Research article

Effect of ***pCO_2*** on direct flue gas mineral carbonation at pilot scale

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Abstract

Concerns about global warming phenomena induced the development of research about the control of anthropogenic greenhouse gases emissions. The current work studies on the scaling up of aqueous mineral carbonation route to reduce the CO_2 emissions at the chimney of industrial emitters. The reactivity of serpentinite in a stirred tank reactor was studied for several partial pressures of CO_2 (pCO_2) (0.4, 0.7, 1.3 and 1.6 bar). Prior to carbonation, the feedstock was finely grinded and dehydroxyled at 650 °C by a thermal treatment. The major content of magnetite was removed (7.5 wt% total weight^{-1}). Experiments were carried out under batch mode at room temperature using real cement plant flue gas (14–18 vol% CO_2) and open pit drainage water. The effect of the raw water and the pCO_2 on the carbonation efficiency was measured. First, the main results showed a positive effect of the quarry water as a slight enhancement of the Mg leaching in comparison with distilled water. Secondly, a pCO_2 of 1.3 bar was the optimal working pressure which provided the highest efficiency of the carbonation reaction (0.8 gCO_2 g residue^{-1}). Precipitation rates of dissolved CO_2 ranged from 7% to 33%. Pure precipitate was obtained and essentially composed of Nesquehonite. At a pCO_2 of 1.3 bar, additional physical retreatment of the solid material after being contacted with 6 batches of gas enhanced considerably mineral carbonation efficiency (0.17 gCO_2 g residue^{-1}.).

Keywords: Mineral carbonation; Serpentinite; Industrial flue gas; Open pit drainage water; CO_2 sequestration; Pilot scale

1 Introduction

The emissions of anthropogenic greenhouse gases have continuously increased during the industrial period and largely contributed to the global warming phenomena (IPCC, 2014). The concentration of CO_2 registered in the atmosphere is gradually rising from 280 ppm in the 19th century to reach 400 ppm nowadays. This is especially due to the intensive use of fossil fuels as a primary energy sources (MacKenzie et al., 2004). Among the different solutions proposed, geological storage and mineral carbonation (MC) processes represent interesting solutions for long term CO_2 disposal. While to date, large-scale capture and storage projects using geological storage are underway, large-scale applications of MC are still limited. In fact, even if MC offers the safest way to store CO_2, its large energy requirement still stand as a major barrier.

The application of MC for the reduction of anthropogenic CO_2 was first proposed by Seifritz (1990). It is based on the magnesium/calcium (Mg/Ca) silicate weathering (Lasaga and Berner, 1998). The reaction is exothermic with a slow kinetic, taking place on a geological time scale (Pan et al., 2012). However, the obtained products are known to be stable for a large range of temperature and pressure (Sipilä et al., 2008). Several feed stocks are known to be efficient for MC, such as natural minerals like wollastonite (≈48,3%/wt CaO), olivine (≈49,5%/wt MgO) and serpentine (≈40%/wt MgO) or industrial wastes or mine tailings (Sanna et al., 2014). The aqueous route is the most effective and can be described by three mechanisms. First, the CO_2 dissolution into the liquid phase, then the Mg/Ca leaching and finally the carbonate precipitation (Huijgen et al., 2006). All steps are critical and contribute to the overall reaction efficiency. Nevertheless, the solid dissolution remains the limiting step which control the cation availability for the carbonate precipitation. For this reason, the particle size is a key point. A fine grinding of the feedstock will increase the specific surface area of solid particles and thus promotes the cation dissolution (Alexander et al., 2007).

Among the different feedstocks studied, serpentinite minerals were intensively studied. As MC was first viewed as an alternative to geological storage, pure CO_2 stream treatment was investigated. The processing of supercritical CO_2 in high temperature and pressure conditions (155 °C, 115 bars) with a carrier solution (0.64 M $NaHCO_3$ and 1 M NaCl) and a reaction time of 60 min led to a satisfying conversion rate of 73.5% (Gerdemann et al., 2007). Nevertheless, these hydrated minerals required a heat activation at 650 °C for 30 min to remove hydroxyl groups and thus to increase the material reactivity (McKelvy et al., 2004). In addition, the use of high temperature and pressure conditions globally limits the potential industrial application due to global high energy demands. To counteract the heat activation step, different indirect methodologies were proposed in order to extract Mg prior to carbonation, such as “pH swing” (Nduagu et al., 2012; Park and Fan, 2004). Nevertheless, feasibility of such processes depends on the ability to recover chemicals/acids used and still requires high temperatures and/or pressure operating conditions. Another alternative is to implement MC as an integrated capture and storage process. This route has the advantage to avoid a capture step which clearly simplifies the process scheme. In this way, different studies focused on using a diluted CO_2 stream, similar at some industrial flue gas (Pasquier et al., 2014a; Werner et al., 2014). Results showed that reaction mechanism, kinetics where similar as observed for pure CO_2 treatments and lead to promising results (Hariharan et al., 2014; Pasquier et al., 2014b). In addition, dissociation of gas treatment steps and carbonates precipitation leads to the production of high purity products giving significant incomes.

The use of alkaline residues as MC feedstock present several advantages. Mostly, the use of an already ground material allows the decrease energy requirements for the particle size reduction (Bobicki et al., 2012). In addition, some of them are available on CO_2 emitting industrial sites such as steel slags or cement kiln dust. This approach allows to answer GHG mitigation jointly with waste valorization and reuse. In the case of serpentine, about 2Gt of chrysotile mining residues (mostly composed of lizardite or antigorite) where generated in Quebec's southern province. Those are known to react spontaneously with CO_2 contained in the air but with geologic scale kinetics (weathering process) (Huot et al., 2003; Wilson et al., 2009). Their reactivity in stirred reactor was also demonstrated using diluted gas (Pasquier et al., 2016). Recently, experiments were performed using such material for the treatment of a real cement plant flue gas at a pilot scale (Kemache et al., 2016). Results showed that the scaling effect was neglectable and that water recirculation enhances carbonates precipitation. The present work is in the continuity of the latter work. The impact of pCO_2 variations and the use of raw industrial water on the reaction efficiency are discussed.

