

Concept Paper

Mineral Carbonation as an Educational Investigation of Green Chemical Engineering Design

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Abstract: Engaging students in the experimental design of “green” technology is a challenge in Chemical Engineering undergraduate programs. This concept paper demonstrates an educational methodology to investigate accelerated mineral carbonation, which is a promising technology related to mitigation of climate change by sequestering carbon dioxide (CO₂) from industrial sources as stable solid carbonates. An experimental investigation is conceived, whereby students test the effect of two process parameters (CO₂ pressure and mixing rate) on the extent of carbonation reaction. The carbonation reaction has been performed using a mineral called wollastonite (CaSiO₃). The experimental study and laboratory report cover principles of reaction kinetics and mass transfer, while illustrating the steps to develop and investigate a green process technology. The results from the experimental investigation, which is carried out by multiple teams of students, are then pooled and used to guide a subsequent design project. Students would conceive a flowsheet, size equipment, and estimate the energy demand and net CO₂ sequestration efficiency of a full-scale implementation of the mineral carbonation technology. This educational investigation aims to help undergraduate students to acquire deeper experiential learning and greater awareness of future green technologies by applying fundamental engineering principles into an engaging experimental and design exercise.

Keywords: mineral carbonation; reaction kinetics; mass transfer; wollastonite; experimental investigation; process design; green chemical engineering; climate change mitigation

1. Introduction

Sustainability planning requires fundamental investment on education, moving towards training students in innovative environmental technologies that they should be aware of to develop cleaner production processes, and to be capable of participating in and promoting continuous improvements in the economy, environment, and society [1]. Green Chemistry is a scientific field created as a consequence of pollution prevention initiatives, and it is based on principles that reduce waste production, promote efficient use of resources, and decrease demands on energy while improving environmental sustainability [2]. The implementation of Green Chemistry has provided many opportunities for professors to design innovative and environmentally friendly experiments as well as developing their secondary courses, to educate and guide the next generation of chemistry professionals [3,4]. This common practice of incorporating Green Chemistry into curricular activities and the design of novel experiments assists students in developing comprehensive perspectives skills, moving them beyond simple yields calculations to environmentally sustainable practices [5].

In the study of applied chemistry and chemical engineering, practical work has unquestionable importance, given its relevance for professional job preparation, and can certainly provide unique opportunities to develop investigative skills [6,7]. However, most laboratory experiments performed by

students in undergraduate programs (at universities, polytechnic institutes, and colleges) are based on well-established reactions and physical phenomena that were originally developed based on industrial practices that are now decades old. The lack of coherent learning objectives and the observed student isolation in laboratories could cause to disengage them from the learning process [8]. Although faculty members have decreased student isolation over the years, assigning students to work in collaborative teams is more effective [8].

In the authors' experiences as teachers and students, it is noticed that many laboratory experiments and design projects used in coursework (apart from capstone projects) are disconnected from one another, and students often perform identical experiments to other students or are not allowed or encouraged to share data. This results in students not having the opportunity to further utilize and build on the experimental data they produce, and the experimental dataset the class produces. Time (i.e., experiment duration), the high cost of laboratory equipment, and, in some cases, excessive procedural complexity, represent constraints to explore innovative ideas and collaborative and progressive work in the educational setting.

It is the authors' conception that students are more likely to feel engaged in this experiential learning when they can see the importance of what they are required to do, be it a skill that they think they will use in the future, or knowledge they will gain about real-world issues and solutions for them. Martínez and Campos [9] discuss how the level of accomplishment between students is directly linked to the commitment level they demonstrate, which is reflected by how they address their inquiry questions and the quality of the concept studied before starting the experimental activity, also improving the scientific thinking ability.

There are plenty of Green Chemistry and sustainable technology topics that are or have recently started finding their way into real-world implementation [10,11]. Carbon sequestration is one of the main strategies available for climate change mitigation via reduction of greenhouse gas emissions, and among the many options for carbon sequestration, mineral carbonation is one that has a potential to sequester significant amounts of carbon dioxide (CO₂) [12–16]. This technology has a high potential to capture and safely store massive amounts of CO₂ to mitigate the increase of the atmospheric concentration, which has risen from around 280 ppm, at the beginning of the industrial revolution, to over 410 ppm, according to National Oceanic and Atmospheric Administration [17] and The International Panel for Climate Change [18].

Mineral carbonation is the reaction between CO₂ and alkaline minerals (i.e., those that contain alkaline earth elements) that produce geologically stable carbonate minerals, such as calcite (CaCO₃), dolomite (CaMg(CO₃)₂), magnesite (MgCO₃), and, in some cases, even siderite (FeCO₃) [12,13]. Alkaline minerals come in different varieties: they include mafic and ultramafic igneous rocks, such as basalt, wollastonite, olivine, and serpentine, but also solid residues from the steelmaking industry, waste incineration, and building demolition, such as slags, ashes, or asbestos [19–22].

Mineral carbonation is a challenging theme to demonstrate to students because the chemical reaction at ambient conditions, also referred by geologists as “weathering”, proceeds extremely slowly over a geological time scale, consequently demanding accelerated process conditions for experimental analysis. This also relates to the need for accelerated carbonation for industrial implementation. To mitigate anthropogenic CO₂ emissions, the reaction must be sped up to the point where CO₂ can be fixated at the same rate that it is generated in the burning of fossil fuels (or calcination of limestone), to create an economically and environmentally sustainable process. Still, after many years of research and development, mineral carbonation is beginning to be implemented at the industrial scale. Examples of companies around the world using mineral carbonation, primarily to produce building materials, include CarbonCure Technologies in Canada [23]; Carbon8 Systems in the United Kingdom [24]; Mineral Carbonation International in Australia [25]; Solidia Technologies in the United States [26].

Aims and Objectives

Given its strong link to concepts of sustainability and Green Chemistry and process requirements that apply principles of reaction kinetics, transport phenomena, and materials characterization, the present work aimed to find a way for accelerated mineral carbonation to earn a place in chemical engineering curricula. To this end, an experimental investigation laboratory procedure and a design project outline were conceived and applied (for the first time in Summer 2017) in the Chemical Engineering Technologist Advanced Diploma program at the Sheridan College Institute of Technology and Advanced Learning. As a way to further engage students in this learning experience, the process conditions for the laboratory work were varied between groups of students, and the experimental data obtained were pooled to be used by every group for the subsequent design exercise. This was meant to give students motivation to generate accurate data that they knew would be useful for the entire class and, at the same time, provide students with the opportunity to use data generated by colleagues, much in the same way the design work is done in the industry.

The experimental investigation and design project, herein presented, are suitable for implementation in upper-year undergraduate (Bachelor or Advanced Diploma) engineering and engineering technology programs, and also for graduate courses at the Master's level. For example, in 3rd or 4th year of University undergraduate degrees and 3rd year of College diplomas in North America, or the 3rd, 4th, or 5th years of higher education programs in countries that follow the Bologna Accord (i.e., Europe).

The ultimate objective was to better train chemical engineering students given their future careers. Graduates with experience in mineral carbonation investigation and design would potentially be better trained to develop engineering solutions that take into account sustainability criteria. Also, having gone through a memorable undergraduate exercise in mineral carbonation investigation and design would potentially reinforce learned concepts of chemical engineering fundamentals, and make it more likely that graduate would recall those fundamental concepts in their future careers.

Section 2, 3, 4, and 5.1 of this concept paper, along with the two Supplementary Materials files, present the information that was provided to students in their laboratory investigation procedure and design project outline. Section 2 gives the background of the mineral carbonation process, which helps students to become familiar with the subject and to see links with fundamental concepts they learned in the classroom, including in previous classes. Section 3 and Supplementary_Material_1 provide students with the knowledge and step-by-step instructions on how to perform the experimental investigation. Section 4 details the calculations required to process the experimental data, and additional questions students must answer related to the investigation and the subject matter to interpret and explain the achieved results. Section 5.1 and Supplementary_Material_2 provide students guidance on the design project (to be implemented in a future course), both in terms of requirements and a general procedure (allowing student some freedom on how they set-up and analyze their design). In Section 5, the experience with running the experimental investigation at Sheridan College is discussed, and, in Section 6, conclusions are offered.

