Solid products characterization in a multi-step mineralization process

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HIGHLIGHTS

- A multi-step pH-swing process makes value-added products from captured CO_2.
- High yields of carbonate precipitate are obtained from carbonation of the extracted magnesium.
- Different forms of magnesium carbonate can be obtained depending on reaction temperature.
- Different forms of iron hydroxide can be obtained depending on reaction pH.
- The precipitate has a purity of 99.9% based on MgO content.

ABSTRACT

In this paper, we describe a carbon dioxide mineralization process and its associated solid products. These solid products include amorphous silica, iron hydroxides and magnesium carbonates. These products were subjected to various characterization tests, and the results are published here. It was found that the iron hydroxides from this process can have different crystalline properties, and their formation depended very much on the pH of the reaction conditions. Different forms of magnesium carbonate were also obtained, and the type of carbonate precipitated was found to be dependent on the carbonation temperature. Hydromagnesite was obtained mainly at low temperatures, while dypingite was obtained at higher temperatures. Near ambient conditions, nesquehonite was the predominant form of magnesium carbonate obtained. The process mass balance shows that 3.1 tonne of hydrated magnesium carbonate with 99.82 wt% purity is obtained for each tonne of CO_2 sequestrated. And for each tonne of carbon dioxide sequestrated, about 3.74 tonnes of mineral ore are needed as a source of magnesium.

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1. Introduction

The world's reliance on using fossil fuels as a cheap and convenient energy source has led to the emission of large amounts of carbon dioxide [1]. As a consequence, CO_2 concentrations in the atmosphere have been on an upward trend, with it currently being 30% above pre-industrial levels. This increase is very likely to lead to irreversible harmful consequences [2,3]. As such, there exists a pressing need to develop carbon dioxide mitigation technologies to address this problem.

The accelerated weathering of minerals, also called mineral carbonation, provides an option for carbon sequestration. This method may be particularly useful in regions where suitable underground geological formations for CO_2 injection are unavailable, the risk of CO_2 leakage from an underground site is considered unacceptable, or where mineral sources for carbonation abound in the vicinity of

large carbon emission sources (such as coal-fired power plants) [4]. The main advantage of mineral carbonation is that the CO_2 is stored as carbonates that are stable over geological time periods (millions of years) [5]. The capacity of mineral carbonation is also huge, and it can potentially store billions of tonnes of carbon dioxide per year permanently [6,7]. However, its typically high energy requirements and poor process economics are two limiting factors for mineral carbonation [8].

One of the more promising routes for mineral carbonation involves aqueous reactions. This process is similar to the natural alteration of ultramafic rocks, also called serpentinization [9]. Currently there are two main approaches for aqueous carbonation of calcium and magnesium silicates: (a) direct carbonation, where mineral dissolution and carbonation take place simultaneously in an aqueous solution, and (b) indirect pH-swing processes which includes the extraction of alkaline-earth metals from a mineral and separate precipitation of the carbonate in subsequent steps [10,11]. In a direct approach, the entire process is thermodynamically favored. As a result, energy inputs are theoretically not

required during the chemical processing of the material. This method is currently regarded as the most economical mineral-carbonation pathway [12]. However, mass transfer limitations arise from the low solubility of CO_2 in the acidic environment which is necessary for mineral dissolution. As a result the direct process may be less favorable kinetically.

On the other hand, if process efficiency and high product purities are desirable, an indirect, multi-step mineral carbonation process appears to be more attractive than a direct single step process [13]. The indirect aqueous approach to CO_2 mineralization has several advantages: the process is kinetically favored and simple, the products are of high purity and the reaction takes place in a very short time [14,15]. Most indirect methods involve the use of HCl, H_2SO_4 or NaOH as reagents in the process [16–20]. Typically the magnesium contained in serpentine dissolves quickly in acid, forming magnesium salts in solution and leaving behind silica:

$$HX + Mg_3Si_2O_5(OH)_4 \rightarrow MgX_2 + SiO_2 + H_2O \qquad (1)$$
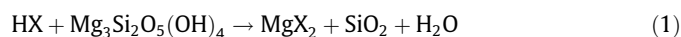
The magnesium in the resulting leachate is filtered from the silica residue, and precipitated as magnesium carbonate in a separate unit operation downstream in the process [21]. However, due to the relatively high cost associated with carbon mineral sequestration, commercial implementations of this technology will not be possible without considering the utilization of solid products [12,22–24]. In order for the products to be marketable, the quality and purity of the products must be sufficiently high [25].