2 Materials and methods

2.1 Analytical methods

For each sample, chemical composition was characterised, before and after each process steps/reaction in order to follow the material and liquid and gaseous stream variations. Solid samples were melted using alkaline fusion with lithium metaborate (Claisse method) (Tertian and Claisse, 1982). The resulting liquids were analyzed by inductively coupled plasma spectrometry of emission (ICP-OES, Varian). Liquid samples were also analyzed using ICP-OES. The inorganic carbon analysis in the solid samples was done with the carbon hydrogen nitrogen sulfur analyser (Leco CHNS). Inorganic carbon concentration was measured in liquid samples using a Total Organic Carbon analyzer (Shimatzu TOC-VCSH). Furthermore, the loss on ignition was performed at a temperature of 1020 °C for 390 min. The sample crystallography was determined using X-RD analysis (Siemens diffractometer D5 000). A copper radiation of ($\lambda = 1.54$ A°) was used with a scan range from 1 to 65°, a step of 0.02 mm and a count time of 1.2 s.

2.2 Methods

The global methodology is illustrated by Fig. 1. Both pre-treatments steps and carbonation procedure are presented and a complete description is provided below.

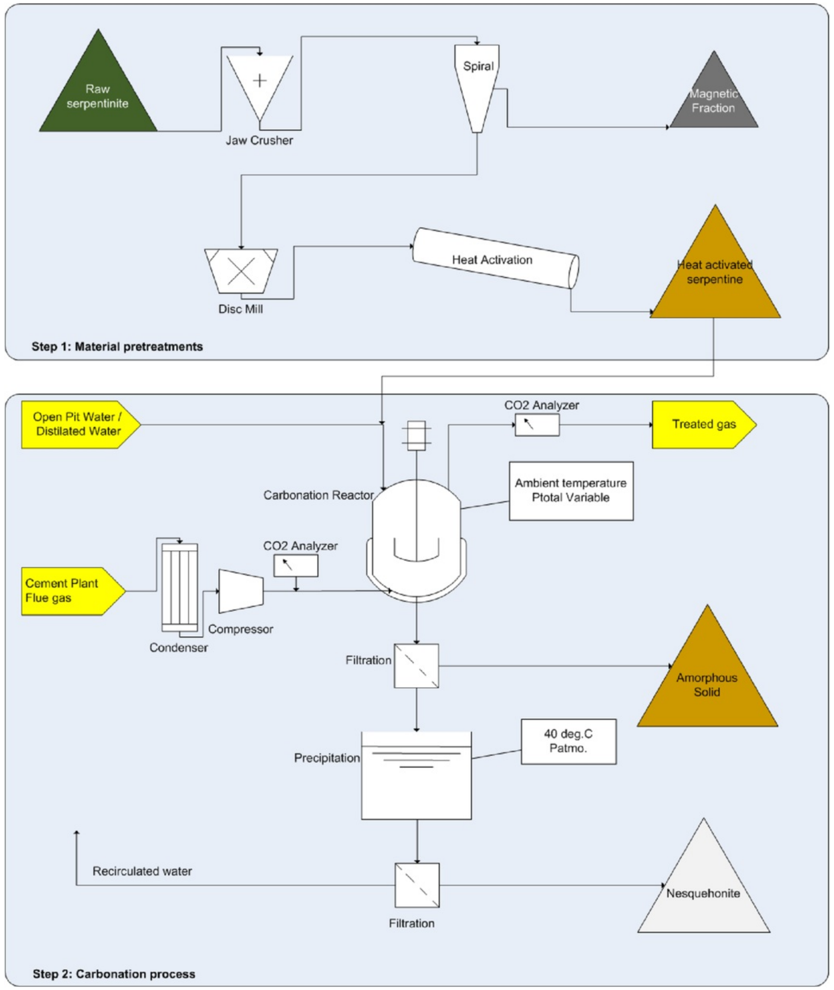

Fig. 1 Overall process diagram.

alt-text: Fig. 1

2.2.1 Material pre-treatment

MC experiences required a mass of 170 kg of solid tailings sampled from the chromite mine of Montreal Coleraine situated in Saint Joseph (Coleraine). The initial granulometric size was around 20–100 mm. Prior to physical separation, the raw material was crushed with a jaw crusher (C-RC-335) and grinded with an oscillating mill discs (Retsch-RS200). The grinding conditions were set at 700 tours.min^{-1} during 75 s. Consequently, the particle size of the solid was determined by a laser particle sizer (Horiba LA-950V2, Laser Scattering Particle Size Distribution Analyzer). The particle sample granulometry was around 142 ± 34 µm. The particles were mixed with water in order to create a pulp. A first separation using a spiral (5LL400 model type) with a water flow of 150 L min^{-1} was made. The light fraction containing various silicates material was not used. The dense fraction obtained was a mixture of magnesium silicates and magnetite and undergone a second separation step by the Wilfley table (Outokumpu Technology, model SA-13A) using a longitudinal inclination of 14°, a speed of strokes of 500 strokes.min^{-1}, a stroke length of 14 mm, a water flow of 0.12 m^3 h^{-1} and a throughput of solid of 5 kg h^{-1}. Both magnesium silicate and magnetic fractions densities were determined by a pycnometer (AccuPyc 1330, Micromeritics).

