



Thermodynamic analysis of theoretical dolomite formation from seawater and captured carbon dioxide

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Abstract

In this study, an integrated system is proposed to form dolomite chemically from seawater and carbon dioxide. The system contains three main chemical processes: formation of magnesium hydroxide and calcium hydroxide, the reaction of magnesium hydroxide and calcium hydroxide with carbon dioxide, and the formation of dolomite. Based on the fundamental thermodynamic laws, energy and exergy analyses, and performance assessment of the proposed system is carried out. Furthermore, the effects of varying temperatures of each process on various energy and exergy efficiencies are assessed through parametric studies. The results show that formation of dolomite is favorable at temperature ranges of 313–470 K based on the thermodynamic study. The exergy efficiency of dolomite formation is found to be about 23.8% and the results reveal that the dolomite formation process has the specific exergy destruction value of 29.6 kJ/mol among other sub-processes. The results suggest that the proposed system may provide enhanced options for low-temperature dolomite formation using seawater and captured carbon dioxide once the reaction kinetics is favored.

Keywords Carbon capture · Dolomite · Energy · Exergy · Efficiency · Building material

1 Introduction

The formation and properties of dolomite have been investigated since the beginning of the 1900s [1]. Dolomite is formed when lime muds or limestone are modified by post-depositional chemical change. Dolomite is used as an aggregate in construction projects, and it is a kiln fired in the manufacturing of cement [2]. Dolomite can be used as a replacement for some conventional materials in the cement sector and it results in suitable raw materials for the production of Portland cement [3, 4]. Conventional materials that are used in cement manufacturing are not favorable due to unavailability of natural material, energy consumption, and carbon dioxide emissions. Replacing conventional materials by alternative materials can recover some of the conventional material in the cement industry especially considering the high CO₂ emissions from the cement industry.

Enhancing renewable based raw materials can contribute significant reduction in energy use and greenhouse gas emissions in building sector [5, 6]. Artificial dolomite can play a role in the transition, however dolomite formation mechanism, kinetics in natural systems and synthesis in laboratory conditions are not clearly studied. Formation of dolomite is favored thermodynamically, and it is related to the difficulties of generating dolomite at low temperature and thermodynamic preference which is called dolomite problem. The dolomite problem has remained one of the most studied topics in geology due to low direct dolomite formation. The dolomite problem is the denial between the difficulties to generate dolomite in the lab at low temperature. The composition and distribution of materials in geochemical systems are strongly controlled by reaction kinetics. Marine carbonates and dolomite are examples of such materials [7]. Therefore, investigators attempt to develop

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geochemical modules to form dolomite [8]. Typically, experimental syntheses regarding dolomite reaction mechanisms, kinetics, and physiochemical conditions can resolve the “dolomite problem” [9, 10]. There are two ways presented in some of the literature studies to form dolomite at low temperatures. Firstly, forming dolomite experimentally by mixing two solutions, one solution contains Mg/Ca ratio ≥ 1 with other solution contains dissolved carbonate ions. The experiment was conducted at one independent parameter which was temperature. The experiment was only successful when the temperature was more than 100 °C [11]. Secondly, the new synthesis pathway for dolomite formation using calcite and magnesite was tested under different temperature ranges from (25 to 200 °C). Other parameters including calcium, magnesium, and reaction solution amount were constant [9]. Due to low direct dolomite formation from seawater naturally, there is a need of research for increasing ways of forming dolomite to be used as a replacement of cement. In addition, the dolomite can also be used as pre-treatment agents for acid mine drainage [12]. There is a lack of information in the literature studying the exergy analysis of artificial dolomite formation through captured carbon dioxide and sea water. Moreover, the reaction mechanism and role of all parameters including the amount of heat needed in the processes to form dolomite, the reaction temperature in each process, heat losses during the processes, energy and exergy efficiencies, and exergy destructions of the reactions are poorly studied. Therefore, identifying all these factors that affect dolomite formation remains a major scientific challenge to obtain a better understanding of dolomite formation to facilitate its production.

Consequently, the specific objectives of this study are listed as follows:

- To propose dolomite formation process utilizing Mg^{2+} and Ca^{2+} ions obtained from seawater and captured carbon dioxide.
- To analyze the proposed artificial dolomite formation process using thermodynamic laws (first and second laws of thermodynamics).
- To determine the specific exergy destruction rates within the proposed system.
- To evaluate the energy and exergy efficiencies of each sub-process and overall process.

