Reaction Mechanism of Wollastonite In Situ Mineral Carbonation for CO₂ Sequestration: Effects of Saline Conditions, Temperature, and Pressure

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ABSTRACT: The research presented here investigates the reaction mechanism of wollastonite in situ mineral carbonation for carbon dioxide (CO₂) sequestration. Because wollastonite contains high calcium (Ca) content, it was considered as a suitable feedstock in the mineral carbonation process. To evaluate the reaction mechanism of wollastonite for geological CO₂ sequestration (GCS), a series of carbonation experiments were performed at a range of temperatures from 35 to 90 °C, pressures from 1500 to 4000 psi, and salinities from 0 to 90,000 mg/L NaCl. The kinetics batch modeling results were validated with carbonation experiments at the specific pressure and temperature of 1500 psi and 65 °C, respectively. The results showed that the dissolution of calcium increases with increment in pressure and salinity from 1500 to 4000 psi and 0 to 90000 mg/L NaCl, respectively. However, the calcium concentration decreases by 49%, as the reaction temperature increases from 35 to 90 °C. Besides, it is clear from the findings that the carbonation efficiency only shows a small difference (i.e., ±2%) for changing the pressure and salinity, whereas the carbonation efficiency was shown to be enhanced by 62% with increment in the reaction temperature. These findings can provide information about CO₂ mineralization of calcium silicate at the GCS condition, which may enable us to predict the fate of the injected CO₂, and its subsurface geochemical evolution during the CO₂–fluid–rock interaction.

1. INTRODUCTION

Global warming has been considered as one of the severe threats to humankind over the last decades. It is caused partially by the uncontrolled release of greenhouse gases, mainly carbon dioxide (CO₂), from anthropogenic sources.¹ There is a recognized need to reduce the uncontrolled emission of CO₂ into the atmosphere to mitigate the harmful effects such as global warming.² Some primary alternatives are adopted for the moderation of atmospheric CO₂ emissions. These alternatives include the improvement of energy-efficient technologies, the use of less carbon-intensive fuels, and CO₂ capture and sequestration (CCS).³⁴ CCS has emerged as the leading alternative compared to the other options because of a substantial CO₂ sequestration potential, which is forecasted to reduce one-sixth of the CO₂ emission by 2050.⁵ CCS involves different approaches of CO₂ sequestration to aid the global decrease of CO₂ emissions by capturing the CO₂ produced. Geological CO₂ storage (GCS), such as in depleted oil and gas reservoirs,⁶⁷ is one of the proposed solutions. These reservoirs contain hydrocarbon at high pressure over the geological period, which proves that they have the potential to be used for the storage of CO₂. Currently, the GCS meets both the technical and economic requirements to sequestre large amounts of CO₂ permanently to the subsurface.⁸⁹ CO₂ sequestered into geological media offers several trapping mechanisms such as structural, residual, solubility, and mineral trapings.¹⁰¹¹ Among all these trapping mechanisms, mineral trapping¹²¹³ has been determined as the safest and permanent form of CO₂ storage.¹⁴ Mineral trapping, which is also referred to as in situ mineral carbonation, implies the transformation of CO₂ into stable carbonate minerals in geological formations.¹⁵ In situ mineral carbonation commences when liquefied CO₂ is injected into the geological formation triggering disequilibrium state on the fluid-rock system and eventually leads to a series of geochemical processes that result in the formation of secondary minerals.¹⁶ The first geochemical process occurs when the injected CO₂ dissolves into the brine to form carbonic acid (Reaction R1), which is described in geochemical textbooks.¹⁷¹⁸

\[
\text{CO}_2(\text{gas}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \\
\leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ 
\]  

(R1)
The carboxylic acid (H\textsubscript{2}CO\textsubscript{3}) produced from Reaction R1 will reduce the pH and initiate a second geochemical process, dissolution of the silicate minerals. Reaction R2 shows the dissolution mechanism as for the case of wollastonite (CaSiO\textsubscript{3}).

\[
\text{CaSiO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{SiO}_2(\text{aq}) \tag{R2}
\]

The third geochemical process occurs when the brine supersaturated with dissociated divalent metal cations (i.e., Ca\textsuperscript{2+}) as a result of silicate mineral dissolution (Reaction R2) reacting with inorganic carbon to generate secondary carbonate phases (Reaction R3).

\[
\text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{H}^+ \tag{R3}
\]

Based on the reaction mechanisms given in Reactions R1–R3, it is clearly shown that the silicate mineral dissolution rate and the conversion rate of the secondary carbonates are the main governing mechanisms for the in situ mineral carbonation.\textsuperscript{14} These mechanisms are influenced by particular in situ factors, including temperature, pressure, and salinity. The temperature and pressure conditions of geological formations vary for the formation pressure and geothermal gradient in the area.\textsuperscript{22} Most saline aquifers and depleted oil reservoirs are located in 400–3000 m range of depth, which corresponds to wide ranges of subsurface temperature (i.e., 31–110 °C) and pressure (i.e., 1060–8700 psi) variations.\textsuperscript{23} The brine salinity may also vary from several thousand mg/L to several hundred thousands of mg/L, depending on the formation depth and basin location.\textsuperscript{24} For example, in the Sleipner Field,\textsuperscript{25} the brine has salinity as low as 7000 mg/L, while in the Ketzn Stuttgart Formation, Germany, a salinity of 250,000 mg/L is reported.\textsuperscript{26} In some of the future CO\textsubscript{2} sequestration projects, co-injection of seawater together with CO\textsubscript{2} into the geological formations is also considered.\textsuperscript{27} Therefore, a significant variation in salinity is foreseen for different geological formations and GCS projects.