The magnesium carbonate products from the indirect process can find use in the paper, polymer, environmental protection and fertilizer industries [26,27]. However, potential lower value applications may include utilizing the product for mine reclamation or soil modification [28]. The disposal of carbonate solids near the surface or underground has low environmental risks. The magnesite product could possibly replace conventional soil liming agents, while the porous silica residue could improve soil water retention in arid environments [29]. Bai et al. [30] showed that the silica residue can also be further processed to produce a purified nanoporous SiO_2. The process includes extraction with NaOH followed by CO_2 bubbling in solution to reprecipitate the silica. At higher purities, magnesite has also been used as a fire retardant and as filler material for the manufacturing of paint, bricks, and ceramics [31,32]. Magnesium carbonate can also be used as structural material for electric arc furnaces, blast furnaces, basic oxygen furnace and housing construction [33].

It is also possible to obtain different morphs of magnesium carbonate from a mineralization process. The properties of magnesium carbonate can vary according to its different morphologies. Therefore it is valuable to be able to control morphologies according to the requirements, and controlled synthesis is important for the practical application of materials [34,35]. Two different morphologies of $MgCO_3 \cdot 3H_2O$ have been reported in literatures by adjusting the reaction conditions in the precipitation process (such as reaction temperature, stirring time, and aging time) to produce either agglomerates consisting of very thin sheets or well-formed needles [35].

The different morphologies of magnesium carbonate usually involve different degrees of hydration or carbonation, for example nesquehonite ($Mg(CO_3) \cdot 3H_2O$) which is thermally stable up to 100 °C [36]. Nesquehonite forms as a mineral in nature at relatively low-temperatures, and the synthetic product can be used in a large number of industrial applications, such as in the production of eco-cement and corrosion-resistant protective coatings [14]. The specifications of different grades of magnesium carbonate for various industrial uses are shown in Table 1 [37].

Other metal cations are also present in magnesium-silicate minerals, the most abundant of these being iron [38,39].

The industrial applications of the solid products from carbon dioxide mineralization are summarized in Table 2.

In this article, we detail the characteristics of the products obtained from a novel carbon mineralization process [41]. In this context, we describe the quantities, purity and morphology of products from a closed loop multi-step mineralization process under different conditions. Moreover, we present the synthesis of different kinds of magnesium carbonates and by-products from a magnesium-silicate mineral with a view to investigate the quality of these products in the CO_2 sequestration process.

2. Material and methods

2.1. Process description

A general scheme of the novel mineralization process is presented in Fig. 1. In the extraction step, magnesium carbonate is reacted with acid to give a magnesium-rich leachate. The residual silica and magnetite is filtered off. The leachate contains mainly magnesium, as well as trivalent and divalent iron. The trivalent iron is removed as a precipitate (P_1) via the careful addition of base to adjust the solution pH to a preset value (pH_I). The remaining solution is then transferred to a second precipitation reactor, where the solution pH is adjusted to another preset pH value (pH_{II}) to remove the divalent iron as a precipitate (P_2). After filtering of P_2, the impurities-free solution is transferred to a third precipitation reactor, where the magnesium is reacted with sodium carbonate to give magnesium carbonate precipitates (P_3) at an even higher pH (pH_{III}). The sodium carbonate used to produce P_3 is obtained from the scrubbing of flue gas CO_2 by NaOH. The resultant sodium chloride salt in the end solution is recycled to a bipolar membrane electro-dialyser, where it is regenerated into HCl and NaOH for re-use in the process.

2.1.1. Mineral pre-treatment

Pre-treatment of the mineral was carried out by milling the magnesium silicate rock with a ball mill to decrease the size particles of the ore (purchased from Quebec) to <56 μm.

2.1.2. Dissolution experiments

4 g of milled mineral ore with 10–56 μm particle size fractions were added into 100 mL 1 M HCl solution. The dissolution experiments were carried out in a three-neck round bottom flask at 80 °C and atmospheric pressure. The mixture was agitated with a magnetic stirrer at a constant rate of 600 rpm. A condensation apparatus was used to prevent vapor losses of HCl and water. After 6 h of dissolution, the mixture was cooled down to ambient temperature and filtered with a 0.45 μm membrane filter paper.

2.1.3. Purification experiments

To obtain P_1, 100 ml of the filtered leachate was prepared and transferred into a conical flask. The initial pH of the leachate was measured and recorded using a METTLER TOLEDO Seven Easy pH meter (S20) with accuracy ±0.01 at 25 °C. 1 M NaOH was added dropwise to the leachate at room temperature and pressure. The solution was constantly stirred at 600 rpm. Addition of NaOH was stopped when the pH of the solution reached a value of 5. The resulting slurry was then filtered using 0.45 μm membrane filter paper to give a filtrate and the P_1 solids.

After removal of P_1, whole amount of filtrate 1 was transferred to a second conical flask. In this step, 1 M NaOH was added until the pH of the solution reached a value of 9. The temperature, pressure and stirring conditions for this step are identical to the previous step where P_1 was obtained. The precipitate in this step (P_2)