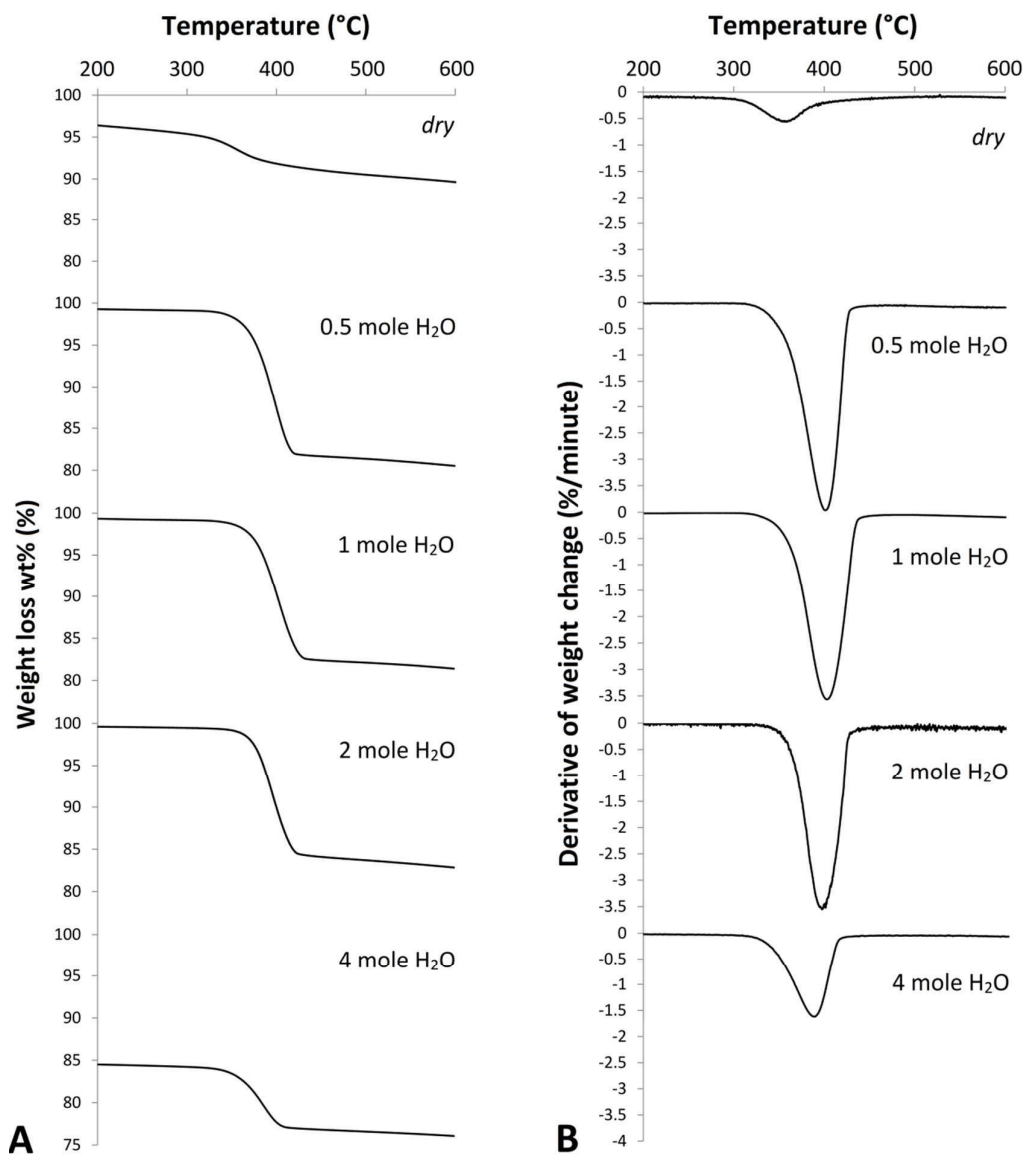


**Figure 4:** XRD patterns of reaction products from Series 2 with different amounts of H<sub>2</sub>O.

The TGA and DTG curves of the reaction products from Series 2 are shown in Figure 5(A) and 5(B), respectively. The sample reacted in *dry* condition had a small weight loss between 300 and 450 °C for the dehydroxylation of Mg(OH)<sub>2</sub>, whereas those reacted in presence of water showed a larger weight loss in this temperature region, indicating that more Mg(OH)<sub>2</sub> was produced when H<sub>2</sub>O was added to the system.

The calculated concentration of  $\text{Mg}(\text{OH})_2$  in the reaction product was 19 wt% for the *dry* dunite- $\text{NaOH}$  mixture, and 57.6, 55.4, 51.2 and 28 wt% with 0.5, 1, 2 and 4 mole of  $\text{H}_2\text{O}$  added per 1 mole of dunite, respectively. Thus, the amount of  $\text{Mg}(\text{OH})_2$  in the products decreases with the increase in  $\text{H}_2\text{O}$  content.

The TGA results are in agreement with the XRD data and indicate that the addition of  $\text{H}_2\text{O}$  was beneficial compared to the *dry* condition, likely because the dissolution of  $\text{NaOH}$  in  $\text{H}_2\text{O}$  favoured the ion exchange and the diffusivity of materials involved in the reaction<sup>18,19</sup>. The addition of smaller amounts of  $\text{H}_2\text{O}$ , i.e. higher  $\text{NaOH}:\text{H}_2\text{O}$  mole ratio, was a more preferable condition for  $\text{Mg}(\text{OH})_2$  formation, which suggests that the concentration of  $\text{NaOH}$  in  $\text{H}_2\text{O}$  played a decisive role for the extraction of  $\text{Mg}(\text{OH})_2$  from dunite.

