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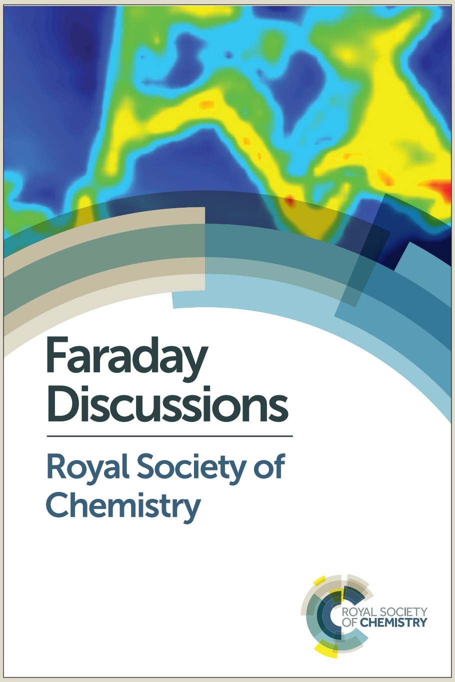

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Extraction of $Mg(OH)_2$ from Mg silicate minerals with NaOH assisted with H_2O: implications for CO_2 capture from exhaust flue gas

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Abstract

The utilisation of $Mg(OH)_2$ to capture exhaust CO_2 has been hindered by the limited availability of brucite, $Mg(OH)_2$ mineral in natural deposits. Our previous study demonstrated that $Mg(OH)_2$ 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, $Mg(OH)_2$ was extracted from dunite reacted in solid systems with NaOH assisted with H_2O. The consumption of NaOH was reduced by 97% respect to the NaOH aqueous systems, maintaining a comparable yield of $Mg(OH)_2$ extraction, i.e. 64.8 - 66%.

The capture of CO_2 from CO_2-N_2 gas mixture was tested at ambient conditions using a $Mg(OH)_2$ aqueous slurry. $Mg(OH)_2$ almost fully dissolved and reacted with dissolved CO_2 by forming $Mg(HCO_3)_2$ which remained in equilibrium storing the CO_2 in the aqueous solution.

The CO_2 balance of the process was assessed from the emission derived from the power consumption for NaOH production and $Mg(OH)_2$ extraction together with the CO_2 captured by $Mg(OH)_2$ derived from dunite. The process resulted carbon neutral when dunite is reacted at 250 °C for durations of 1 and 3 hours and CO_2 is captured as $Mg(HCO_3)_2$.

Introduction

Carbon Capture and Storage (CCS) is a portfolio of technologies developed for the abatement of anthropogenic CO_2 emissions via permanent isolation of CO_2 from the atmosphere [1]. CCS includes the separation of CO_2 from exhaust flue gases and its storage either underground, in seawater or through the fixation into stable mineral carbonates via mineral carbonation [1].

$Mg(OH)_2$ can capture CO_2 in a wide range of conditions: it can permanently and safely store CO_2 into solid Mg carbonate minerals upon the exposure to gaseous or supercritical CO_2 or via dissolution in H_2O with purged CO_2 [2, 3, 4]. $Mg(OH)_2$ aqueous slurries have been successfully tested to separate CO_2 from gas mixtures via liquid-gas scrubbing, and the technology has been proposed to separate CO_2 from exhaust flue gases [5]. $Mg(OH)_2$ and CO_2 dissolved in H_2O can react to form $Mg(HCO_3)_2$ which remains in solution as soluble phase under controlled pH [5, 6]. This chemistry is suited to industrial applications such as coastal industry and power plants or ships, where CO_2 can be separated from exhaust flue gases using $Mg(OH)_2$ slurries and permanently stored in seawater as dissolved $Mg(HCO_3)_2$ [7]. This technology combines the separation and storage of CO_2 into a single stage, which is favourable because it avoids the capture and conversion of CO_2 into a pure CO_2 stream, as well as the compression and transport operations, all of which are expensive and energy demanding [8, 9]. Despite the wide range of possible applications and potential advantages, $Mg(OH)_2$ utilisation for CO_2 capture has been hindered due to its rare occurrence in natural outcrops [1,10].

Mg silicate minerals, on the other hand, in particular serpentine and forsterite have been the preferred feedstock materials for CO_2 sequestration due to their vast availability in natural deposits which provides large storage capacity [1, 11, 12]. 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 [1, 13].

The extraction of $Mg(OH)_2$ 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 $Mg(OH)_2$ has a faster kinetic in carbonation than these Mg silicate minerals and allows greater flexibility in the design of the CCS technologies [4]. There are technologies currently available to obtain $Mg(OH)_2$ from Mg silicate minerals, e.g. a solid state reaction with ammonium salts at 400 - 500 °C or dissolution with HCl at 150 °C [4, 14]. These technologies involve a second step where the pH of the system is increased by introducing another reactant to favour the precipitation of $Mg(OH)_2$ in alkaline condition [4, 14].

In a previous study we investigated the alkaline digestion of Mg silicate minerals to obtain $Mg(OH)_2$ using highly concentrated NaOH aqueous systems [15]. 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 $Mg(OH)_2$. 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 [15].

The present study proposes a new technique for the extraction of $Mg(OH)_2$ 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_2O on the efficiency of $Mg(OH)_2$ extraction from the dunite-NaOH solid mixtures. The effects of temperature and duration of reaction were also studied for a dunite-NaOH-H_2O 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_2 sequestration using $Mg(OH)_2$ was also demonstrated using a Downflow Gas Contactor (DGC) reactor. CO_2 was separated from a flow of CO_2-N_2 mixture at ambient conditions using an aqueous slurry of reagent grade $Mg(OH)_2$, and the implications of using $Mg(OH)_2$ derived from dunite for CO_2 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_2, and 6.16 wt% Fe_2O_3, while other oxides were present at < 1 wt%. The X-ray diffraction (XRD) analysis revealed that dunite was mainly composed of forsterite, Mg_2SiO_4, the Mg-rich member of the olivine group. The minor components were also Mg-bearing minerals, i.e. clinochlore, 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 $Mg(OH)_2$ 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 $Mg(OH)_2$

NaOH pearl, reagent grade provided by Fisher Chemical was mixed with powdered dunite, with or without addition of distilled H_2O, 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_2SiO_4. For all series, the samples were prepared at different NaOH:H_2O mole ratio of 4:1, 2:1, 1:1, and 1:2. Series 2 also includes a sample reacted without H_2O 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_2O 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_2O** (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_2SiO_4.
** Different amounts of H_2O were tested at NaOH:H_2O mole ratio of 4:1, 2:1, 1:1 or 1:2 for each series. Series 2 also includes a *dry* system without H_2O.

CO_2 capture with $Mg(OH)_2$ 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_2 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_2 and 4 – 5% CO_2 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_2, i.e. the concentration of CO_2 in the outlet gas became the same in the inlet gas, 50.8 g of powdered $Mg(OH)_2$ was added to the circulating H_2O.

The $Mg(OH)_2$ 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_2 and Fe_2O_3 as impurities.

The CO_2 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_2 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_2 flow. The first derivative of the TG curve, DTG, was also determined to assist the analysis. The amount of $Mg(OH)_2$ was calculated based on the dehydroxylation of $Mg(OH)_2$ (Reaction 1) taking place at 350 – 450 °C [16].

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)} \qquad (1)$$

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 [17]. The calculation was also performed for the minor mineral phases in the dunite. The calculation was not performed for clinochlore and hornblende due to the lack of available data in SSUB5.

The carbon content in the solid residue recovered from the CO_2 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_2 wt% to assess the CO_2 captured in the solid phase.

Results and Discussion

Extraction of $Mg(OH)_2$

The reaction of dunite with NaOH usually resulted in formation of brucite, Na_2SiO_3 and natrite, i.e. Na_2CO_3, 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_2O mole ratio of 1:2:0.5, before and after being washed with distilled H_2O, respectively. The by-products, Na_2SiO_3 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 $Mg(OH)_2$ and remaining dunite components (Figure 1).