The resulting silicate fraction obtained after physical separation was finely ground through a series of three grinding steps. An average granulometry of 57µm with a median of 25µm were measured. The material was then heat treated at 650 °C using a modified electric rotary kiln (Pyromaître Pyro 106-HE). The thermal treatment was carried out in continuous mode with a feeding rate of 200 g min^{-1} of dry solid. The tube was inclined to an angle of 9.45° to create combined tumbling and rolling down effect to respect a residence time of 30 min. The treated solid was characterized by XRD to monitor the change in its mineral structure with the following scan parameters.

2.2.2 Mineral carbonation procedure

The experimental unit was installed at a cement plant site. The gas was directly pumped from one of the plant chimneys. It was at first cooled and condensed in a plate heat exchanger. The cooling fluid used was tap water. At this point, most of the NO_x and SO_x gasses were condensed. Then, once cooled, the gas was compressed using a double stage compressor to 12 barg and stored in the compressor tank (model 2340L5-V from Ingersoll Rand the company). Prior to experiments, the gas composition was measured using an infra-red analyzer from MRU Instrument (NOVA plus IV) calibrated to measure the amounts of CO_2, NO_x, SO_x, and oxygen O_2. The experiences were carried out at ambient temperature in a stirred reactor type “Floor stand 4555 reactor” (Parr Instrument Company) with a total volume of 18.7 L. A mass of 705 g of solid was mixed with 4.68 L of raw water coming from the quarry of the cement plant. The resulting pulp has a 15 wt% of solid. Before each experiment, the pH of the pulp was measured using a pH meter (Orion star A111). Once filled with the pulp, the gas was introduced into the vessel until reaching the desired working pressure. As the experiments were realized following a batch mode, all the valves were closed during the tests. The stirring speed was set to 600 rpm, and the reaction started. After 15 min of the reaction, the gas was removed, and its composition measured. Usually, the same pulp was contacted with a second batch of gas for another 15 min as previously described in the previous laboratory conducted work (Pasquier et al., 2014a). The operating parameters were monitored during the reaction using a control unit (Parr 4848 controller). Following the treatment of two successive batches of gas, the pulp was retrieved, the pH measure and the liquid and solid fraction were separated by filtration. The resulting solid was recirculated to be contacted with more batches of gas. The filtrate was sent to the precipitation system, stirred at 300 rpm and heated at a temperature around 40 ± 15 °C for 6 h. The obtained carbonates were dried, weighed and analyzed.

2.3 Calculations

Calculation of the mass of CO_2 captured (Eq (1));

$$Treated\ CO_2\ (g) = mCO_{2\ inlet} - \mathrm{m}CO_{2\ outlet} \qquad \textbf{(1)}$$

Each mass of CO_2 was calculated using the following (Eq (2));

$$mCO_2\ (g) = \frac{\left(p_{CO_2} \times V_{gaz} \times M_{CO_2}\right)}{(R \times T)} \qquad \textbf{(2)}$$

with pCO_2: partial pressure of CO_2 (bar), V_{gaz}: Volume of the gas in the reactor (m^3), M_{CO2}: Molar mass of CO_2 (g. mol^{-1}), R: Ideal gas law constant (m^3.bar.K^{-1}.mol^{-1}), T: Temperature inside the reactor (K).

3 Results and discussion

3.1 Feedstock pre-treatment

As previously mentioned, using serpentine minerals for MC requires several pre-treatments to increase conversion rates. The initial chemical composition of the feedstock (CR) can be seen in Table 1. It highlights that the major elements of the solid are Mg and Si. The magnetic fraction is also defined by the significant iron content.

Table 1 Major Oxides and Lost on Ignition of the raw sample.

alt-text: Table 1

Sample ID	CaO	Cr_2O_3	Fe_2O_3	MgO	SiO_2	LOI
CR	0.9	2.1	7.9	42.1	33.9	12.9

The X-RD analysis confirms the presence of lizardite ($Mg_3Si_2O_5\ (OH)_4$) as the main mineral phase (Fig. 2). The iron is mainly present as magnetite (Fe_3O_4). Chromite ($FeCr_2O_4$) signature was also identified in a further analysis of the magnetic fraction.

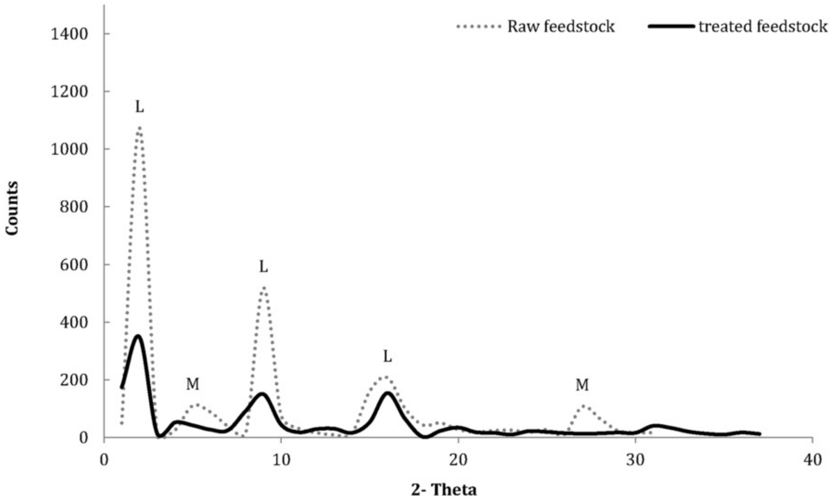

Fig. 2 X-ray patterns of both of raw and treated feedstock with L: Lizardite, M: Magnetite.

alt-text: Fig. 2

The first pre-treatment step consisted in the removal of the magnetic fraction (i.e. the magnetite and the chromite) by gravimetric separation. The different proportions of generated products can be shown in Table 2.