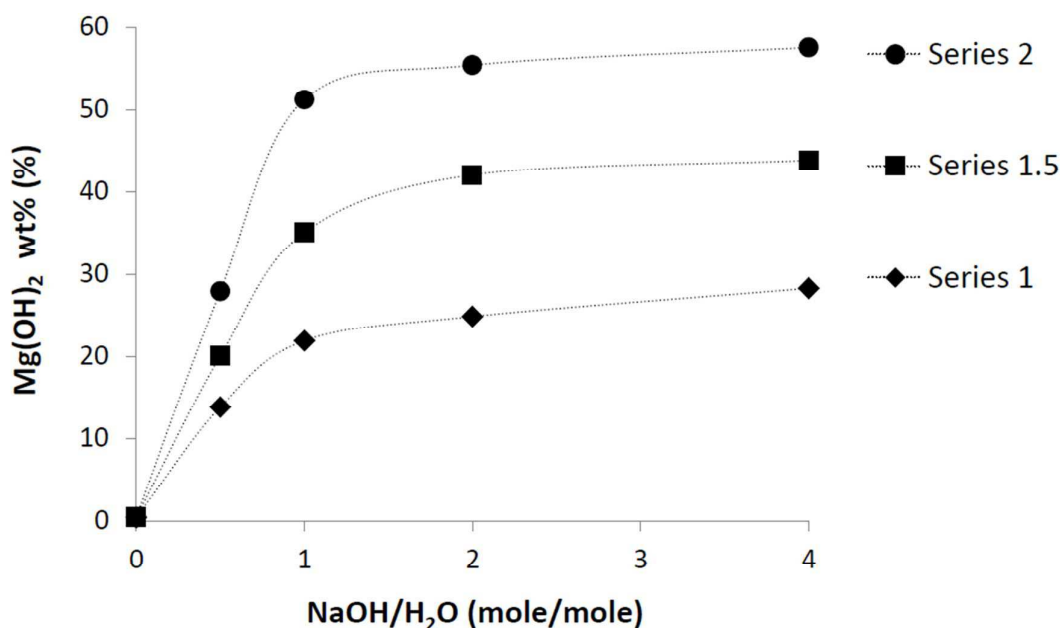


**Figure 5:** (A) TGA and (B) DTG curves of reaction products from Series 2.

### Effect of NaOH concentration

The  $\text{Mg}(\text{OH})_2$  content in the reaction products were estimated via TGA for Series 2, 1.5 and 1, and compared in Figure 6. The data are plotted against NaOH:H<sub>2</sub>O mole ratio to study the effects of NaOH concentration in H<sub>2</sub>O.

The reaction products from Series 2 showed the highest concentration of  $\text{Mg}(\text{OH})_2$ , followed by those from Series 1.5 and 1, indicating the advantage of having higher NaOH content in the system. The three series showed the same trend in presence of H<sub>2</sub>O, and the wt% of  $\text{Mg}(\text{OH})_2$  in the reaction products increased with the increase of NaOH:H<sub>2</sub>O mole ratio. However, this effect becomes less significant at higher NaOH:H<sub>2</sub>O mole ratio. In fact, at higher NaOH:H<sub>2</sub>O mole ratio the concentration of NaOH in H<sub>2</sub>O is higher but the amount of H<sub>2</sub>O in the system is lower, and thus the positive effect of H<sub>2</sub>O, such as the improvement of the reactants diffusion is reduced.

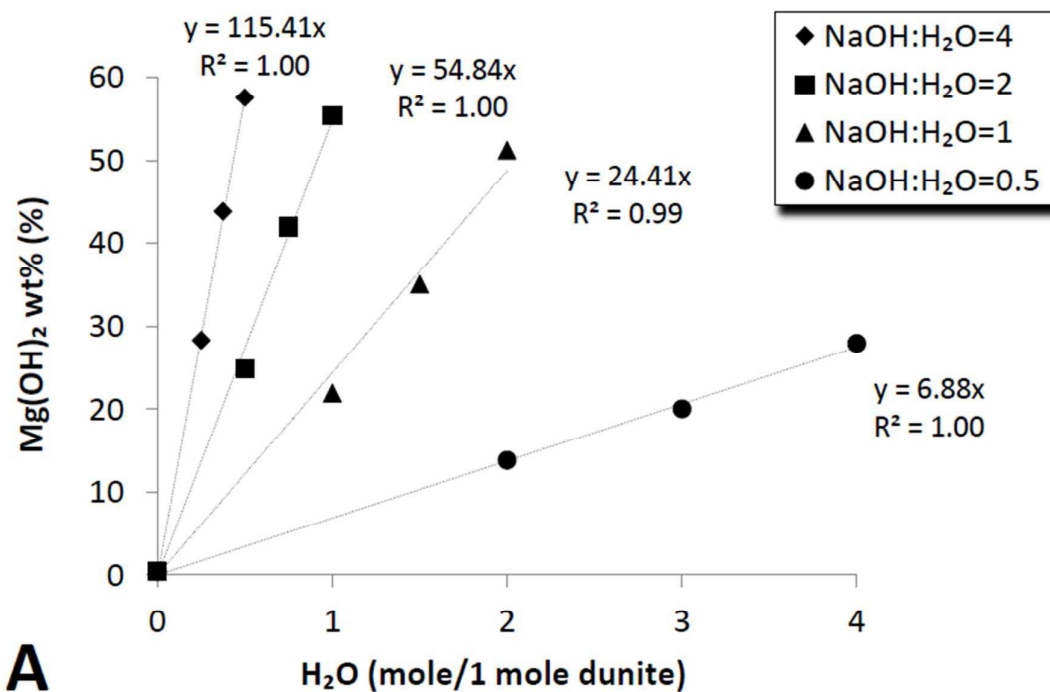


**Figure 26:**  $\text{Mg}(\text{OH})_2$  concentrations estimated via TGA in reaction products from Series 1, 1.5, and 2.

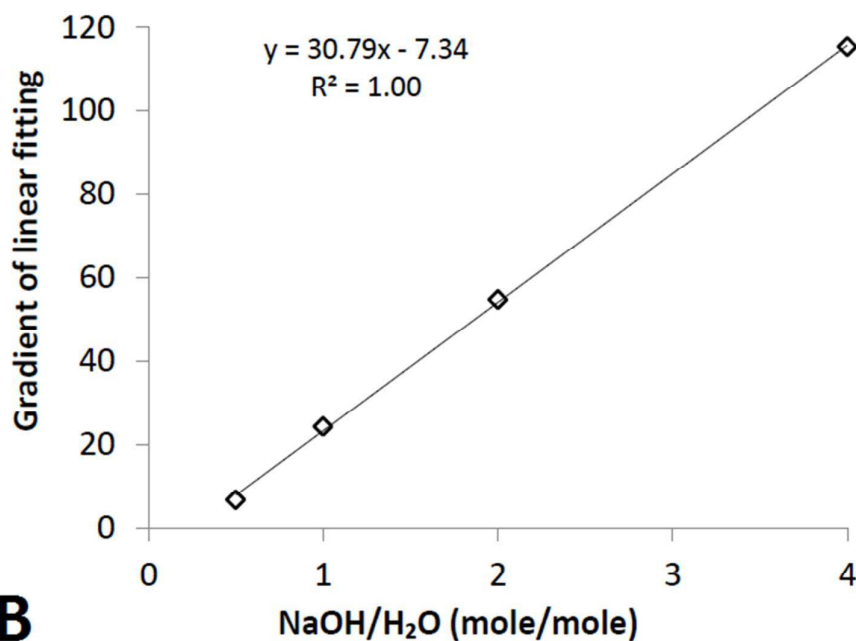
The data shown in Figure 6 are also plotted against the amount of H<sub>2</sub>O added to the system in Figure 7(A), grouped by the same NaOH:H<sub>2</sub>O mole ratio.