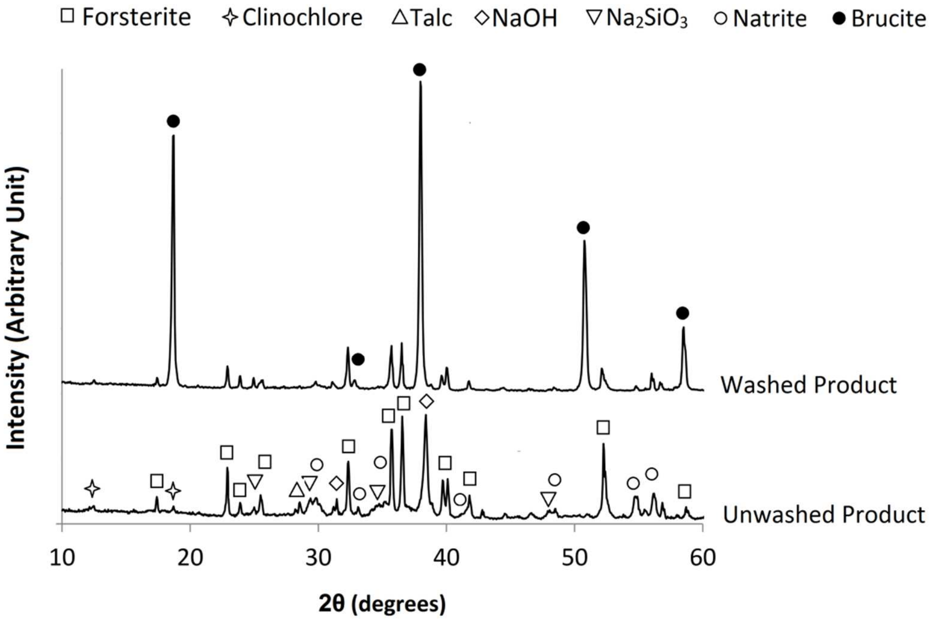


Figure 1: XRD patterns of selected reaction products from solid systems with dunite:NaOH mole ratio of 1:2 and dunite:NaOH:H_2O mole ratio of 1:2:0.5 before and after washing, respectively.

It is expected to be difficult to obtain Na_2SiO_3 from the reaction of dunite and NaOH. Reactions 2, 3 and 4 are examples of reactions for Mg_2SiO_4 and NaOH which assume Na_4SiO_4, Na_2SiO_3 and $Na_2Si_2O_5$ as reaction products, respectively. Mg_2SiO_4 was chosen as representative of dunite because it is the main mineral component. The calculation of the Gibbs energy change, (ΔG^o), for Reactions 2, 3 and 4 showed that only the formation of Na_4SiO_4 is thermodynamically favoured, as indicated by the negative ΔG^o of reaction in Figure 2, whereas, the formation of Na_2SiO_3 or $Na_2Si_2O_5$ is not possible because of ΔG^o >0.

$$Mg_2SiO_4 + 4NaOH \rightarrow 2Mg(OH)_2 + Na_4SiO_4 \qquad (2)$$

$$Mg_2SiO_4 + 4NaOH \rightarrow 2Mg(OH)_2 + Na_2SiO_3 + Na_2O \qquad (3)$$

$$Mg_2SiO_4 + 4NaOH \rightarrow 2Mg(OH)_2 + \frac{1}{2}Na_2Si_2O_5 + \frac{3}{2}Na_2O \qquad (4)$$

However, when H_2O is involved in the reactions (Reactions 5, 6 and 7), the formation of these Na silicate species becomes possible because their ΔG^o are all negative, as shown in Figure 2.

$$Mg_2SiO_4 + 2NaOH + H_2O \rightarrow 2Mg(OH)_2 + \frac{1}{2}Na_4SiO_4 + \frac{1}{2}SiO_2 \qquad (5)$$

$$Mg_2SiO_4 + 2NaOH + H_2O \rightarrow 2Mg(OH)_2 + Na_2SiO_3 \qquad (6)$$

$$Mg_2SiO_4 + NaOH + \frac{3}{2}H_2O \rightarrow 2Mg(OH)_2 + \frac{1}{2}Na_2Si_2O_5 \qquad (7)$$

It should be noted that the formation of Na_2SiO_3 in the presence of H_2O becomes thermodynamically more favourable than that of Na_4SiO_4 in *dry* reaction. These data suggest the involvement of H_2O in the studied reaction and its thermodynamical advantage over the *dry* reaction. The carbonation of NaOH could also aid the involvement of H_2O 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_2O through the following reaction.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (8)$$

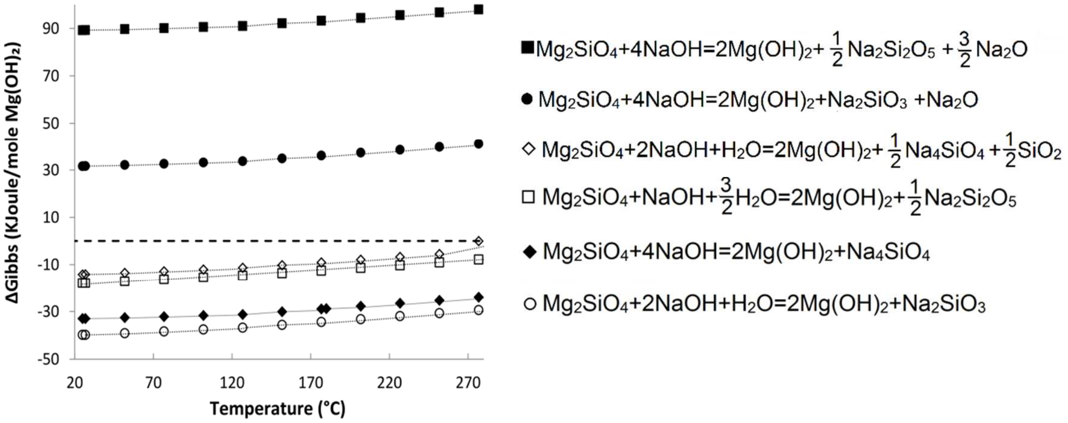


Figure 2: ΔG^o per 1 mole of $Mg(OH)_2$ produced calculated for possible reactions for Mg_2SiO_4 and NaOH. Closed data points are for the *dry* reactions, and open data points for those involving H_2O.

The *ΔG°* for the reactions of NaOH and minor phases in the dunite i.e., serpentine ($Mg_3Si_2O_5(OH)_4$), talc ($Mg_3Si_4O_{10}(OH)_2$), and enstatite ($MgSiO_3$) are showed in Figure 3 and suggests that the formation of $Mg(OH)_2$ and Na_2SiO_3 from these Mg silicate minerals is also thermodynamically possible ($\Delta G^o < 0$). The thermodynamical feasibility of $Mg(OH)_2$ 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 [4].