Table 2 Results of magnetic removal and thermal treatment of the feedstock.

alt-text: Table 2

Treatment	Inlet	Outlet		Mass loss
	kg	kg	%	%
Initial	170			
Gravimetric separation (Spiral)	Magnetic fraction	16.2	9.5	
	Silicate fraction	150	88.2	
Total	170	166~~.2~~	97.8	2.2
Heat Activation	146	136		7.31

Serpentine contains generally 5 to 15% (by weight) of magnetite. (Huot et al., 2003). Consequently, the gravimetric separation efficiency measured was acceptable with 9.5 wt% of magnetic fraction obtained after treatment. The density of the product was equivalent to 4.5 g cm^{-3} confirming its relative purity. For comparison, pure magnetite and hematite have a density of 5.15 and 5.3 g cm^{-3} respectively. Removing the magnetite helps generally MC process by avoiding the oxidation mechanism of iron oxides during the heat treatment and the formation of passive layer (Fauth et al., 2002). Additionally, this fraction can be potentially valuable (O'Connor et al., 2005). Afterward, the silicate fraction was heat treated to remove the hydroxyl groups from the crystal lattice (Li et al., 2009; McKelvy et al., 2004). A mass loss of~~of of~~ 7.31% (weight :~~.~~ total weight^{-1}) was measured (Table 2). Moreover, the comparison of the X-ray pattern of non-treated and heat treated serpentinite shows that Lizardite signal is still present but with a lower intensity after the heat treatment (Fig. 2). This shows that an incomplete amorphization of the sample was achieved. Thus, the efficiency of heat treatment step can be judged non-optimal. This can be attributed to a non-homogenous roasting of the sample, due to a too rapid heating rate.

3.2 Effect of open pit drainage water

Fig. 3 compares the effect of the use of open pit drainage water (QDW) and distilled water on the CO_2 treated and Mg leached during the different batches of gas conducted at pCO_2 of 1.2 bar.

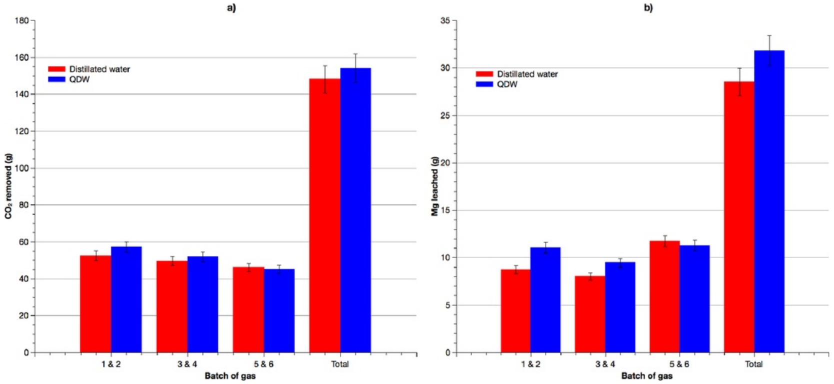

Fig. 3 Comparative analysis of the effect of water compositions on CO_2 removal (a) and Mg leached as function of the batch of gas treated (b). Error bars stands for a 5% error.

alt-text: Fig. 3

The QDW is the runoff water collected in the calcite pit near the cement plant. It was characterized by an alkaline pH (pH = 9) and higher ionic strength than distilled water. The QDW showed concentration of Mg, Ca, K and Na of 6.68, 19.4, 257 and 60 ppm respectively. As mentioned in previous works, the aqueous phase salinity can affect minerals dissolution (Johnson et al., 2014; McKelvy et al., 2001; Pokrovsky and Schott, 2000). From the batches 1 to 6, the quantity of CO_2 treated with QDW are in a similar range when distilled water is used. On the other hand, the amount of Mg leached were slightly superior when using the QDW compared to the distilled water for the four first batch. A light decrease was registered with the batches 5 and 6. However, the cumulative quantity of Mg leached were higher in the case of QDW. From these~~is~~ results, it can be assumed that the CO_2 solubility is not significantly favored, whereas the Mg dissolution seems to be promoted. At first, the alkaline pH offered favorable conditions regarding the dominance of HCO_3^- and CO_3^{2-}. In addition, the elevated ionic strength of the aqueous phase when using QDW enhanced the bulk solution diffusion process. In these conditions, the proton and ligand exchange is thus promoted resulting in a higher Mg dissolution. Such observations are in accordance with previously published studies were organic and inorganic salts such as NaCl, $NaHCO_3$ and $KHCO_3$ promoted MC rate (Harrison et al., 2012; O'Connor et al., 2002; Prigiobbe et al., 2009). Moreover, it must be mentioned that the regular changes of the aqueous phase, after each two successive batches of gas, limits the supersaturation. This allows to avoid carbonates precipitation on particle surfaces to have a subsequent separate precipitation of nearly pure magnesium carbonate. Through these results, it can be concluded that QDW can be used to conduct MC experiments. In a larger way, the use of raw effluent present on some industrial site could be considered as a water source. This can have multiple advantages regarding the applicability of such process. For instance, in the case of cement plant, calcite open pit is often nearby the plant and similar stream might be available. Moreover, effluents management on industrial sites can be problematic and their use for mineral carbonation, depending on their composition and prominently on the pH of the solution, can enlarge the solutions available.

3.3 Effect of pCO_2

Considerable fluctuation of CO_2 composition was observed within the chimney gas of the cement plant (14–18 vol% CO_2). This led to continuous change of pCO_2. Therefore, the effect of different pCO_2 on MC efficiency was investigated. Fig. 4 shows the effect of the pCO_2 on CO_2 uptake and on Mg dissolution for six successive batches of gas.