The gradients of the linear fitting for these data sets are proportional to the NaOH:H<sub>2</sub>O mole ratio as shown in Figure 7 (B). Based on these results, it is possible to estimate the approximate wt% of  $\text{Mg}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2(\%)$ , expected in the reaction product under the condition studied, using the following empirical equation with the amount of NaOH ( $X_{\text{NaOH}}$ ) and H<sub>2</sub>O ( $X_{\text{H}_2\text{O}}$ ).

$$\text{Mg}(\text{OH})_2(\%) = 30.79 \cdot (X_{\text{NaOH}}) - 7.34 \cdot (X_{\text{H}_2\text{O}}) \quad (9)$$



A



B

**Figure 7:**  $\text{Mg(OH)}_2$  concentrations estimated via TGA in reaction products: (A) effect of  $\text{H}_2\text{O}$  content for different NaOH:H<sub>2</sub>O mole ratio, and (B) the gradient of the linear fitting for datasets shown in (A).

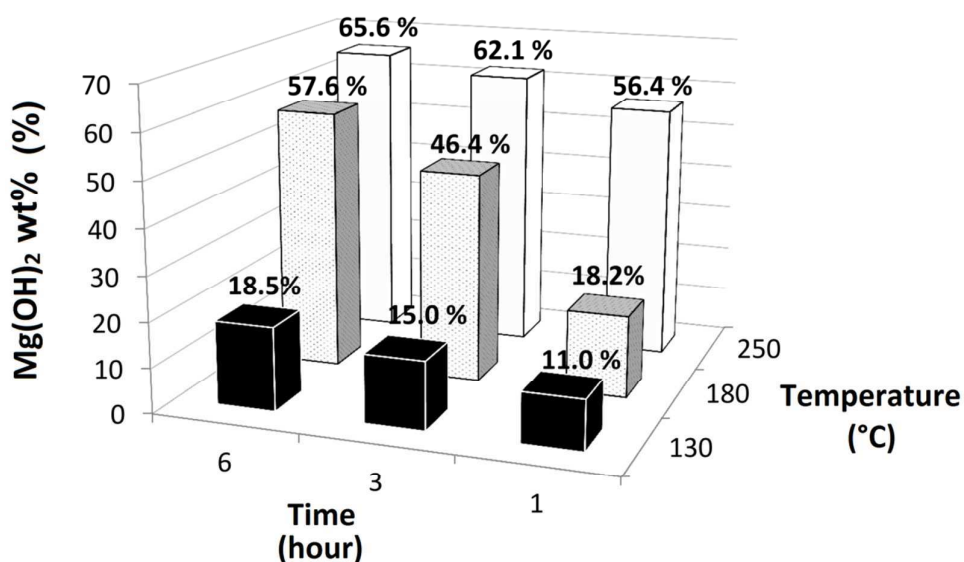
These data together with those previously discussed for Series 2, indicate that the extraction of  $\text{Mg(OH)}_2$  from dunite in NaOH-H<sub>2</sub>O solid systems is the result of a combined effect of NaOH concentration in H<sub>2</sub>O and amount of liquid phase present in

the system. At 180 °C, the NaOH in the systems should be fully dissolved at NaOH:H<sub>2</sub>O mole ratio of 1:2 and 1:1, or constitute a solid system with partially dissolved NaOH at NaOH:H<sub>2</sub>O mole ratio of 2:1 and 4:1<sup>20</sup>. The optimal conditions for the extraction of Mg(OH)<sub>2</sub> appears to be found when H<sub>2</sub>O is present in sufficient quantity to help the diffusion of the reactants but not in excess to reduce the relative concentration of NaOH in the liquid.

### ***Effect of temperature and time***

Amongst the compositions investigated, the system with the mole ratio of dunite:NaOH:H<sub>2</sub>O = 1:2:0.5 gave the highest Mg(OH)<sub>2</sub> extraction. The effect of reaction conditions was further investigated for this system, using three durations of reaction, i.e. 1, 3 and 6 hours, at different temperatures, i.e. 130, 180 and 250 °C. The reaction products were analysed via TGA, and the wt% of Mg(OH)<sub>2</sub> in the reaction product are compared in Figure 8.

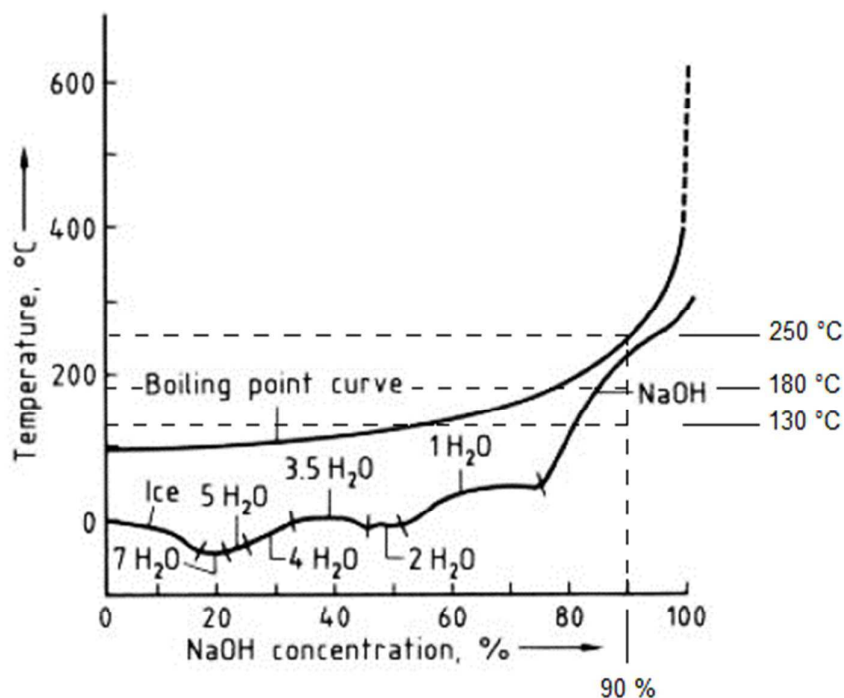
As expected, increasing the duration and temperature of reaction was beneficial for the extraction of Mg(OH)<sub>2</sub>. At 130 °C the formation of Mg(OH)<sub>2</sub> was limited, achieving only 18.5 wt% after 6 hours which is comparable with 18.2 wt% obtained at 180 °C in 1 hour. The reaction conducted at 180 °C resulted in a significant Mg(OH)<sub>2</sub> extraction of 46.4 wt% after 3 hours reaction. Increasing the temperature to 250 °C significantly improved the extraction of Mg(OH)<sub>2</sub>, and a concentration of 56.4 wt% Mg(OH)<sub>2</sub> was achieved after 1 hour, which increased to 65.6 wt% in 6 hours. The Mg(OH)<sub>2</sub> extraction obtained within 1 hour at 250 °C is comparable with 57.6 wt% attained at 180 °C over 6 hours of reaction. The reaction at 250 °C is faster than at the other temperatures, and the majority of reaction appears to have taken place in the first hour. This is highly advantageous for the industrial application of the process, as it would allow the reduction of reaction time from 6 to 1 hour to achieve the same degree of Mg(OH)<sub>2</sub> extraction obtained at 180 °C.