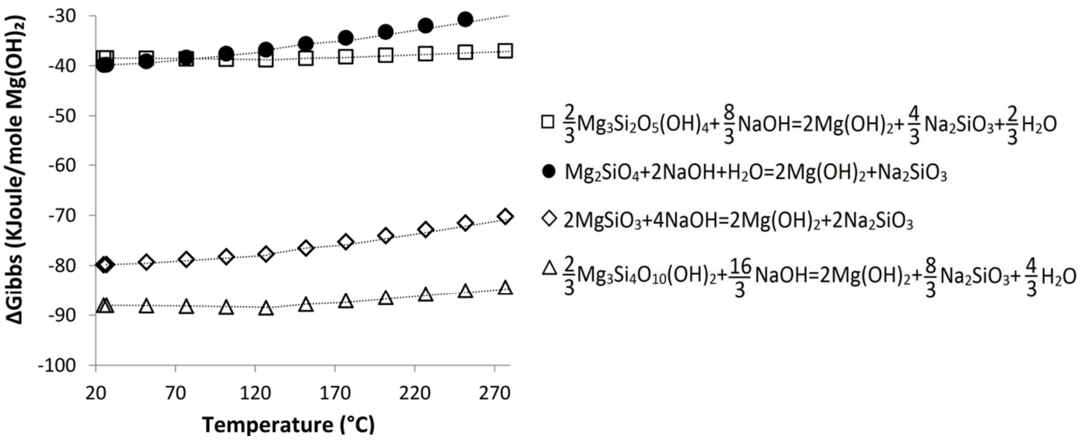


Figure 3: *ΔG°* per 1 mole $Mg(OH)_2$ produced calculated for possible reactions for serpentine ($Mg_3Si_2O_5(OH)_4$), talc ($Mg_3Si_4O_{10}(OH)_2$), and enstatite ($MgSiO_3$) with NaOH in comparison with that for forsterite (Mg_2SiO_4).

The enthalpy change (*ΔH°*) 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 *ΔH°* in the temperature range of interest and the lowest was found at 250 °C. The values of *ΔH°* 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 $Mg(OH)_2$ from dunite should be energetically favoured.

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

Reactions	*ΔH°* (KJ)*
$Mg_2SiO_4 + 2NaOH + H_2O \rightarrow 2Mg(OH)_2 + Na_2SiO_3$	-58
$\frac{2}{3}Mg_3Si_2O_5(OH)_4 + \frac{8}{3}NaOH \rightarrow 2Mg(OH)_2 + \frac{4}{3}Na_2SiO_3 + \frac{2}{3}H_2O$	-44
$2MgSiO_3 + 4NaOH \rightarrow 2Mg(OH)_2 + 2Na_2SiO_3$	-98
$\frac{2}{3}Mg_3Si_4O_{10}(OH)_2 + \frac{16}{3}NaOH \rightarrow 2Mg(OH)_2 + \frac{8}{3}Na_2SiO_3 + \frac{4}{3}H_2O$	-99
$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$	-176

Effect of added H_2O

The introduction of H_2O into the system had a significant effect on the extraction of $Mg(OH)_2$. Figure 4 compares the XRD patterns of the reaction products from the *dry* reaction and reaction with added H_2O in Series 2. These samples were washed with distilled water and Na_2SiO_3, Na_2CO_3 had been removed. The extraction of brucite ($Mg(OH)_2$), 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_2O 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 clinochlore and forsterite, respectively, but are distinguishable based on the proportion of the other peaks intensity. The introduction of H_2O is beneficial and the intensity of the reflection peaks for brucite considerably increases in systems with 0.5, 1 and 2 moles of H_2O, although, the intensity significantly decreases in the system with 4 moles of H_2O. A similar trend was observed also in Series 1.5 and 1.

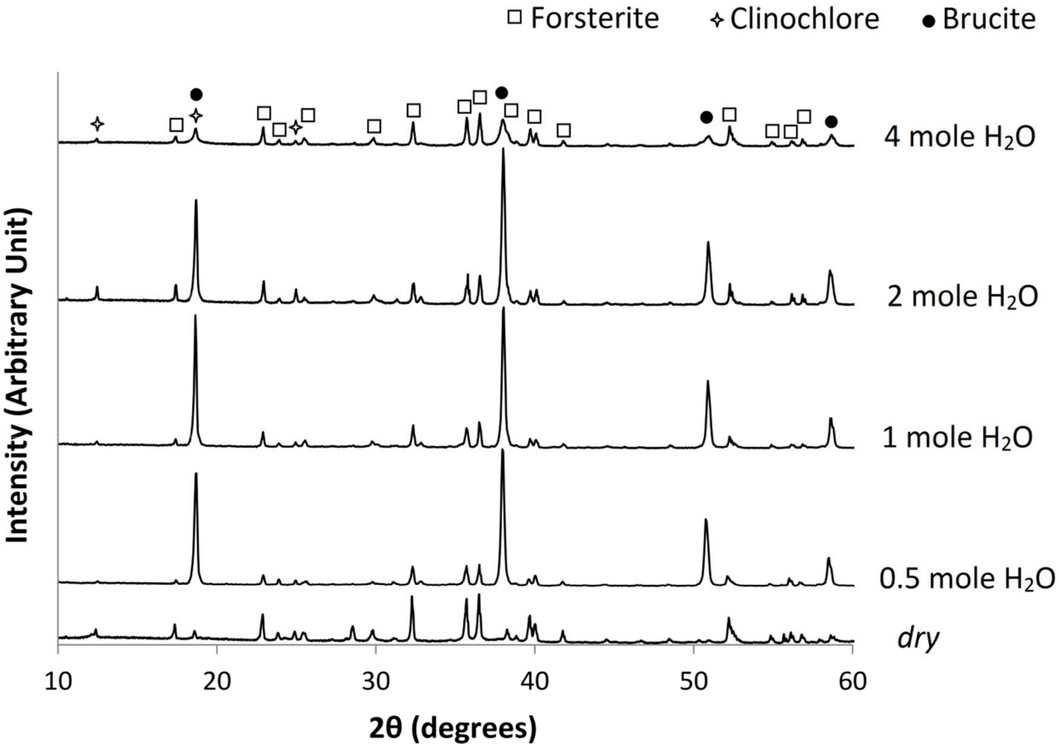


Figure 4: XRD patterns of reaction products from Series 2 with different amounts of H_2O.

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 $Mg(OH)_2$, whereas those reacted in presence of water showed a larger weight loss in this temperature region, indicating that more $Mg(OH)_2$ was produced when H_2O was added to the system.

The calculated concentration of $Mg(OH)_2$ in the reaction product was 19 wt% for the *dry* dunite-NaOH mixture, and 57.6, 55.4, 51.2 and 28 wt% with 0.5, 1, 2 and 4 mole of H_2O added per 1 mole of dunite, respectively. Thus, the amount of Mg(OH) in the products decreases with the increase in H_2O content.

The TGA results are in agreement with the XRD data and indicate that the addition of H_2O was beneficial compared to the *dry* condition, likely because the dissolution of NaOH in H_2O favoured the ion exchange and the diffusivity of materials involved in the reaction [18, 19]. The addition of smaller amounts of H_2O, i.e. higher NaOH:H_2O mole ratio, was a more preferable condition for $Mg(OH)_2$ formation, which suggests that the concentration of NaOH in H_2O played a decisive role for the extraction of $Mg(OH)_2$ from dunite.