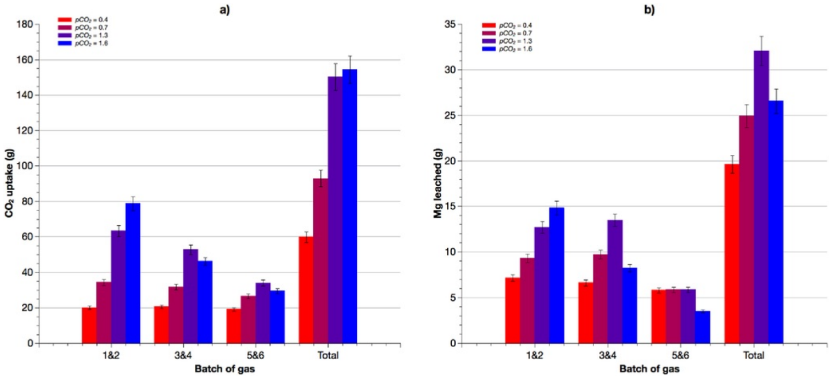

Fig. 4 The effect pCO_2 on gas removal (a) and serpentine dissolution (b).

alt-text: Fig. 4

At low pCO_2 (0.4 and 0.7 bars), the CO_2 uptake and Mg leached remain constant during each of the six batches of gas. In fact, the pH slurry values measured stayed closed to 9 ± 1 for the whole series batches of gas. The increase of pCO_2 to 1.3 and 1.6 bars led to a considerable enhancement of both cumulative quantities of CO_2 treated and Mg leached. In each case, the CO_2 uptake and Mg leaching were higher for batches 1 and 2. According to Henry's law, at high pCO_2, the amount of dissolved CO_2 is higher. The slurry phase acidification for the last batch of gas (pH = 7) can explain the reduction of the CO_2 uptake.

While the trend is similar for both results, the decrease along the batches is different for the CO_2 uptake and the Mg leaching. It can be observed that the higher the pCO_2 is, the higher is the CO_2 uptake (Fig. 4a). A similar trend is reported for Mg leaching with a pCO_2 of 1.6. However, such trend is not true for experiments performed with a lower pCO_2 of 1.3 bar. Indeed, the amount of Mg measured in solution is still increasing after batches 3&4 and then stabilized with an identic value for each condition.

The similar trends for the CO_2 uptake and Mg leaching are explained by the promoting effect of the ligand $HCO_3^-$and protons exchange on the solid surface (Berg and Banwart, 2000; Hänchen et al., 2006). Previous thermodynamic studies showed that at slightly acidic conditions, Mg can be complexed by bicarbonate which consequently helps the ~~Mg leaching step~~ Olivine dissolution and carbonation under conditions relevant for in situ carbon storage (Chen et al., 2006; Jarvis et al., 2009).

As mentioned above, the increase of pCO_2 from 0.4 to 1.6 bar induced different pattern for the Mg leaching. In fact, with a pCO_2 of 1.3 bar, the decrease in terms of dissolution efficiency started at the batches 5 and 6. However, at a pCO_2 of 1.6 bar, it started at the batches 3 and 4. The decrease of Mg leaching can be explained by incongruent dissolution known to happen at ambient temperature (Daval et al., 2009). In addition, several studies also mentioned the development of Si rich layer through the leaching/precipitation process, which hindered the Mg disponibilty (Daval et al., 2011; King et al., 2014; Park et al., 2003; Pokrovsky and Schott, 2000; Teir et al., 2007). The passivating layer thickness grows as the Mg is removed from the solid lattice (Pokrovsky and Schott, 2004). As the increase of the pCO_2 enhances the Mg solubilisation, the passivation might appear quicker in this case. Nevertheless, the assays performed at 1.3 bar showed a higher Mg dissolution. Such variability could be too explained by the solid heterogeneity, and or a better activation of the sample which favored the Mg availability.

In the present study, working with 1.3 bar appears to be the most interesting condition which ensures comparable quantity of CO_2 treated than at 1.6 bar with higher quantity of Mg leached. Hence, the highest efficiency of MC reaction was obtained at a pCO_2 of 1.3 bar with a conversion of 0.08 g of CO_2 treated g of residue^{-1} compared with 0.05, 0.06, 0.07 g of CO_2 treated g of residue^{-1} for 0.4, 0.7 and 1.6 bar, respectively.

The results, in accordance with the literature highlight the importance of the pCO_2 for MC reaction efficiency at ambient temperature for the treatment of industrial flue gas. Beyond the applicability, the flue gas composition variation introduces another variable to be investigated. While the assays where performed using a batch wise mode, where the amount of CO_2 could be controlled by increasing or lowering the total pressure, operation under continuous flows will require a precise control of the amount of CO_2 entering the vessel. Depending on the CO_2 quantity, the retention of the pulp might be adapted to keep the amount of CO_2 and Mg high enough to reach sufficient reaction yields.

3.4 Carbonate precipitation

Table 3 highlights a simplified CO_2 mass balance for the precipitation step. Precipitation rates ranged from 7 to 30%. Before discussing the effect of the pCO_2, it is first important to remind that the experiments were performed on the liquid phase only (after filtration). In addition, the assays were realized at atmospheric pressure in a vessel open to the atmosphere.

Table 3 CO_2 mass balance for the precipitation step (40 °C, 300 rpm, 6 h).

alt-text: Table 3

pCO_2 bar	CO_2 Inlet g	CO_2/precipitate g	CO_2/filtrate g	Precipitation %	Mass balance %	Balance Error %
0.4 ± 0.03	56.3	4.13	37.7	7.34	74.3	25.7
0.7 ± 0.03	70.6	23.5	28.1	33.3	73.1	26.9
1.3 ± 0.03	119	33.7	39.5	28.4	61.8	38.2
1.6 ± 0.07	107	29.6	11.4	27.2	104	4.0

A similar trend as previously discussed for the Mg leaching is observed. Indeed, the link between dissolved Mg and precipitation is highlighted. On the other hand, no clear relation between the pCO_2 and the precipitation efficiency can be highlighted. Nevertheless, by comparing the mass of carbonates precipitated, a relationship with the amount of dissolved CO_2 can be identified (Fig. 4a). Logically, a more concentrated solution of dissolved CO_2 and Mg leads to a higher precipitation rate. Thus, the pCO_2 defines serpentine dissolution and the availability of HCO_3^-, CO_3^{2-} and Mg^{2+} in the solution. However, from the results, it seems that a higher amount of Mg will promote the precipitation compared with the amount of CO_2. Such results are explained by the composition of Nesquehonite, where 17.~~,57~~6% of the molecular weight is Mg, while Carbon stands for 8.68%. In this way, the formation of the carbonates involves a quicker decrease in the Mg concentration, making it the limiting element.