**Figure 8:** Mg(OH)<sub>2</sub> concentration estimated via TGA in reaction products of dunite:NaOH:H<sub>2</sub>O systems with 1:2:0.5 mole ratio at different temperatures and times of reaction.



Figure 9 shows the NaOH-H<sub>2</sub>O phase diagram<sup>20</sup>. The diagram has been adapted to show the temperatures and NaOH concentration used in this study. The NaOH:H<sub>2</sub>O mole ratio of 4:1 corresponds to a NaOH concentration in H<sub>2</sub>O of approximately 90% by weight. The diagram shows that there could be a solid portion remaining at 130 and 180 °C in the NaOH-H<sub>2</sub>O system at 90 wt% NaOH whereas, only liquid or gas can be present at 250 °C, similar to molten salt systems<sup>20</sup>. Consequently, at 250 °C dunite reacted with a highly alkaline melt instead of a solid system with a limited amount of NaOH dissolved in H<sub>2</sub>O, which should have favoured the diffusion of reactants<sup>21</sup>, contributing to the much faster kinetic of Mg(OH)<sub>2</sub> extraction observed within the first hour of reaction at this temperature. Although the increase of pressure in the closed vessel at higher temperature may shift the melting temperature, based on the obtained results it appears to be still below 250 °C.



**Figure 9:** NaOH-H<sub>2</sub>O phase diagram, modified from Kurt and Bittner, 2003<sup>20</sup>.

### Efficiency of reaction

The efficiency of Mg(OH)<sub>2</sub> extraction is estimated through the yield of reaction which calculates the percentage of Mg(OH)<sub>2</sub> produced with respect to the maximum amount of Mg(OH)<sub>2</sub> theoretically producible from dunite<sup>15,22</sup>. The procedure adopted for the yield calculation is described in Madeddu *et al*<sup>15</sup>. In the present study, the yield was calculated using Eqs. 10 and 11 from which the amount of Mg(OH)<sub>2</sub> extracted from dunite was obtained, based on the wt% estimated via TGA.

The wt% of Mg(OH)<sub>2</sub> in the reaction products determined via TGA,  $Mg(OH)_{2(\%)}$ , can be expressed according to Equation 10, where  $Mg(OH)_{2(rp)}$  and  $Dunite_{(rp)}$  are the amount of Mg(OH)<sub>2</sub> and dunite in the reaction products, respectively. Equation 11, on the other

hand calculates the amount of MgO involved in the reaction.  $Dunite_{(i)}$  is the initial feed of dunite, and 48.3 is the wt% of MgO in  $Dunite_{(i)}$ . 48.21 is the wt% of MgO in dunite excluding the MgO initially presented as 0.42 wt% of  $Mg(OH)_2$ , and 40.3 and 58.3 are the molecular weights of MgO and  $Mg(OH)_2$ , respectively.

$$Mg(OH)_{2(\%)} = \frac{100 \cdot Mg(OH)_{2(rp)}}{Mg(OH)_{2(rp)} + Dunite_{(rp)}} \quad (10)$$

$$\frac{48.3 \times Dunite_{(i)}}{100} = \frac{48.21 \times Dunite_{(rp)}}{100} + \frac{40.3 \times Mg(OH)_{2(rp)}}{58.3} \quad (11)$$

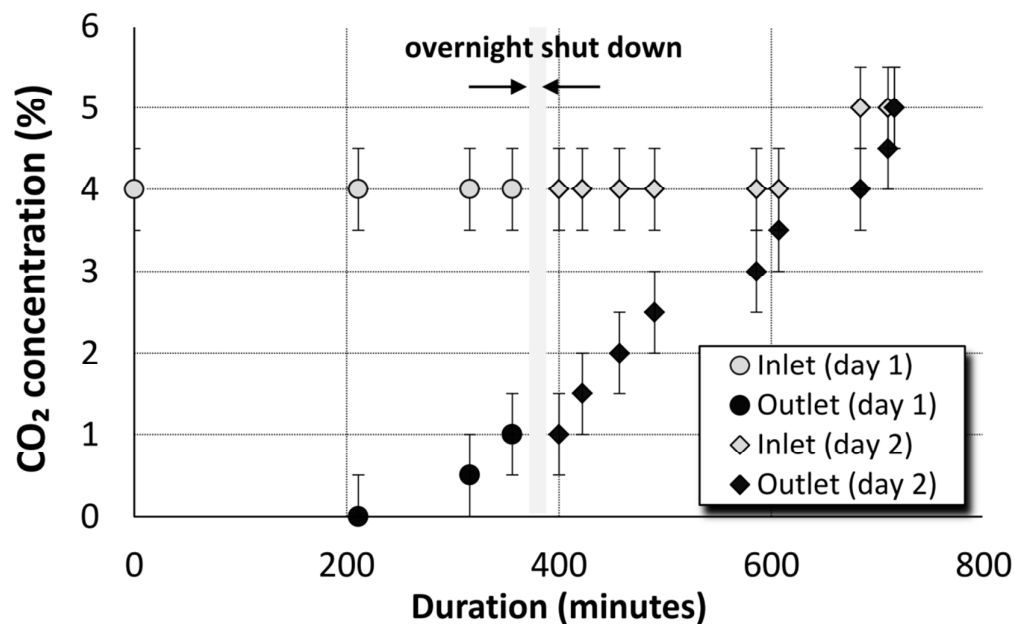
With the values of  $Mg(OH)_{2(\%)}$  and  $Dunite_{(i)}$ , it is possible to obtain  $Mg(OH)_{2(rp)}$  and  $Dunite_{(rp)}$  by solving the system of Eqs. 10 and 11.