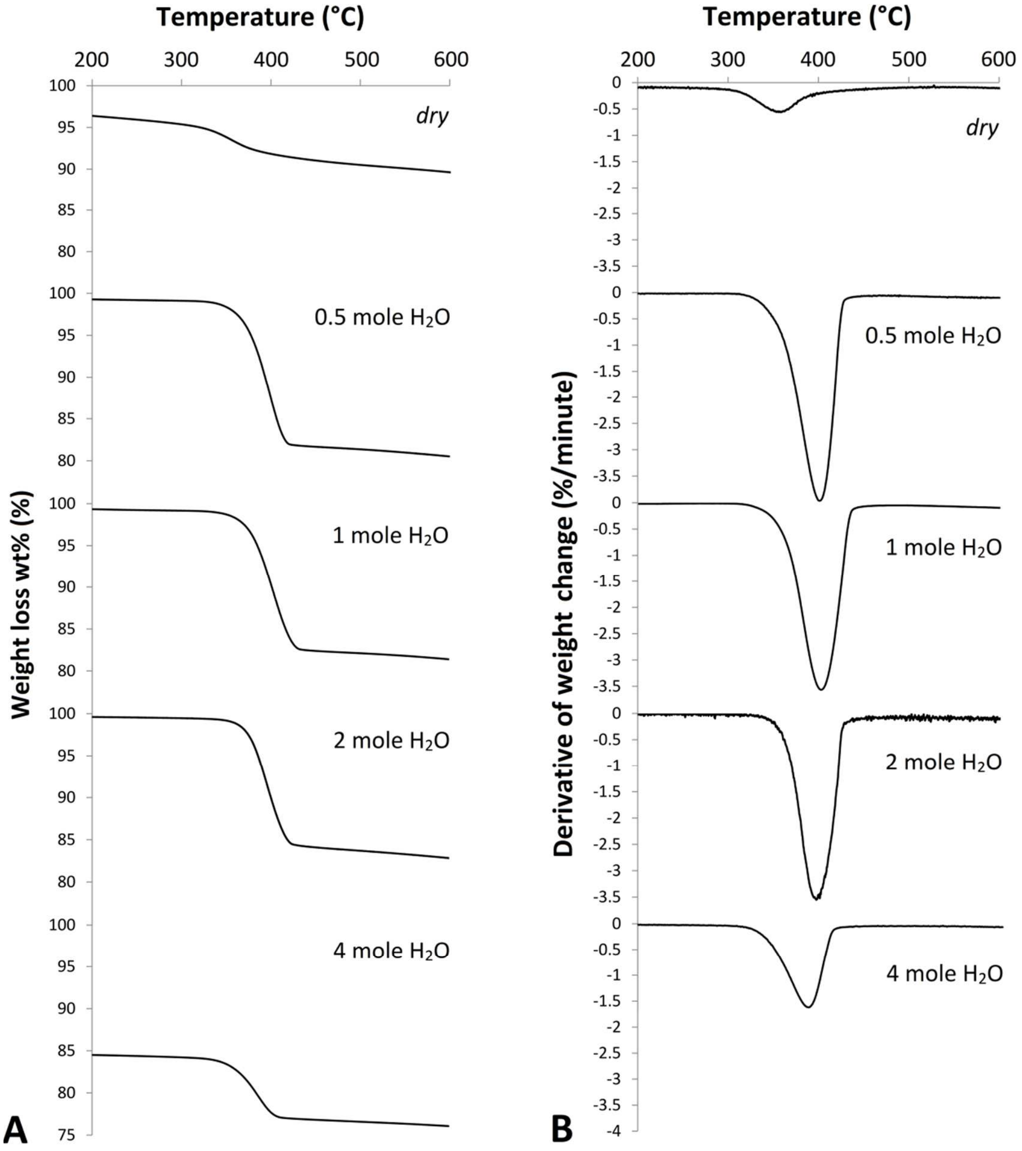


Figure 5: (A) TGA and (B) DTG curves of reaction products from Series 2.

Effect of NaOH concentration

The $Mg(OH)_2$ 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 $NaOH:H_2O$ mole ratio to study the effects of NaOH concentration in H_2O.

The reaction products from Series 2 showed the highest concentration of $Mg(OH)_2$, 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_2O, and the wt% of $Mg(OH)_2$ in the reaction products increased with the increase of $NaOH:H_2O$ mole ratio. However, this effect becomes less significant at higher $NaOH:H_2O$ mole ratio. In fact, at higher $NaOH:H_2O$ mole ratio the concentration of NaOH in H_2O is higher but the amount of H_2O in the system is lower, and thus the positive effect of H_2O, such as the improvement of the reactants diffusion is reduced.

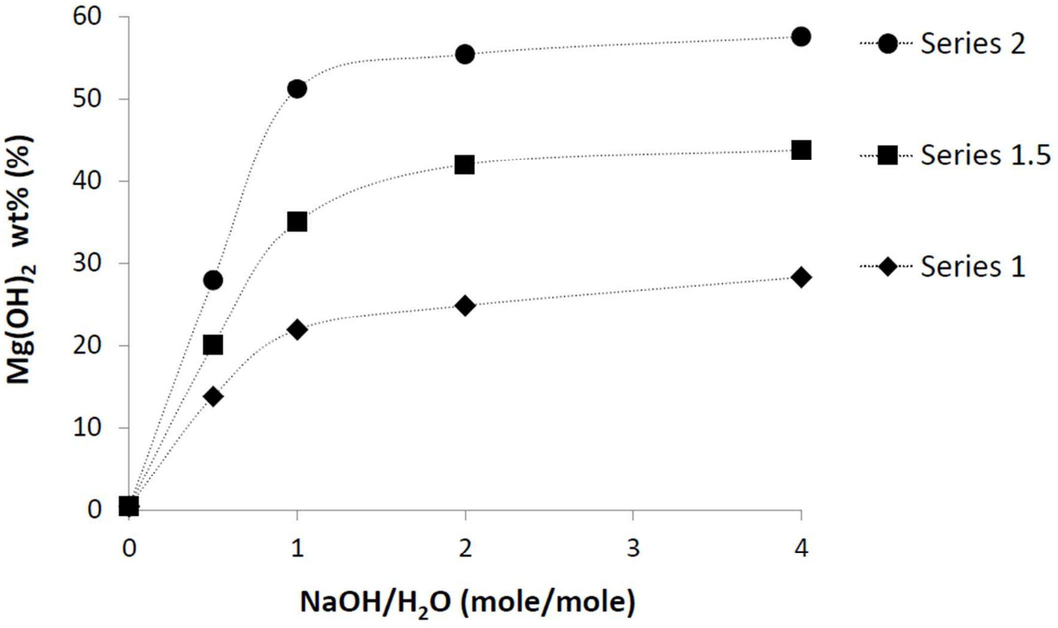


Figure 2~~6~~: $Mg(OH)_2$ concentrations estimated via TGA in reaction products from Series 1, 1.5, and 2.

The data shown in Figure 6 are also plotted against the amount of H_2O added to the system in Figure 7(A), grouped by the same $NaOH:H_2O$ mole ratio.
The gradients of the linear fitting for these data sets are proportional to the $NaOH:H_2O$ mole ratio as shown in Figure 7 (B). Based on these results, it is possible to estimate the approximate wt% of $Mg(OH)_2$, $Mg(OH)_2(\%)$, expected in the reaction product under the condition studied, using the following empirical equation with the amount of NaOH (X_{NaOH}) and H_2O (X_{H2O}). ·