2. Experimental Investigation Part A: Background of Mineral Carbonation

Fundamentally, mineral carbonation occurs when carbon dioxide reacts with metal oxides or natural alkaline silicates (containing calcium or magnesium). The corresponding carbonate is formed, releasing heat, according to the following chemical reaction (Equation (1)), where M represents a divalent metal [27]:



Silicates rocks are available in vast amounts worldwide and represent the ideal material for mineral carbonation. Often used minerals include olivine ((Mg,Fe)SiO₄) [28], forsterite (Mg₂SiO₄) [29], serpentine (Mg₃Si₂O₅(OH)₄) [30], and wollastonite (CaSiO₃) [31]. Several industrial residues (such as combustion/incineration ashes, mining tailings, and metallurgical slags) also contain alkaline silicates,

often more complex, such as chrysotile ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$) [32] and brownmillerite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$) [33] and, at times, amorphous (lacking crystal structure). Calcium-based minerals are usually more reactive than magnesium-based minerals, basically, because the Ca atom is larger than the Mg atom, and consequently the valence electron is less tightly bound to the Ca atom. Wollastonite is one of the most reactive natural minerals to carbonation, but it is also less abundant than other less reactive minerals [34]. When milled, its particles normally have an acicular (needle-like) morphology of high aspect ratio (i.e., much longer in one dimension and much narrower in the others) [35] (Figure 1). Stoichiometrically, 1.16 t of wollastonite can sequester 1 t of CO_2 .

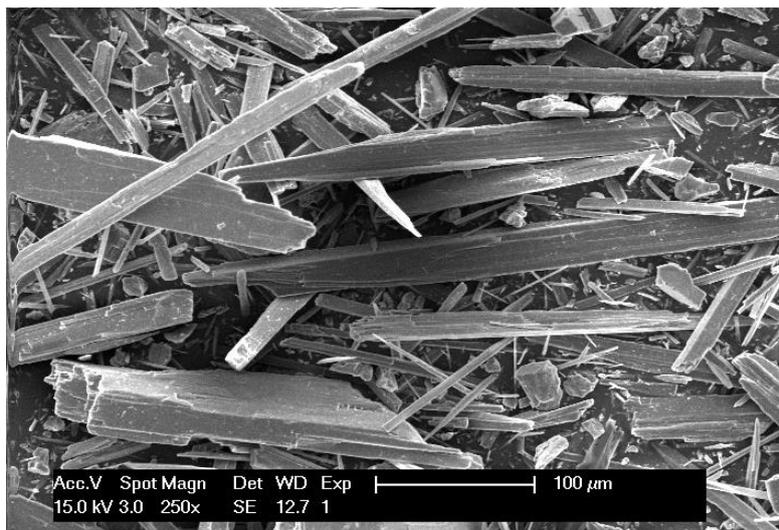
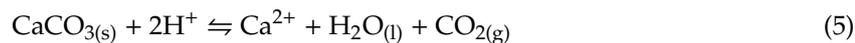
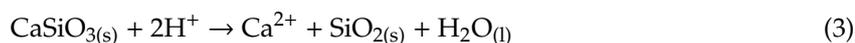
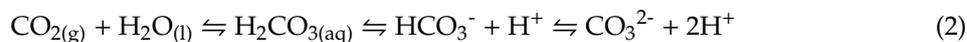


Figure 1. Electron Microscopy image of acicular (needle-like) wollastonite particles (Casiflux®F 125 (NYCO Minerals, Willsboro, NY, USA), $D_{50} = 57 \mu\text{m}$) used in the present experiments.

According to the dissolution reaction of carbon dioxide (Equation (2)) and the principle of le Chatelier-Braun, the carbonate and bicarbonate anion and hydronium cation concentrations increase as the CO_2 partial pressure rises. Thus, the diffusion rate, silicate dissolution rate (Equation (3)), and the rate of calcium carbonate precipitation (Equation (4)) also increase, up to a point, where the pH becomes too low and the carbonate begins to dissolve again (Equation (5)). This is not so problematic, as gas compression is also costly, so an optimal level of compression would exist that maximizes the rate of CO_2 sequestration while maintaining reasonable cost. It is important to note that because several chemical reactions occur simultaneously in the system, it could happen that a change in processing conditions would improve one reaction, but be detrimental to the overall reaction (Equation (6)) rate.



The more acidic the bulk solution is, more free protons are available to attack the mineral and leach the Ca from its matrix. Looking at the reactions above, this also becomes clear using the Le Chatelier-Braun principle. The lowering of the pH could be achieved by increasing the CO_2 pressure or by adding external acids. The carbonate would eventually have more trouble to precipitate; however, it dissolves when the pH is too low. This is not usually a problem when solely carbonic acid is the acidic

species since the dissolution of the silicate (Equation (3)) consumes the acid formed (Equation (2)). Daval et al. [36] reported that, with $p\text{CO}_2 = 250$ bar and $T = 90$ °C, the equilibrium pH of an aqueous solution of CO_2 was 3.07, but increased to 4.61 in the presence of carbonating wollastonite.

Because the mineral carbonation reaction (illustrated in Figure 2 for steelmaking slag) proceeds by the diffusion of carbonate anions into a solid mineral matrix, it is imperative that a high surface-to-volume ratio is created by first crushing the mined ore and subsequently milling the particles to a specified particle size [37–39]. To further improve the overall reaction rate, aside from reducing the particle size and increasing the CO_2 pressure, another strategy is to introduce chemical additives to the aqueous phase. These additives could help to increase the CO_2 solubility and carbonic acid dissociation (by shifting Equation (2) equilibrium), increase the mineral dissolution rate (by shifting Equation (3) equilibrium), or reduce the acidification (to avoid the reaction of Equation (5)). Chemicals, such as NaOH , NaHCO_3 , NH_4Cl , and acetic acid, have been used for these purposes [40]. Additives do pose challenges; however, they can be costly and need to be separated and regenerated to be recycled.

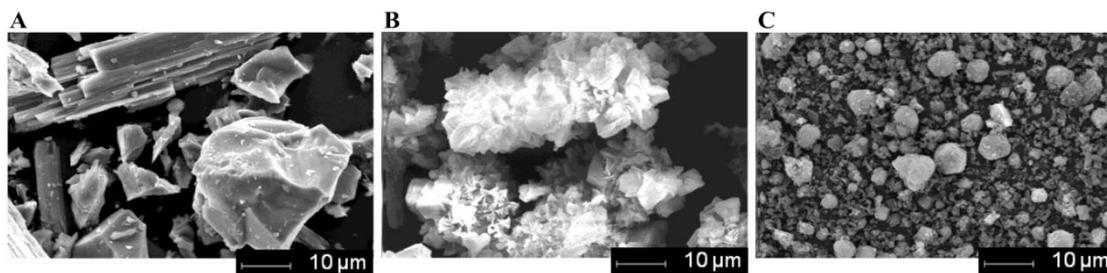


Figure 2. Comparison of particle morphology of original (A); stirred carbonated (B); sonicated carbonated (C) Continuous Casting slag powders [41] (CC BY).

2.1. Reaction Rate and Kinetics

The reaction rate (r) of wollastonite dissolution in acidic medium is reported to obey the following expression (Equation (7)) [42]:

$$\ln(r_{\min}) = \ln(A) - E_A / (R \times T) \quad (7)$$

where r_{\min} is the mineral dissolution rate ($\text{mol}/(\text{m}^2 \cdot \text{s})$), A is the pre-exponential empirical factor ($(1.8 \pm 0.9) \cdot 10^3 \text{ mol}/(\text{m}^2 \cdot \text{s})$ in the case of wollastonite dissolution in acetic acid [42]), E_A is the apparent activation energy of dissolution ($47 \pm 1 \text{ kJ}/\text{mol}$ [42]), R is the universal gas constant ($\text{kJ}/(\text{mol} \cdot \text{K})$), and T is the temperature (K).

