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Effect of H_2O on $Mg(OH)_2$ carbonation pathways for combined CO_2 capture and storage

Kyle J. Fricker [a], Ah-Hyung Alissa Park [a,b,*]

[a] Department of Earth and Environmental Engineering, Lenfest Center for Sustainable Energy, Columbia University, 918 S.W. Mudd Hall, Mailcode 4711, 500 W. 120th Street, New York, NY 10027, United States
[b] Department of Chemical Engineering, Columbia University, 918 S.W. Mudd Hall, Mailcode 4711, 500 W. 120th Street, New York, NY 10027, United States

HIGHLIGHTS

- The extent of gas-solid $Mg(OH)_2$ carbonation is limited in dry conditions.
- The presence of H_2O can enhance $Mg(OH)_2$ carbonation in gas-solid and slurry modes.
- $Mg(OH)_2$ carbonation often involves the formation of hydrated intermediate phases.
- Anhydrous carbonate formation is favored at high temperature and H_2O loading.
- $Mg(OH)_2$ has shown potential to be used as a combined CO_2 capture and storage media.

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ABSTRACT

Mg-bearing sorbents, derived from silicate minerals and industrial wastes, can act as combined carbon capture and storage media in various energy conversion systems. $Mg(OH)_2$ carbonation in the slurry phase occurs spontaneously and recent results show improved gas–solid carbonation with comparable materials in the presence of H_2O vapor; however, the reaction mechanism is still poorly understood at high temperature and pressure conditions. This study investigated the pathways of H_2O enhanced $Mg(OH)_2$ carbonation at elevated temperatures and CO_2 pressures (up to 673 K and 1.52 MPa) in the presence of steam and in the slurry phase. For a given reaction temperature, carbonation conversion showed dramatic increase with increasing H_2O loading. Comprehensive solid analyses via thermogravimetric analysis, X-ray diffraction, and UV-Raman allowed for qualitative and quantitative compositional characterization of reacted solids. The results suggest that a hydrated environment facilitates the formation of intermediate hydrated magnesium carbonate species. The hydrated carbonates form relatively quickly and can transform into anhydrous carbonates while subjected to greater H_2O loading, higher temperature, and/or longer reaction time.

1. Introduction

The rapid increase in carbon dioxide (CO_2) emissions from industrial sources is considered one of the main causes for the Earth's changing climate (IPCC, 2007). Reduction of CO_2 emissions can be achieved by improving energy efficiency, implementing renewable carbon-free energy sources, and developing carbon capture, utilization and storage (CCUS) technologies. Worldwide energy use will continue increasing (IEA, 2010), and thus, CCUS could provide an immediate solution to the global carbon imbalance while renewable energy technologies develop. By sequestering CO_2, the atmospheric CO_2 concentration can be stabilized or reduced. Most focus in the CCUS field has been placed on amine-based CO_2 capture combined with geological storage. While these technologies have already been demonstrated in large scales (Rochelle, 2009), amine-based CO_2 capture process and the geological storage of CO_2 still face challenges, such as high parasitic energy consumption during solvent regeneration and the permanence and accountability issues for long term CO_2 storage. Furthermore, these schemes would not allow direct integration of carbon capture and storage with high temperature energy conversion systems.

A few high temperature carbon capture schemes exist that utilize a metal oxide as a carbon capture medium such as Zero Emission Coal Alliance (ZECA) process and calcium looping technologies (Feng et al., 2007). Numerous studies have shown

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[*] Corresponding author at: Department of Earth and Environmental Engineering, Lenfest Center for Sustainable Energy, Columbia University, 918 S.W. Mudd Hall, Mailcode 4711, 500 W. 120th Street, New York, NY 10027, United States.
Tel.: +1 212 854 8989; fax: +1 212 854 7081.
E-mail address: ap2622@columbia.edu (A.-H.A. Park).