Several laboratory studies and conceptual geochemical models have reported the effect of temperature, pressure, and salinity on the mineral carbonation mechanism. Most of these research studies, however, were carried out under the atmospheric and high-temperature conditions to understand the in situ carbonation mechanism of alkaline rocks such as peridotite, serpentinite, and basalt at the hydrothermal environment\textsuperscript{28–33} and during the natural weathering process.\textsuperscript{34–37} Moreover, researchers have not treated the in situ mineral carbonation in much detail as a fully coupled problem in rock deformation, pore-fluid flow, heat transfer, mass transport, and chemical reaction processes and structurally simple calcium-bearing silicates like wollastonite. Thus, the effect of variation in the stated in situ parameters on the leaching rate of divalent metal cations and the rate of wollastonite carbonation is still unclear at the conditions relevant to the GCS.

More recently, literature studies have emerged to offer contradictory findings to determine the CO\textsubscript{2}−fluid–mineral interaction mechanism for in situ or ex situ mineral carbonation of wollastonite.\textsuperscript{38–40} Ca silicates like wollastonite have a comparatively weak Ca−O bond rather than Mg−O bond in Mg silicates. Therefore, Ca silicates tend to dissolve at a faster rate than Mg silicates for a given connectedness.\textsuperscript{41} Besides, the crystallinity of the mineral wollastonite influences its rate of dissolution.\textsuperscript{42} Search of the literature revealed that few studies had used wollastonite as an analogue to other silicates that occurred on the Earth’s surface.\textsuperscript{33–35} In a study conducted by Min et al.,\textsuperscript{14} the interaction between wet supercritical CO\textsubscript{2} and wollastonite was investigated, and a significant change in mineral thickness was observed within 40 h of experimental procedure even with a relatively large particle size. Also, Miller et al.\textsuperscript{35} found that the carbonation of wollastonite reaches a pseudo-equilibrium state in less than 30 h. It is apparent that wollastonite, even with large particle sizes, shows a detectable geochemical reaction within reasonably short experimental timeframes. However, much uncertainty still exists about the impact of temperature, pressure, and salinity on the reaction mechanisms of wollastonite carbonation under typical GCS conditions. In this research, the focus is on the release rate of divalent metal cations from wollastonite in the dissolution process and the conversion rate of the liberated cations into secondary carbonate minerals. In regard, the effects of pH evolution, wollastonite dissolution, and carbonate precipitation on the mineral carbonation efficiency are investigated at different temperatures, pressures, and saline conditions. Drawing upon the strand of research into the reaction mechanism of wollastonite for CO\textsubscript{2} sequestration, this study attempts to better understand the in situ mineral carbonation of wollastonite by simulating the water–rock–gas interaction and carbon dioxide solubility through reaction modeling software of PHREEQC (version 3.3.8) and Geochemist’s Workbench (GWB–14).

### 2. EXPERIMENTAL AND MODELING SECTION

#### 2.1. Experimental Setup

**2.1.1. Materials.** Wollastonite samples were acquired from Kaolin Sdn Bhd, Malaysia. The samples were pulverized into a fine powder and treated to remove all the impurities and gangue materials. The pacified wollastonite gives a result superior to unpacified ones; therefore, the wollastonite samples were treated with dilute sulfuric acid (normality of 0.015). Shimadzu energy-dispersive X-ray fluorescence (XRF) spectrometry was used to determine the chemical composition of wollastonite samples. The unique wavelength characteristics and fluorescence intensity emitted from the mineral allow determination of the elements and their respective concentration in the sample. Field-emission scanning electron microscopy (FESEM, SU8030 Hitachi) was employed to analyze the sample microstructures, including grain morphology, surface roughness, and identification of secondary phases. FESEM allows a higher magnification (nanoscale) of the sample surface. FESEM is linked with energy-dispersive X-ray (EDX) spectroscopy, which enables to analyze the elemental composition of the sample at specific surface locations. To generate better quality FESEM images, the powdered sample was coated with gold foil before FESEM analysis.\textsuperscript{16} The particle size distribution of the powdered wollastonite has been determined using a Malvern Mastersizer 2000 analyzer. It works on the Mie theory, wherein the dispersion pattern produced by the Malvern Mastersizer analyzer indicates the mineral grain size. Also, water sample analysis was conducted using inductively coupled plasma optical emission spectrometry (ICP–OES) before and after the batch reactions. This analysis was conducted to document the changes in water chemistry, which may provide some indication of the dissolution and precipitation mechanism that could occur during CO\textsubscript{2}–water–rock interactions. ICP–OES determines the concentration of the ionic elements in the fluid from the electromagnetic radiation, which is emitted from the
excited atoms and ions.47 The wavelength characteristics and the emission intensity are used to identify the elements and quantify their concentration in the solution. Besides, thermogravimetric analysis (TGA, Q500 TA Instrument) was carried out on the reacted sample to determine the weight loss (%) of powdered wollastonite. Besides, according to Rahmani,48 a total carbon analyzer (TCA, CS844, LECO Corp.) was applied to examine the carbonation efficiency of wollastonite samples.