2 System description

A schematic diagram of the proposed system is presented in Fig. 1. The system contains two main inlets: sea water and carbon dioxide, and the system has three processes. The first process is when seawater enters the system to form magnesium hydroxide and calcium hydroxide. Seawater is used as a source of magnesium ions, calcium ions, and hydroxide ions. These three ions are present after seawater passes through the ion separator. The ion separator makes 1 mol of magnesium ions and 1 mol of calcium ions and 4 mol of hydroxide ions. One mole of magnesium ion reacts with 2 mol of hydroxide ions to form magnesium hydroxide with the addition of heat, and the other 2 mol of hydroxide react calcium ions to form calcium hydroxide with the addition of heat. The heat source that comes from the third process is used in the second process to supply the endothermic process. The second process is the reaction when the formed magnesium hydroxide and formed calcium hydroxide reacts with carbon dioxide to form magnesium carbonate and calcium carbonate. Both the processes generate heat as output due to the chemical reaction. The third process is the mixture of the output

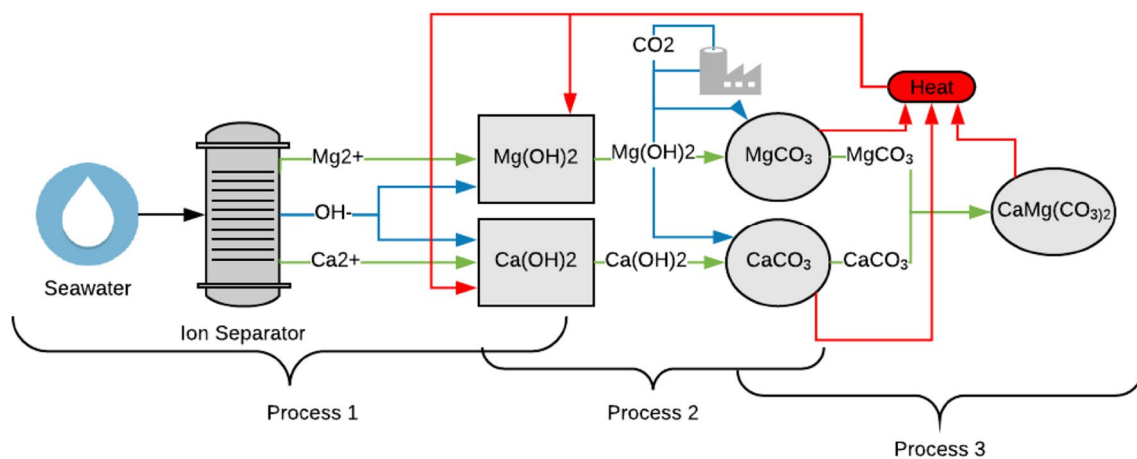
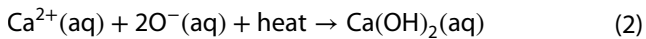
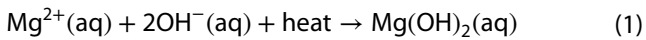


Fig. 1 A schematic diagram of dolomite formation from seawater

of the second process which the reaction of magnesium carbonate with calcium carbonate to form dolomite which can be used as cement substitute.

2.1 Process 1

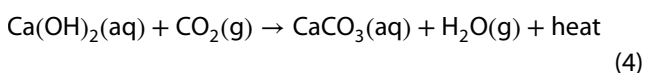
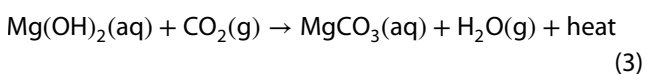
The first process contains the formation of two chemicals: magnesium hydroxide and calcium hydroxide as presented in the following chemical reactions:



When seawater enters the ion separator, chemical compositions of seawater turn to ions [13]. Magnesium ions, calcium ions, and hydroxide ions are absorbed by the system where the other ions are neglected. The reaction of 1 mol of aqueous magnesium ions with 2 mol of aqueous hydroxide form magnesium hydroxide. The same process happens when 1 mol of aqueous calcium ions react with 2 mol of hydroxide ions to form calcium hydroxide. Both processes are endothermic, so they require heat to occur and the reactions are held in room temperature around 25 °C. The source of heat is taken from the third process to supply this process. It is noted that there should be a suitable engineering design for capturing the heat and providing to other processes. For instance, this can be overcome by thermal energy storage units where the exothermic heat is supplied to a molten salt medium or a phase change material and later on provided to the endothermic reaction.

2.2 Process 2

The outputs of the first process are used as inputs in the second process. Both magnesium hydroxide and calcium hydroxide react with pressured carbon dioxide gas from industry to form magnesium carbonate, calcium carbonate, water vapor, and heat respectively as shown in the chemical reactions. Here, the reaction occurs when the temperature is 20 °C and the carbon dioxide pressure is 50 bar.

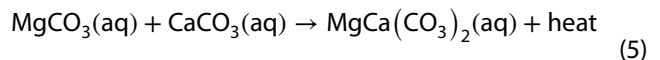


2.3 Process 3

The third process shows the formation of dolomite when both products from the second process react together.