Since mineral dissolution is seen as the rate-limiting step in mineral carbonation (CO_2 dissolution and carbonate precipitation are comparatively fast [36]), the rate of carbonation (R_{carb} (mol/s)) can be estimated from the rate of dissolution and the available mineral surface area ($A_{\min,(t)}$ (m^2)) by the following expression (Equation (8)):

$$R_{\text{carb}} = r_{\min} \times A_{\min,(t)} \quad (8)$$

The available mineral surface area is a function of time (t) since it will gradually reduce as carbonation proceeds (i.e., the reaction front shrinks from the surface of the particle towards its core, as illustrated in Figure 3). It can be approximated by the product of the initial specific surface area (SSA (m^2/g)) of the mineral, the fractional extent of carbonation conversion of the mineral at the reaction time ($\xi_{(t)}$), and the initial mass of wollastonite being carbonated ($m_{\text{wo,init}}$ (g)) (Equation (9)):

$$A_{\min,(t)} = \text{SSA} \times (1 - \xi_{(t)}) \times m_{\text{wo,init}} \quad (9)$$

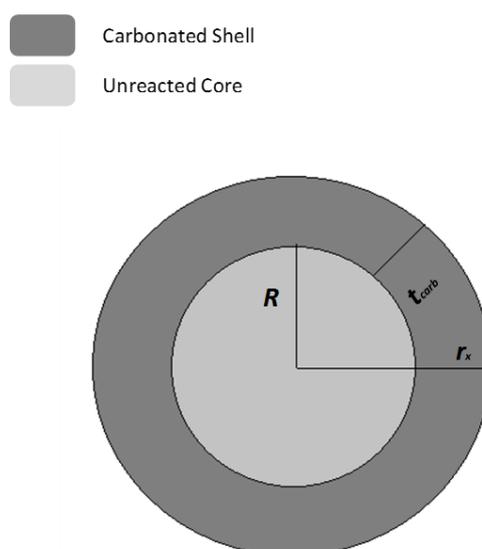


Figure 3. Illustration of the partially carbonated mineral particle, according to shrinking core model [43], where r_x is the original particle radius, R is the radius of the unreacted core of the particle, and t_{carb} is the thickness of the carbonated shell. Re-used with permission from John Wiley and Sons (4592190232399).

The fractional extent of carbonation conversion of the mineral at the reaction time is the ratio of the number of mols of calcium that have become CaCO_3 at the reaction time ($n_{\text{CaCO}_3(t)}$) over the total number of mols of calcium in the wollastonite being carbonated ($n_{\text{wo,init}}$), according to Equation (10):

$$\xi_{(t)} = n_{\text{CaCO}_3(t)} / n_{\text{wo,init}} \quad (10)$$

Reacted Particle Morphology

When wollastonite carbonates, two solid products form: calcium carbonate (typically as the calcite polymorph) and amorphous silica. The behavior of these two product phases, in terms of where they end up, differs. Daval et al. [44] observed that at the micrometer-scale, wollastonite replacement occurred pseudomorphically: the acicular shape of the wollastonite grains was preserved, as the silica product remained in the place where wollastonite originally existed. Thus, in each particle, the silica layer remains adjacent to the unaltered wollastonite core. Daval et al. [44] postulated that the pseudomorphic texture implied an intrinsic silica precipitation rate much greater than the dissolution reaction. As a result, silica product that detaches from the reacting wollastonite interface is immediately reprecipitated by the silica layer-wollastonite core interfacial region, thus preserving the original particle morphology.

In cases where the wollastonite particle contains secondary phases (such as diopside ($\text{MgCaSi}_2\text{O}_6$), this phase may further slow the carbonation reaction, especially if it is inert to carbonation, or has much slower carbonation kinetics (which tends to be true for magnesium-based silicates). Depending on the degree of mixing of wollastonite with diopside, the diopside may appear as separate grains upon milling, or as micro-crystals within the wollastonite matrix [34]. In the former case, its effect on carbonation kinetics of wollastonite should be minimal, but in the latter, where it would accumulate in the calcium-depleted layer surrounding the unreacted core, it could have a significant effect in hindering ion diffusion.

2.2. Effects of Process Parameters

2.2.1. Temperature and CO_2 Pressure

Temperature is an important process parameter that can be adjusted to improve the overall rate of reaction. There are two phenomena that are dependent on temperature: (i) the solubility of

carbon dioxide, which decreases with higher temperatures, and this results in a higher pH, which is detrimental for the mineral dissolution rate; (ii) the dissolution rate of silicate minerals, which, on the other hand, increases with higher temperatures.

Because of the opposite direction of these two concurrent effects, an optimum temperature exists for the carbonation of each mineral. In the case of wollastonite, it has been reported that the process should be conducted below 200 °C [45], depending on the CO₂ pressure [46]. The higher the pressure, the higher the optimum temperatures would be.

2.2.2. Agitation

CO₂ in the gas phase is transported across a gas-liquid interface, as it dissolves from the headspace into the slurry below. The mechanism of calcium ions reaction is less clear; there are two scenarios. In one scenario, calcium ions move as ions from the surface of the solid particles to the liquid phase and then react with carbonate ions to precipitate as calcium carbonate crystals. Another scenario is that calcium ions precipitate at the surface of particles, where they meet the carbonate coming from the liquid phase, and later calcium carbonate crystals are dislodged from the surface due to agitation [47].

Mass transfer can be improved in the liquid phase, to aid in CO₂ dissolution and calcium carbonate crystallization, by agitation. Agitation improves the convective mass transfer mechanism, which is more important than diffusion in the liquid phase [48]. Convection enhances mass transfer across interfaces by reducing the thickness of boundary layers (the region near an interface where ions accumulate), thus increasing the driving force: the concentration difference. Ideally, for ions to leach out from a solid surface, the concentration of that ion in the liquid phase, at the interface, should be as close to zero as possible, which is possible in a system where the ion later precipitates in the liquid [49].

2.3. Determination of the Reaction Extent

As wollastonite (and any other calcium- or magnesium-rich mineral) reacts with CO₂, solid carbonates form. These carbonates can be Ca-carbonates, Mg-carbonates, and a variety of Ca-Mg-carbonates [50]. The most common Ca-carbonate is CaCO₃, referred to as calcium carbonate, which forms under a range of process conditions. Calcium carbonate is particularly special as it can have three polymorphs: calcite, aragonite, and vaterite. All have the same chemical composition, but different crystal structures (and consequently particle morphologies). A less common Ca-carbonate would be monohydrocalcite (CaCO₃·H₂O). When magnesium is also present in appreciable quantities in the mineral ore, calcium can co-precipitate with magnesium to form Mg-rich carbonates, such as huntite (Mg₃Ca(CO₃)₄), and Ca-rich carbonates, such as magnesian-calcite (Mg_{0-0.15}Ca_{0.85-1}CO₃). Finally, when Mg-carbonates are the predominant carbonation products, possible forms include anhydrous MgCO₃ (magnesite), its hydrated form as nesquehonite (MgCO₃·3H₂O), among others.

For CO₂ sequestration by wollastonite, and for kinetics and mass transfer determinations, the principal need is to determine the total amount of CO₂ bound in mineral form. Also, given the chemical composition of wollastonite ore, it can be assumed that CaCO₃ is the predominant carbonate product. Thus, how does one determine the amount of CaCO₃ in a solid sample? Four common approaches are briefly described next. In addition to these, other more specialized techniques exist that can identify and/or quantify the presence of carbonates. Some are standalone techniques, and others are used in combination with other techniques; examples include: Energy Dispersive Spectrometry (can detect elemental carbon and its spatial association with other elements), Fourier Transform Infrared (can detect chemical bonding of carbonates in solid phase, and CO₂ in gas phase), Mass Spectrometry (can detect CO₂ in gas phase), Total Carbon Analyzers (can determine total carbon, total organic carbon, and total inorganic carbon contents), among others.

2.3.1. X-ray Diffraction (XRD)

The most direct method of detection is by X-ray Diffraction (XRD) analysis. This is a technique that determines the distance between atoms in a crystal, thus allowing precise determination of the

types of minerals present in a sample. Using the Rietveld Refinement Method and internal standards, it is possible to estimate with reasonable accuracy and precision ($\pm 2\text{--}3$ wt %) the mass fractions of different crystalline minerals in the sample, as well as the total mass fraction of amorphous content [51]. Of the four methods described here, this is the only one that could differentiate calcite from aragonite (polymorphs of CaCO_3) [52]. An example of an X-ray diffractogram showing this distinction is seen in Figure 4.