The relatively low precipitation rates can be attributed to non-optimal precipitation conditions. Further work in this study proved the possible enhancement of the precipitation reaction by liquid recirculation (Kemache et al., 2016). This ensures to reach supersaturation more quickly and allows the secondary nucleation process. Further investigations on operating parameters such as temperature and stirring conditions rate are recommended. In addition, the amount of CO_2 released in the gas phase due to the temperature increase should be investigated. The obtained precipitate showed a very high purity with 96.4 ± 0.9% moles of Mg per moles of the total analysed chemical elements. Nesquehonite ($MgCO_3$.~~·~~$3H_2O$), known to be formed during ambient conditions was identified as the main compound (Hänchen et al., 2008).

3.5 Effect of heat-treatment of mineral carbonation residue

Additional heat-treatment of the residue obtained after the treatment of six batches of gas was performed. Such activation showed in other research studies an enhancement of the MC rate (Pasquier et al., 2014a). Consequently, the solid obtained from a series of experiments conducted at 1.3 bar, was grinded and then heat treated at 650 °C for 30 min. Fig. 5 compares the quantities of CO_2 treated and Mg leached with and without the residue treatment.

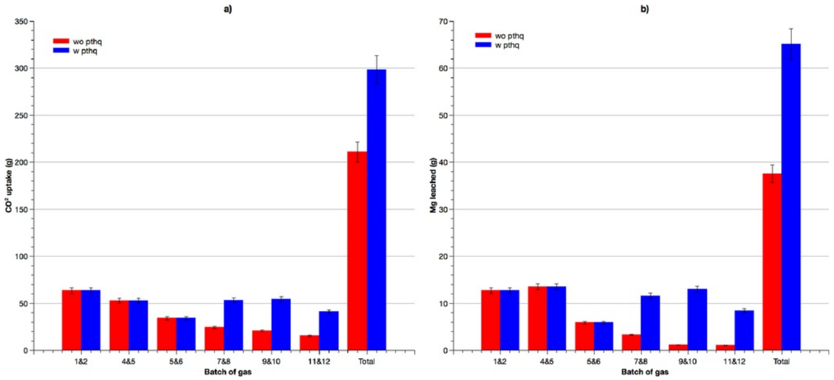

Fig. 5 Comparative analysis of the effect of grinding and heat treatment on the CO_2 uptake (a) and Mg leached (b). (error bars stands for 5% error).

alt-text: Fig. 5

By comparing the observed trends from the 12 batches, physical re-treatments showed a remarkable promoting effect of the reaction. An improvement of the cumulative CO_2 removal and Mg leaching with a factor of 1.43 and 1.63 were respectively observed. First, as previously mentioned, the initial heat treatment of the solid was partially efficient. It can explain the important gain of reactivity after the second re-activation of serpentinite by heat treatment. Secondly, both grinding and heat treatment can induce the exfoliation of the passivating layer. Some researchers reported that the amorphous silica showed several particles in the range of tens of micrometers (Jarvis et al., 2009). Tensile stress caused by grinding can lead the detachment of these formed particles from the serpentinite by a cracking process (McKelvy et al., 2006). In addition, the second heat treatment induces the reduction of inherent moisture content which causes the solid surface fracturation. Indeed, the characterization of deshydroxylated serpentine showed an increase of the pore volume and the generation of mesoporous product (Alizadehhesari et al., 2012). Additionally, the enhancement of MC reaction was reported through a partial destruction of the passivating layer achieved by mechanical treatments such as energetic agitation (attrition phenomena) or the use of abrasive slurry component like quartz, zircon or glass balls (Julcour et al., 2015; McKelvy et al., 2006).

The retreatment of the solid followed by MC reaction led to an overall efficiency of 0.17 g of CO_2 converted .~~·~~ g of residue^{-1}. Similar work conducted in laboratory scale led to a reaction efficiency of 0.28 g of CO_2 converted~~ per~~ .g of serpentine^{-1} (Pasquier et al., 2014b). The difference between the results can be attributed to several factors. First, the feedstock used are not equivalent. The mineralogical composition changes can induce reactivity variation. In addition, the heat activation was more controlled in the laboratory conditions. Activation is a crucial aspect of serpentine MC which will drive the global reaction efficiency. Besides the results obtained under real conditions, with an inherent lower degree of control on the input, mainly the gas and the feedstock composition, shows encouraging results proving the feasibility of the process under real conditions.

4 Conclusion

At ambient temperature and several pCO_2 varying from 0.4 to 1.7 bar, aqueous MC of lizardite was assessed in stirred tank reactor (18 L). Experiments were performed using a real cement plant flue gas that was directly pumped from the chimney. In addition, raw water, here QDW, was used for conducting the experiments and did not limit the MC reaction efficiency. The feedstock treatment allowed an efficient magnetite and chromite removal. Such by-product can be further considered as a marketable product. Incomplete amorphization of the solid was shown after the initial heat treatment. This low efficiency is attributed to a non-optimized heat activation process. Increasing the pCO_2 showed considerable enhancement of MC efficiency. However, a pCO_2 of 1.3 bar appeared to be the optimal working pressure in the conditions tested. It allowed the highest Mg leaching and consequently the highest reaction efficiency after the treatment of 6 batches of gas (0.08 g of CO_2 treated g of residue^{-1}). Relatively low precipitation rates were obtained, but the importance of the amount of Mg dissolved compared with the dissolved CO_2 was highlighted. The improvement of the feedstock treatment and the mechanically exfoliation of SiO_2 through additional grinding and heat treatment of the residue was observed. At working a pCO_2 of 1.3 bar, this re-treatment led to the enhancement of the reaction efficiency after 12 successive batches of gas (0.17 g of CO_2 converted g of residue^{-1}). To conclude, encouraging results under real conditions and pilot scale conditions were obtained for aqueous MC route. Nonetheless, additional research is needed to improve the optimisation of the feedstock treatment and the precipitation conditions.