According to Montes-Hernandez et al. [9], dolomite is precipitated directly and homogeneously by mixing two solutions, one contains magnesium, calcium and other contains dissolved carbonate ions [1:1:2]. Better dolomite formation occurs when 1.0 M solution mixed in Ca^{2+} , Mg^{2+} , and CO_3^{2-} ration of 1:1:2 where the PH of the precipitation medium ranges from 9.7 to 9.1 and temperature ranges from 25 to 100 °C [10, 14].

Reacting magnesium carbonate with calcium carbonate form dolomite and heat as presented in the following chemical equation:



Dolomite can be formed by mixing 1 mol of calcite (CaCO_3) and 1 mol of magnesite (MgCO_3) [9, 15].

Note that the composition and distribution of materials in geochemical systems are strongly controlled by reaction kinetics. However, the dolomite formation step is spontaneous at low temperature in the third process even though the production rate is limited due can be the kinetic limitation of the reaction.

3 Analysis and assessment

Thermodynamic analysis of the system is conducted using Engineering Equations Solver (EES) [16] by thermodynamic laws using energy, entropy, and exergy balance equations. These balance equations are applied for all the processes individually and integrated together by assigning appropriate state points. The main assumptions in the analysis for the state operation are listed as follows:

- The ambient conditions are considered as $T_o = 298 \text{ K}$ and $P_o = 101.325 \text{ kPa}$.
- The sink temperature is taken as $T_{si} = 298 \text{ K}$.
- Ion separation makes 1 mol of Mg^{2+} , Ca^{2+} , and OH^{-} .
- CO_2 is taken from the carbon capture unit at 50 bar.
- All the chemical reactions take place according to their stoichiometry and goes to completion.

For the system analysis, each process has been analyzed thermodynamically (energy, entropy, exergy balance equations). After developing the governing thermodynamic equations of each process, they are integrated by assigning appropriate inputs and outputs for each process. Since all processes contain chemical reactions, reactants are as input to the process and products are output to the process. Defining all these processes, equations represent the thermodynamic model of the whole system. Additionally,

boundary condition such as ambient conditions for each process is constrained to perform the parametric study.

The system contains three main processes. Formation of magnesium hydroxide $Mg(OH)_2$, calcium hydroxide $Ca(OH)_2$, magnesium carbonate $MgCO_3$, calcium carbonate $CaCO_3$ and dolomite $MgCa(CO_3)_2$. For analysis, energy balance for all the processes of the system is applied according to the first law of thermodynamics. In fact, the energy balance equation of any steady state flow process in molar form is shown as follows:

$$\sum \dot{Q}_{net} + \sum \dot{W}_{net} + \sum \dot{n}_{in}h_{in} - \sum \dot{n}_{out}h_{out} = 0 \quad (6)$$

where \dot{Q} is heat rate required or released, \dot{W} is work rate required or produced through the boundary, \dot{n} is the mole flow rate required and h is the specific enthalpy of each compound in kJ/mol. Energy balance equations for all the processes in the system are presented in Table 1. The enthalpy of magnesium hydroxide, calcium hydroxide, water, and carbon dioxide are defined using NASA library in EES software [16]. The enthalpy of the ions magnesium ions, calcium ions, hydroxide, and dolomite are defined from literature [17]. Once the energy balance equations for each process in the system is defined, they are integrated by defining the appropriate inputs to each process. Generally, the output of one process is input to another process.

Energy analysis by itself is not satisfactory for detailed thermodynamic analysis of a system [18–20]. Therefore, exergy analysis, which is based on the second law of thermodynamics, has been implemented for each process in the system. The specific physical exergy equation for each process is presented in the following equation:

$$ex_{ph_i} = h_i - h_o - T_o(s_i - s_o) \quad (7)$$

where s represents the specific entropy of a compound in each process, subscript i is i th state point and subscript o represents the reference conditions. The entropy of magnesium hydroxide, calcium hydroxide, water and carbon dioxide are defined using NASA library in EES software. The entropy of the ions magnesium ions, calcium ions, hydroxide and dolomite are defined from literature [17]. The exergy balance equation of a steady state process is governed by the following equation:

$$\dot{E}x_{d_i} = \dot{E}x^{Q_i} - \dot{E}x_{W_i} + \sum \dot{n}_{in}ex_{in} - \sum \dot{n}_{out}ex_{out} \quad (8)$$

where $\dot{E}x_{d_i}$ is the rate of exergy destruction occurring in a compound i , $\dot{E}x^{Q_i}$ is the exergy of heat rate required, $\dot{E}x_{W_i}$ is work related exergy rate, $\dot{n}_{in}ex_{in}$ is the exergy carried by 1 mol into the system while $\dot{n}_{out}ex_{out}$ is the exergy carried out of the system by 1 mol. $\dot{E}x^{Q_i}$ is expressed by the following equation:

$$\dot{E}x^{Q_i} = \dot{Q}_i \left(1 - \frac{T_o}{T_{s_i}} \right) \quad (9)$$

where \dot{Q}_i represents the heat rate required, T_o represents the ambient temperature and T_{s_i} is sink temperature when there is heat loss from the system. Since all the processes contain chemical reactions, chemical exergy is incorporated in the equation to calculate specific exergy for each compound. The total specific exergies are calculated using the following equation:

$$ex_i = h_i - h_o - T_o(s_i - s_o) + ex_{ch_i} \quad (10)$$

Table 1 Energy balance equations for all the processes in the system

Processes	Energy balance equation
Process 1 $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(aq)$ $Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(aq)$	$\dot{n}_{Mg^{2+}}h_{Mg^{2+}} + 2\dot{n}_{OH^-}h_{OH^-} + \dot{Q}_{in,1} = 1\dot{n}_{Mg(OH)_2}h_{Mg(OH)_2}$ $1\dot{n}_{Ca^{2+}}h_{Ca^{2+}} + 2\dot{n}_{OH^-}h_{OH^-} + \dot{Q}_{in,2} = 1\dot{n}_{Ca(OH)_2}h_{Ca(OH)_2}$
Process 2 $Mg(OH)_2(aq) + CO_2(g) \rightarrow MgCO_3(aq) + H_2O(g)$ $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(aq) + H_2O(g)$	$1\dot{n}_{Mg(OH)_2}h_{Mg(OH)_2} + 1\dot{n}_{CO_2}h_{CO_2} = 1\dot{n}_{MgCO_3}h_{MgCO_3} + 1\dot{n}_{H_2O}h_{H_2O} + \dot{Q}_{out,3}$ $1\dot{n}_{Ca(OH)_2}h_{Ca(OH)_2} + 1\dot{n}_{CO_2}h_{CO_2} = 1\dot{n}_{CaCO_3}h_{CaCO_3} + 1\dot{n}_{H_2O}h_{H_2O} + \dot{Q}_{out,4}$
Process 3 $MgCO_3(aq) + CaCO_3(aq) \rightarrow CaMg(CO_3)_2(aq)$	$1\dot{n}_{MgCO_3}h_{MgCO_3} + 1\dot{n}_{CaCO_3}h_{CaCO_3} = 1\dot{n}_{MgCa(CO_3)_2}h_{MgCa(CO_3)_2} + \dot{Q}_{out,5}$

Table 2 Exergy balance equations for all the processes in the system

Processes	Exergy balance equation
Process 1 $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(aq)$ $Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(aq)$	$1\dot{n}_{Mg^{2+}}ex_{Mg^{2+}} + 2\dot{n}_{OH^-}ex_{OH^-} + \dot{E}x^{Q_1} = 1\dot{n}_{Mg(OH)_2}ex_{Mg(OH)_2} + \dot{E}x_{d_1}$ $1\dot{n}_{Ca^{2+}}ex_{Ca^{2+}} + 2\dot{n}_{OH^-}ex_{OH^-} + \dot{E}x^{Q_2} = 1\dot{n}_{Ca(OH)_2}ex_{Ca(OH)_2} + \dot{E}x_{d_2}$
Process 2 $Mg(OH)_2(aq) + CO_2(g) \rightarrow MgCO_3(aq) + H_2O(g)$ $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(aq) + H_2O(g)$	$1\dot{n}_{Mg(OH)_2}ex_{Mg(OH)_2} + 1\dot{n}_{CO_2}ex_{CO_2} = 1\dot{n}_{MgCO_3}ex_{MgCO_3} + 1\dot{n}_{H_2O}ex_{H_2O} + \dot{E}x_{d_3} + \dot{E}x^{Q_3}$ $1\dot{n}_{Ca(OH)_2}ex_{Ca(OH)_2} + 1\dot{n}_{CO_2}ex_{CO_2} = 1\dot{n}_{CaCO_3}ex_{CaCO_3} + 1\dot{n}_{H_2O}ex_{H_2O} + \dot{E}x_{d_4} + \dot{E}x^{Q_4}$
Process 3 $MgCO_3(aq) + CaCO_3(aq) \rightarrow CaMg(CO_3)_2(aq)$	$1\dot{n}_{MgCO_3}ex_{MgCO_3} + 1\dot{n}_{CaCO_3}ex_{CaCO_3} = 1\dot{n}_{MgCa(CO_3)_2}ex_{MgCa(CO_3)_2} + \dot{E}x_{d_5} + \dot{E}x^{Q_5}$