$$Mg(OH)_2(\%) = 30.79 \cdot (X_{NaOH}) - 7.34 \cdot (X_{H2O}) \qquad (9)$$

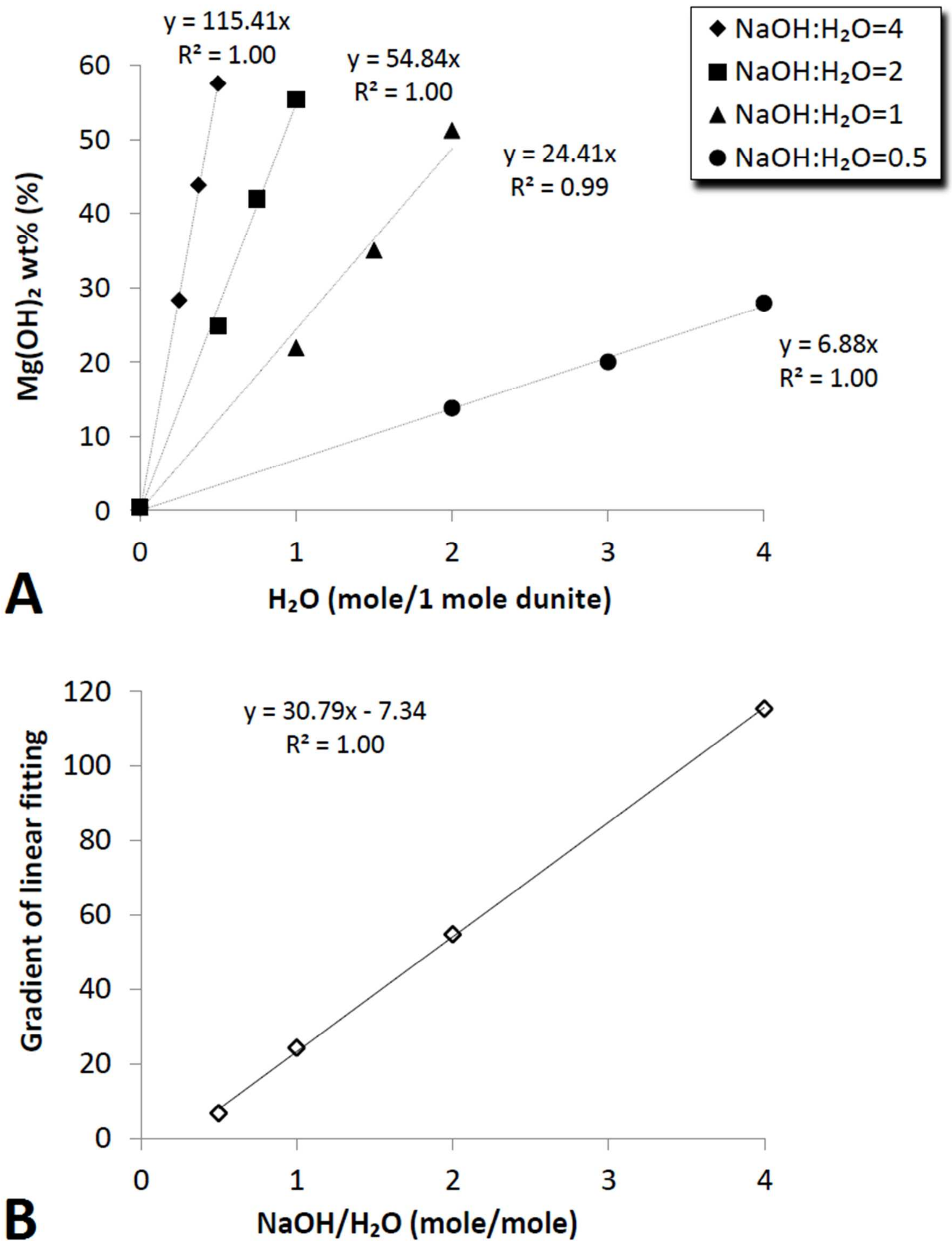


Figure 7: $Mg(OH)_2$ concentrations estimated via TGA in reaction products: (A) effect of H_2O content for different $NaOH:H_2O$ mole ratio, and (B) the gradient of the linear fitting for datasets shown in (A).

These data together with those previously discussed for Series 2, indicate that the extraction of $Mg(OH)_2$ from dunite in $NaOH$-H_2O solid systems is the result of a combined effect of NaOH concentration in H_2O and amount of liquid phase present in the system. At 180 °C, the NaOH in the systems should be fully dissolved at NaOH:H_2O mole ratio of 1:2 and 1:1, or constitute a solid system with partially dissolved NaOH at NaOH:H_2O mole ratio of 2:1 and 4:1 [20]. The optimal conditions for the extraction of $Mg(OH)_2$ appears to be found when H_2O 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_2O = 1:2:0.5 gave the highest $Mg(OH)_2$ 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 $Mg(OH)_2$ in the reaction product are compared in Figure 8.

As expected, increasing the duration and temperature of reaction was beneficial for the extraction of $Mg(OH)_2$. At 130 °C the formation of $Mg(OH)_2$ 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 $Mg(OH)_2$ extraction of 46.4 wt% after 3 hours reaction. Increasing the temperature to 250 °C significantly improved the extraction of $Mg(OH)_2$, and a concentration of 56.4 wt% $Mg(OH)_2$ was achieved after 1 hour, which increased to 65.6 wt% in 6 hours. The $Mg(OH)_2$ 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 $Mg(OH)_2$ extraction obtained at 180 °C.

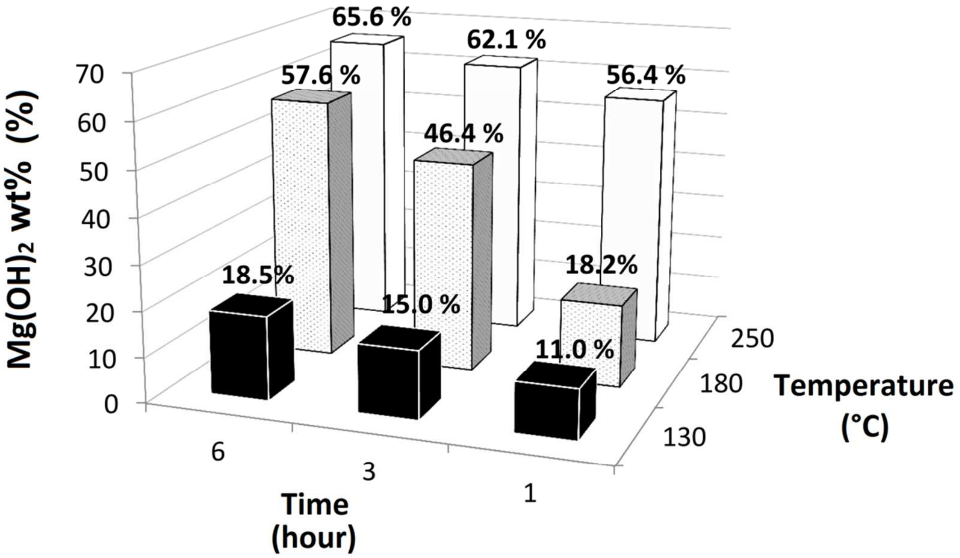


Figure 8: $Mg(OH)_2$ concentration estimated via TGA in reaction products of dunite:NaOH:H_2O systems with 1:2:0.5 mole ratio at different temperatures and times of reaction.

Figure 9 shows the NaOH-H_2O phase diagram [20]. The diagram has been adapted to show the temperatures and NaOH concentration used in this study. The NaOH:H_2O mole ratio of 4:1 corresponds to a NaOH concentration in H_2O 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_2O system at 90 wt% NaOH whereas, only liquid or gas can be present at 250 °C, similar to molten salt systems [20]. 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_2O, which should have favoured the diffusion of reactants [21], contributing to the much faster kinetic of $Mg(OH)_2$ 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.

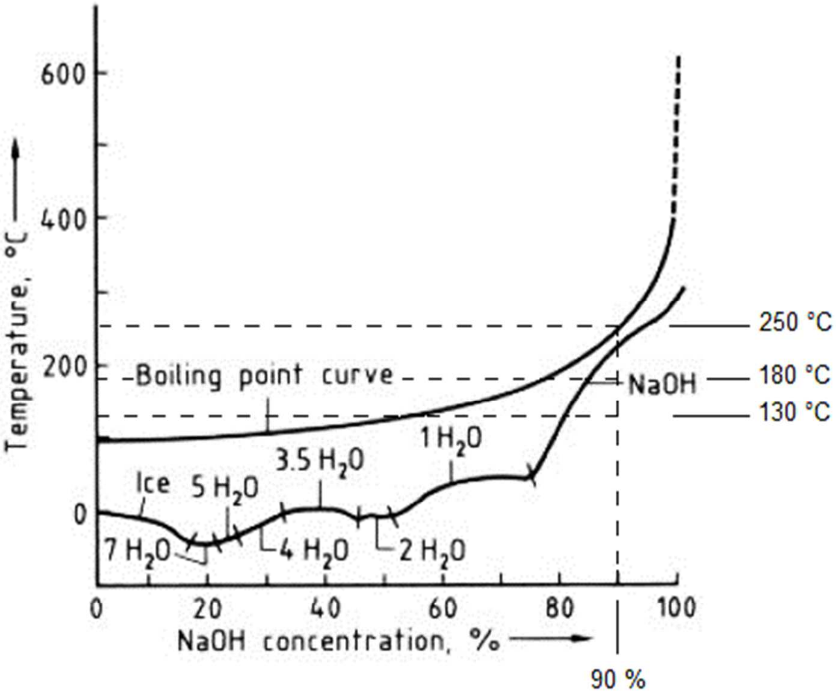


Figure 9: NaOH-H_2O phase diagram, modified from *Kurt and Bittner, 2003* [20].