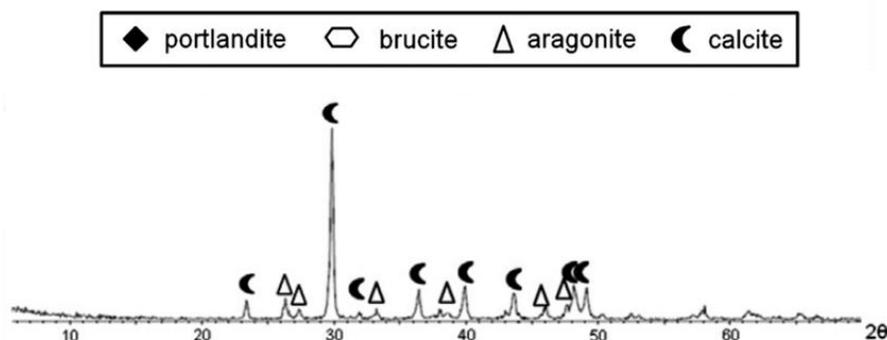


Figure 4. X-ray diffractogram of carbonated calcium hydroxide, with major crystalline phases indicated [51]; re-used with permission from Elsevier (4592190838155).

2.3.2. Thermogravimetric Analysis (TGA)

Another instrumental method to detect carbonate content of solid samples is Thermogravimetric Analysis (TGA). This method relies on the thermal decomposition of carbonates when samples are heated to elevated temperatures, which causes the solid sample to lose mass. In theory, different carbonates will demonstrate different decomposition temperatures. However, the method is not able to precisely discern carbonates with close decomposition temperature [53]. Most commonly, the mass losses are divided into two stages: between approximately $300\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$, MgCO_3 decomposes, and between $500\text{ }^{\circ}\text{C}$ and $800\text{ }^{\circ}\text{C}$, CaCO_3 decomposes [54]. Hydrated and hydroxylated carbonates will experience some mass loss at lower temperatures, as a result of water release, but the carbonate groups should still decompose in the aforementioned ranges. To avoid overestimation of carbonate content, evolved gas analysis can be used to discern CO_2 from other volatiles [55]. Figure 5 shows examples of TGA curves for CaCO_3 , MgCO_3 , and $\text{Ca}(\text{OH})_2$.

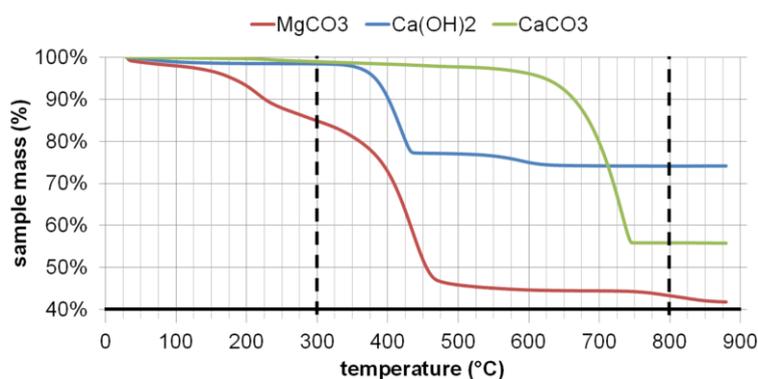


Figure 5. Thermal gravimetric analysis of analytical grade solids [54]; re-used with permission from Elsevier (4592190653818).

2.3.3. Calcimetry

The third method also relies on the decomposition of carbonates, but, rather than using heat, the method uses acidification. This method is called calcimetry or gasometric analysis and is performed

using a calcimeter. The working principle is based on Equation (5); when a carbonate is exposed to a sufficiently strong acid (typically HCl or HNO₃), CO₂ gas is released. The calcimeter measures the volume (or pressure) of released gas, which is used to estimate the carbonate content of the sample. Figure 6 illustrates the use of this method, based on pressure, for determination of MgCO₃ content. An advantage of this method over the TGA method is that only CO₂ is released by acidification, so it avoids possible overlap with vapor release (which is more problematic for samples containing Mg-carbonates). Some disadvantages include lower accuracy, greater detection limit, and the inability to discern between different carbonates, including Mg- and Ca-carbonates [55,56].

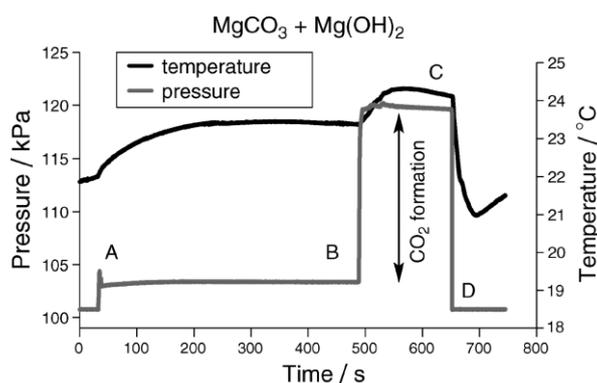
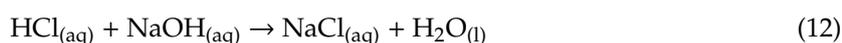
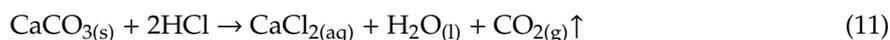


Figure 6. Temperature and pressure profiles of gasometric carbonate analysis experiment, where the letters denote container sealed (A), sample and HCl mixed (B), maximum pressure (C), and container opened (D) [57]; reprinted with permission from Fagerlund et al. [57], copyright 2010 American Chemical Society.

2.3.4. Acid-Base Titration

The last method herein described is the acid-base titration. This method is similar to the previously described gasometric analysis, in that acid is used to dissolve the carbonates. However, detection is done by chemical (pH) rather than physical (volume or pressure) means. The method consists of two steps [58,59]. In the first step, the sample is gradually acidified, typically using HCl, while the pH is monitored. The pH will indicate when the carbonates have been fully consumed (Equation (11)). Before they are consumed, carbonates will buffer the pH, which will remain relatively constant. When the carbonates fully dissolve, a pH step occurs, where the pH will decrease until another component in the mineral becomes the pH-controlling mineral. An example is shown in Figure 7 for the acidification of red mud (a by-product of aluminum production). In red mud, an aluminate controls the pH of the material at first, followed by a silicate at lower pH, and followed by calcite at an even lower pH [60]. As can be seen, the pH of calcite is near nine, and when it is fully consumed by the acid, the pH drops to below six.



At this point in the acid-base titration method, phenolphthalein is added, and the solution is back-titrated with NaOH (Equation (12)), until the phenolphthalein endpoint (pink color). The difference between the amount of acid added and the amount of excess acid neutralized by sodium hydroxide is the amount of acid that is consumed in dissolving the minerals. Back-titration is used because the acid titration reaction cannot be used directly to titrate the CaCO₃, as it is very slow when the reaction is close to the endpoint. Heating the solution can help degas the release CO₂, and thus sharpen the endpoint [61]. Disadvantages of this method are similar to those for gasometric analysis.

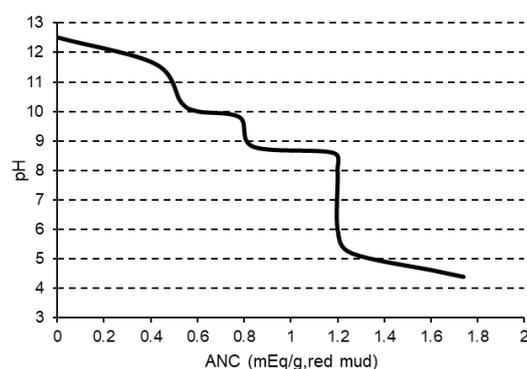


Figure 7. Hydrochloric acid titration curve of red mud, re-plotted using data as simulated by Khaitan et al. [62].

3. Experimental Investigation Part B: Materials and Methods

In the following sub-sections, the materials and equipment utilized for the accelerated mineral carbonation experimental investigation developed and performed at Sheridan College are described. Several other types of alkaline minerals and different types of pressurized reactors can replace those specified below, though process conditions may need to be altered from those described here.