2.1.2. Experimental Apparatus. A piston-assisted high-pressure accumulator with a fluid capacity of 600 mL, an Autoclave reactor, was used to conduct the carbonation experiment. The design of the apparatus was based on the reaction temperature and the working pressure of up to 300 °C and 10,000 psi, respectively. The equipment was commonly used to recombine dead oil and hydrocarbon before pressure volume temperature (PVT) fluid analysis. To fit this experimental requirement, a modification was required on the equipment for carrying out a long-term rocking-batch experiment; hence, a water-bath equipment and a pressure maintenance system were added to the piston-assisted high-pressure accumulator. The water-bath equipment was attached to the piston-assisted high-pressure accumulator for maintaining the system at the desired temperature throughout aging. A temperature controller was also embedded in the Autoclave reactor to control the temperature of the rocking system. The pressure maintenance system was made up of three main components: a pressure gauge with a manually controlled valve, an injection pump to input CO₂, and a flow meter to measure the carrying fluid. Two pumps were embedded in the system to work either independently or in synchronized mode, depending on the selected setting. In the carbonation experiment, the independent model was chosen for the pumps, wherein the first pump was responsible for pressurizing the accumulator, with the CO₂ coming from the fluid sample tank. The other pump was used to inject the distilled water into the rocking system. The flow meters were applied to ensure that the CO₂ pressure and injected distilled water are well-maintained from the top and bottom of the accumulator. The critical wetted parts of the setup were made up of titanium and super duplex stainless steel, which were highly resistant toward acidic and high chloride concentration environments. Moreover, the pressure, volume, and temperature were recorded from each data logging or monitoring system throughout the carbonation experiment. Figure 1 represents a schematic of the rocking-batch experimental setup.

2.1.3. Experimental Procedure. Before the batch experiment, the accumulator and the flow line were cleaned with toluene and acetone to remove contaminants (if any), and 10 g of powdered wollastonite with specific volumetric mean diameters and 100 mL of deionized water were prepared and placed into the accumulator. The water volume/rock mass ratio of 10 was used in the carbonation experiment based on the ratio used in the CO₂-batch experiment conducted by Sterpenich et al.49 Besides, Huijgen et al.49 examined the effect of the liquid-to-solid ratios of 3, 5, and 10 kg/kg on the mineral carbonation of wollastonite. However, their result concludes the uncertain effect of the liquid-to-solid ratio on the mineral carbonation, and the highest reaction carbonation of wollastonite was observed at the liquid-to-solid ratio of 10, which was adopted in this study. After that, the accumulator lid was secured, and the accumulator was vacuumed to remove any trapped air inside the system. The pressure inside the accumulator was then increased to 2200 psi using the CO₂, which was transferred via a pump from the fluid sample bottle. Once the pressure stabilized, the temperature was increased to 65 °C in the water-bath equipment. The range of temperature and pressure was selected according to the Frio Formation, which was considered a typical condition for geological CO₂ sequestration.50 The system was left for 24 h to stabilize the pressure. The rocking process was initiated after monitoring for 24 h. The pressure and temperature were frequently logged to observe any fluctuations during the carbonation experiment. After 10 days of experimental duration, a mixture of wollastonite and water was retrieved. The retrieved mixture was then filtered to separate suspension and water samples. Once the suspension samples were extracted, it was first necessary to place and dry them in an oven at 50 °C overnight.

Figure 1. Schematic of the rocking-batch experimental setup.
Then, the dried samples as a powder form were further studied by FESEM and TGA analyses, while the collected water sample was analyzed using the ICP–OES technique.

2.1.4. Quantification of the Mineral Carbonation Efficiency. Quantification of the number of carbonates formed during the mineral carbonation process of wollastonite was determined based on TGA results. To this aim, the powdered wollastonite was heated in aluminum oxide ceramic cups at a rate of 10 °C/min from ambient up to 1000 °C under a N2 flow (50 mL/min). Approximately 20 mg of the powdered sample was used for each of the TGA results. The rate of CO2 conversion into carbonated minerals was defined based on the weight loss between 150 °C and 1000 °C. According to Miller et al., wollastonite is stable below 900 °C; however, CaCO3 is completely decomposed into CO2 and CaO. Therefore, the mass loss at a temperature interval between 150 and 1000 °C TGA was attributed to CO2 resulting from CaCO3 decomposition. The mass of calcium in calcite (CaCO3) was determined using eq 1. The mineral carbonation efficiency and the reacted fraction of wollastonite were calculated using eqs 2 and 3, respectively.

Calcium mass in CaCO3 (g/mol) 
= ∆W(150°–1000°) × MWCO2(g) / MW (g) 
× mass of residue (g/mol) 
(1)

carbonation efficiency (%) 
= calcium mass in CaCO3 / total calcium mass in primary mineral × 100 
(2)

reacted fraction = mass of reacted wollastonite (g) / mass of powdered wollastonite (g) 
(3)

From eq 1, ∆W(150°–1000°) is the weight loss of the reactants measured by TGA at the temperature interval between 150 and 1000° and MW denotes the molecular weight. In eq 3, the mass of reacted wollastonite referred to the mass loss of carbon dioxide adsorbed by wollastonite in the mineral carbonation process.

From eq 4, the sequestration rate of CO2 was calculated. WCO2 is the weight (g) of CO2 sequestered in calcite. WC presents the weight (g) of wollastonite used for the process of mineral carbonation. YCa is the mass fraction (%) of Ca2+ in wollastonite samples that can react with CO2 to form the calcite.

\[ \frac{W_{CO2}(g)}{W_C(g)} = \frac{Y_{Ca}(\%)}{MW_{Ca}(g)} \times MW_{CO2}(g) \]

2.2. Geochemical Modeling. 2.2.1. Modeling Approach. In this study, kinetics batch modeling was conducted to assess the geochemical interaction between the CO2, water, and wollastonite, neglecting the effect of aqueous species transport via fluid flow. The reaction rate was assessed with an assumption that CO2, water, and wollastonite are always in mutual contact with the model. The kinetics batch modeling was initialized with 100 mL of deionized water and 10 g of wollastonite mineral, where the water/rock (liquid to solid) ratio was set to 10:1. The kinetics batch modeling was performed for 10 days to observe geochemical changes at the laboratory duration. However, the most prolonged duration of the batch experiment that has been conducted for CO2–wollastonite reaction in the literature is 138 days. Under this water/rock ratio (i.e., 10:1) and duration (i.e., 10 days), the geochemical interaction was not constrained by the availability of the mineral and CO2. It is referred to the unlimited supply of CO2 and mineral sources for the geochemical interaction to occur. The justification of the high volume of CO2 and wollastonite initialization in this study is to ensure that the full potential of geochemical reactivity can be captured within 10 days and not constrained by the supply of CO2 and mineral. A low amount of reactant would lead to inhibition of the conversion process.