Acknowledgements

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References

Alexander G., Maroto-Valer M.M. and Gafarova-Aksoy P., Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation, *Fuel* **86**, 2007, 273–281.

Alizadehhesari K., Golding S.D. and Bhatia S.K., Kinetics of the dehydroxylation of serpentine, *Energ Fuel* **26**, 2012, 783–790.

Berg A. and Banwart S.A., Carbon dioxide mediated dissolution of Ca-feldspar: implications for silicate weathering, *Chem. Geol.* **163**, 2000, 25–42.

Bobicki E.R., Liu Q., Xu Z. and Zeng H., Carbon capture and storage using alkaline industrial wastes, *Prog. Energy Combust. Sci.* **38**, 2012, 302–320.

Chen Z.Y., O'Connor W.K. and Gerdemann S.J., Chemistry of aqueous mineral carbonation for carbon sequestration and explanation of experimental results, *Environ. Prog.* **25**, 2006, 161–166.

Daval D., Martinez I., Corvisier J., Findling N., Goffe B. and Guyot F., Carbonation of Ca-bearing silicates, the case of wollastonite: experimental investigations and kinetic modeling, *Chem. Geol.* **265**, 2009, 63–78.

Daval D., Sissmann O., Menguy N., Saldi G.D., Guyot F., Martinez I., Corvisier J., Garcia B., Machouk I. and Knauss K.G., Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 C and elevated pCO 2, *Chem. Geol.* **284**, 2011, 193–209.

Fauth D.J., Baltrus J.P., Soong Y., Knoer J.P., Howard B.H., Graham W.J., Maroto-Valer M.M. and Andresen J.M., Carbon Storage and Sequestration as Mineral Carbonates, Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century2002, 101–117, 447.

Gerdemann S.J., O'Connor W.K., Dahlin D.C., Penner L.R. and Rush H., Ex situ aqueous mineral carbonation, *Environ. Sci. Technol.* **41**, 2007, 2587–2593.

Hänchen M., Prigiobbe V., Baciocchi R. and Mazzotti M., Precipitation in the Mg-carbonate system-effects of temperature and CO_2 pressure, *Chem. Eng. Sci.* **63**, 2008, 1012–1028.

Hänchen M., Prigiobbe V., Storti G., Seward T.M. and Mazzotti M., Dissolution kinetics of fosteritic olivine at 90-150 °C including effects of the presence of CO_2, *Geochim. Cosmochim. Ac* **70**, 2006, 4403–4416.

Hariharan S., Werner M., Hänchen M. and Mazzotti M., Dissolution of dehydroxylated lizardite at flue gas conditions: II. Kinetic modeling, *Chem. Eng. J.* **241**, 2014, 314–326.

Harrison A.L., Power I.M. and Dipple G.M., Accelerated carbonation of brucite in mine tailings for carbon sequestration, *Environ. Sci. Technol.* **47**, 2012, 126–134.

Huijgen W.J.J., Witkamp G.J. and Comans R.N.J., Mechanisms of aqueous wollastonite carbonation as a possible CO_2 sequestration process, *Chem. Eng. Sci.* **61**, 2006, 4242–4251.

Huot F., Beaudoin G., Hébert R., Constantin M., Dipple G.-M. and M, R, Le piégeage du CO2 anthropique dans les parcs à résidus d'amiante du sud du Québec: Concept et valorisation, 2003, Université Laval, Geologie et génie

Géologique, Faculté des sciences et de génie; Québec, Canada, 167.

IPCC, Summary for policymakers, In: Edenhofer O., Pichs-Madruga R., Sokona Y., Farahani E., Kadner S., Seyboth K., Adler A., Baum I., Brunner S., Eickemeier P., Kriemann B., Savolainen J., Schlo¨mer S., von Stechow C., Zwickel T. and Minx J.C., (Eds.), *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change,* 2014, Cambridge University Press Cambridge, United Kingdom and New York, NY, USA, 33.

Jarvis K., Carpenter R., Windman T., Kim Y., Nunez R. and Alawneh F., Reaction mechanisms for enhancing mineral sequestration of CO2, *Environ. Sci. Technol.* **43**, 2009, 6314–6319.

Johnson N.C., Thomas B., Maher K., Rosenbauer R.J., Bird D. and Brown G.E., Olivine dissolution and carbonation under conditions relevant for in situ carbon storage, *Chem. Geol.* **373**, 2014, 93–105.

Julcour C., Bourgeois F., Bonfils B., Benhamed I., Guyot F., Bodénan F., Petiot C. and Gaucher É.C., Development of an attrition-leaching hybrid process for direct aqueous mineral carbonation, *Chem. Eng. J.* **262**, 2015, 716–726.

Kemache N., Pasquier L.-C., Mouedhen I., Cecchi E., Blais J.-F. and Mercier G., Aqueous mineral carbonation of serpentinite on a pilot scale: the effect of liquid recirculation on CO2 sequestration and carbonate precipitation *Appl. Geochem* **67**, 2016, 21–29.

King H.E., Satoh H., Tsukamoto K. and Putnis A., Surface-specific measurements of olivine dissolution by phase-shift interferometry, *Am. Mineral.* **99**, 2014, 377–386.

