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Aqueous mineral carbonation of serpentinite on a pilot scale: The effect of liquid recirculation on CO_2 sequestration and carbonate precipitation

Nassima Kemache, Louis-César Pasquier*, Ikbel Mouedhen, Emmanuelle Cecchi, Jean-François Blais, Guy Mercier

Institut National de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC G1K 9A9, Canada

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A B S T R A C T

Following the promising results obtained on the laboratory scale, an aqueous mineral carbonation process was tested under industrial conditions as part of a pilot project conducted in a cement plant in Quebec. Experiments were conducted using a Parr 18.7 L reactor with cement plant flue gas (14–18 vol.% CO_2) and serpentinite tailings as a source of magnesium. The gas was not concentrated or separated before use. The reactions occurred at a solid/liquid ratio of 150 g/L, 22 ± 3 °C and a total pressure between 2 and 10 bar. To decrease water consumption, the effect of liquid recirculation on the rates of CO_2 sequestration, Mg leaching and carbonate precipitation were studied. The solid reacted with 6 successive batches of gas (15 min each), and the liquid was recovered for the carbonate precipitation after every two batches. For the recirculation assays, after carbonate filtration, the liquid was reused with subsequent batches.

The results showed that the dissolution of CO_2 was not affected by the liquid recirculation since 72.5% of the CO_2 introduced was dissolved; in comparison to 77% when fresh liquid was used. The captured CO_2 resulted in 0.215 and 0.211 g CO_2/g of residue in the experiments with and without liquid recirculation, respectively. This result corresponds to approximately 45% of serpentinite's total capacity for CO_2 sequestration, which is 0.47 g CO_2/g of residue. The carbonate precipitation experiments were conducted in a separate system at low temperatures (32–40 °C) and included 2 h of stirring. When the liquid was recirculated, supersaturation was reached more quickly because of the accumulation of Mg^{2+} and HCO_3^-/$CO^{2-}{}_3$ ions. Therefore, the rate of precipitation and the amount of carbonate formed were significantly more important when the liquid was recirculated. However, the overall efficiency corresponding to the captured CO_2 under carbonate form does not exceed 9% even with liquid recirculation.

1. Introduction

In its April 2014 report, the Intergovernmental Panel on Climate Change (IPCC) recommended reducing greenhouse gas (GHG) emissions to between 40 and 70% of the 2010 values by 2050. Carbon dioxide (CO_2) is the primary GHG, and the highest CO_2 emissions (32 $GtCO_2$-eq in 2010) come from fossil fuel combustion and industrial processes (IPCC, 2014). To reach the IPCC's goals, both industrialized and emerging countries must find more viable solutions for storing CO_2 that are affordable and easy to implement. Different technologies are being investigated. These include geological storage, which consists of injecting CO_2 into petroleum and natural gas fields or deep saline formations, biological storage, which is primarily based on increasing photosynthesis to produce fossil fuel, and mineral carbonation, which is based on the weathering process of natural rock in the presence of acidic rain that contains dissolved CO_2 (Seifritz, 1990). Chemically, the mineral carbonation consists of a reaction between CO_2 and an alkali, alkaline earth or oxide silicate such as magnesium oxide, MgO, or calcium oxide, CaO. Natural silicates are present in minerals such as serpentinite ($Mg_3Si_2O_5(OH)_4$) (Lackner et al., 1995) and wollastonite ($CaSiO_3$) (Huijgen et al., 2006). However, in the province of

* Corresponding author.
E-mail address: louis-cesar.pasquier@ete.inrs.ca (L.-C. Pasquier).

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Quebec, serpentinite is available in greater quantities than wollastonite. They can also be found in some percentages in alkaline industrial residues such as steelmaking slags (Bobicki et al., 2012). Storing CO_2 in mineral carbonates (Mg/Ca carbonates) offers several advantages, including long-term stability and the safety associated with it and the availability of large amounts of raw material around the world (IPCC, 2005). The serpentinite generally used for mineral carbonation is an ultramafic rock composed of one or more serpentine minerals. This mineral group contains three polymorphs: chrysotile, antigorite, and lizardite. Serpentine minerals contain magnesium silicate; therefore, their makeup is 35–40% MgO, the same amount of SiO_2 and 12–13.5% water (Wicks and Ohanley, 1988). The structure consists of alternating tetrahedrons of silica and octahedral sheets of $Mg(OH)_2$. Because serpentinite is used as the source of Mg in mineral carbonation, its dissolution and, therefore, the liberation of Mg is an important step in the process. To improve the rate of leaching, the serpentinite undergoes the following pre-treatments: grinding and size reduction, magnetic separation to remove iron oxides and spinel and heat treatment. The effect of reducing the particle size on the reaction rate was observed by O'Connor et al. (2000). They reported an increase in the amount converted from 10 to 90% when the particle size was decreased from 150 to 37 μm. The chemically bonded hydroxyl groups surrounding the Mg atoms were removed in the form of H_2O vapor by heating the serpentinite, generally to 600–650 °C. Heating serpentinite results in an open structure (O'Connor et al., 2000) and, in some cases, in the complete destruction and amorphization of the structure (Brindley and Zussman, 1957). The high energy consumption of these treatments significantly increases the cost of the process.

