Synthesis of nesquehonite by reaction of gaseous CO_2 with Mg chloride solution: Its potential role in the sequestration of carbon dioxide

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ABSTRACT

In this paper is reported a novel method to synthesize nesquehonite, $MgCO_3 \cdot 3H_2O$, *via* reaction of a flux of CO_2 with Mg chloride solution at $20 \pm 2\,°C$. The reaction rate is rapid, with carbonate deposition almost complete in about 10 min. The full characterization of the product of synthesis has been performed to investigate its potential role as a "CO_2-sequestering medium" and a means of disposing Mg-rich wastewater. We investigated the nesquehonite synthesized using SEM, XRD, FTIR and thermal analysis. The thermodynamic and chemical stability of this low-temperature hydrated carbonate of Mg and its possible transformation products make our method a promising complementary solution to other methods of CO_2 sequestration. Carbonation *via* magnesium chloride aqueous solutions at standard conditions represents a simple and permanent method of trapping CO_2. It could be applied at point sources of CO_2 emission and could involve rejected brine from desalination plants and other saline aqueous wastes (i.e., "produced water"). The likelihood of using the resulting nesquehonite and the by-products of the process in a large number of applications makes our method an even more attractive solution.

1. Introduction

We are all bombarded daily by alarming news about the rising levels of CO_2 in the atmosphere, caused largely by the combustion of fossil fuels, and about the deleterious impact of such loadings on our climate. According to the Intergovernmental Panel on Climate Change [1], new emissions for the period 2000–2005 were about 6 Gt C/year (23.5 Gt CO_2/year). With the continued growth of emerging densely populated countries like China and India, there is the prospect of tripling the loading of CO_2 to the atmosphere by the end of the 21st century. Clearly, the scientific community must seek to implement quickly the results of research on effective methods of sequestering CO_2 [1,2]. All approaches to reduce the global CO_2 emission must be examined carefully. Here, is presented a novel approach involving the synthesis of nesquehonite, $MgCO_3 \cdot 3H_2O$.

Numerous approaches to CO_2 sequestration, including ocean, terrestrial, geological, biological and chemical options are currently being studied [1,3–18]. As a substantial share of CO_2 emissions must be stored, the retention or sequestration of CO_2 in geological reservoirs is currently the option being applied (e.g., Weyburn, Canada; Sleipner, North Sea [14]). Deep aquifers and depleted reservoirs in oil and gas fields offer possible sites of storage of CO_2, with the fraction retained exceeding 99% over 1000 years [1,7,8]. However,

the behavior of CO_2 in such porous and permeable media, and the physical and chemical changes that can be expected in rocks if CO_2 is injected, still raise concerns in the scientific community [14,15].

Complementary technologies applied to CO_2 sequestration, such as neoformation of minerals *via* reaction of CO_2 with Mg–Ca silicate rocks or of carbonate minerals in aqueous solutions, offer attractive options for the permanent and safe storage of CO_2 in a solid form [19,20]. The methods based on neoformation of carbonates or bicarbonates require cations to neutralize CO_2 [11–13,18]. If a supply of the appropriate cations can be assured, such carbonation reactions offer virtually unlimited capacity and the promise of safe, permanent storage of CO_2. This idea was first proposed by Seifritz [21] in 1990. There is little risk of unexpected release of CO_2 back to the atmosphere, because the resulting carbonates are thermodynamically stable at ambient conditions [19,22]. The process occurs naturally on a small scale during the weathering of rocks, and has been shown to be important locally in ultrabasic complexes [23]. The source of the neutralizing ions could be silicates of Mg and Ca such as olivine, serpentine-group minerals and clinopyroxene. Unfortunately, the industrial extraction of Ca and Mg from silicate minerals requires expensive pre-processing, which contributes to the problem rather than to the solution [24]. Furthermore, this option is not at all practical in many countries owing the paucity of exposed basic and ultrabasic rocks.

An attractive alternative involves the interaction of ions in aqueous solution with CO_2. In this case, the precipitation of carbonates of Ca and Mg proceeds much more rapidly than if the cations are

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locked in a silicate structure. The source of such a process could be a "brine" [15] or even seawater. There is an advantage in focusing on Mg, because a greater weight proportion of CO_2 is found in Mg carbonates than in Ca carbonates. Moreover, Mg is readily available as an important constituent of seawater (about $1.3\,g\,L^{-1}$). The process, a variant of the Solvay process [19], is based on carbonating alkaline brines derived from deep saline aquifers, which would produce carbonates from a chloride-rich reactant and hydrochloric acid as a by-product [19]. It is a variant of this approach that we report in what follows, with a focus on nesquehonite.