Efficiency of reaction

The efficiency of $Mg(OH)_2$ extraction is estimated through the yield of reaction which calculates the percentage of $Mg(OH)_2$ produced with respect to the maximum amount of $Mg(OH)_2$ theoretically producible from dunite [15, 22]. The procedure adopted for the yield calculation is described in *Madeddu et al* [15]. In the present study, the yield was calculated using Eqs. 10 and 11 from which the amount of $Mg(OH)_2$ extracted from dunite was obtained, based on the wt% estimated via TGA.

The wt% of $Mg(OH)_2$ 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 $Mg(OH)_2$ 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.

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

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

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_2O 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 [15]. 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% [15]. The H_2O consumed was also reduced by 99% [15]. 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_2 capture with $Mg(OH)_2$

Figure 10 shows the CO_2 concentration in the flow gas measured at the inlet and outlet of GDC reactor during the experiment. The CO_2 concentration at the outlet was initially negligible, and all CO_2 in the flow gas appeared to be retained in the circulating solution by reacting with $Mg(OH)_2$ in the system. The CO_2 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_2. The overnight shut down period did not cause any obvious change in the system. The obtained results clearly show the CO_2 capture capability of this system.

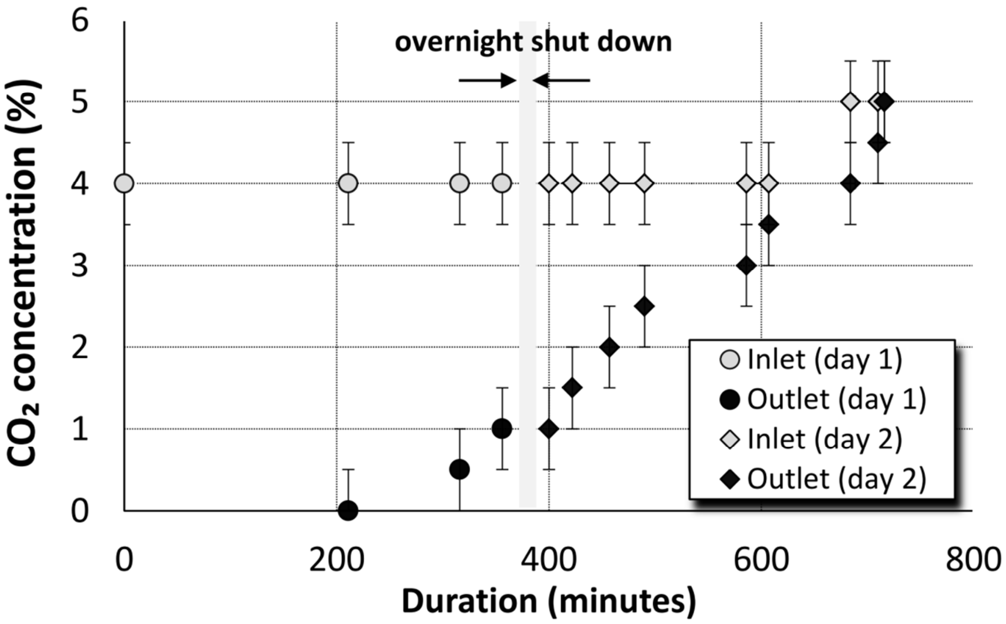


Figure 10: CO_2 concentration in the flow gas at the inlet and outlet of DGC reactor.

The amount of CO_2 captured from the flow gas was estimated using Eq. 12 where $CO_2 i$ % and $CO_2 o$ % are the concentration of CO_2 in the inlet and outlet gas, respectively. The volume of gas under atmospheric pressure at 10 °C was estimated as 23.2 L/mole.

$$\mathrm{CO_2(mole)} = \frac{2.25(\mathrm{L \cdot min^{-1}})}{23.2(\mathrm{L \cdot mole^{-1}})} \times \frac{\mathrm{CO_2}i(\%) - \mathrm{CO_2}o(\%)}{100} \times \mathrm{time(min)} \qquad (12)$$

The amount of captured CO_2 is plotted in Figure 11 together with the pH of the circulating solution. CO_2 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 $Mg(OH)_2$ available for reaction.

In total, 1.80 ± 0.19 moles of CO_2 were sequestered over the 2 days of experimental run.

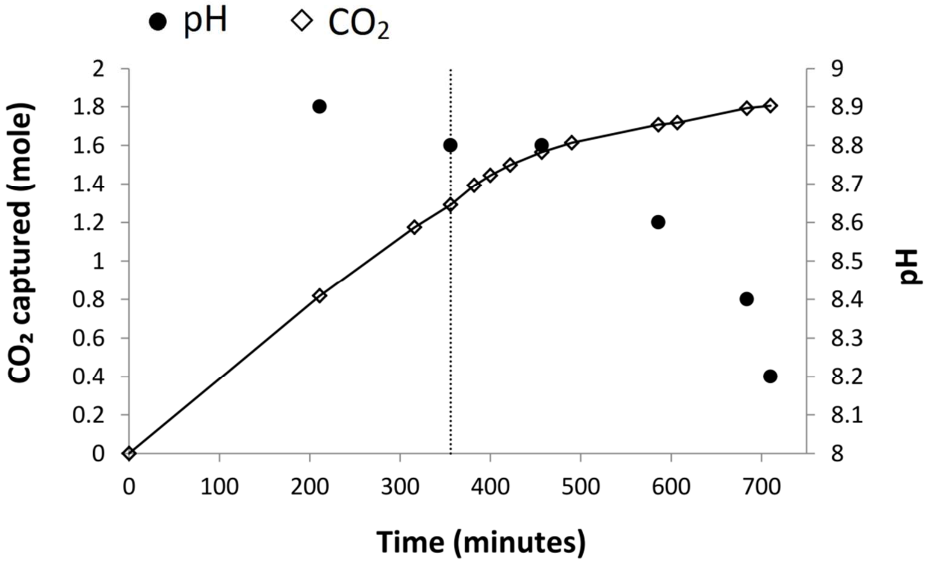


Figure 11: Amount of CO_2 captured and pH of the circulating solution in the liquid-gas scrubbing with $Mg(OH)_2$-H_2O slurry

Since the circulating solution used in the present study contained approximately 0.85 mole of $Mg(OH)_2$, the maximum CO_2 to be captured is 1.71 mole (1.72 mole if CaO presented as an impurity is also counted) assuming the reaction product is $Mg(HCO_3)_2$, and 0.86 mole if $MgCO_3$ was produced. Although our estimation, 1.80 ± 0.19 mole, contains a significant deviation, it is clear that the reaction product in the tested system was mainly $Mg(HCO_3)_2$. It is known that the formation of $Mg(HCO_3)_2$ is favoured when the pH of the solution is around 8.4 where HCO_3^- ions are the predominant species of CO_2 dissolution, whereas $MgCO_3$ preferentially forms when the pH of the solution is above 10 as the CO_3^{2-} ions are the predominant species [5, 23, 24]. The obtained results confirms that $Mg(HCO_3)_2$ 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 ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) and another poorly crystalline phase which was not identified. The amount of CO_2 in the collected solid was determined via CHN analysis and estimated as 0.01 mole. These results indicate that $Mg(OH)_2$ almost fully dissolved and captured CO_2 by forming $Mg(HCO_3)_2$ which remained in equilibrium in solution while only a small fraction reacted forming Mg carbonate phases.