Besides, typical examples for CO2 geological storage conditions are 35 °C, 1500 psi, and 35,000 mg/L at the Sleipner site; 65 °C, 2200 psi, and 92,633 mg/L in the Frio Formation; and 100 °C, 3200 psi, and 7000 mg/L at the Gorgon site. Thus, the simulation was performed at various pressures of 1500–4000 psi, temperatures of 35–90 °C, and salinities of 0–90,000 mg/L NaCl to observe the effect of those variables on the mineral carbonation of wollastonite. Two variables were kept constant during each batch modeling to distinguish the individual impact of the variable on the process of mineral carbonation. For example, the variables of temperature and salinity were kept constant in the batch modeling to investigate the effect of pressure on the fluid mineral reaction. All the values fall within the typical conditions of GCS sites. In doing so, the kinetics batch modeling was run with different investigated variables of temperature, pressure, and salinity (Table 1).

Table 1. List of the Kinetics Batch Modeling Sensitivity Cases

| sensitivity run | pressure (psi) | temperature (°C) | salinity (mg/L) |
|-----------------|---------------|-----------------|-----------------|
| 1               | 1500          | 65              | 0               |
| 2               | 2200          | 35              | 0               |
| 3               | 2200          | 65              | 0               |
| 4               | 2200          | 65              | 35,000          |
| 5               | 2200          | 65              | 90,000          |
| 6               | 2200          | 90              | 0               |
| 7               | 4000          | 65              | 0               |

2.2.2. Modeling Code. The kinetics batch modeling was conducted using the PHREEQC (version 3.3.8) code and GWB-14. This modeling can simulate complex geochemical interactions between dissolved gases, aqueous solutions, and minerals in batch reaction mode. The llnl.dat database developed by Lawrence Livermore National Laboratory was converted to the PHREEQC format and used in all the kinetics batch modeling. As some simulations dealt with a high salinity brine, the Pitzer speciation model was initially considered because of its suitability in a high ionic strength condition. Because the Pitzer speciation approach was not taken into account on the distribution of SiO2 in solution, which constrains the mineral reaction of wollastonite, the Debye–Hückel model was adopted to calculate the aqueous species activity coefficient for SiO2. Under simulated conditions (i.e., various temperature, pressure, and salinity), the CO2 fugacity coefficients were estimated using the Peng–Robinson equation of state based on the critical temperature, pressure, and the acentric factor of CO2. According to Appelo et al., the Peng–Robinson model provides a...
reasonable estimation of CO2 fugacity and CO2 solubility in water at a system relevant to GCS sites.

2.2.3. Kinetics Parameters. During the batch modeling, the Lasaga kinetic rate law was applied to describe mineral dissolution and precipitation mechanisms. Based on the kinetic rate law, mineral reactive surface area and reaction rate constants were determined as controlling factors in kinetics rates. Equation 5 describes the mineral dissolution/precipitation rate suggested by Lasaga.

\[ r = A k \left[ 1 - \left( \frac{Q}{K} \right)^n \right] \]

where \( r \) denotes the mineral dissolution/precipitation rate in which positive values imply dissolution and negative values mean precipitation, \( A \) is the mineral reactive surface area, \( k \) is the temperature-dependent rate constant, \( Q \) is the reaction quotient, and \( K \) is the equilibrium constant for the dissolution/precipitation fluid mineral reaction. A simplified assumption was made where the precipitation rate is proportional to the dissolution rate. In the absence of final dissolution and precipitation parameters for simulated conditions, this type of simplified approximation is acceptable. To extrapolate the rate constant to different temperatures, the temperature-dependent reaction rate (eq 6) was adopted from Arrhenius.

\[ k = k_{298} \exp \left( -\frac{E_A}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \]

where \( k_{298} \) denotes the rate constant at 298 °C, \( E_A \) is the activation energy, \( R \) is the ideal gas constant (i.e., 8.314 J/mol.K), and \( T \) is reaction temperature. The mineral dissolution and precipitation are always being influenced by H⁺ (acid stem) or OH⁻ (base system). In this complex geochemical system, the reaction rate is calculated using eq 7, which incorporates all the three mechanisms.

\[ k = k_{298}^{nu} \exp \left( -\frac{E_A}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) + k_{298}^H \exp \left( -\frac{E_A}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) a^H + k_{298}^{OH} \exp \left( -\frac{E_A}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) a^{OH} \]

where \( a \) is the species activity and \( k_{298}^{nu}, k_{298}^H, \) and \( k_{298}^{OH} \) represent the neutral, acid, and base mechanism, respectively. To calculate the kinetics rate parameters of wollastonite, the input data were adopted from the work by Palandri et al. The input data were limited by a lack of information on the surface area of wollastonite; therefore, it was experimentally determined using the Malvern Mastersizer 2000 analyzer (Table 2).