In this context, we describe here encouraging results of our experiments on the reaction of gaseous CO_2 with $MgCl_2$ solutions through a kinetically rapid process, and the production of nesquehonite, $MgCO_3\cdot3H_2O$. Nesquehonite is a low-temperature carbonate encountered in alkaline soils, in cave deposits and as a weathering product of ultramafic rocks. It generally forms euhedral prismatic crystals, but also is found in fibroradial and botryoidal arrays. Here, we present data on experimental synthesis of nesquehonite, the full characterization of the solid product, necessary to confirm that the synthetic nesquehonite obtained in our experiments behaves in the same way as natural nesquehonite and the synthetic analogue, as reported in previous papers, and finally, its potential application to the problem. Various procedures for the synthesis of nesquehonite have been documented over the last century [25–31]. However, the differences between the methods cited and the one described in this study involve the source of CO_2, as those methods generally make use of solid carbonates as the source of carbon dioxide, or the source of Mg for the aqueous solution. Moreover, to our knowledge, the synthesis of nesquehonite by flushing CO_2 in a magnesium chloride solution with a view to investigate a possible role for this carbonate in a "CO_2-sequestering process" and disposing of Mg-rich wastewater has not been carried out until now. The procedure described here is inspired by that of Towe and Malone [32].

1.1. The properties of nesquehonite

Nesquehonite is a monoclinic hydrated carbonate of Mg, space group $P2_1/n$, with unit-cell parameters: a 7.701 Å, b 5.365 Å, c 12.126 Å, β 90°.41′ as reported by Giester et al. [33]. Its structure consists of infinite flat ribbons of corner-sharing MgO_6 octahedra along the b axis of the crystal, which is the fiber axis, linked by hydrogen bonds. Within the chains, CO_3 groups link three MgO_6 octahedra by one edge and two common corners. The Mg atoms are in a distorted coordination, and each atom is coordinated by two H_2O ligands; one free H_2O molecule is located between the chains [33–35].

2. Experimental methods

We carried out experiments using both doubly distilled and tap water from Rome (Italy), compressed CO_2 from SAPIO (Italy), and analytical grade reagents ($MgCl_2\cdot6H_2O$ and aqueous ammonia (25%) NH_3, Merck p.a.). In our syntheses $MgCl_2\cdot6H_2O$ was used as a source of magnesium. In thirty-two experiments, we synthesized nesquehonite by sparging CO_2 for 15 min at a rate of ~$100\,mL/min$ through 200 mL of the Mg chloride solution (~$7\,g\,L^{-1}$ of Mg) at $20\pm2\,°C$.

The pH, upon stopping the flow of CO_2, ranged between 5.20 and 5.70. Because pH has a significant influence on the precipitation of carbonates, it was measured continuously during the experiments. The suitable range of pH for the formation of nesquehonite in our experimental conditions was obtained by adding ammonia.

The kinetics of the formation of the solid products were followed by sampling the solution at time intervals of 2 min within the first
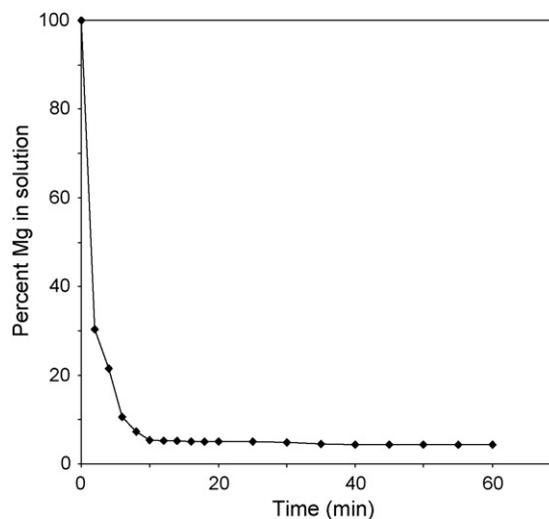

Fig. 1. Kinetics of the carbonation reaction.

20 min and then of 5 min, and measuring the concentration of Mg in the solution. The suspension was filtered using $0.20\,\mu m$ Nucleopore polycarbonate membrane filters, and the solid products were washed with doubly distilled water and dried in air. The influence of the duration of settling on the crystallinity of the solid products was investigated by filtering the suspension at the end of the experiment, after 24 and 48 h.