The exact quantification of CO_2 captured by the reaction with $Mg(OH)_2$ is challenging and requires further analysis. Nevertheless, these preliminary results suggest that at least 93.6% of CO_2 potentially capturable by the $Mg(OH)_2$ suspension was effectively captured.

Implications of $Mg(OH)_2$ extraction for CCS

The consumption of NaOH was identified as one of the major drawbacks for the extraction of $Mg(OH)_2$ in the NaOH aqueous system [15] because the production of

NaOH involves a significant energy consumption and thus CO_2 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_2 balance was evaluated based on the emissions associated with the NaOH, $Mg(OH)_2$ extraction and the sequestration potential of $Mg(OH)_2$ 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 $Mg(OH)_2$ extracted was estimated from the yield of reaction achieved. The CO_2 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_2 per 1 kWh, when natural gas is used [25, 26]. The CO_2 emission from the extraction of $Mg(OH)_2$ 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 [27]. The CO_2 sequestration was calculated based on the full conversion of $Mg(OH)_2$ into either $MgCO_3$ or $Mg(HCO_3)_2$.

Figure 12 compares the CO_2 potentially captured by the $Mg(OH)_2$ 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_2 emissions from the NaOH production and $Mg(OH)_2$ extraction. The graph shows that the potential CO_2 capture naturally increases with the improvement of the yield of $Mg(OH)_2$ extraction, but the estimated CO_2 emission from NaOH production and $Mg(OH)_2$ 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_2 emission for all series when $Mg(OH)_2$ is fully converted into $Mg(HCO_3)_2$. On the other hand, the CO_2 captured into $MgCO_3$ would not be sufficient to offset the CO_2 emission even at the maximum yield of $Mg(OH)_2$ extraction. According to Reaction 6, 1 mole $Mg(OH)_2$ requires the consumption of 1 mole NaOH, and from the amount of $Mg(OH)_2$ 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 $Mg(OH)_2$ extraction.

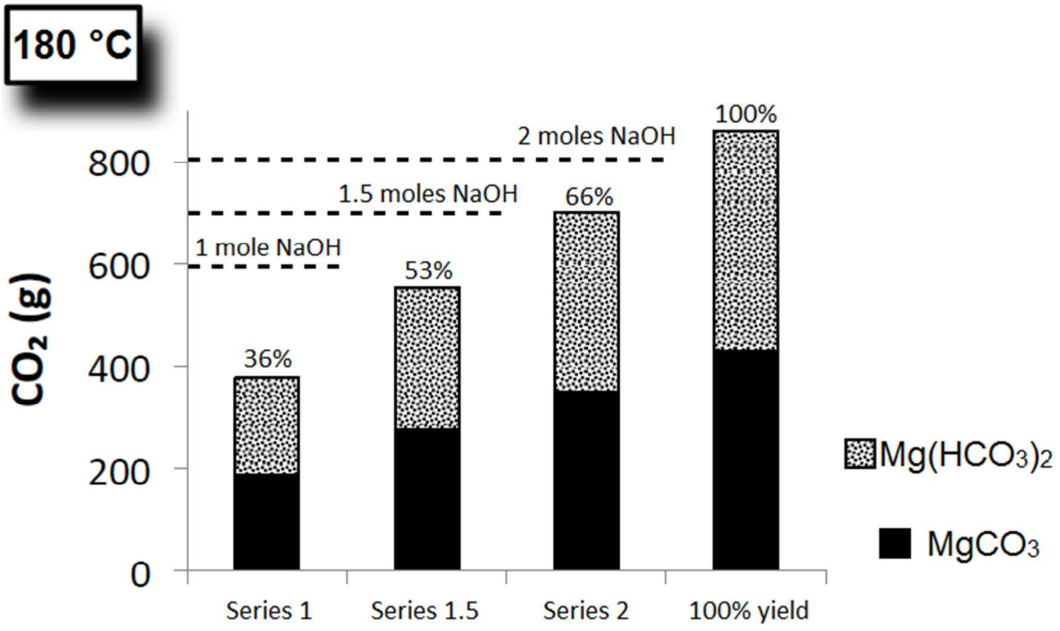
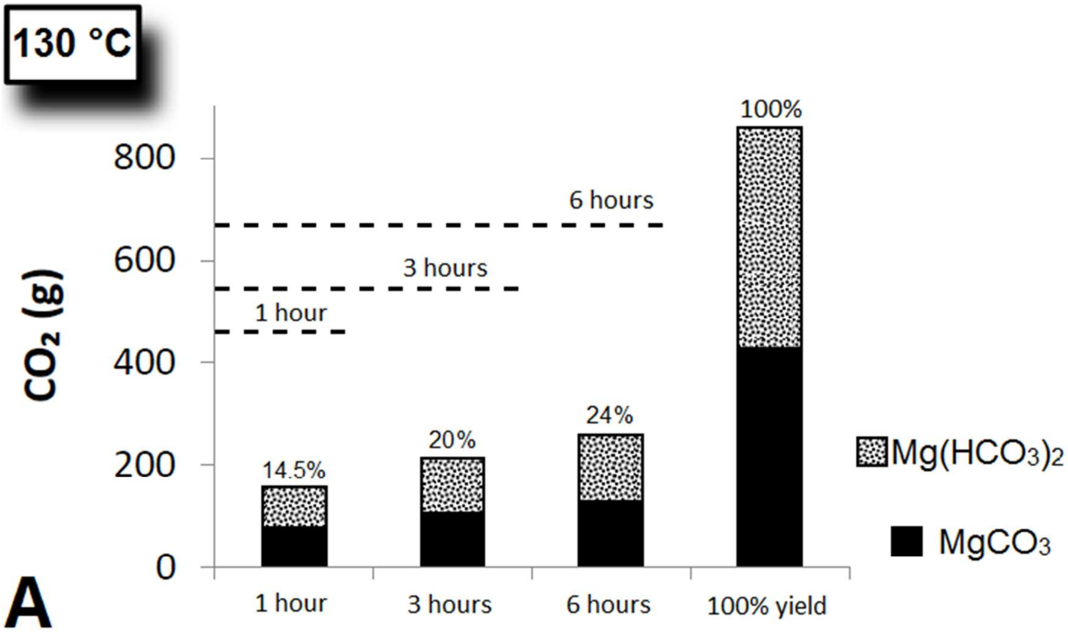
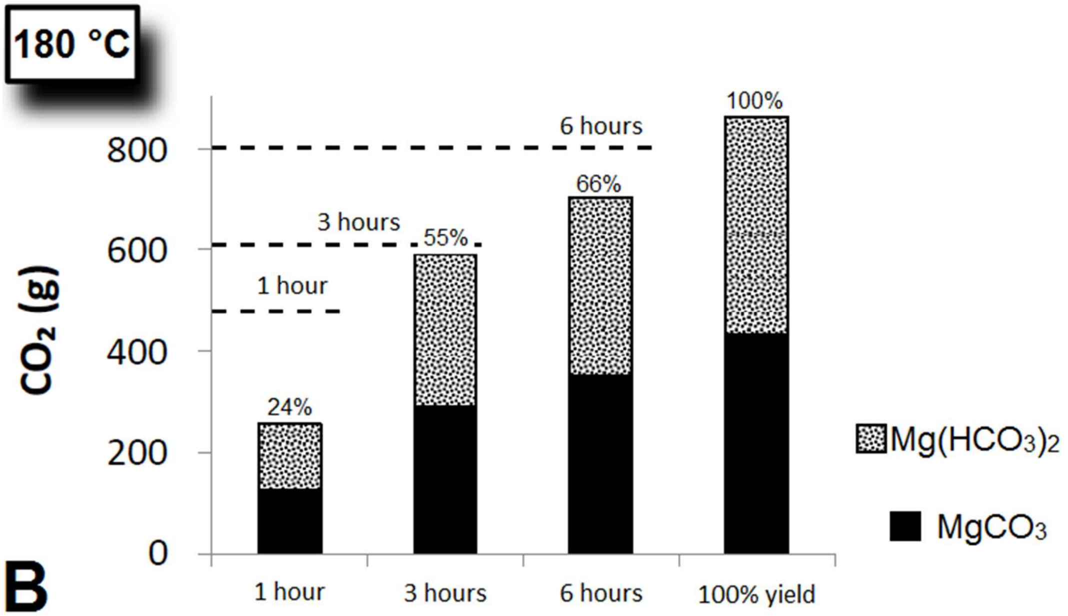


Figure 12: Potential CO_2 capture by $Mg(OH)_2$ conversion into $MgCO_3$ or $Mg(HCO_3)_2$ (columns). The estimated CO_2 emission associated with the NaOH production and $Mg(OH)_2$ extraction at 180 °C for 6 hours are also shown (dotted lines) for Series 1, 1.5 and 2 for comparison. The yield of $Mg(OH)_2$ extraction is reported on top of the columns for each series.