For the three series tested at 180 °C in the present investigation, the highest yield of reaction of 66% was achieved in the reaction product of Series 2, with a NaOH:H<sub>2</sub>O mole ratio of 4:1 reacted for 6 hours. The same yield was obtained from the alkaline digestion of dunite with NaOH 50 mol/Kg aqueous system at the same temperature and same duration of reaction<sup>15</sup>. The NaOH consumed in the solid system reaction was 0.57 g per 1 g of dunite, whereas 20.6 g of NaOH was demanded in the aqueous system to process 1 g of dunite, which corresponds to the reduction of NaOH usage by 97%<sup>15</sup>. The H<sub>2</sub>O consumed was also reduced by 99%<sup>15</sup>. When the system reacted at 130 °C, the yield of reaction was 24% after 6 hours, whereas, at 250 °C the yield was 64.8, 70 and 73% after 1, 3, and 6 hours, respectively. As expected the yield achieved after 1 hour reaction at 250 °C is comparable with that achieved at 180 °C after 6 hours. The NaOH was reduced by 97.9% in Series 1.5 and 98.6% in Series 1, although the yield of reaction was reduced to 53% and 36%, respectively, after 6 hour reaction at 180 °C.

These results shows that the extraction of  $Mg(OH)_2$  via reaction of dunite with NaOH in solid system is preferable than the alkaline digestion with NaOH aqueous systems as the amount of NaOH required can be significantly reduced while maintaining the same efficiency of  $Mg(OH)_2$  extraction.

#### **Feasibility of CO<sub>2</sub> capture with $Mg(OH)_2$**

Figure 10 shows the CO<sub>2</sub> concentration in the flow gas measured at the inlet and outlet of GDC reactor during the experiment. The CO<sub>2</sub> concentration at the outlet was initially negligible, and all CO<sub>2</sub> in the flow gas appeared to be retained in the circulating solution by reacting with  $Mg(OH)_2$  in the system. The CO<sub>2</sub> concentration started increasing after approximately 200 minutes due to the consumption of  $Mg(OH)_2$  in the system, and became equal to that in the inlet gas at 720 minutes where the system no longer captures CO<sub>2</sub>. The overnight shut down period did not cause any obvious change in the system. The obtained results clearly show the CO<sub>2</sub> capture capability of this system.

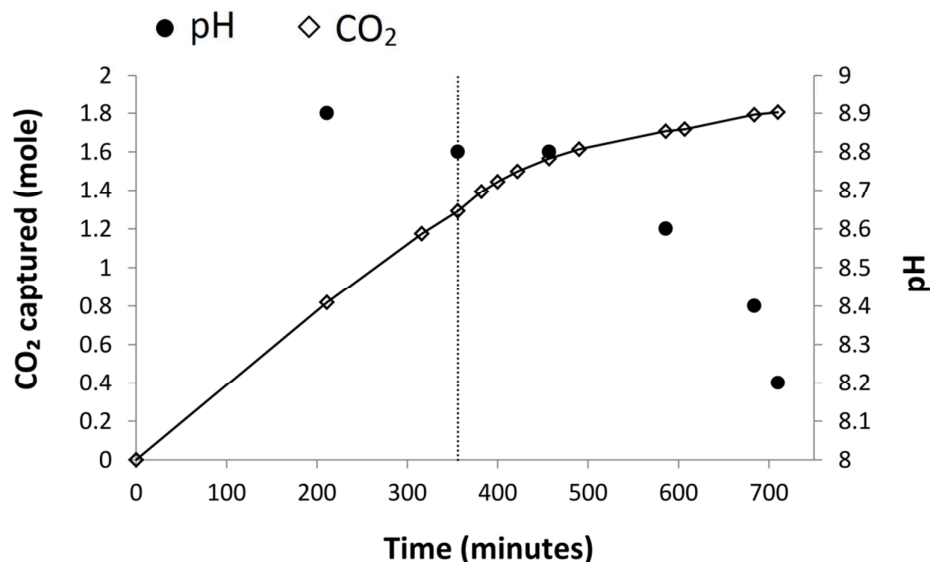


**Figure 10:** CO<sub>2</sub> concentration in the flow gas at the inlet and outlet of DGC reactor.

The amount of CO<sub>2</sub> captured from the flow gas was estimated using Eq. 12 where CO<sub>2*i*</sub> % and CO<sub>2*o*</sub> % are the concentration of CO<sub>2</sub> in the inlet and outlet gas, respectively. The volume of gas under atmospheric pressure at 10 °C was estimated as 23.2 L/mole.

$$\text{CO}_2(\text{mole}) = \frac{2.25(\text{L} \cdot \text{min}^{-1})}{23.2(\text{L} \cdot \text{mole}^{-1})} \times \frac{\text{CO}_{2i}(\%) - \text{CO}_{2o}(\%)}{100} \times \text{time}(\text{min}) \quad (12)$$

The amount of captured CO<sub>2</sub> is plotted in Figure 11 together with the pH of the circulating solution. CO<sub>2</sub> was steadily captured up to around 400 minutes, and then the rate of capture slightly decreased. The significant reduction in pH at this period suggests the exhaustion of the dissolved Mg(OH)<sub>2</sub> available for reaction. In total, 1.80 ± 0.19 moles of CO<sub>2</sub> were sequestered over the 2 days of experimental run.