### Table 2. Input Parameters for the Kinetics Batch Modeling of Wollastonite

| mineral | moles | specific surface area (m²/g) | acid mechanism | base mechanism |
|---------|-------|-----------------------------|----------------|---------------|
| Wollastonite | 0.0861 | 0.8512 | \( k_{298} \) (mol/m²/s) | \( E_A \) (kJ/mol) | \( n \) | \( k_{298} \) (mol/m²/s) | \( E_A \) (kJ/mol) | \( n \) |
|          |       |                              | 4.266 \( \times \) \( 10^{-6} \) | 54.7 | 0.4 | 1.318 \( \times \) \( 10^{-9} \) | 54.7 | 0.5 |

### 3. RESULTS

3.1. Characterization of Wollastonite. The concentration of major oxides in the wollastonite sample is listed in Table 3. Based on the chemical composition, the ratio of calcium oxide to silica (CaO/SiO₂) is 0.931, consistent with data in the literature. The total concentration of SiO₂ and CaO accounted for 96 wt % of the sample. Also, minor impurities of potassium, magnesium, iron, and aluminum oxides were detected, which are consistent with the theoretical composition of wollastonite.

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It can be observed that the particle size of the unreacted wollastonite powder is in the range of 0.4–120 μm with a volumetric mean diameter (d_v) of 16.1 μm and a specific surface area of 0.8512 m²/g (Figure 2).

**Figure 2.** Particle size distribution of the powdered wollastonite.
wollastonite grain surfaces. The EDX spectra (Figure 3d) confirmed the formation of calcite as a new mineral phase. It may contribute to the increased occurrence of particles with irregular morphology in the carbonated samples. From Figure 3d, it can be stated that calcite has been derived from wollastonite particles as the Ca peak shows a high concentration in the energy-dispersive system (EDS) analysis. Haque et al. stated that because carbon content is likely organic matter, the samples with silicon and calcium but no carbon may be considered as residual particles of unreacted wollastonite (Figure 3a,b). Regions with calcium and carbon but no silicon could be calcite (Figure 3c,d). Based on the EDX spectra in Figure 3b, the wollastonite grain surface (Figure 3a) exhibits the element of silicon and oxygen.

3.2. TGA Analysis. Figure 4 represents the decomposition behaviors of wollastonite as a function of temperature for pre- and post-CO$_2$ reacted wollastonite samples. For the pre-CO$_2$ reacted sample, the weight loss behavior of wollastonite is 0.08 mg, decreased from 20 to 19.92 mg, which is equivalent to 0.4% of the original weight. For the CO$_2$-reacted sample, the weight loss behavior of wollastonite is 5.16 mg, which decreased from 20 to 14.84 mg. This reaction corresponds to 25.80% of the original weight and refers to the decomposed sample below 1000 °C. Out of the total weight loss, 3.90% of the weight loss occurs between 133 and 261 °C, and 21.90% of the weight loss occurs between 525 and 751 °C. Huijgen et al. reported that the decomposition temperature range for CaCO$_3$ is approximately 500–800 °C. As can be seen from Figure 4, the TGA graph shows a greater mass loss in this high-temperature range for wollastonite. As mentioned above, however, the mass loss is about 3.90% at a temperature from 133 to 261 °C because of (bi)carbonate decomposition. The mass loss at the high-temperature range progressively increased, though quantitative conclusions about CO$_2$ sequestration still cannot be made with the lack of a control plot. As shown in Figure 4, the TGA data confirm that the application rate of wollastonite increases while a more significant mass loss from 600 to 751 °C results (i.e., weight loss of 21.90%), indicating calcium carbonate decomposition temperature.

Figure 5 displays the concentration of cations in the post-CO$_2$-batch experiment resulted from the ICP–OES technique. The results show that 60 mL out of 100 mL of the aqueous solution was retrieved. This volume reduction could be attributed to the evaporation process during the depressurization stage at the end of the batch experiment. Based on the ICP–OES results, it was observed that the aqueous solution at ambient condition contains 157 mg/L of calcium, 68 mg/L of
potassium, 26 mg/L of sodium, and 19 mg/L of magnesium. The concentration of strontium and barium was found to be below the detection limit of the ICP−OES analysis. It is also shown that the highest number of cations was observed to be calcium ions, followed by potassium, sodium, and magnesium. The detection of sodium, magnesium, and potassium might dissociate the trace impurities present in the wollastonite sample. The dissociation of potassium is relatively high, accounting for 25% of all the dissociated ions in the water. It might be attributed to the slight potassium concentration present in the wollastonite powder (see Table 3).

3.3. Kinetics Batch Modeling. The kinetics batch modeling was performed at a range of temperatures from 35 to 90 °C, pressure from 1500 to 4000 psi, and salinity from 0 to 90,000 mg/L NaCl. The effect of assessed variables on the mineral carbonation process of wollastonite is presented in the following subsections.