Figures 13 (A), (B) and (C) show the CO_2 balance for Series 2 extracted at 130, 180 and 250 °C, respectively. As shown in Figure 13 (A), the yield of $Mg(OH)_2$ extraction at 130 °C is too low and the CO_2 emission from the power consumption is considerably larger. Figure 13 (B) shows that the CO_2 balance is significantly improved at 180 °C. In fact, at this temperature the potential CO_2 capture becomes close to the CO_2 produced in the case of 3 hours of extraction, when CO_2 is captured as $Mg(HCO_3)_2$. 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_2 is emitted. The CO_2 balance for the extraction at 250 °C is much better. As shown in Figure 13 (C), at 1 and 3 hours extraction, the CO_2 capture exceeds the CO_2 produced from the NaOH production and $Mg(OH)_2$ extraction, and CO_2 is successfully reduced. At this temperature, a shorter duration is clearly more beneficial. It should be noted that the CO_2 capture exceeds the CO_2 emission only when $Mg(HCO_3)_2$ is produced as a reaction product. The achievement of 100% yield of extraction at 130, and 180 °C would reduce CO_2 under the studied conditions when $Mg(HCO_3)_2$ is formed, while at 250 °C, this occurs only for the extraction of 1 and 3 hours, and with 6 hours CO_2 is emitted. When $MgCO_3$ is produced as the reaction product, the amount of CO_2 to be captured is less than the CO_2 produced during the process, even at 100% yield, and thus the production of $Mg(HCO_3)_2$ is a key factor to offset the CO_2 produced during the extraction.


130 °C
CO₂ (g)
800
600
400
200
0
6 hours
3 hours
1 hour
14.5%
20%
24%
100%
1 hour
3 hours
6 hours
100% yield
▨ Mg(HCO3)2
■ MgCO3

A


180 °C
CO₂ (g)
800
600
400
200
0
6 hours
3 hours
1 hour
24%
55%
66%
100%
1 hour
3 hours
6 hours
100% yield
▨ Mg(HCO3)2
■ MgCO3

B

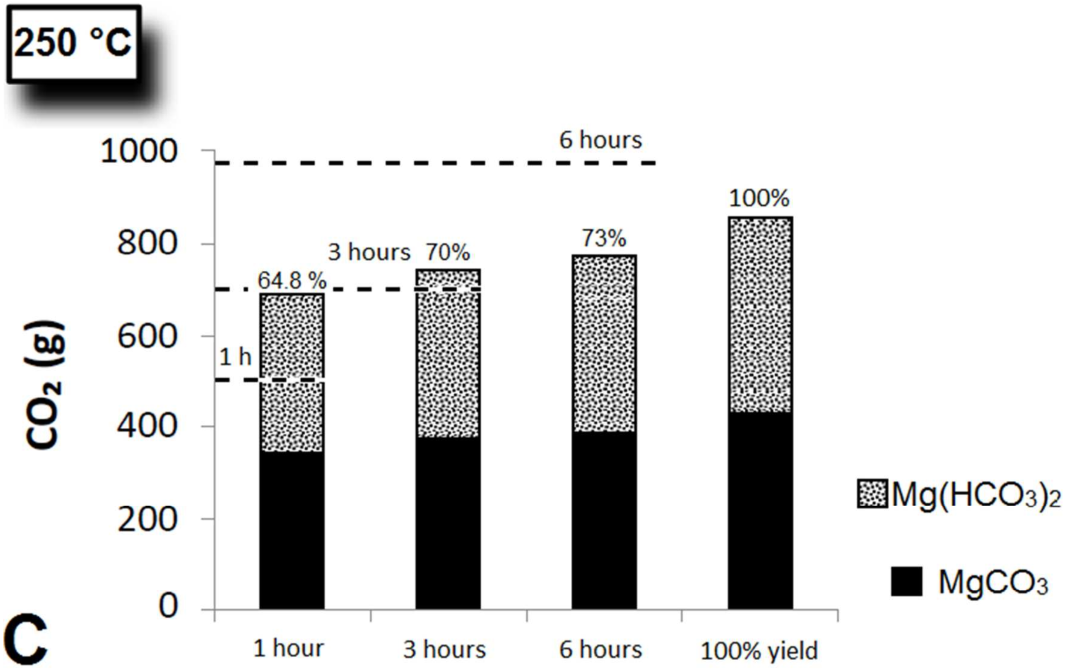


Figure 13: Potential CO_2 capture by $Mg(OH)_2$ conversion into $MgCO_3$ or $Mg(HCO_3)_2$ (columns) for Series 2 at (A) 130 °C, (B) 180 °C and (C) 250 °C. The estimated CO_2 emission associated with the NaOH production and $Mg(OH)_2$ extraction for 1, 3 and 6 hours are also shown (dotted lines) for comparison. The yield of $Mg(OH)_2$ extraction is reported on top of the columns for each series.

Conclusions

The present study demonstrated that the NaOH required to extract $Mg(OH)_2$ from dunite can be reduced to a stoichiometric ratio with the reaction in the solid system assisted with H_2O.

H_2O considerably improved the extraction of $Mg(OH)_2$ compared with the reaction in *dry* condition, favouring the diffusion of the reactants involved. Both NaOH concentration in H_2O and the amount of liquid phase in the system played a significant role in the extraction of $Mg(OH)_2$ from dunite and the best results were achieved in systems with dunite:NaOH:H_2O 1:2:0.5 mole ratio. Decreasing the NaOH below the stoichiometric ratio resulted in less $Mg(OH)_2$ extraction.

At 180 °C, the maximum yield of $Mg(OH)_2$ extraction was 66% over 6 hours reaction for solid systems with dunite:NaOH:H_2O 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_2O consumption was also reduced by 99%. At 250 °C, the extraction of $Mg(OH)_2$ was significantly accelerated and 64.8% yield was achieved in 1 hour for solid systems with dunite:NaOH:H_2O mole ratio of 1:2:0.5.

CO_2 was successfully separated from a gas mixture composed of 4 – 5% CO_2 and N_2 via liquid-gas scrubbing using a $Mg(OH)_2$ aqueous slurry and stored in the solution as $Mg(HCO_3)_2$. 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_2 in one single step and may improve the efficiency of the overall CCS process.

The CO_2 balance of the process was estimated from the emission associated with the power consumed for NaOH production and $Mg(OH)_2$ extraction together with the CO_2 captured by $Mg(OH)_2$ 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 $Mg(OH)_2$ is converted into $Mg(HCO_3)_2$. The CO_2 balance becomes negative when dunite is processed at 250 °C for 1 or 3 hours and CO_2 is captured as $Mg(HCO_3)_2$. This is promising for the possible application of $Mg(OH)_2$ derived from dunite for CO_2 separation from flue gases and storage in H_2O.

Acknowledgements

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