Table 3 Definition of exergy efficiencies for all the processes

	Process	Exergy efficiency
Process 1	$Mg^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mg(OH)_2(aq)$	$\eta_{ex,1} = \frac{ex_{Mg(OH)_2}}{(ex_{Mg^{2+}} + 2ex_{OH^{-}} + \dot{E}X^{Q_{in,1}})}$
	$Ca^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ca(OH)_2(aq)$	$\eta_{ex,2} = \frac{ex_{Ca(OH)_2}}{(ex_{Ca^{2+}} + 2ex_{OH^{-}} + \dot{E}X^{Q_{in,2}})}$
Process 2	$Mg(OH)_2(aq) + CO_2(g) \rightarrow MgCO_3(aq) + H_2O(g)$	$\eta_{ex,3} = \frac{ex_{MgCO_3}}{(ex_{Mg(OH)_2} + ex_{CO_2})}$
	$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(aq) + H_2O(g)$	$\eta_{ex,4} = \frac{ex_{CaCO_3}}{(ex_{Ca(OH)_2} + ex_{CO_2})}$
Process 3	$MgCO_3(aq) + CaCO_3(aq) \rightarrow CaMg(CO_3)_2(aq)$	$\eta_{ex,5} = \frac{ex_{MgCa(CO_3)_2}}{(ex_{MgCO_3} + ex_{CaCO_3})}$

where, ex_{ch_i} is the chemical exergy content of each compound. The values of specific chemical exergies of reactants and products are available in the literature [21]. The exergy balance equations for all the processes in the system are presented in Table 2 and the exergy efficiency for all the processes are in Table 3.

Change in enthalpy of the reaction in each process is defined by a change in enthalpy of product substitute with a change in enthalpy of reactants as shown in the following equation [22].

$$H_{rxn} = H_{products} - H_{reactants} \tag{11}$$

Change in entropy of the reaction is defined by a change in entropy of product substitute with a change in entropy of reactants as shown in the following equation.

$$S_{rxn} = S_{products} - S_{reactants} \tag{12}$$

Change in entropy is found to determine Gibbs free energy of the reaction because Gibbs free energy is combination of enthalpy change and entropy change. Gibbs free energy is defined by a change in enthalpy substitute with a change in entropy multiplied by reference temperature as shown in the following equation [22].

$$G_{rxn} = H - TS \tag{13}$$

Equilibrium constant in each process is defined as per the following equation:

$$K_{eq} = \exp\left(\frac{-G_{rxn}}{RT}\right) \tag{14}$$

where K_{eq} represents equilibrium constant, $-G_{rxn}$ is Gibbs free energy change, R is the gas constant and T is the temperature of each process.

4 Results and discussion

The analysis of the system is performed using Engineering Equation Solver Software which is a powerful tool for thermodynamic analysis through energy, entropy, exergy balance equations. Values of temperature, pressure, specific enthalpy, specific entropy, specific exergy, standard chemical exergy are determined for all the states in the system as shown in Table 4.

Table 5 shows the change in specific entropy, change in specific enthalpy, specific Gibbs free energy for the three

Table 4 Thermodynamic properties for all the states in the system

	Specific enthalpy (kJ/kmol)	Specific entropy (kJ/kmol K)	Specific exergy (kJ/kmol)	Specific chemical exergy (kJ/kmol)	Reference specific enthalpy (kJ/kmol)	Reference specific entropy (kJ/kmol K)
Mg ²⁺ (aq)	-467,000	-137	754,100	754,100	-467,000	-141
OH ⁻ (aq)	-230,000	-10.7	120,300	120,300	-230,000	-10.7
Mg(OH) ₂ (aq)	-924,293	63.18	40,900	40,900	-924,293	63.18
Ca ²⁺ (aq)	-544,000	-56.2	831,400	831,400	-544,000	-57.2
Ca(OH) ₂ (aq)	-985,840	83.39	53,700	53,700	-985,840	83.39
CO ₂ (g)	-393,486	180.6	29,537	19,870	-393,676	213.7
MgCO ₃ (aq)	-1,096,000	63.77	37,903	37,900	1,096,000	65.09
H ₂ O(g)	-241,811	155.7	19,166	9500	-241,984	188.7
CaCO ₃ (aq)	-1,207,000	90.26	1004	1000	-1,207,000	91.7
CaMg(CO ₃) ₂ (aq)	-2,325,000	127.7	9259	15,100	-2,324,000	105

processes in the system and its spontaneity. Magnesium hydroxide and calcium hydroxide processes have large positive enthalpy change, therefore, they absorb a large amount of heat which is said to be strongly endothermic. However, dolomite process has large negative specific enthalpy change hence it releases a large amount of heat which is called to be exothermic. Moreover, experimental observations have shown that a decrease in free energy is associated with reactions which occur spontaneously. All the reactions have negative specific Gibbs free energy, so they are all spontaneous, the tendency to occur.