**Figure 11:** Amount of CO<sub>2</sub> captured and pH of the circulating solution in the liquid-gas scrubbing with Mg(OH)<sub>2</sub>-H<sub>2</sub>O slurry

Since the circulating solution used in the present study contained approximately 0.85 mole of Mg(OH)<sub>2</sub>, the maximum CO<sub>2</sub> to be captured is 1.71 mole (1.72 mole if CaO presented as an impurity is also counted) assuming the reaction product is Mg(HCO<sub>3</sub>)<sub>2</sub>, and 0.86 mole if MgCO<sub>3</sub> was produced. Although our estimation,  $1.80 \pm 0.19$  mole, contains a significant deviation, it is clear that the reaction product in the tested system was mainly Mg(HCO<sub>3</sub>)<sub>2</sub>. It is known that the formation of Mg(HCO<sub>3</sub>)<sub>2</sub> is favoured when the pH of the solution is around 8.4 where HCO<sub>3</sub><sup>-</sup> ions are the predominant species of CO<sub>2</sub> dissolution, whereas MgCO<sub>3</sub> preferentially forms when the pH of the solution is above 10 as the CO<sub>3</sub><sup>2-</sup> ions are the predominant species<sup>5, 23, 24</sup>. The obtained results confirms that Mg(HCO<sub>3</sub>)<sub>2</sub> can form in the pH ranging between 8.2 – 8.9.

The amount of solid material collected upon completion of the experiment was 2 g. The XRD analysis showed that the solid residue was constituted by brucite and poorly crystalline hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) and another poorly crystalline phase which was not identified. The amount of CO<sub>2</sub> in the collected solid was determined via CHN analysis and estimated as 0.01 mole. These results indicate that Mg(OH)<sub>2</sub> almost fully dissolved and captured CO<sub>2</sub> by forming Mg(HCO<sub>3</sub>)<sub>2</sub> which remained in equilibrium in solution while only a small fraction reacted forming Mg carbonate phases.

The exact quantification of CO<sub>2</sub> captured by the reaction with Mg(OH)<sub>2</sub> is challenging and requires further analysis. Nevertheless, these preliminary results suggest that at least 93.6% of CO<sub>2</sub> potentially capturable by the Mg(OH)<sub>2</sub> suspension was effectively captured.

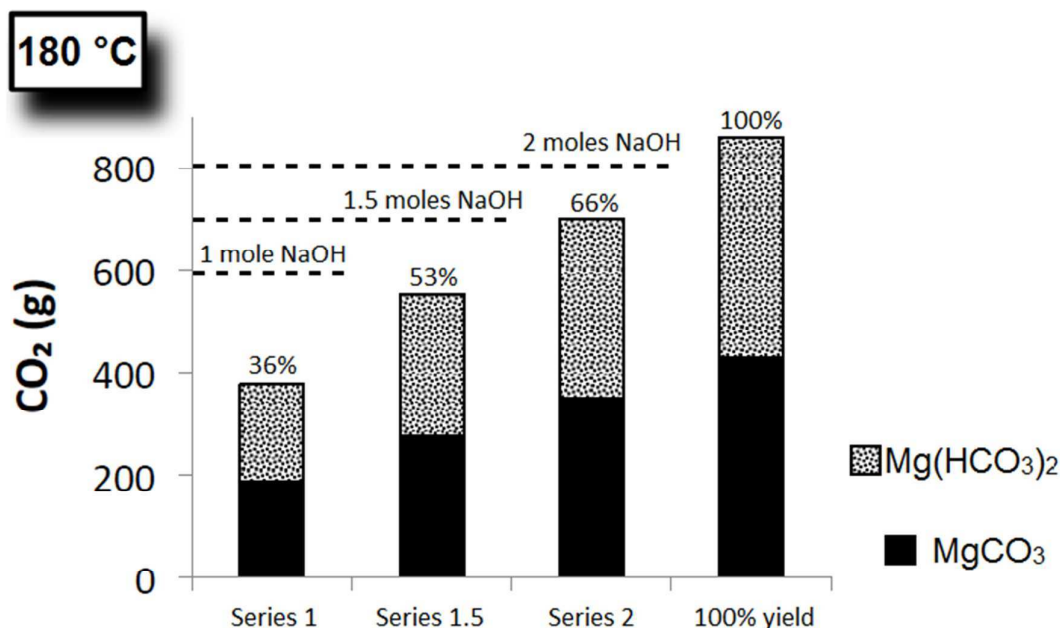
### **Implications of Mg(OH)<sub>2</sub> extraction for CCS**

The consumption of NaOH was identified as one of the major drawbacks for the extraction of Mg(OH)<sub>2</sub> in the NaOH aqueous system<sup>15</sup> because the production of

NaOH involves a significant energy consumption and thus CO<sub>2</sub> emissions. Therefore, the reduction in NaOH achieved in the present study is significant and it would reduce the environmental impact of the process.

In the present study, the CO<sub>2</sub> balance was evaluated based on the emissions associated with the NaOH, Mg(OH)<sub>2</sub> extraction and the sequestration potential of Mg(OH)<sub>2</sub> derived from dunite. The assessment is based on the mass balance of the materials used assuming that 1 kg of dunite is processed with the corresponding amount of NaOH used for Series 1, 1.5 and 2. The amount of Mg(OH)<sub>2</sub> extracted was estimated from the yield of reaction achieved. The CO<sub>2</sub> emission from the NaOH production was calculated assuming that 2.9 kWh electricity is required to produce 1 kg of NaOH, which corresponds to the emission of at least 250 g of CO<sub>2</sub> per 1 kWh, when natural gas is used<sup>25,26</sup>. The CO<sub>2</sub> emission from the extraction of Mg(OH)<sub>2</sub> is based on the use of an electric oven with 28 litres capacity to process 1 kg of dunite. The oven consumes 0.17, 0.26 and 0.385 kWh of energy to operate at 130, 180 and 250 °C, respectively, according to the manufacturer's specification<sup>27</sup>. The CO<sub>2</sub> sequestration was calculated based on the full conversion of Mg(OH)<sub>2</sub> into either MgCO<sub>3</sub> or Mg(HCO<sub>3</sub>)<sub>2</sub>.