The product of our synthesis was investigated morphologically by scanning electron microscopy (SEM) using a FEI Quanta 400 operating at 30 kV, equipped with X-ray energy-dispersive spectroscopy (EDS). X-ray powder-diffraction patterns were obtained using a Seifert diffractometer operating at 40 kV and 30 mA. The XRD patterns were recorded from 5° to 60° 2θ at a rate of 0.02° per step and with a counting time of 8 s per step using Cu Kα radiation. For Fourier transform infrared (FTIR) analysis, powdered samples were dispersed in KBr in excess without further manipulation. The spectra were obtained in Diffuse Reflectance (DRIFT) using an Equinox 55 Interferometer (Bruker) in the 7500–$400\,cm^{-1}$ interval. The resolution was $2\,cm^{-1}$.

The thermal measurements, thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA), were carried out using a Thermal Analyst model 2920 instrument. The heating rate was $10\,°C\,min^{-1}$ with samples of 5–10 mg, with a modulation amplitude $\pm0.5\,°C$ every 60 s in temperature range between 25 and $1000\,°C$. The Mg content in the residual solution was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Varian Vista RL CCD simultaneous spectrometer. The detection limit was $0.01\,mg\,L^{-1}$, and the analytical error was estimated to be in the order of 3%.

3. Results of the syntheses

Information on the kinetics of the reaction is summarized in Fig. 1. The reaction rate is rapid, with carbonate deposition almost complete in about 10 min. The solid product that formed shows a variable grain size and degree of crystallinity as a function of time taken for settling. Samples obtained after 24 or 48 h exhibit well-formed needles up to 0.5 mm in length and 30 μm in diameter under the optical and electron microscope (Fig. 2).

Fig. 3 shows a typical XRD pattern; narrow peaks reflect the high degree of crystallinity of the precipitate. All patterns are in agreement with those reported in JCPDS card 20-669 for nesquehonite. In our experiments the formation of nesquehonite occurred in a range of pH 7.8–8.2. The above pH conditions were obtained
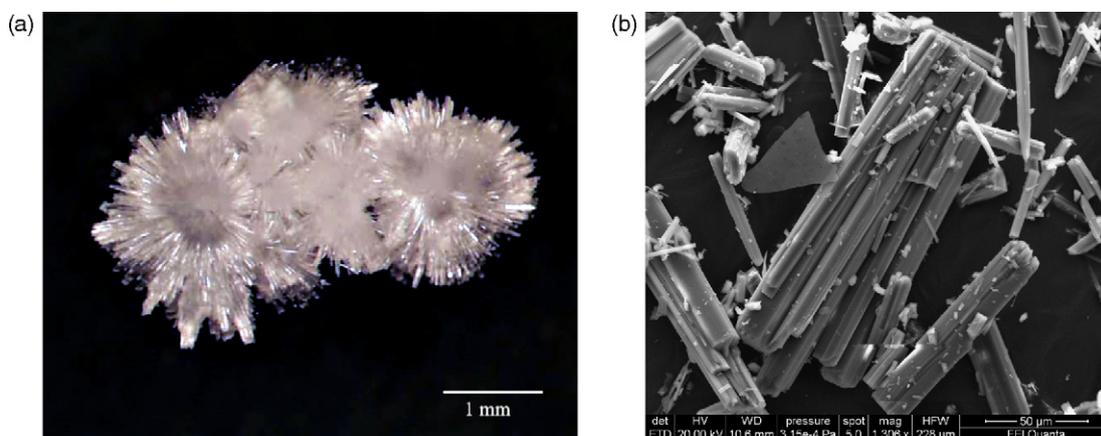
Fig. 2. Images of nesquehonite. (a) Optical micrograph exhibits clusters showing the typical elongate habit; (b) SEM image of nesquehonite at high magnification.
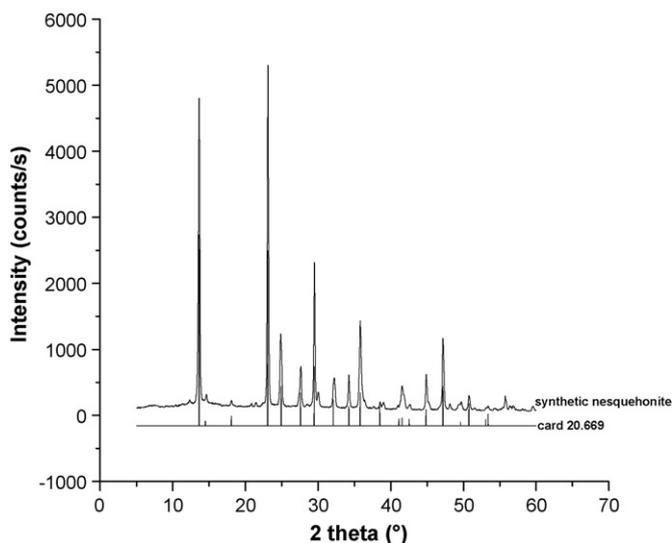