3.3.1. Effect of the Pressure. Figure 6 shows the kinetics batch modeling results from the effect of pressure in wollastonite mineral carbonation. Looking at Figure 6a, it is apparent that the modeled pH of the aqueous solution instantaneously decreases from 7 to 3.03, 2.94, and 2.81 for the pressure of 1500, 2200, and 4000 psi, respectively. Then, the pH was slowly buffered up to 4.5 at the end of the experimental period (i.e., 240 h). The calcium leaching profile is shown in Figure 6b. The concentration of calcium was increased up to 895, 1038, and 1308 mg/L for the pressure of 1500, 2200, and 4000 psi, respectively, before reaching constant values. No calcite was precipitated up to 30 h, and precipitation started to increase with time (Figure 6b); however, the amount of precipitated calcite was less for the higher pressure (Figure 6c). The carbonation efficiency at 1500, 2200, and 4400 psi is 23.1, 22.5, and 21.4%, respectively (Figure 6d). High pressure of 2200 psi can be used to enhance both the dissolution of CO2 in the water media and the diffusion of the gas into the solid matrix. CO2 pressure can significantly influence the reaction rate in the aqueous carbonation at the optimum temperature range (150−200 °C). Operating above those values, carbonation was considered independent of the CO2 pressure. The carbonation of wollastonite at constant temperature (150 °C) remains constant between 1500 and 2200 psi and decreases at CO2 pressure below 1500 psi because of deficiency of (bi)carbonate activity. On the other hand, the wollastonite carbonation increases when the CO2 pressure is increased to 1500 psi at 200−225 °C. Therefore, it can be concluded that the carbonation efficiency decreases with increasing pressure.

3.3.2. Effect of the Reaction Temperature. Figure 7 shows the effect of temperature on the kinetics batch modeling results in terms of (a) pH evolution, (b) calcium leaching profile, (c) calcite precipitation, and (d) carbonation efficiency. Closer inspection of Figure 7a shows that the simulated pH rapidly decreased from 7 to 2.85, 2.94, and 3.04 for 35, 65, and 90 °C, respectively. The pH then gradually increases to 4.5 at the end of simulation time (i.e., 240 h). The calcium leaching profile shows that the calcium concentration rises initially for all the cases (Figure 7b); however, the calcium concentration at 65
and 90 °C becomes constant once the level reached 1428 and 921 mg/L, respectively. For the case of 35 °C, the leaching of calcium continuously increases to 1840 mg/L at the end of simulation time. From Figure 7c, there was no calcite precipitation observed at 35 °C. The calcite precipitation was shown to be higher at 90 °C compared to 35 °C. In Figure 7d, the carbonation efficiency is 0.0, 22.5, and 62.1% at the temperature of 35, 65, and 90 °C, respectively. The carbonation efficiency of “zero” means there is no carbonate being formed at 35 °C within the stipulated duration. This carbonation rate is because the saturation index of calcite is <1, which is undersaturated to commence calcite precipitation. It should be noted that research by Huijgen et al.49 showed that the carbonation efficiency of wollastonite at 25 °C is less than 5%, which is comparable with this study, considering the experiment by Huijgen et al.49 was enhanced significantly by the stirring at 500 rpm. Thus, based on the experimental data from the literature, these simulation results are reasonable, considering the experimental procedure adopted in this study. Based on the geochemical simulation, 337 h is needed to initiate precipitation of calcite at 35 °C. Also, at a temperature of 35 °C, the concentration of Ca is yet to reach supersaturation for the precipitation of calcite to take place. Afterward, the initiation of calcite precipitation will lead to constant Ca concentration because of the incorporation of Ca during calcite precipitation. Therefore, it can be seen from the data in Figure 7 that the carbonation efficiency significantly increases as the temperature increases.

3.3.3. Effect of the Salinity. An instantaneous decrease in pH from 7 to 2.95, 2.89, and 2.85 was observed once the reaction was started at 0, 35,000, and 90,000 mg/L salinity, respectively (Figure 8a). The pH was then slowly buffered to 4.6 at the end of the simulation time. An increase in calcium concentration was observed for all the cases until it reached 1428, 2057, and 2430 mg/L for 0, 35,000, and 90,000 mg/L salinity, respectively (Figure 8b). Afterward, the calcium concentration becomes constant until the end of simulation time (i.e., 240 h). The calcite precipitation was constrained up to 48 h before the precipitation process was started to increase (Figure 8c). As shown in Figure 8d, the carbonation efficiencies for 0, 35,000, and 90,000 mg/L are 22.5, 20.95, and 20.03%, respectively. The results indicated that the carbonation efficiency increases with decreasing salinity in the aqueous solution.

3.4. Results Comparison. The lack of effluent analysis during the experimental procedure does not allow the calibration of the geochemical model to take place. However, the model prediction was validated via observation from SEM−EDS and TGA data, which confirms the modeling results qualitatively and quantitatively. Calcite precipitation was observed in the geochemical model as well as in the SEM−EDS analysis. Meanwhile, based on the TGA analysis, the reacted fraction of wollastonite is 25.80%, while the modeling result shows 30% of the wollastonite reacted fraction within the typical simulation experiment difference (±4%).

Also, from TGA results and eqs (R1−1), 10 g of wollastonite with a weight loss of 25.80% could produce 5.52 g of CaCO3 and sequester 3.42 g of CO2 as measured by the TCA. This finding also showed a positive statistical relationship between the amount of consumed wollastonite and sequestered CO2. If the aim is to apply 1 Mt of CO2 per year, 5.160 Mt of wollastonite is utilized. As a result, the rate of CO2 sequestration is in equilibrium with the precipitation of CaCO3.

4. DISCUSSION

In the mechanism of mineral carbonation, availability or scarcity of divalent cations is one of the main factors affecting the conversion of CO2 into stable carbonate minerals. According to the concentration of cations after 240 h (see
Figure 8. Influence of the salinity on the mineral carbonation of wollastonite in the kinetics batch modeling: (a) pH evolution, (b) calcium leaching profile, (c) calcite precipitation, and (d) mineral carbonation efficiency at a fixed pressure of 1500 psi and temperature of 90 °C over 240 h.