Table 6 lists the results of the energy and exergy analysis. The specific heat required input to form magnesium hydroxide and calcium hydroxide are theoretically found

as 2707 kJ/kmol and 18,160 kJ/kmol, respectively. The exergy efficiency of both magnesium hydroxide and calcium hydroxide are low due to the absorption of heat of reaction however the exergy efficiency of other three processes (magnesium carbonate, calcium carbonate, and dolomite) are high because of production of the heat of the reaction. The exergy efficiency of magnesium carbonate is 53.8% which is the highest among all the other processes due to its high chemical exergy at reference state [21]. The exergy destruction and efficiency of all the system process are shown in Fig. 2.

The specific exergy destruction is found to be large in both processes forming magnesium hydroxide and calcium hydroxide because of the input heat required

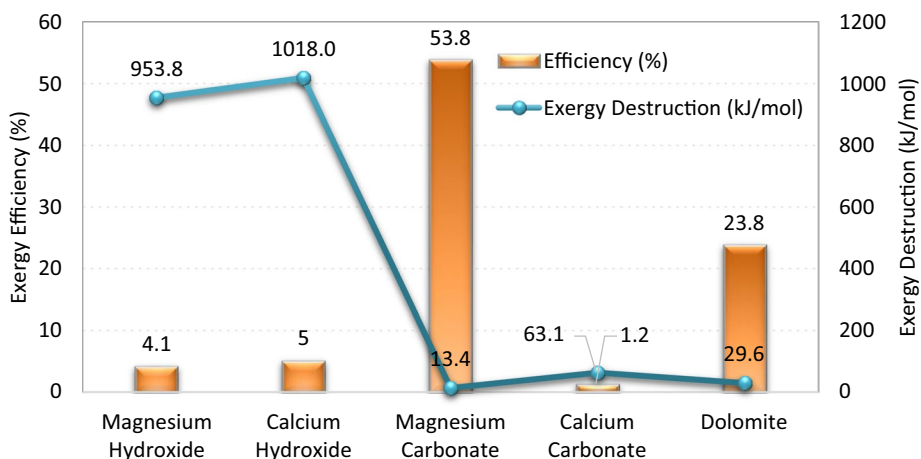
Table 5 The change in entropy, change in enthalpy Gibbs free energy for the five processes in the system and its spontaneity

Processes	Specific entropy change Δs (J/kmol K)	Specific enthalpy change Δh (kJ/kmol)	Specific gibbs free energy change Δg (kJ/kmol)
Process 1 $Mg^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mg(OH)_2(aq)$	225.6	2707	-64,549
$Ca^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ca(OH)_2(aq)$	162	18,160	-30,138
Process 2 $Mg(OH)_2(aq) + CO_2(g) \rightarrow MgCO_3(aq) + H_2O(g)$	-24.31	-20,338	-13,215
$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(aq) + H_2O(g)$	-18.04	-69,422	-64,138
Process 3 $MgCO_3(aq) + CaCO_3(aq) \rightarrow CaMg(CO_3)_2(aq)$	-26.3	-20,519	-11,313

Table 6 The results of the energy and exergy analysis

Parameters	Value
Specific heat required for magnesium hydroxide formation (kJ/kmol)	2707
Specific heat required for calcium hydroxide formation (kJ/kmol)	18,160
Exergy efficiency of magnesium hydroxide formation process (%)	4.1
Exergy efficiency of calcium hydroxide formation process (%)	5.0
Exergy efficiency of magnesium carbonate formation process (%)	53.8
Exergy efficiency of calcium carbonate formation process (%)	1.2
Exergy efficiency of dolomite formation process (%)	23.8

Fig. 2 The specific exergy destruction and exergy efficiency of all the processes



to make the reaction occur. The specific exergy destruction values for both the processes are 953.8 kJ/mol and 1018 kJ/mol, respectively. Therefore, the exergy efficiencies are low due to the required input heat. The specific exergy destruction of dolomite formation step is 29.6 kJ/mol, which is the lowest because of its favorability of forming from magnesium carbonate and calcium carbonate [9].

The change in exergy efficiency and required heat input with respect to the temperature of both processes (magnesium hydroxide and calcium hydroxide) are illustrated in Fig. 3. Increasing reaction temperature increases the required heat input and increase exergy efficiency slightly. As temperature increases in both processes, the specific free Gibbs energy required increases resulting in an increase in required heat input. Since the reactions for the processes have a large positive change in enthalpy,

both reactions are strongly endothermic which shows that the chemical reactions absorb a large amount of heat to occur [23]. Increasing in temperature results in an increase in exergy efficiency by 0.22% for magnesium hydroxide and 0.03% for calcium hydroxide. Therefore, these two processes are favorable to be implemented at slightly higher temperatures and increasing the temperature enhances the performance of the process.