Fig. 3. XRD pattern of synthetic nesquehonite compared with the strongest lines recorded in JCPDS card 20-669.

adding an amount of ammonia solution representing about 2% of the total volume of the Mg chloride solution. The pH range that we determined partially overlaps that reported in the literature [36].

Infrared spectra recorded for our synthetic nesquehonite are in agreement with those reported in the literature [28,37–39]. Fig. 4a illustrates the internal modes of nesquehonite in which the internal vibrations ν_1 (symmetric stretching) and ν_2 (bending) of CO_3^{2-} appear as sharp bands. The three bands near 1425, 1471 and 1519 cm^{-1} are ascribed to the split ν_3 (antisymmetric stretching), characteristic of nesquehonite [28,35,37]. The 1648 cm^{-1} band can be ascribed to an OH-bending mode of H_2O [39]. The broad absorption band around 972 cm^{-1}, not observed in every case [28,38], has been explained as the characteristic absorption band of O–H···O out-of-plane bending mode in the bicarbonate ion [39] (Fig. 4a); however, the results of Giester et al. [33] and Coleyshaw et al. [35] do not confirm the presence of bicarbonate groups in the structure of nesquehonite. The stretching of the hydroxyl group and the H_2O molecule gives rise to broad bands in the region near 3000–3600 cm^{-1} (Fig. 4b).

The TG–DTG curves given in Fig. 5 document the thermal decomposition of nesquehonite during gradual heating, proceeding *via* dehydration at a low-temperature (below 350 °C) and, above that threshold, complete loss of CO_2 (427 °C). By comparing the curves (Fig. 5), we can conclude that dehydration of the mineral takes place at the following endothermic steps: 98, 117, 144 and 220 °C. The total amount of H_2O liberated is ~34 wt.% (see tangent lines on the TG plot). On the basis of stoichiometry, we infer that the mass loss over the interval 100–200 °C marks the loss of two molecules of H_2O from nesquehonite (Fig. 5, DTG curve). The loss of OH groups occurs at a temperature above 250 °C, and it is partially
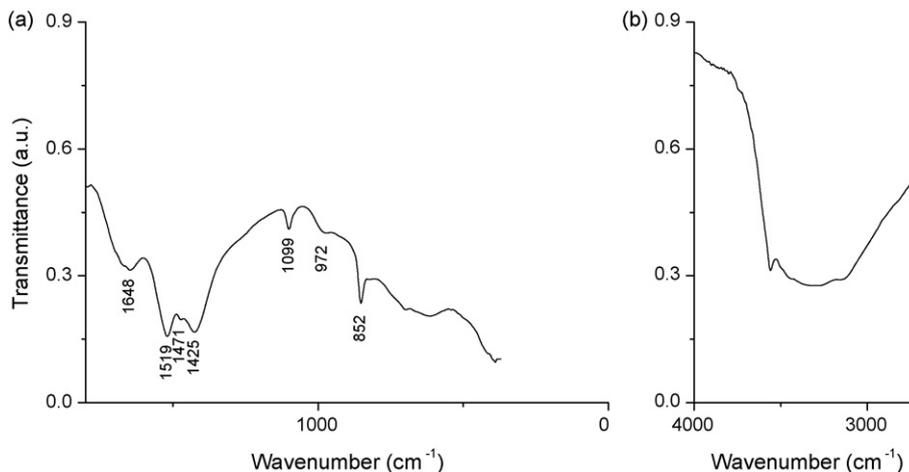