3.1. Mineral

The wollastonite material used in this lab was obtained from NYCO Minerals (Willsboro, NY, USA). The chemical composition of the material was determined by X-ray Fluorescence (XRF) and is presented in Table 1. It consists mainly of calcium and silicon oxides, consistent with the chemical formula of wollastonite, CaSiO_3 . The Ca:Si molar ratio is 1.18, slightly higher than that of pure wollastonite mineral, which is 1. The maximum CO_2 sequestration capacity, based on the calcium and magnesium contents (i.e., if they all become carbonated), would be 409.9 grams of CO_2 per kilogram of wollastonite material. (i.e., if all calcium is carbonated). The resulting product would contain 29.1 wt. % CO_2 . Additional characterization data (mineralogical and particle size analyses) are presented in the Appendix.

Table 1. Chemical composition of wollastonite material, determined by XRF (X-ray Fluorescence) and expressed as oxides.

Oxide	Wt %
CaO	51.2 ± 0.6
SiO ₂	46.4 ± 0.3
Al ₂ O ₃	0.79 ± 0.04
MgO	0.70 ± 0.05
Fe ₂ O ₃	0.52 ± 0.06
K ₂ O	0.14 ± 0.02

3.2. Pressurized Reactor

The reactor used for carbonation was from Parr Instrument Company (Moline, IL, USA), model 4525, which is a continuously stirred, pressurized, and jacket-heated tank reactor. The nominal reactor volume is 1000 mL, and the material of construction of the head, cylinder, and internal wetted parts is Alloy C-276 (commonly referred to as Hastelloy). The reactor sits on a bench-top stand, and is removable, including the head. Figure 8 shows the reactor, with major components indicated, and additional details are illustrated in Supplementary_Material_1. This reactor is capable of withstanding temperatures up to 300 °C (using PTFE flat gasket) and pressures up to 200 bar (2900 psi). The carbon dioxide compressed gas cylinder is supplied by Praxair (Guildford, United Kingdom) (CAS

12-38-9) and is of industrial grade (min. 99.5% purity). Heating is provided by an aluminum-block electrically heated jacket, energized, and regulated by a Parr 4848 proportional-integral-derivative (PID) temperature control unit. Cooling is done by water circulating through the heating jacket, controlled manually via a needle valve. The pressure is provided by the connected gas cylinder, and autogenously by vaporization of water content. Stirring is enabled by a mechanical shaft and impeller, externally coupled to a variable speed 1/4 hp motor and an rpm controller. The stirring shaft is fitted with dual Rushton turbine impellers, and a baffle is present to ensure adequate mixing. The reactor's bottom drain was fitted with a simple plug (replacing the original valve) to allow drainage of liquid and slurry from the reactor.

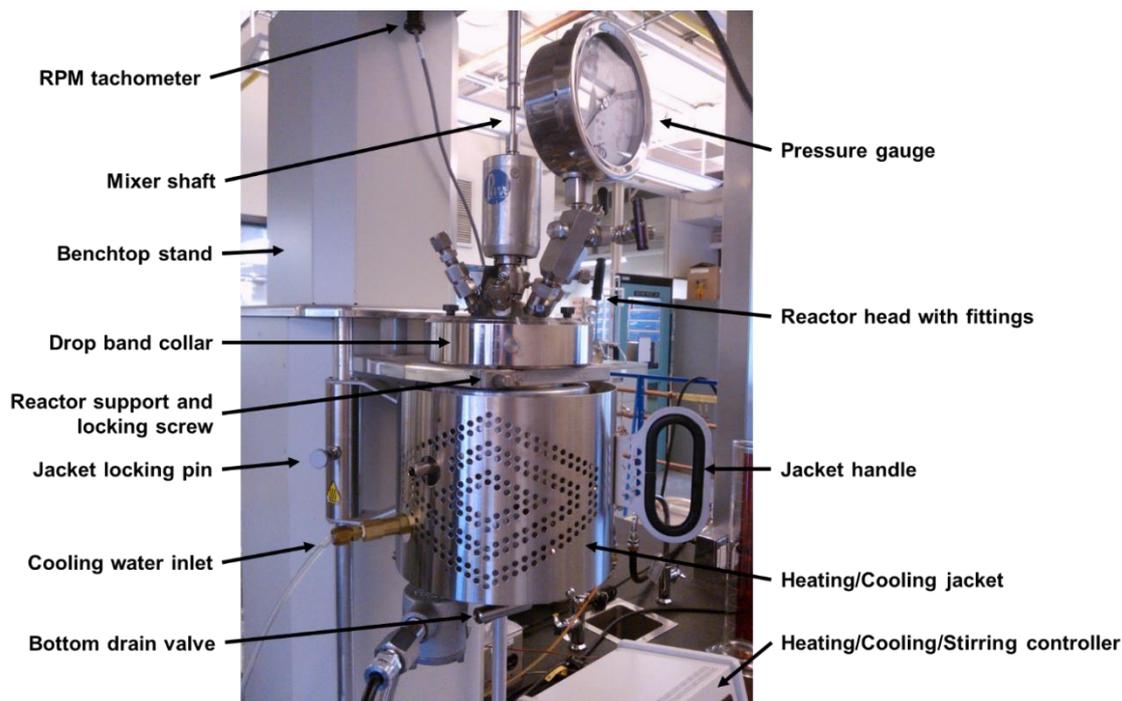


Figure 8. Parr 4525 pressurized reactor, with main components indicated.

3.3. Process Parameters

It is possible to vary several process parameters to study the carbonation of wollastonite in the continuously stirred pressurized reactor. For this lab, which is the study of reaction kinetics and mass transfer, and based on the number of experiments planned, some parameters were kept constant. These include:

- The volume of water in the reactor: the stirrer blades were fixed to a certain height, so changing the amount of water would imply that mixing would become difficult if the water level became too low. Thus, a value that is well suited for the 1 L reactor was used: 800 mL H₂O.
- Mass of solids in the reactor: decreasing the liquid-to-solid (L/S) mass ratio could help promote particle-particle interaction, which might aid in carbonation conversion by eroding the silica layer, but, at too low values, mixing becomes problematic. To ensure good mixing, a relatively high L/S ratio was used: 20 (i.e., 40 g wollastonite material).
- Residence time: the higher the residence time, the higher the carbonation conversion [45]. However, to study the effect of process parameters on reaction extent, differences were magnified at intermediate conversion values, so the residence time should be limited. The reaction residence time was fixed to 30 min.
- Temperature: wollastonite reportedly carbonates best when the temperature is sufficiently high to aid in calcium leaching but not so high that it reduces the solubility of CO₂ too greatly [45].

The temperature choice also impacts the duration of start-up, since heating from room temperature to the reaction temperature takes time, and of shut-down, since the reactor must be sufficiently cooled before it can be depressurized (<100 °C) and before its contents can be drained safely (<80 °C). Hence the temperature to be used was 120 °C (at this temperature, the steam pressure was 0.974 bar, gauge).

- Particle size: particle size is one of the most important parameters for mineral carbonation, as an increase in surface area (i.e., particle size reduction) contributes to the rate of carbonation (Equation (8)). However, reducing the particle size of mined minerals is costly, and the more milling is done, the lower the net CO₂ sequestration for the process (the process can even become a net CO₂ emitter). The material used in this project was milled by NYCO Minerals to the maximum extent that the company still deems economical for commercialization of the mineral; particle size data is presented in the Appendix. According to the results of Huijgen et al. [45], an average particle size below 100 µm is needed for satisfactory kinetics, which is the case for the present material. Hence, the material was used as is, and the initial particle size was constant for all experiments.

Two important process parameters remain for the study of reaction kinetics and mass transfer of wollastonite carbonation: (a) the CO₂ partial pressure, and (b) the stirring rate. Based on the findings of Huijgen et al. [45], the following conditions (two factors with four levels) were used in this experimental investigation:

- CO₂ gauge pressure (barg): 2, 5, 10, 40.
- Stirring rate (rpm): 100, 200, 400, 600.

Based on these parameters, a total of 16 experiments can be performed with unique conditions, according to Factorial Design (4²). Figure 9 indicates these conditions and highlights the conditions that should preferably be used in this lab to study the effect of the process variables (factors) on the reaction kinetics and mass transfer. Each student group shall use a different set of conditions. It should be noted that students only have time to perform a single experiment in a three-hour period, hence replicating experiments to increase the reliability of the experimental results, while important in the professional and research settings, is not expected for these experiments.