Figure 4 shows the relationship between equilibrium constant and exergy efficiency with temperature for magnesium carbonate and calcium carbonate. Equilibrium constant relates the equilibrium compositions of a chemical reaction system to measurable physical properties of reactants and products. As the temperature increases, it results in decreasing in equilibrium constant which shows decreasing in products. The equilibrium constant

Fig. 3 The change in exergy efficiency and required heat input with respect to the temperature of both processes (magnesium hydroxide and calcium hydroxide)

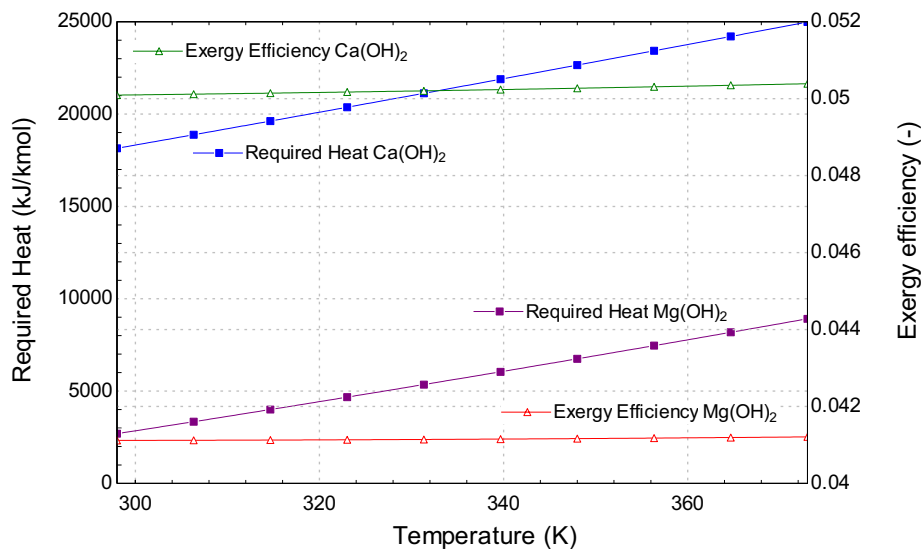
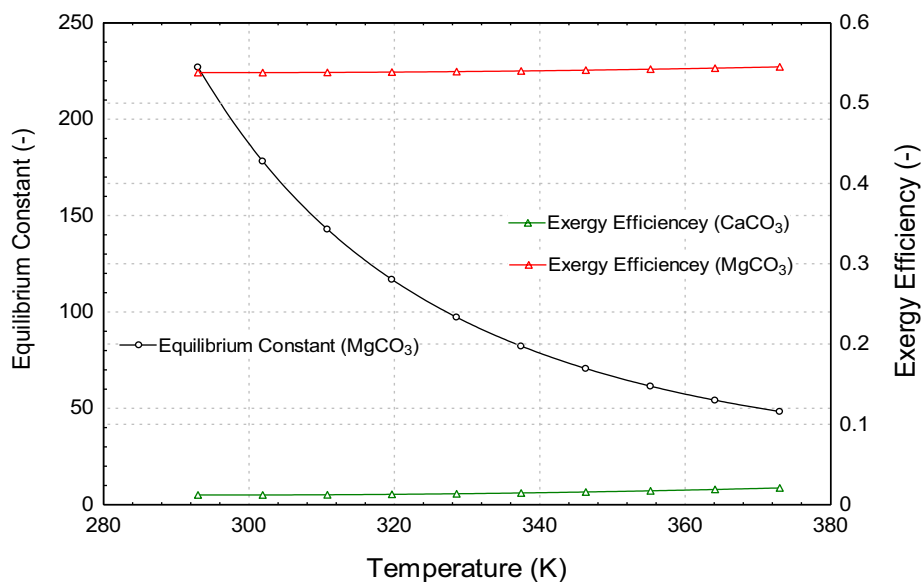


Fig. 4 The effects of temperature on the equilibrium constant and exergy efficiencies of the magnesium carbonate and calcium carbonate processes



of calcium carbonate decreases significantly from 293 to 373 K comparing to magnesium carbonate due to its high free energy of formation. The exergy efficiency increases by 1.3% in magnesium carbonate and calcium carbonate by 72.1% as the temperature increases from 293 to 373 K. Therefore, both processes are favorable at low temperature and increasing the temperature slightly improves the performance of the process.

The variation of the exergy efficiency and equilibrium constant with the temperature of dolomite formation is shown in Fig. 5. As the temperature increases from 348 to 423 K, the exergy efficiency decreases by 89%. Dolomite starts forming at a temperature of 348.15 K when it reacts with magnesium carbonate and calcium carbonate

[9]. Thus, the formation of dolomite is favorable at higher temperatures.

