Journal of Environmental Chemical Engineering 5 (2017) 3362–3372

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Research Paper

Directed precipitation of anhydrous magnesite for improved performance of mineral carbonation of CO_2

S. Atashin, R.A. Varin, J.Z. Wen*

Department of Mechanical and Mechatronics Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L3G1, Canada

ARTICLE INFO

Keywords:
CO_2 sequestration
Mineral carbonation
Aqueous carbonation
Directed anhydrous precipitation

ABSTRACT

This paper studies the indirect aqueous carbon sequestration via $Mg(OH)_2$ using directed precipitation technique. This technique produces anhydrous $MgCO_3$ (magnesite), the most desirable carbonated phase for sequestration. The formation of magnesite is significantly affected by its kinetics of precipitation in an aqueous carbonation medium. This study considers directed precipitation strategy to control precipitation of anhydrous magnesite through enhancement of the heterogeneous precipitation. Heterogeneous precipitation is implemented using seeding material that could improve the conversion efficiency of the directed carbonation of $Mg(OH)_2$. A ternary phase diagram is achieved which represents the relative concentration of possible precipitated phases: brucite ($Mg(OH)_2$), magnesite and hydromagnesit ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$). The results reveal the fundamental role of heterogeneous precipitation on the magnesite concentration and conversion percentage of $Mg(OH)_2$ wet carbonation process. Two seeding materials, hydrophobic activated carbon and hydrophilic alumina, were tested and the influence of the surface chemistry of varying seeding sites (hydrophobic vs. hydrophilic seeds) was elaborated. At the carbonation temperature of 100 °C and 150 °C, a heterogeneous precipitation using hydrophilic alumina results in lower concentrations of anhydrous magnesite in precipitated compounds, even as compared to the seedless solution, owing to the hydrophilic properties of alumina. In contrast, use of activated carbon as heterogeneous nucleation sites in an aqueous medium results in a magnesite concentration of around 60% and the corresponding carbonation conversion of about 72% under the controlled condition of 200 °C and 30 bar CO_2 pressure.

1. Introduction

Energy production and use cause almost two-thirds of global greenhouse gas (GHG) emission [1–6]. The goal of limiting the global temperature increase to within 2 °C by 2100, as set at the 21 st Conference of the Parties (COP21) [1], necessities effective strategies for controlling global CO_2 levels. Carbon capture and sequestration (CCS) technologies including mineral carbonation (MC) are considered promising solution that can be implemented immediately while other emission controlling strategies such as renewable energy replacement and energy efficiency improvement are developed [7–14]. Although MC-CCS is thermodynamically favorable, its slow kinetics greatly hinders its use. Various kinetic improvement methods have been suggested to speed up the overall rate of carbon sequestration, such as pre-activation techniques (e.g. mechanical activation, thermal activation and chemical activation). The author's previously explored mechanical pre-activation [15]. However, there is still an urgent need to study the carbonation parameters to enhance the kinetics of carbonation process and achieve favorable carbonated products.

Aqueous indirect carbonation has received significant industrial attention, as it combines the benefits of improved kinetics in aqueous approaches and the process controllability of indirect carbonation [16]. During indirect carbonation route, the overall mineralization process is staged into two major steps; extraction of reactive compounds from original feedstock and later carbonation of extracted compounds. The attraction toward indirect carbonation approach over the direct route is mostly ascribed to its higher efficiency and enhanced overall kinetics of storage. This superiority can be attributed to initial separation of rate controlling silica layers and also, the more efficient control over carbonation parameters [16]. Among the different types of divalent cation bearing feedstock used in mineral carbonation, Mg-bearing materials are the most preferred resources, due to their great abundancy, high theoretical CO_2 storage capacity, and noticeable absorbent element content [9,17,18]. $Mg(OH)_2$ is the major reactive compound extracted from such feedstock for indirect carbon sequestration.