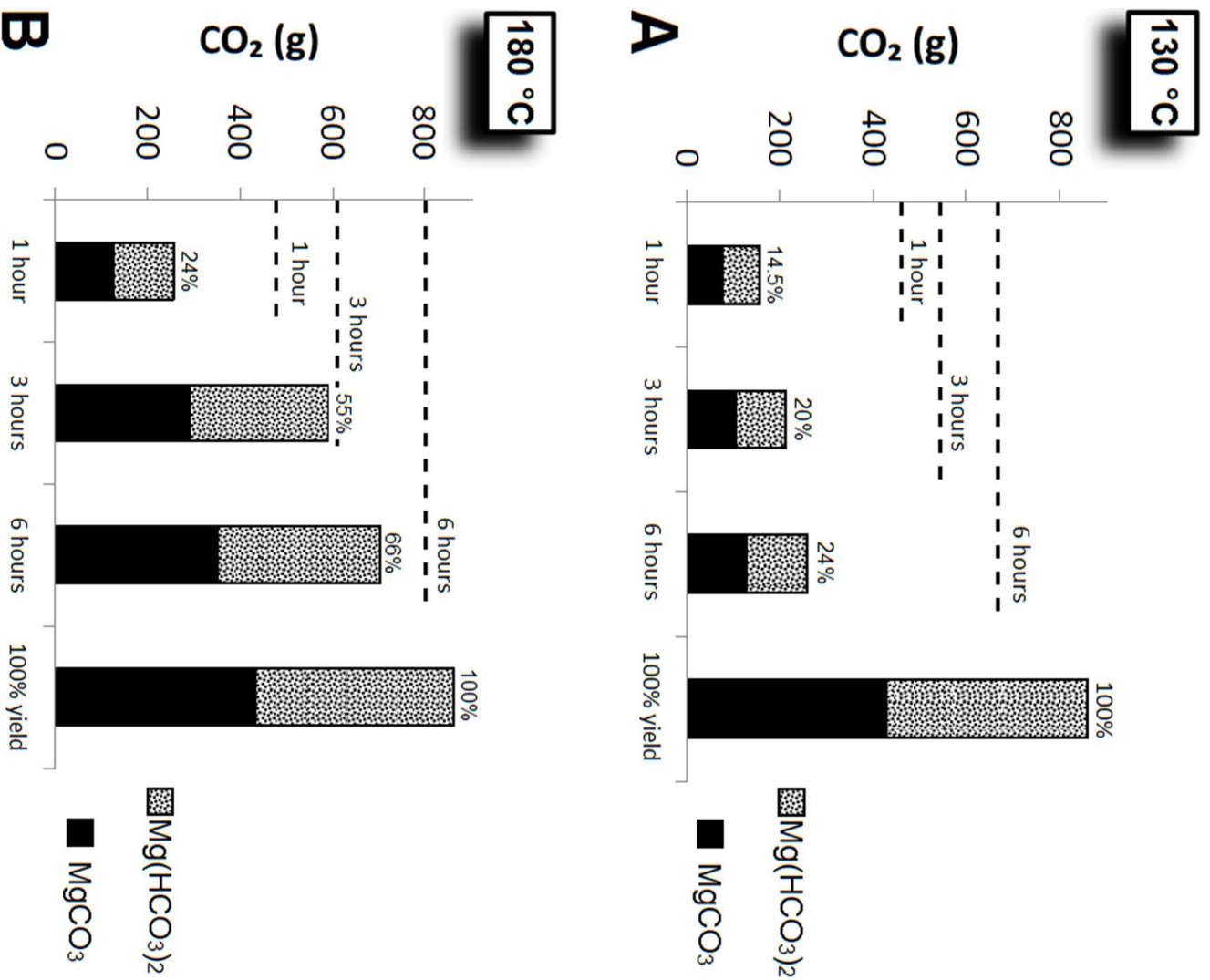
Figure 12 compares the CO<sub>2</sub> potentially captured by the Mg(OH)<sub>2</sub> extracted at 180 °C in 6 hours for Series 1, 1.5, and 2, together with that achievable at 100% yield of reaction. The dotted lines represent the sum of the CO<sub>2</sub> emissions from the NaOH production and Mg(OH)<sub>2</sub> extraction. The graph shows that the potential CO<sub>2</sub> capture naturally increases with the improvement of the yield of Mg(OH)<sub>2</sub> extraction, but the estimated CO<sub>2</sub> emission from NaOH production and Mg(OH)<sub>2</sub> extraction is still larger, indicating the importance of process optimisation. The achievement of 100% yield at 180 °C in 6 hours would effectively reduce CO<sub>2</sub> emission for all series when Mg(OH)<sub>2</sub> is fully converted into Mg(HCO<sub>3</sub>)<sub>2</sub>. On the other hand, the CO<sub>2</sub> captured into MgCO<sub>3</sub> would not be sufficient to offset the CO<sub>2</sub> emission even at the maximum yield of Mg(OH)<sub>2</sub> extraction. According to Reaction 6, 1 mole Mg(OH)<sub>2</sub> requires the consumption of 1 mole NaOH, and from the amount of Mg(OH)<sub>2</sub> in the reaction products it was estimated that only 55, 59 and 60% NaOH reacted with dunite in Series 2, 1.5 and 1, respectively, suggesting that there is still a wide margin for improvement of Mg(OH)<sub>2</sub> extraction.

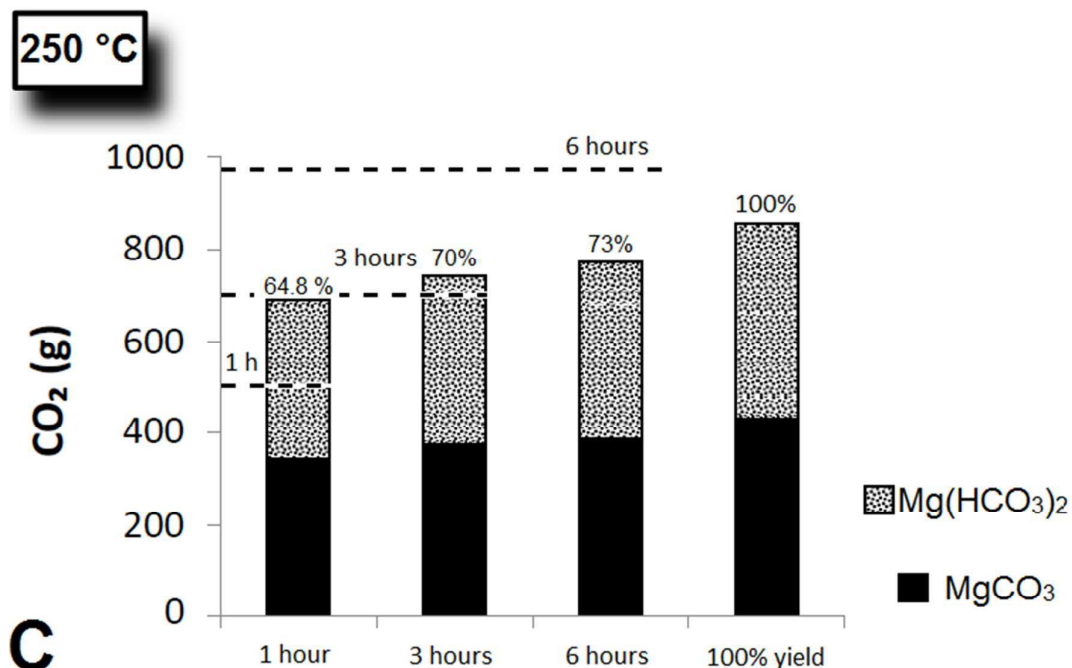


**Figure 12:** Potential CO<sub>2</sub> capture by Mg(OH)<sub>2</sub> conversion into MgCO<sub>3</sub> or Mg(HCO<sub>3</sub>)<sub>2</sub> (columns). The estimated CO<sub>2</sub> emission associated with the NaOH production and Mg(OH)<sub>2</sub> extraction at 180 °C for 6 hours are also shown (dotted lines) for Series 1, 1.5 and 2 for comparison. The yield of Mg(OH)<sub>2</sub> extraction is reported on top of the columns for each series.