<u>E8</u>	<u>E9</u>	<u>E10</u>	<u>E7</u>
2 barg CO ₂ + 100 rpm	5 barg CO ₂ + 100 rpm	10 barg CO ₂ + 100 rpm	40 barg CO ₂ + 100 rpm
<u>E11</u>	<u>E15</u>	<u>E16</u>	<u>E6</u>
2 barg CO ₂ + 200 rpm	5 barg CO ₂ + 200 rpm	10 barg CO ₂ + 200 rpm	40 barg CO ₂ + 200 rpm
<u>E12</u>	<u>E13</u>	<u>E14</u>	<u>E5</u>
2 barg CO ₂ + 400 rpm	5 barg CO ₂ + 400 rpm	10 barg CO ₂ + 400 rpm	40 barg CO ₂ + 400 rpm
<u>E1</u>	<u>E2</u>	<u>E3</u>	<u>E4</u>
2 barg CO ₂ + 600 rpm	5 barg CO ₂ + 600 rpm	10 barg CO ₂ + 600 rpm	40 barg CO ₂ + 600 rpm

Figure 9. Factorial design of experimental variables. Shading indicates the order of preference (darker = greater priority) if less than the full design is tested. Experiment number (e.g., E1) indicates a suggested order.

3.4. Experimental Procedure

The experiment would involve high pressure and temperature. Safety precautions should be followed precisely, and caution should be constantly exercised during permanency in the laboratory. In the first step, students should determine operational conditions they would run according to the schedule presented in Figure 9. The following three steps would consist of: loading the reactor; running the reactor; analyzing the product. Complete procedural details that would be followed by the students, in chronological order, are provided in Supplementary_Material_1, along with a data

table (Table S1) for recording observations and values obtained during the experiment. The duration of each experiment would be approximately 3 hours, and the work would be ideally carried out in groups of 2 or 3 students.

4. Experimental Investigation Part C: Calculations and Questions

4.1. Moisture Content in Collected Filter Cake

Using the weighing data recorded, calculate the moisture content (MC (%)) of the filter cake, according to Equation (13), and the total mass of reacted solids collected. If m_{ws} is mass of wet solids (Equation (14)) and m_{ds} is mass of dry solids (Equation (15)), then:

$$MC = \frac{m_{ws} - m_{ds}}{m_{ds}} \times 100 \quad (13)$$

$$m_{ws} = (m_C + m_F + m_{RC}) - (m_C + m_F) \quad (14)$$

$$m_{ds} = (m_C + m_F + m_{RC} - m_{H_2O}) - (m_C + m_F) \quad (15)$$

where m_C : a mass of crucible; m_F : a mass of filter paper; m_{RC} : a mass of remaining cake (after retrieving a sample for titration test); m_{H_2O} : a mass of moisture. This methodology should be employed when executing the experiment.

4.2. CO₂ Content in Fresh and Carbonated Wollastonite

Using the acidification data recorded, determine the CO₂ content of the original wollastonite as well as the carbonated wollastonite. Report the CO₂ content in units of mg, CO₂/g, wollastonite (Equation (20)) and wt % (Equation (21)). Then, compared to the theoretical maximum value (in a unit of mg/g), report the fractional extent of carbonation conversion ($\xi(t)$) from Equation (25).

If m_i (Equation (17)) is initial mass of acidification vessel and its contents just before start of reaction, and m_f (Equation (18)) is final mass of acidification vessel when reaction between CaCO₃ (in the sample (m_{sample})) and HCl reaction has been completed, then mass of CO₂ lost (m_{CO_2}) is determined according to Equation (16):

$$m_{CO_2} = m_i - m_f \quad (16)$$

$$m_i = (m_{test\ tube} + m_{sample}) + m_{HCl} \quad (17)$$

$$m_f = m_{test\ tube} + m_{sample} + m_{HCl} - m_{CO_2} \quad (18)$$

To calculate the HCl mass, use the Equation (19), where V_{HCl} is the volume of HCl used (15,000 mL), and ρ_{HCl} is the density of 6 M HCl (1.0939 g/mL):

$$m_{HCl} = V_{HCl} \times \rho_{HCl} \quad (19)$$

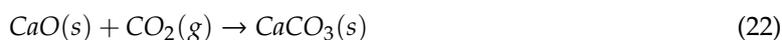
The CO₂ content is then calculated as (Equations (20) and (21)):

$$C_{CO_2} \left(\frac{mg\ CO_2}{g\ wollastonite} \right) = \frac{m_{CO_2}}{m_{sample} - m_{CO_2}} \quad (20)$$

$$C_{CO_2} (wt\ \%) = \frac{m_{CO_2}}{m_{sample}} \times 100 \quad (21)$$

The fractional extent of carbonation ($\xi(t)$) is calculated taking into account two assumptions: wollastonite mass % of CaO 51.2%, and only calcium carbonate (CaCO₃) forms (Equation (22)).

The theoretical maximum concentration of CO₂ is defined as the concentration of CO₂ present in wollastonite if all CaO present is converted into CaCO₃, as described by Equations (23–25):



$$C_{\text{CO}_2, \text{max}} = \frac{51.2 \text{ g CaO}}{100 \text{ g wollastonite}} \times \frac{1 \text{ gmole CaO}}{56.077 \text{ g CaO}} \times \frac{1 \text{ gmole CO}_2}{1 \text{ gmole CaO}} \times \frac{44.009 \text{ g CO}_2}{1 \text{ gmole CO}_2} \times \frac{10^3 \text{ mg CO}_2}{1 \text{ g CO}_2} = \frac{401.8155 \text{ mg CO}_2}{\text{g wollastonite}} \quad (23)$$

$$C_{\text{CO}_2, \text{reacted}} = C_{\text{CO}_2}(\text{Carbonated Wollastonite}) - C_{\text{CO}_2}(\text{Fresh Wollastonite}) \quad (24)$$

$$\xi(t) = \frac{\text{Reacted concentration of CO}_2 \left(\frac{\text{mg CO}_2}{\text{g sample}} \right)}{\text{Theoretical concentration of CO}_2 \left(\frac{\text{mg CO}_2}{\text{g Sample}} \right)} = \frac{C_{\text{CO}_2, \text{reacted}}}{C_{\text{CO}_2, \text{max}}} \quad (25)$$

4.3. Laboratory Report Questions

After the initial calculations, the students answer several questions, as part of their experimental investigation report, to evaluate their progress and knowledge. The following is a list of questions used at Sheridan College. Some questions directly relate to the experiment conducted and data collected, while others challenge students to hypothesize based on fundamental engineering concepts and to explore available literature.

1. Present all experimental data in well-formatted lists and/or tables (in addition to the photocopy of your lab notebook notes).
2. Present answers to the calculation questions and show calculations.
3. Comment on your confidence in the acidification results for the original and carbonated solids, and make any additional remark about using this method for CO₂ uptake determination.
4. Comment on the carbonation extent achieved. Is it as expected based on the theory on process conditions and mechanism?
5. How can the reaction progress be followed in real-time (on-line)? Research and summarize at least two instrumental methods that can be coupled to a pressurized high-temperature reactor.
6. Would it make any difference to the reaction if impure CO₂ was used (e.g. direct flue gas, or CO₂ of lower purity than used)? Think about chemical and physical aspects.
7. Explain the function of a rupture disk and how it is selected for a reactor. In what cases is a rupture disk used versus a relief valve?
8. Research literature to find out what the pH and CO₂ solubility (mol/L) at the operating temperature and pressure you used would be if the reaction medium was pure water (i.e. no mineral).
9. Following up on question 8, do you think the pH and CO₂ solubility with the reacting wollastonite present (as in the experiment) would be higher or lower than the values you found for pure water?

5. Discussion

The experimental investigation presented in this paper was conducted in Summer 2017 for the first time, with three two-member groups of students, as a laboratory assignment in the “Air Pollution Chemistry” course at Sheridan College. However, this conceptualized experiment can be applied in a range of multidisciplinary courses at the 3rd or 4th-year levels in Bachelor or Advanced Diploma programs and the 1st or 2nd-year levels of a Master’s program. Suitable courses include titles, such as “Reaction Kinetics”, “Reactor Design”, “Unit Operations”, “Mass Transfer Operations”, “Materials Chemistry”, among others. It is crucial that students performing the conceptualized lab possess prior knowledge, and preferably laboratory experience, in fundamental topics that include physical chemistry and transport phenomena.