Figure 6 shows the relationship between exergy efficiency and specific exergy destruction with temperature for dolomite formation. As the temperature of the dolomite process increases, the specific exergy destruction increases while the exergy efficiency decreases. The exergy destruction increases by 28.7% as temperature increases from 348 to 423 K which is reasonable since the reaction is exothermic.

Fig. 5 The variation of exergy efficiency and equilibrium constant with the temperature of dolomite formation

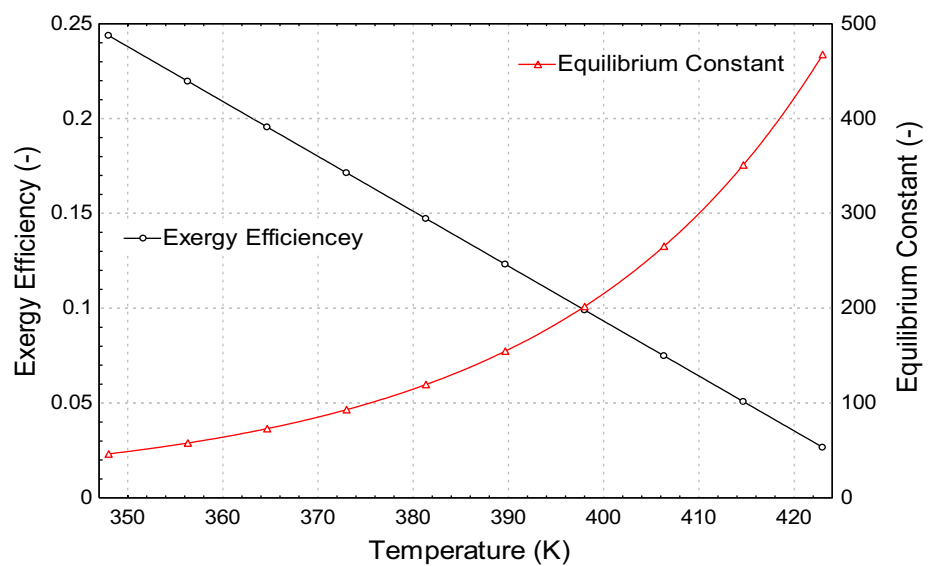
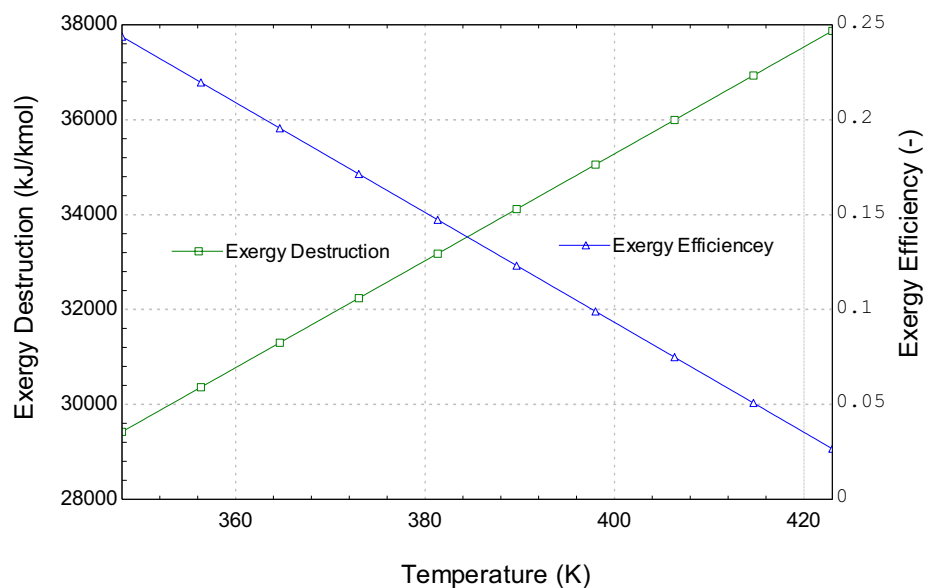


Fig. 6 The relationship between exergy efficiency and specific exergy destruction with temperature for dolomite formation



5 Conclusions

This study investigates the thermodynamic analysis of a new system that captures carbon dioxide and use seawater to form dolomite. There are three main processes in the system: formation of magnesium hydroxide and calcium hydroxide, the reaction of carbon dioxide with magnesium hydroxide and calcium hydroxide to form magnesium carbonate and calcium carbonate and formation of dolomite. Based on the thermodynamic study, the simulation results show that formation of dolomite is favorable at temperature ranges of 313–470 K. The exergy efficiency and specific exergy destruction of dolomite formation process are calculated as 23.8% and 29.6 kJ/mol, respectively. Dolomite can be used as a building material in certain applications and reduce the dependency on highly pollutant cement industry if it can be produced from captured CO₂ and seawater in a well-engineered system.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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