Figures 13 (A), (B) and (C) show the CO<sub>2</sub> balance for Series 2 extracted at 130, 180 and 250 °C, respectively. As shown in Figure 13 (A), the yield of Mg(OH)<sub>2</sub> extraction at 130 °C is too low and the CO<sub>2</sub> emission from the power consumption is considerably larger. Figure 13 (B) shows that the CO<sub>2</sub> balance is significantly improved at 180 °C. In fact, at this temperature the potential CO<sub>2</sub> capture becomes close to the CO<sub>2</sub> produced in the case of 3 hours of extraction, when CO<sub>2</sub> is captured as Mg(HCO<sub>3</sub>)<sub>2</sub>. Thus, a small improvement of the extraction condition could result in a carbon neutral process. Extending the duration of reaction to 6 hours is not energetically beneficial as more CO<sub>2</sub> is emitted. The CO<sub>2</sub> balance for the extraction at 250 °C is much better. As shown in Figure 13 (C), at 1 and 3 hours extraction, the CO<sub>2</sub> capture exceeds the CO<sub>2</sub> produced from the NaOH production and Mg(OH)<sub>2</sub> extraction, and CO<sub>2</sub> is successfully reduced. At this temperature, a shorter duration is clearly more beneficial. It should be noted that the CO<sub>2</sub> capture exceeds the CO<sub>2</sub> emission only when Mg(HCO<sub>3</sub>)<sub>2</sub> is produced as a reaction product. The achievement of 100% yield of extraction at 130, and 180 °C would reduce CO<sub>2</sub> under the studied conditions when Mg(HCO<sub>3</sub>)<sub>2</sub> is formed, while at 250 °C, this occurs only for the extraction of 1 and 3 hours, and with 6 hours CO<sub>2</sub> is emitted. When MgCO<sub>3</sub> is produced as the reaction product, the amount of CO<sub>2</sub> to be captured is less than the CO<sub>2</sub> produced during the process, even at 100% yield, and thus the production of Mg(HCO<sub>3</sub>)<sub>2</sub> is a key factor to offset the CO<sub>2</sub> produced during the extraction.







**Figure 13:** Potential CO<sub>2</sub> capture by Mg(OH)<sub>2</sub> conversion into MgCO<sub>3</sub> or Mg(HCO<sub>3</sub>)<sub>2</sub> (columns) for Series 2 at (A) 130 °C, (B) 180 °C and (C) 250 °C. The estimated CO<sub>2</sub> emission associated with the NaOH production and Mg(OH)<sub>2</sub> extraction for 1, 3 and 6 hours are also shown (dotted lines) for comparison. The yield of Mg(OH)<sub>2</sub> extraction is reported on top of the columns for each series.

## Conclusions

The present study demonstrated that the NaOH required to extract Mg(OH)<sub>2</sub> from dunite can be reduced to a stoichiometric ratio with the reaction in the solid system assisted with H<sub>2</sub>O.

H<sub>2</sub>O considerably improved the extraction of Mg(OH)<sub>2</sub> compared with the reaction in *dry* condition, favouring the diffusion of the reactants involved. Both NaOH concentration in H<sub>2</sub>O and the amount of liquid phase in the system played a significant role in the extraction of Mg(OH)<sub>2</sub> from dunite and the best results were achieved in systems with dunite:NaOH:H<sub>2</sub>O 1:2:0.5 mole ratio. Decreasing the NaOH below the stoichiometric ratio resulted in less Mg(OH)<sub>2</sub> extraction.

At 180 °C, the maximum yield of Mg(OH)<sub>2</sub> extraction was 66% over 6 hours reaction for solid systems with dunite:NaOH:H<sub>2</sub>O 1:2:0.5 mole ratio. The NaOH consumption was reduced by 97% without affecting the efficiency of extraction with respect to the NaOH aqueous systems used in the previous study reacted at the same temperature and time. The H<sub>2</sub>O consumption was also reduced by 99%. At 250 °C, the extraction of Mg(OH)<sub>2</sub> was significantly accelerated and 64.8% yield was achieved in 1 hour for solid systems with dunite:NaOH:H<sub>2</sub>O mole ratio of 1:2:0.5.

CO<sub>2</sub> was successfully separated from a gas mixture composed of 4 – 5% CO<sub>2</sub> and N<sub>2</sub> via liquid-gas scrubbing using a Mg(OH)<sub>2</sub> aqueous slurry and stored in the solution as Mg(HCO<sub>3</sub>)<sub>2</sub>. At least 93.6% capture efficiency was achieved over 12 hours of duration at ambient conditions. This technology integrates the separation and capture of CO<sub>2</sub> in one single step and may improve the efficiency of the overall CCS process.

The CO<sub>2</sub> balance of the process was estimated from the emission associated with the power consumed for NaOH production and Mg(OH)<sub>2</sub> extraction together with the CO<sub>2</sub> captured by Mg(OH)<sub>2</sub> derived from dunite. At 130 and 180 °C, the process is carbon neutral only at yields of reaction higher than those achieved in the present study when Mg(OH)<sub>2</sub> is converted into Mg(HCO<sub>3</sub>)<sub>2</sub>. The CO<sub>2</sub> balance becomes negative when dunite is processed at 250 °C for 1 or 3 hours and CO<sub>2</sub> is captured as Mg(HCO<sub>3</sub>)<sub>2</sub>. This is promising for the possible application of Mg(OH)<sub>2</sub> derived from dunite for CO<sub>2</sub> separation from flue gases and storage in H<sub>2</sub>O.

### Acknowledgements

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