In the first implementation of this methodology, students were required to perform this investigation within an approximately three-hours duration in the laboratory, and write a report (one per student) with the data and results obtained that was due one week after the lab. Lab experiments

in this course are alternated between groups, so each week one group performed the Accelerated Carbonation lab. As this was the most comprehensive lab students performed in the course, all groups were scheduled to perform the lab during the last three weeks of the course, so that students would be experienced in air pollution experiments before attempting this lab. Students were also required to read the extensive lab procedure before arriving in the lab and were required to show notes they had made in preparation for the lab. This was done to ensure students worked efficiently to be able to conclude the experiment in the allotted time and to ensure students were well aware of the safety precautions that had to be taken. All six students who experimented understood and concluded the experiment in the time proposed, describing the procedures, data, calculations (Sections 4.2 and 4.3) in detail in the report, adequately answering the questions (Section 4.3), and correctly filling out the data table (Table S1). It is thus concluded that the conceptualized experimental investigation has been validated both procedurally and pedagogically. Furthermore, this experimental investigation showed (from the instructor's perspective based on lab performance and quality of reports) that students were more engaged when they had a clear purpose and knew the value of the experimental data.

After the collection of the student's results obtained using different parameter conditions, the reaction efficiency obtained in the experiments, which is the relation between the maximum theoretical and actual experimental CO₂ uptake values, was on average 22.5%, ranging from 17 to 28%. These results are in good agreement with those of Huijgen et al. [45]. They reported an efficiency of 39% for the same reaction duration used herein (30 min.), and using the following parameters: particle size <106 μm (D(4,3) = 51.1 μm), T = 150 °C, P_{CO₂} = 20 bar, L/S = 5 kg/kg, 500 rpm. The higher efficiency obtained in that study compared to the students' results could be attributed primarily to the particle size. The students used material with 75 wt % having particle size below 100 μm and D(4,3) equal to 82.7 μm. Thus, it was expected that the students' coarser material would carbonate less in the same reaction duration, and hence could be said that their results were adequate.

The fact that all groups obtained reasonable efficiency values is also evidence that students not only performed the experiments adequately but were able to apply the required calculations correctly, even though such calculations were different from the calculations they performed in prior labs. Strong student performance in this experimental lab is evidence of strong student engagement. Student engagement was also verified by inspecting their laboratory procedures at the beginning of the lab period. Students were asked to highlight and make hand-written notes on the procedure before coming to the lab to be well prepared, and all students turned up with significantly marked up copies of the procedure.

Students were also able to provide thoughtful answers to the questions presented in Section 4.3; the following are some examples of the answers provided for selected questions:

- Q3) Students commented on the increase in the CO₂ content of wollastonite after reaction versus the original mineral. Comments were also made regarding possible vapor losses from the acidification tube due to heating, and water condensation into the tube due to an ice bath, as potential sources of error in the quantitative determination.
- Q5) Two approaches to follow reaction progress in real-time were commonly mentioned. One is to use instrumentation that analyzes the reaction medium in-situ, such as in-situ FTIR. The other is by collecting samples while the reactor operates at elevated temperatures and pressures, using appropriate sampling techniques.
- Q6) Students recalled the concepts of partial and total pressures to answer this question. They realized that it is the CO₂ partial pressure that drives the carbonation reaction, thus impure CO₂, in the form of flue gases, would require greater total pressure to achieve similar reactivity as pure CO₂. From a physical perspective, the implication of this includes the need for reactors that can withstand higher pressures and compressors that can pressure flue gases to very high pressures, both of which affect process costing.
- Q7) This question about rupture disks and relief valves can easily be answered by searching the internet, but it was selected for this lab for a special purpose. Sheridan students perform another

lab experiment using a climbing film evaporator, which uses a boiler that has a pressure relief valve. Thus answering this question enabled the students to recall that experiential learning event, which is a pedagogical approach to reinforce learned concepts, thus making the experience of researching the answer to this question more engaging.

- Q8) The answer to this question comes from published literature and can be most readily be found in journal articles. This question is thus designed to expose students to journal literature, and an example of a paper that students found to answer this question is that of Duan and Sun [63].
- Q9) Students analyzed the effect of wollastonite on CO₂ solubility, and consequently pH, by looking at chemical equilibrium equations. They verified that wollastonite consumes acidity, thus shifts the carbonic acid equilibria towards the greater dissolution of CO₂ and increases the pH.

It is also worth briefly discussing the potential industrial implementation of wollastonite mineral carbonation, given the results obtained by the students, and those reported in the literature. The students achieved up to 28% calcium conversion efficiency with 30 min duration, and Huijgen et al [45] reported a value of 45% with 60 min duration (using the aforementioned parameters). For industry, close to 100% efficiency would be desirable, to maximize the CO₂ sequestration potential of the technology and to minimize the expenditure on wollastonite mineral. Full conversion of minerals is not commonly reported in the literature because of the long durations required and other conversion limiting factors (e.g., passivation). Santos et al. [64] have reported full conversion of olivine (0.515 g, CO₂/g, olivine = 99.0% ± 3.9%), which is a magnesium-based natural silicate, by carbonating it for 72 h at 200 °C and 35 bar P_{CO₂}, with the addition of 1 M NaCl and L/S = 4. From an industrial perspective, long durations (> few hours) would not be feasible due to throughput and energy demand limitation; thus, it is important to assess with partial conversion at reasonable durations to make it an industrially implementable process. This can be done by performing energy analyses, such as that discussed in Section 5.1.

Going back to the conceptualized two-stages project, the experimental results presented by each work are to be combined to yield a dataset that can be applied in the subsequent design project. In the design project, students would use the experimental data obtained by themselves and classmates on the accelerated mineral carbonation of wollastonite, to determine if this is a feasible process for industry to sequester carbon dioxide, in view of mitigating climate change. Also, they would use the experimental data, acquired using a range of process conditions, to study the effect of the process variables (CO₂ pressure and mixing rate) on the carbonation kinetics and mass transfer rate. When students receive the dataset, they would carefully inspect the experimental data to investigate if any of the data is not reliable, either due to experimental or data processing error. If the error is correctable, students would be encouraged to do so; otherwise, they would use their engineering know-how to discard outliers. Students should be mindful that each data point would not be replicated (as each group runs a different condition), so they should observe and foresee trends in the data for signs of unreliable data.

The first step of the design project is to be done by way of an energetic analysis, whereby students would design a process flowsheet to sequester CO₂, determine how much energy it will consume to perform this task, and assess if the CO₂-intensity of the process is low enough so that it can achieve net CO₂ sequestration. The second step is to be done by way of data analysis and modeling. The effect of pressure at constant mixing rate will enable finding a rate law that predicts reaction kinetics as a function of pressure. The effect of the mixing rate at constant pressure will enable determining if the mass transfer of calcium ions from the mineral particles to the bulk solution, where they precipitate as carbonate, is dominated by diffusion or convection, and if the latter, how much benefit increasing the rate of mixing brings to the carbonation rate. Section 5.1 and Supplementary_Material_2 provide more details on the design project requirements and procedure that would be (or could be) provided to students.

5.1. Energetic Analysis and Design Project

One of the biggest concerns with the accelerated mineral carbonation technology is that if it is implemented as an industrial process, it will not deliver net CO₂ sequestration. The reason behind this is that all process equipment in the industry requires energy to function, and, in most cases, that energy is supplied from CO₂-intensive processes. Even so-called “green energy” has a CO₂ footprint. Hydroelectric fares the best, at 4 g, CO₂-eq/kWh_e, while wind and solar emit (over the life-cycle) 12 and 22 g, CO₂-eq/kWh_e, respectively (CO₂-eq stands for CO₂-equivalent, and kWh_e is the rate of electrical energy generation) [65]. At the other end of the spectrum, the median CO₂ intensity of coal power generation, the worst performer, is a whopping 1001 g, CO₂-eq/kWh_e. Thus, if too much energy is used for accelerating mineral carbonation, the process may end up emitting more CO₂ than sequestering it.