Figure 8), the high concentration of calcium could be associated with the dissolution mechanism of the initial wollastonite structure in releasing more calcium cations. Wollastonite reacts with the H+ ions in the slurry and dissociates into silicon and calcium ions. Gopinath and Mehra\(^+\) stated that the rate of wollastonite dissociation depends on the concentration of H+ ions in the slurry and also the maximum solubility of calcium ions in the dissolution process. The kinetics batch modeling was conducted at the same experimental condition (see Figures 6–8) and showed a significant dissolution of calcium that occurs once the injected CO2 is dissolved into the water. Figures 6–8 illustrate the change in the concentration of calcium ions with time. At the optimum conditions, that is, a temperature of 90 °C, pressure of 1500 psi, and salinity of 0 ppm, a high rate of calcium concentration is observed during 7.2, 21.6, and 26.4 h reaction time, respectively. There was no observed difference in the concentration rate of calcium after these reaction times. At the same experimental condition (see Reaction R1) the calculated pH to decrease from 7 to approximately 2.95, which eventually initiates the dissolution of wollastonite (see Reaction R2). It is consistent with the findings of Daval et al.,\(^{41}\) where the dissociation of calcium cations in the wollastonite structure was initiated under the acidic condition of the CO2-saturated solution. A decrease in wollastonite surface thickness was also expected based on the mass loss observed from the TGA analysis in Figure 4. A study conducted by Min and Jun\(^{51}\) indicated that the reacted thickness of wollastonite increases as the mass loss resulted from the TGA analysis increases. Changes in thickness observed by Min and Jun\(^{51}\) were due to the diffusion of supercritical CO2 on the mineral surface, which eventually triggers the dissociation of wollastonite grains.

Noticeable growth of secondary mineral was observed on surfaces of wollastonite grains after being exposed to CO2 for 240 h (see Figure 3c). The peaks from EDX spectra (see Figure 3d) showed that the secondary mineral growth contains calcium, carbon, and oxygen, which are the main components for calcium carbonate crystals. Most of calcium carbonate crystals formed in this experiment possess a rhombohedral crystal habit, which is a typical crystal structure for carbonate minerals such as calcite (CaCO3), magnesite (MgCO3), rhodochrosite (MnCO3), siderite (FeCO3), and smithsonite (ZnCO3). However, the absence of Mg, Mn, Fe, and Zn for the stated common carbonate minerals in the FESEM–EDX (see Figure 3) suggests that the rhombic crystal is calcite. Also, the precipitation of calcite was observed in the kinetic batch modeling (see Figure 6c), wherein the brine was supersaturated with calcium. These results seem to be consistent with other research studies, which found the formation of calcite as the secondary product in the mineral carbonation of wollastonite.\(^{42,44}\) Although there is a possibility to form another byproduct amorphous calcium carbonate in the carbonation reaction,\(^{45}\) it has not been detected during the analytical characterization, as the intermediate phases are easily transformable to more stable phases. Moreover, amorphous silica, which is also referred to as a pervasive layer or passivating layer, was detected in the reacted wollastonite sample of this study (see Figure 3a). The formation of an amorphous silica layer was also observed in another experimental research study as well. For example, Daval et al.\(^{41}\) reported a silica-rich passivating layer as the reaction product from the wollastonite carbonation experiment. Miller et al.\(^{44}\) also detected this passivating amorphous phase through X-ray diffraction and solid-state nuclear magnetic resonance spectroscopy. Even though we have witnessed that the wollastonite carbonation reaction yielded stable calcium carbonate mineral (calcite) and pervasive silica layer as shown in Reactions R2 and R3, the reaction rate and carbonation efficiency are influenced by affective variables of pressure, temperature, and salinity.

Furthermore, the instantaneous pH drop can be observed because of the rapid dissociation of CO2 into the aqueous solution that is not affected much by pressure (see Figure 6a). However, these small changes in pH significantly affect the amount of calcium extracted during the initial reaction. Little
difference in pH serves as a driving force for the calcium leaching mechanism and results in an increment of calcium concentration in the solution (see Figure 6b). Despite the increase in the dissolution reaction mechanism, the CO\textsubscript{2} conversion efficiency at different pressures was nearly constant (see Figure 6d). Rising pressure was observed to have a small influence on the CO\textsubscript{2} conversion during the in situ mineral carbonation of wollastonite. The calcite precipitation profile also confirmed this observation in Figure 6c, where there was not much difference in terms of CO\textsubscript{2} conversion into calcite. Because there were insufficient carbonate activities at different pressures, the precipitation of the carbonated mineral was almost unaffected by pressure. The simulation of pure water saturated with CO\textsubscript{2} at pressure values between 1500 and 4000 psi and a temperature of 65 °C was conducted to examine the log activity of carbonated mineral. The results showed that the log activities for the carbonated mineral are −10.123, −10.123, and −10.124 at simulated pressures of 1500, 2200, and 4000 psi, respectively, which is near constant at all examined pressures (Figure 9). This outcome is contrary to the work by Li et al.\textsuperscript{68} who found that a reduction in pressure lightly increases the aqueous carbonate concentration. Although the various ranges of working pressure from less than 1 MPa to more than 10 MPa have been examined in the kinetics batch modeling, the results from kinetics batch modeling showed that the factor of working pressure has a constant effect on the concentration of calcium in the in situ mineral carbonation mechanism.

An additional simulation was performed at a lower pressure of 150, 300, and 500 psi to assess the influence of pressure on mineral carbonation. The results showed that changes in pressure have a minor impact (±2%) on carbonation efficiency (Figure 10). Nevertheless, the carbonation efficiency shows a considerable increment, specifically in the pressure range of 150 psi to 500 psi, when the reaction temperature was extended for 200 °C.