Lasaga A.C. and Berner R.A., Fundamental aspects of quantitative models for geochemical cycles, *Chem. Geol.* **145**, 1998, 161–175.

Li W.Z., Li W., Lia B.Q. and Bai Z.Q., Electrolysis and heat pretreatment methods to promote CO2 sequestration by mineral carbonation, *Chem. Eng. Res. Des.* **87**, 2009, 210–215.

MacKenzie S.H., Field C.B. and Raupach M.R., The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World, 2004, Island Press.

McKelvy M., Chizmeshya A., Bearat H., Sharma R. and Carpenter R., Developing Mechanistic Understanding of CO2 Mineral Sequestration Reaction Processes, 2001, 5–8.

McKelvy M., Chizmeshya A., Squires K., Carpenter R. and Bearat H., A Novel Approach to Mineral Carbonation: Enhancing Carbonation while Avoiding Mineral Pretreatment Process Cost, 2006, Arizona State University; Tempe, AZ, US, 45.

McKelvy M.J., Chizmeshya A.V.G., Diefenbacher J., Béarat H. and Wolf G., Exploration of the Role of heat activation in enhancing serpentine carbon sequestration reactions, *Environ. Sci. Technol.* **38**, 2004, 6897–6903.

Nduagu E., Björklöf T., Fagerlund J., Mäkilä E., Salonen J., Geerlings H. and Zevenhoven R., Production of magnesium hydroxide from magnesium silicate for the purpose of CO2 mineralization – Part 2: Mg extraction modeling and application to different Mg silicate rocks, *Min. Eng.* **30**, 2012, 87–94.

O'Connor W.K., Dahlin D.C. and GE G., Aqueous Mineral Carbonation, Final Report, 2005, Albany Research Center (ARC); Albany, OR, 21.

O'Connor W.K., Dahlin D.C., Rush G.E., Dahlin C.L. and Collins W.K., Carbon dioxide sequestration by direct mineral carbonation: process mineralogy of feed and products, *Min. Metall. Proc.* **19**, 2002, 95–101.

Pan S.Y., Chang E.E. and Chiang P.C., CO 2 capture by accelerated carbonation of alkaline wastes: a review on its principles and applications, *Aerosol Air Qual. Res.* **12**, 2012, 770–791.

Park A. and Fan L., CO2 mineral sequestration: physically activated dissolution of serpentine and pH swing process, *Chem. Eng. Sci.* **59**, 2004, 5241–5247.

Park A.H.A., Jadhav R. and Fan L.S., CO2 mineral sequestration: chemically enhanced aqueous carbonation of serpentine, *Can. J. Chem. Eng.* **81**, 2003, 885–890.

Pasquier L.C., Mercier G., Blais J.F., Cecchi E. and Kentish S., Parameters optimization for direct flue gas CO2 capture and sequestration by aqueous mineral carbonation using activated serpentinite based mining residue, *Appl. Geochem* **50**, 2014a, 66–73.

Pasquier L.C., Mercier G., Blais J.F., Cecchi E. and Kentish S., Reaction mechanism for the aqueous-phase mineral carbonation of heat-activated serpentine at low temperatures and pressures in flue Gas conditions, *Environ. Sci. Technol.* **48**, 2014b, 5163–5170.

Pasquier L.C., Mercier G., Blais J.F., Cecchi E. and Kentish S., Technical and economic evaluation of a mineral carbonation process using southern Québec mining wastes for CO2 sequestration of raw flue gas with by-product recovery, *Int. J. Greenh. Gas. Con* **50**, 2016, 147–157.

Pokrovsky O.S. and Schott J., Kinetics and mechanism of forsterite dissolution at 25°C and pH from 1 to 12, *Geochim. Cosmochim. Ac* **64**, 2000, 3313–3325.

Pokrovsky O.S. and Schott J., Experimental study of brucite dissolution and precipitation in aqueous solutions: surface speciation and chemical affinity control, *Geochim. Cosmochim. Ac* **68**, 2004, 31–45.

Prigiobbe V., Costa G., Baciocchi R., Hanchen M. and Mazzotti M., The effect of CO2 and salinity on olivine dissolution kinetics at 120 degrees C, *Chem. Eng. Sci.* **64**, 2009, 3510–3515.

Sanna A., Uibu M., Caramanna G., Kuusik R. and Maroto-Valer M., A Review of Mineral Carbonation Technologies to Sequester CO 2, 2014, Chemical Society Reviews.

Seifritz W., CO2 disposal by means of silicates, *Nature* **345**, 1990, 486.

Sipilä J., Teir S. and Zevenhoven R., Carbon Dioxide Sequestration by Mineral Carbonation Literature Review Update 2005–2007. Report for Faculty of Technology Heat Engineering Laboratory, 2008, Åbo Akademi University.

Teir S., Eloneva S., Fogelholm C.J. and Zevenhoven R., Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production, *Energy* **32**, 2007, 528–539.

Tertian R. and Claisse F., Principles of Quantitative X-ray Fluorescence Analysis, 1982, John Wiley and Son.

Werner M., Hariharan S. and Mazzotti M., Flue gas CO2 mineralization using thermally activated serpentine: from single- to double-step carbonation, *Phys. Chem. Chem. Phys.* **16**, 2014, 24978–24993.

Wilson S.A., Dipple G.M., Power I.M., Thom J.M., Anderson R.G., Raudsepp M., Gabites J.E. and Southam G., Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: examples from the Clinton Creek and Cassiar chrysotile deposits, Canada, *Econ. Geol.* **104**, 2009, 95–112.

Highlights

- Pilot scale mineral carbonation process study using a real cement plant flue gas.
- The effect of the CO_2 partial pressure and the use of raw water were addressed.
- The gas composition variation can affect the carbonation efficiency.
- The use of a raw water did not impact the overall process efficiency.

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