Both extraction and carbonation of $Mg(OH)_2$ need to be kinetically

---

* Corresponding author.
E-mail address: john.wen@uwaterloo.ca (J.Z. Wen).

http://dx.doi.org/10.1016/j.jece.2017.06.048
Received 22 March 2017; Received in revised form 19 May 2017; Accepted 25 June 2017
Available online 27 June 2017

improved to facilitate rapid indirect carbon sequestration. The authors studied enhancing the kinetics of extraction stage in their previous research [19] and kinetic enhancement of carbonation stage has been elaborated in current work. Eqs. (1)–(3) summarize the generally accepted elementary steps of the $Mg(OH)_2$ aqueous carbonation process. Eq. (1) shows a dissolution of CO_2 in water (Eq. (1)) which is not permanent and it may go both ways (a double headed arrow). Therefore, a dissolution of $Mg(OH)_2$ material is needed to liberate divalent cations in the solution (Eq. (2)), and finally, the precipitation of carbonated product occurs (Eq. (3)) [9,15,20–24]. Precipitation (Eq. (3)) may result in the formation of water as a reaction product, depending upon the type of Mg-carbonate produced. The stoichiometry balance of Eq. (3) also depends upon these products.

$$H_2O + CO_2 \leftrightarrow H^+{}_{(aq)} + HCO^-_{3(aq)} \leftrightarrow CO^{-2}_{3(aq)} + 2H^+_{(aq)} \tag{1}$$

$$Mg(OH)_{2(s)}+2H^+{}_{(aq)} \rightarrow Mg^{+2}{}_{(aq)}+2H_2O_{(l)} \tag{2}$$

$$Mg^{+2}{}_{(aq)}+(2HCO_3{}^-{}_{(aq)}/CO_3{}^{-2}{}_{(aq)}) \rightarrow \text{Mg-Carbonates} \tag{3}$$

Varying the temperature and pressure results in different hydrous and anhydrous carbonate products during aqueous carbonation of $Mg(OH)_2$ [24,25]. In the common applicable range of a carbonation process, hydrous carbonates require a higher level of super-saturation (a higher equilibrium constant) than the anhydrous magnesium carbonate ($MgCO_3$-magnesite), suggesting a higher thermodynamic tendency for the formation of anhydrous carbonates vs. hydrous ones. The hydrous precipitates are thermodynamically metastable. In addition, they offer a lower saturation index (SI) of precipitation than anhydrous magnesium carbonates. A saturation index (SI) is the factor which determines solution tendency to form precipitates. This factor compares the actual concentration of solutes under the term of Ion Activation Product (IAP) with thermodynamic solubility product (KSP) to predict the tendency of precipitates formation [26]. However, hydrous carbonate formation can occur more easily due to better kinetics of formation and the formation of the anhydrous magnesite phase is strongly limited by the kinetics of the precipitation process Eq. (3) [25–28].

Anhydrous carbonates are much more favorable compared to hydrous ones owing to their higher storage capability (a lower molecular weight) and thermodynamic stability. So, it is very important to stimulate the kinetics of anhydrous carbonates formation to improve a total carbonation performance. Thus, directing the precipitation toward the formation of anhydrous carbonate phases is desirable, and is referred to as "directed precipitation" in this work. This study aims to promote formation of anhydrous magnesite for the final goal of more efficient $Mg(OH)_2$ carbonation process with the more stable carbonated products. Since the formation of favorable magnesite compound is mainly limited by the kinetics of formation, heterogeneous precipitation strategy is proposed to improve the efficiency of directed precipitation by enhancing the kinetics of magnesite formation.