Mineral carbonation can be performed under dry or aqueous conditions. Direct gas–solid carbonation (or carbonation in a low-humidity environment) consists of a direct reaction between a metal oxide and CO_2 gas that may also be supercritical. The process is simple, but the rate of the reaction is slow and the capacity for carbon sequestration is low (Baciocchi et al., 2006; Eloneva et al., 2009; Lackner et al., 1997, 1995; Larachi et al., 2010; Rendek et al., 2006). Several reactions are involved in aqueous mineral carbonation (AMC); they include the dissolution of CO_2 and its dissociation to bicarbonates and H^+ (Mackenzie and Lerman, 2006). These reactions cause the pH to decrease and are followed by the dissolution of Mg silicates and the liberation of Mg in the presence of H^+ (Stumm and Morgan, 1996).

The dissolution of silicates and the availability of Mg control the reaction rate (Stumm and Morgan, 1996). To improve the leaching rate, some studies have proposed the use of acids such as ammonium bisulphate (NH_4HSO_4) (Park and Fan, 2004, Wang and Maroto-Valer, 2011). In this study, the authors increased the pH of the Mg-leached solution by adding ammonia to water to cause carbonates to precipitate. This pH-swing-based method requires several steps and large amounts of acids and bases. Other authors proposed the use of additives such as sodium chloride and sodium bicarbonate (O'Connor et al., 2002). NaCl has been used to increase the ionic strength to decrease the ionic activity and, consequently, increase the rate of Mg leaching. The addition of bicarbonate increases the concentration of carbonate ions in the solution and accelerates the formation of Mg carbonates. This additive has also been used to maintain an alkaline pH, which favors magnesite precipitation (Chen et al., 2006). In addition to using additives, O'Connor and co-workers conducted their experiments at high pressure (150 bar) and high temperature (115 °C). The authors concluded that the process could be expensive to implement on an industrial scale (O'Connor et al., 2005). However, recent studies have demonstrated the feasibility of AMC at room temperature and moderate total pressure (10 bar) for the treatment of a flue gas (Pasquier et al., 2014). The experiments were performed using mining residues composed of Mg silicates. The composition of the gas (18% CO_2) was close to that of the flue gas found in the cement industry. In addition, carbonate was precipitated outside of the reactor, and this step was separated from the carbonation reaction. Therefore, the carbonates obtained were very pure. To increase the sequestration rate, the same solid was reacted with several successive batches of gas. The authors observed that after 6 batches, which corresponds to 90 min of solid residence time, the reactivity decreased significantly because a passive layer of silica formed on the surface of the mineral undergoing dissolution (Huijgen et al., 2004). The solid was regenerated by grinding it a second time before being reacted with the next 6 batches of gas. In this study, a high rate of magnesium leaching (50%) was reached without using any acids or additives. The total CO_2 uptake after 12 batches was approximately 63%. These results were the subject of a patent (Mercier et al., 2013). In addition to realize the carbonation under mild pressure and temperature conditions, Pasquier and his team succeeded in precipitating pure Mg carbonates outside of a reactor (Pasquier et al., 2014). Following the laboratory good results, the process has now been tested on a pilot scale. The pilot was implemented in a cement plant, and the project continued for one year. This paper presents results of this pilot test. Cement flue gas was directly used without any pre-concentration or separation. First, the same laboratory conditions were used to verify the results. Subsequently, some parameters, such as the gas pressure and the source of Mg silicates, were varied. The effects of liquid recirculation on the rates of CO_2 sequestration and carbonate precipitation were also investigated.

2. Materials and methods

2.1. Raw material pre-treatments and characterization

The serpentinite-based tailings used in this work were samples of residue from a mine in the south of the province of Quebec. The material is being referred as MJ serpentinite. It was primarily composed of lizardite ($Mg_3Si_2O_5(OH)_4$) with minor mineral phases such as brucite ($Mg(OH)_2$), magnetite (Fe_3O_4) and forsterite (Mg_2SiO_4). Before grinding, the samples underwent physical separation to recover their magnetic fractions. The first separation was performed using a spiral (model 5LL400). The serpentinite powder was driven down the spiral by water flowing at a rate of 0.15 m^3/min. Two fractions were recovered by means of gravity and centrifugal force at the end of this step. The light fraction, which contained various silicates, was not used in our experiments. The second fraction was the dense fraction that contained the magnetic portion and the remaining silicates. These portions were separated using a Wilfley table (Outokumpu Technology, model SA-13A). Vibrations with an amplitude of 500 strokes/min and an inclination of 14° were used to create longitudinal motion. The water and powder flow rates were 0.12 m^3/h and 5 kg/h, respectively. To guarantee that magnetite was recovered well, two passes through the Wilfley table were necessary. At the end of this treatment, two fractions were recovered: the magnetic fraction and the silicate fraction. These fractions' densities were determined using a Micromeritics Accupyc 1330 pycnometer. The silicate fraction was ground 3–4 times for 75 s each time using a Retsch Rs-2000 disc mill and then, heat treated using a continuous electric rotary kiln (Pyromaître Pyro 106-HE). Calcination was performed at 650 °C for 30 min with a throughput of 200 g/min. To ensure that the residence time in the kiln reached 30 min, an inclination of 9° was used. The chemical compositions of the solid samples (the serpentinite and carbonate) were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). First, the samples were subjected to