Fig. 4. FTIR spectra of nesquehonite. (a) Internal modes of the CO_3^{-2} (ν_2 mode occurs at 852 cm^{-1}; ν_1 mode at 1099 cm^{-1}; ν_3 mode at 1519, 1471, and 1425 cm^{-1} adsorption bands), and the O–H bending mode of H_2O at 1648 cm^{-1}; (b) the hydroxyl group and H_2O molecules stretch in the region near 3600 cm^{-1}.
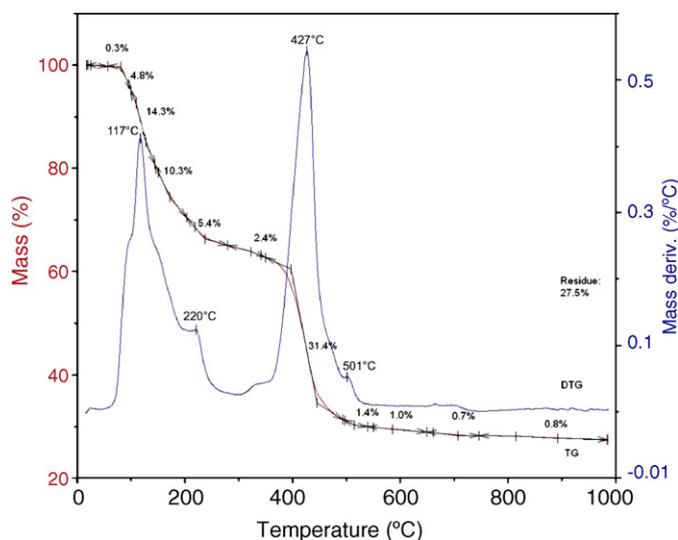
Fig. 5. TG–DTG curves of nesquehonite. The loss of H_2O molecules starts at about 110 °C; whereas the decarbonation process takes place above 350 °C, and mostly at 427 °C. The green line represents the profile of TG analysis, blue line DTG and mass percent losses calculated as tangent lines on the TG curve are shown in black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

hidden by the endothermic reaction due to the release of CO_2. The decarbonation process takes place mainly in the endothermic step at 427 °C, with a pronounced loss in mass (Fig. 5, DTG curve). The total amount of carbon dioxide liberated is ∼32 wt.% (see tangent lines on the TG curve).

Our thermal data on the field of stability of nesquehonite are in good agreement with those reported in the literature [27,38,40–43]; minor discrepancies in the temperature of the endothermic steps can be ascribed to differences in the experimental conditions. Vágvölgyi et al. [44] showed that better resolution and a more detailed interpretation of the decomposition processes of magnesium carbonates could be obtained using controlled rate thermal analysis (CRTA).

The efficiency of the CO_2 mineralization process has been tested by measuring the amount of synthesized nesquehonite and the concentration of Mg in the residual solutions. The amount of nesquehonite produced in our 32 experiments ranged from 4.86 to 5.15 g. On the basis of these experimental data, about $81.7 \pm 0.7\%$ of the sparged CO_2 was captured to form nesquehonite. Only ∼350 mg L^{-1} of Mg are left in the solution after the carbonate formation, representing ∼5% of the starting concentration of Mg.

4. Discussion

4.1. Sources of magnesium available

Potential magnesium sources involve seawater, artificial salt-pans, and evaporitic saline deposits. Currently, most of them are unsuitable for a cost-effective and energy-efficient process of CO_2 sequestration; to transport these sources of magnesium to industrial sites emitting CO_2 for the application of the carbonation process is, in general, too costly. In addition, these sources are abundant only locally to realistically be feedstock for the broad application of the carbonation process. However, they locally can represent point sources for small-scale industrial applications of the proposed method of carbonation.

A massive supply of magnesium could be provided by saline aqueous wastes produced as a by-product of oil and gas production, the so-called produced water (PW), as well as rejected brines from the desalination process. Approximately 70 billion barrels of PW are generated worldwide each year [45]. About 65% of PW is re-injected into wells to enhance oil recovery, whereas the remaining water is managed by treatment followed by surface discharge. However, the re-injection process and methods of treatment are costly. Currently, in many countries, the regulatory standards for the discharge of PW are becoming very stringent [46,47]. The amount and quality of PW depend mainly on the geological conditions, the method of extraction, and the chemical process used for the treatment. The average composition of PW, as reported by Kanagy et al. [48], includes 6% Mg chloride. Our experimental work was performed using Mg chloride solution having a concentration factor about 1/10 of PW to verify the efficiency of the method even at this low concentration. Therefore, PW after treatment for the abatement of residue hydrocarbons, metals, and treatment chemicals could be a suitable source of magnesium for the proposed method, contributing to abatement of their discharge in massive quantities.