A number of researchers have investigated the kinetics and mechanism of magnesite ($MgCO_3$) precipitation during aqueous carbonation of $Mg(OH)_2$. Their main focus has been on predicting most likely carbonate precipitates to be formed as a function of applied conditions such as temperature and pressure [29–33]. The enhancement of precipitation kinetics was studied in [24,34–36]. For example, the effect of heterogeneous nucleation on precipitation of calcium carbonate in an aqueous solution was studied by Chevalier [35] considering two different hydrophobic and hydrophilic nucleation sites. However that research is aimed to inhibit the formation of calcium carbonates in heat exchangers and the possible effect of heterogeneous precipitation on the improvement of carbonation process, under applicable carbonation conditions is not the focus. Similarly, Swanson et al. [24] studied the effect of heterogeneous precipitation on the aqueous carbonation of $Mg(OH)_2$ using magnesite and alumina seeds with the goal of directed carbonation. Their results show that the magnesium carbonate seeds are more prone to form favorable magnesium carbonate precipitates as compared to the alumina seeds. This effect was mainly attributed to similarity between the crystal orientation of magnesium carbonate seeds and magnesite precipitates. The possible effect of surface wettability was not evaluated [24].

Considering the previously proven effect of heterogeneous seeding on the formation of precipitates, this study aimed to improve the process of directed carbonation of $Mg(OH)_2$ using heterogeneous precipitation sites. The effect of wettability parameter was evaluated, addressing the current gap in the effect of surface wettability of heterogeneous nucleation sites (seeds) on directed carbonation. This effect was considered through the comparison of the effects of hydrophobic and hydrophilic seeds on carbonation efficiency and magnesite concentration.

The first phase of this study thoroughly explored the quantitative effects of temperature and pressure on magnesite content and carbonation conversion percentage, in order to understand the path of directed carbonation of $Mg(OH)_2$ toward favorable anhydrous carbonates. In this phase, the correlation between the concentration of magnesite and overall carbonation conversion was assessed. The results of first phase was used as a baseline to clarify the effect of heterogeneous precipitation strategy, investigated in the second phase. In the second phase, a heterogeneous precipitation through seeding to enhance the rate of magnesite formation, was studied. Two different seeding materials with varying wettability properties were used with the objective of enhancing the kinetics of precipitation using the general effect of heterogeneous nucleation sites. The possible effects of different precipitation sites with varying wettability properties on the water content of precipitated carbonates were examined. The main objectives of this study are, to quantitative evaluation of the effect of carbonation temperature and pressure on the directed precipitation of $MgCO_3$ during the aqueous carbonation of $Mg(OH)_2$, by investigating the variation in the magnesite concentration and the total extent of carbonation conversion; to assess the general effect of heterogeneous nucleation on the kinetics enhancement of the anhydrous magnesite formation, under varying temperature and pressure conditions; and to investigate the influence of dissimilar surface properties of heterogeneous nucleation sites on directed precipitation, under different temperature and pressure conditions, during aqueous carbonation. A ternary phase diagram, which represents the relative concentration of possible precipitated phases: brucite ($Mg(OH)_2$), magnesite and hydromagnesit ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) under different carbonation conditions, is to be plotted.

2. Experimental methods

Magnesium hydroxide ($Mg(OH)_2$) powders (Alfa Aesar 1039-42-8; 95–100% assay) were used in this research as a Mg-bearing source during aqueous carbonation. In each carbonation test, 3 g of $Mg(OH)_2$ was added to 100 cc distilled water (a concentration of around 0.5 molar).

Carbonation reactions were performed in a 4650 Parr high-temperature, high-pressure reaction vessel. The vessel was evacuated and purged with CO_2 gas prior to setting the desired carbonation pressure and temperature. In all cases, the reactor was heated from room temperature to the desired carbonation temperature, at a rate of about $10^\circ\ \min^{-1}$, and then was kept under adjusted constant temperature for 60 min. In all cases the carbonation pressure was adjusted to the desired value through opening the valve connected to inlet CO_2 bottle. Fig. 1 shows a schematic of the carbonation setup. A combination of reaction temperatures and pressures was selected based on the saturated water thermodynamic table [37], such as to ensure that the solvent water would not evaporate under applied conditions and the gas phase remained pure CO_2. Carbonation temperatures of 100, 150 and 200 °C and CO_2 pressure of 10, 20, 25 and 30 bar were tested.

The experimental occur under either seedless or seeding conditions. The alpha alumina (Al_2O_3) particles (Alfa Aesar 1344-21-1; 99.9%