Due to the energetic challenges posed, it is vital to conduct an energetic analysis of any proposed accelerated mineral carbonation process. For example, Santos et al. [66] found that, for an ultrasound-enhanced mineral carbonation process (at lab-scale), for every 2.3 g of CO₂ sequestered, 79.2 g would be emitted (based on the energy-mix of Belgium). They proposed some strategies to reduce the CO₂ emissions further at the industrial-scale, such as securing a less CO₂-intensive energy source, increasing the solids loading in the reactor (i.e., more solids per volume of liquid), and improving the design of the reactor to maximize the utilization of sonication energy. Still, a 100-factor reduction in CO₂-intensity would be necessary to achieve net CO₂ sequestration, so it is not easy and perhaps not feasible.

More recently, for a more conventional carbonation process, utilizing steelmaking slag as the carbon sink, Costa et al. [67] estimated an energy requirement of 272–1750 kWh/tonne CO₂ sequestered. Based on the aforementioned energy-intensity of wind power generation, this would represent 38 kg, CO₂ emitted per 1000 kg, CO₂ sequestered. Hence, this would be a feasible process for net CO₂ sequestration. It should be noted, however, that steelmaking slags require less intense carbonation conditions compared to wollastonite (as the material is more reactive). Unfortunately, there is far less steelmaking slag being produced than CO₂ being emitted by steelmaking, so this material alone cannot substantially reduce emissions from this CO₂-intensive industry. Thus, natural materials, such as wollastonite, more abundantly available (though more expensive due to mining and transportation costs), are required to curtail industrial emissions.

So the question is, can accelerated carbonation of wollastonite become a feasible industrial process for net CO₂ sequestration? This would be addressed in the design project, that should include the following analyses:

- Energetic analysis: (a) explain how you adapted the proposed procedure to reach the energy consumption and net CO₂ sequestration results (what assumptions had to be made, what changes you made, if any, to the proposed procedure, etc.); (b) show values (and sources) of all parameters used in the equations; (c) show the energy consumption value of each individual process/equipment; (d) show the calculation procedure of converting energy consumption to CO₂ emissions (footprint) and compare the CO₂ emissions rate to the CO₂ sequestration rate to determine if net CO₂ sequestration is achieved; (e) discuss what process changes you may make, if more experimental or modeling information, to improve the efficiency of the process; (f) write conclusions and recommendations on whether accelerated mineral carbonation can become an industrially feasible process for CO₂ sequestration.
- Reaction rate law: (a) explain the procedure used to develop the rate law(s), including data and graphs used; (b) explain assumptions taken and any limitation of the applicability of the rate law(s); (c) comment on what you learned about the mineral carbonation reaction based on the rate law(s) obtained; (d) comment on how the rate law(s) can aid in improving the process design and energy consumption presented earlier.

- Mass transfer analysis: (a) explain the procedure used in the analysis, including data and graphs used; (b) explain assumptions taken and any limitation on validity of the analysis results; (c) comment on what you learned about the mineral carbonation reaction based on the results obtained; (d) comment on how the analysis can aid in improving the process design and energy consumption presented earlier.

More detail on the design procedure can be found in Supplementary_Material_2.

6. Conclusions

The experimental approach and formulas presented in this work demonstrated a potential pedagogic complement, introducing students to the mineral carbonation process and helping to increase interest in this subject. This methodology is easy to apply, with the possibility of different types of reactor available in the market and minerals (i.e., olivine, serpentine, etc.) or residues (i.e., ashes, tailings, and slags) and could be used to expose students to an environmental concept and engage into opportunities of application of this technology with the visible results obtained after the investigation.

After working in small groups, the learning outcomes for this practical experiment are that students should also be able to design experiments, to test a hypothesis, and work in groups to solve a shared problem. This work demonstrates the importance of the practical investigation to get a deeper understanding and engage students in chemical engineering or other courses related to applied chemistry.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/11/15/4156/s1>, Supplementary_Material_1 and Supplementary_Material_2.

Author Contributions: Conceptualization, R.M.S.; Methodology, R.M.S., J.S.S.; Validation, J.S.S.; Writing—Original Draft Preparation, H.F., R.M.S.; Writing—Review and Editing, R.M.S.; Supervision, R.M.S.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

The mineralogical composition of the wollastonite material was determined by XRD. The diffractogram is presented in Figure A1. The diffraction peaks match well with those of wollastonite 1A (the most common polymorph of CaSiO_3 , which crystallizes in the triclinic system). Quantification by Rietveld Refinement indicates the presence of 82 wt % wollastonite, with minor quantities of quartz (SiO_2), portlandite ($\text{Ca}(\text{OH})_2$), and merwinite ($\text{MgCa}_3(\text{SiO}_4)_2$). The pH of a wollastonite material–water slurry at a liquid-to-solid ratio of 10 kg/kg was determined to be 10.6, after 24 h shaking, which is close to the theoretical value for wollastonite of 10.7.

The particle size distribution of the wollastonite material was determined by wet Laser Diffraction Analysis (LDA) and is presented in Figure A2. The material has a relatively wide particle size distribution (as observed in Figure 1), ranging from sub-micron to ~600 μm , which partly owes to the acicular shape of the material (i.e., a combination of long needles and small needle fragments). The average particle size ($D(4,3)$) of this material was 82.7 μm , with a D_{50} (median diameter) by volume of 44.5 μm . The specific surface area (SSA) was determined to be 0.8903 m^2/g .

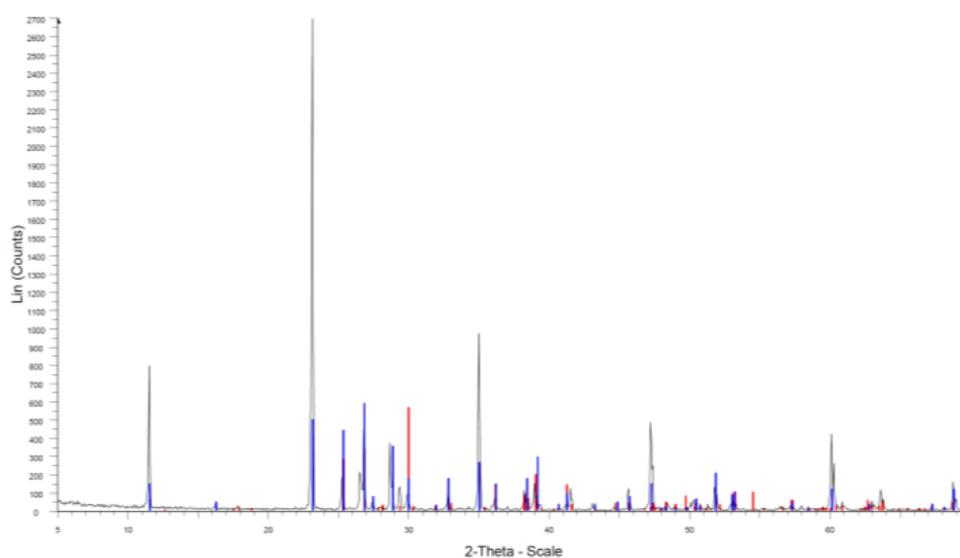


Figure A1. X-ray diffractogram of wollastonite material; wollastonite mineral peaks indicated by colored lines (red = wollastonite 2M; blue = wollastonite 1A).

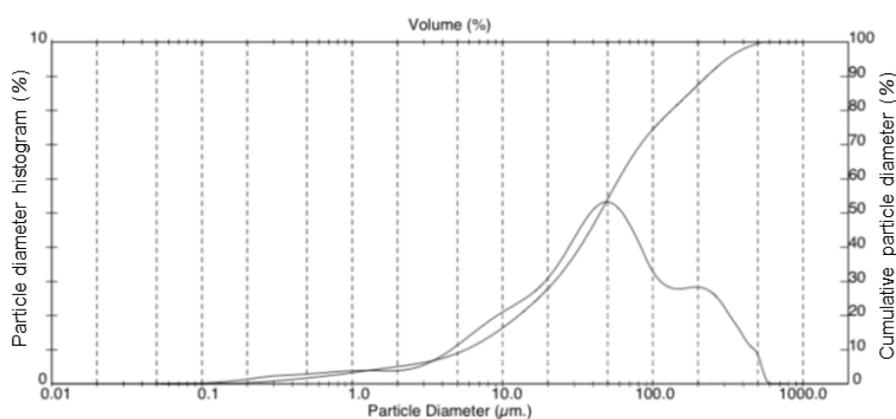


Figure A2. The particle size distribution of wollastonite material, determined by LDA (Laser Diffraction Analysis).

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