4.2. The stability of nesquehonite in an acidic environment

Although nesquehonite is thermodynamically stable under ambient conditions [19,31], possible leakage of CO_2 could occur if it is exposed to rain. Teir et al. [22] reported stability of magnesium and calcium carbonate minerals in nitric acid solutions at various conditions of acidity. They demonstrated that no appreciable CO_2 release will occur if a mixture of Mg hydrate + anhydrous carbonate is leached in solution of pH > 2. Their results also showed a higher stability of Mg carbonate than Ca carbonate in order to dispose CO_2. Because the pH of acid rain is unlikely to be below ∼2.5 [49], the possible release of CO_2 from sites of nesquehonite storage due to acid rain should be unimportant.

4.3. Possible uses for the nesquehonite and recycling of the by-products of the process

The sequestration of CO_2 *via* carbonation produces a solid material that can be utilized as aggregate in bricks, blocks, mortars, and other building materials. This mineral can be used in the production of eco-cement concretes [50,51]. Nesquehonite contributes to strength of the concrete, most likely because growth of fibrous and acicular crystals improves microstructural strength by about 50% compared to rounded or tabular crystals such as calcite [52]; particle size does not seem to be significant in this respect. However, the use of nesquehonite is obviously unsuitable for the production of materials that will be submitted to a thermal treatment above 100 °C, because structural changes caused by dehydration process could result in variations in mechanical strength. Nesquehonite storage in suitable sites below 350 °C presents limited risk with respect to the possible release of CO_2. However, nesquehonite in arid conditions or at temperature above 50 °C transforms in other hydrated Mg carbonate minerals thermodynamically more stable (e.g., dypingite and hydromagnesite) [53–55] that have a CO_2:Mg ratio lower than that of nesquehonite. The sequence of transformation of hydrated Mg carbonates at higher temperature could ultimately produce magnesite, resulting in a CO_2 storage stable for millions of years.

The CO_2 mineralization process leaves behind two moles of hydrochloric acid for every mole of CO_2 captured. As adjusting the pH of the solution involves adding of 2% ammonia solution (aqueous ammonia 25%), recycling the solution several times means that the final by-product will be an NH_4Cl–H_2O mixture. Two different approaches are possible in order to regenerate or recover the by-products. Firstly, the ammonium chloride–H_2O mixture can be used to prepare crystalline ammonium chloride, which has specific fields of application such as electrolyte in dry cell batteries, pharmaceuticals, fertilizers, mordant, dye, soldering flux, melting snow, etc.

Ammonium chloride crystallization from aqueous solutions can be obtained by different methods according to the way which is used to create supersaturation [56,57].

An alternative approach is the regeneration of ammonia using activated carbon (AC) [58]. These authors found that AC can decompose NH_4Cl and separate it into NH_3 and HCl at 25 °C following the equation

$$NH_4Cl + AC \leftrightarrow NH_3 + AC\cdot HCl$$

The resulting ammonia can be recycled for the carbonation process, whereas the activated carbon can be regenerated by water extraction from the adsorbed HCl [58]. The hydrochloric acid produced is sought for a large number of applications, such as leather processing, building construction, and household cleaning.

Indications on costs, including energy, for producing nesquehonite will be evaluated when we apply the method to a pilot plant whose production is in progress.

4.4. Advantages of CO_2 sequestration in synthetic nesquehonite

While awaiting alternative carbon-free sources of energy, the scientific community must propose and develop carbon-capture technologies [17,18,59] necessary to mitigate the amount of carbon dioxide in the atmosphere [60–62], which must be reduced with some urgency in the short term. The application of the nesquehonite approach as a complementary solution to point source CO_2-emitting plants could contribute to compliance with the Kyoto Protocol, which would help industrialized countries satisfy part of their obligations to reduce their emission of greenhouse gases.

Several advantages make the application of the nesquehonite approach attractive: (i) the process is kinetically favored and simple; (ii) nesquehonite formation occurs in a very short time; (iii) it is a thermodynamically and chemically stable solid product, allowing for long-term storage of CO_2; (iv) the starting reactants are locally abundant, and there is the prospect that our method can occupy a cost-effective niche in the sequestration of CO_2 *via* a mineral phase; (v) nesquehonite can potentially be used for industrial purposes, and its disposal near the surface or underground involves limited environmental risks.

Our method, which requires Mg in aqueous solution in large quantities, could use Mg from evaporitic saline deposits, seawater, rejected brine from desalination plants, and saline wastewater produced as a by-product of oil and gas production as the main source. Even if our method should be considered a complementary method of CO_2 sequestration, it could become a main approach for CO_2 abatement locally, in countries where these sources of Mg are significant.

Acknowledgements

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