At a fixed pressure, an increment in temperature would lead to an increase in initial pH due to the lower solubility effect of CO\textsubscript{2} at higher temperatures. It can be observed in Figure 7a, where the initial pH of CO\textsubscript{2}-saturated aqueous solution becomes more elevated at higher temperatures. Therefore, the rate of dissolution was determined to be impacted by pH, in which the dissolution rate is high at lower pH. Besides, the amount of calcium dissolved during the dissolution reaction decreases with temperature (see Figure 7b). The dissolution of calcium reduces by 50% as the temperature increased from 35 to 90 °C. Thus, the increase in temperature was shown to reduce the kinetics of the surface reaction significantly, decreasing the calcium leaching mechanism from the wollastonite (Figure 11).

From Figures 7c and 10, the carbonation efficiency is the same at a temperature of 65 °C and working pressure of 2200 psi, which is 22.49%. The scale of the y-axis in the bar chart of Figure 7d is more extensive, making the small difference significant. In contradiction to the above, the carbonation efficiency was shown to increase with the increase in the reaction temperature (see Figure 7d). The enhancement of the carbonation rate with temperature might be due to an increase in the carbonate activity with the increasing reaction temperature. Based on Figure 9, it can be observed that the log activity for the carbonated mineral is −10.277, −10.123, and −10.071 at 35, 65, and 90 °C, respectively. There is no CO\textsubscript{2} conversion into calcite (see Figure 7c) that occurred at 35 °C because the calcium is yet to reach supersaturation level to commence calcite precipitation. As a result of the simulation, 337 h is needed to initiate precipitation of calcite at 35 °C.

Looking at Figure 8b, it is apparent that a higher salinity can promote the dissociation of calcium from wollastonite. An enhancement in the dissolution rate was observed even at a salinity as low as 5000 mg/L of NaCl. The dissolution of
calcium was 1.2 times higher than in deionized water. The salinity was known to decrease the CO2 solubility in water.69 As a result of simulation at 2200 psi and 65 °C, the CO2 solubility decreases 25% as the aqueous salinity increases from 0 to 90,000 mg/L NaCl. However, pH decreases with an increase in NaCl concentration in the CO2−H2O−NaCl solution due to a significant rise in the H+ activity coefficient, causing a drop in the pH value. Although the pH drop in 90,000 mg/L NaCl is only 0.09, the concentration of calcium is 42% higher compared with deionized water. The decline in the pH value causes a significant increase in terms of calcium dissociation in the wollastonite sample.

From Figure 8d, it can be seen that there is no much difference in terms of mineral carbonation for all salinity cases (±2%). Though an increase in the salinity enhances the calcium extraction rate, the carbonate activity is low at a high saline solution, which lowered the potential of mineral carbonation. In contrast, the carbonate activity is increased in a low saline solution. However, the low dissolution rate in low saline solution impedes the carbonation efficiency in wollastonite. The opposite effect between the dissolved calcium and carbonate activity causes the carbonation rate of all saline solutions near the same.

5. CONCLUSIONS

The reaction mechanism of wollastonite in situ mineral carbonation for CO2 sequestration was evaluated under various reaction temperatures, pressures, and salinities. In this investigation, the aim was to assess the impact of temperature, pressure, and salinity on the release rate of divalent metal cations during silicate mineral dissolution and the conversion rate of liberated cations into the carbonated mineral. A rocking system was used to ensure that all the wollastonite grains are homogeneously reacted with the CO2-dissolved water. The rocking system might not have a direct representation in real conditions. Nevertheless, as the factor of pressure, temperature, and salinity is the focus of this research, the rocking system eliminates other parameters that might conflict the geochemical analysis during the CO2−water−wollastonite interaction. The results revealed that these in situ parameters have a significant impact on the CO2−fluid−mineral interaction in wollastonite samples. A substantial increase in the rate of calcium dissolution was documented when the factor of pressure and salinity was increased. The calcium concentration increases as the pressure and salinity change from 1500 to 4000 psi and 0 to 90,000 mg/L NaCl, respectively. However, a different trend was shown in the calcium concentration (49% decrease) as the reaction temperature increases from 35 to 90 °C. Also, the results indicated that the carbonation efficiency increases with decreasing pressure and salinity in the aqueous solution. Moreover, the kinetics batch modeling was validated using experimental results to assess the geochemical interaction between the CO2 water, and wollastonite. Furthermore, the results showed that the carbonation efficiency increases with the decreasing pressure and salinity from 90,000 to 0 mg/L and 4000 to 1500 psi, respectively, whereas the mineral carbonation efficiency was shown to be enhanced by 62% with increasing temperature. For all applied temperatures, the calcium concentration increases initially and then becomes constant for the cases of 65 and 90 °C. For instance, at 35 °C, the leaching of calcium continuously increases. Also, the calcite precipitation was shown to be higher at 90 °C compared to 35 °C. Thus, it could be concluded that the reaction temperature mainly controls wollastonite in situ mineral carbonation. Simultaneously, the dissolution mechanism is significantly affected by all factors of pressure, temperature, and salinity. Based on the findings, this study can be applied to extensive accessibility feedstocks rich in Ca, Mg, and Fe because of the research on CO2 sequestration. Future works may focus more on the mineralogy containing calcium, magnesium, and iron to enhance the rate of carbon dioxide sequestration and the recovery of potential metals.

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ABBREVIATIONS

GCS, geological CO2 sequestration; CO2, carbon dioxide; Ca, calcium; mg/L, milligram per liter; psi, pound-force per square inch; °C, degree centigrade; %, percent; GHGs, greenhouse gases; CCS, CO2 capture and sequestration; aq, aqueous; m, meter; GWB, Geochemist’s Workbench; EDX, energy
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