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that Ca-based sorbents, often in the form of $Ca(OH)_2$ or CaO derived from $CaCO_3$, provide substantial carbonation conversion and kinetics (Feng et al., 2007). Ca-based sorbents are attractive because they can be prepared using inexpensive resources such as limestone; however, since they are derived from carbonate mineral, Ca-based sorbents cannot be used as direct carbon storage. The spent sorbents need to be regenerated, which requires significant energy and cost, especially when accounting for sorbent degradation (Dasgupta et al., 2008; Senthoorselvan et al., 2009).

On the other hand, carbon mineralization technology that converts Mg-bearing minerals into mineral carbonates is a CCUS scheme that could combine CO_2 capture and storage technologies (IPCC, 2005). Research has shown that the abundance of suitable minerals, particularly those containing high magnesium fractions (e.g., olivine and serpentine), far exceeds the total CO_2 that could be produced from fossil fuel reserves (Lackner et al., 1995). Mineralized carbon is significantly more thermodynamically stable than gaseous carbon, and carbonation reactions are exothermic. Thus, carbon mineralization is the most secure and permanent solution for carbon storage that does not require long-term monitoring (Lackner et al., 1995). Unfortunately, mineral weathering naturally occurs on geological timescales; therefore, feasible carbon mineralization processes must provide significant enhancement to mineral dissolution and carbonation rates. As a result, most of the research in this area has been focused on the enhancement of silicate mineral dissolution (1), CO_2 hydration (2)–(3), and carbonation (4) (Park and Fan, 2004):

$$Mg_3Si_2O_5(OH)_4(s)+6H^+=3Mg^{2+}+2Si(OH)_4+H_2O \tag{1}$$

$$CO_2(g)=CO_2(aq) \tag{2}$$

$$CO_2(aq)+H_2O=H_2CO_3(aq)=HCO_3^-+H^+=CO_3^{2-}+H^+ \tag{3}$$

$$Mg^{2+}+CO_3^{2-}=MgCO_3(s) \tag{4}$$

These reactions have generally been performed in the aqueous phase, which limits their application to relatively low reaction temperatures. By raising the pH without introducing CO_2 and producing $Mg(OH)_2$ instead of $MgCO_3$, a solid $Mg(OH)_2$ sorbent can be formed to capture CO_2 via high temperature gas–solid reactions:

$$Mg(OH)_2(s)=MgO(s)+H_2O(g) \tag{5}$$

$$MgO(s)+CO_2(g)=MgCO_3(s) \tag{6}$$

The overall reaction becomes:

$$Mg(OH)_2(s)+CO_2(g)=MgCO_3(s)+H_2O(g) \tag{7}$$

Carbonation of Mg-based sorbents extracted from silicate minerals has seen less research interest, mainly due to its slower kinetics, though optimized reaction conditions and sorbent characteristics, such as surface area, can improve sorbent reactivity (Béarat et al., 2002; Butt et al., 1996; Fagerlund et al., 2010; Fagerlund and Zevenhoven, 2011; Goff and Lackner, 1998; Lin et al., 2008; Zevenhoven et al., 2008). Much of the complexity of the $Mg(OH)_2$ carbonation system arises from the simultaneous dehydroxylation and carbonation reactions (reactions (5) and (6)), which occur in similar temperature ranges (Butt et al., 1996). MgO carbonation has been shown to be considerably slower than $Mg(OH)_2$ carbonation. In fact, MgO is effectively unreacitve at low partial pressures of CO_2 (Béarat et al., 2002; Zevenhoven et al., 2008). Though $Mg(OH)_2$ is more reactive, the carbonation reaction can produce a diffusion limited carbonate shell which restricts the overall carbonation conversion (Butt et al., 1996). Some argue that the effect of water on $Mg(OH)_2$ carbonation was to prevent dehydroxylation (Fagerlund et al., 2011). Other literature available on carbonation of Mg and Ca bearing oxides, hydroxides, and raw minerals supports a water enhanced carbonation theory under a wide range of reaction conditions (Beruto and Botter, 2000; Kwak et al., 2010, 2011; Kwon et al., 2011; Larachi et al., 2012; Loring et al., 2012; Schaef et al., 2011; Shih et al., 1999; Torres-Rodríguez and Pfeiffer, 2011). Considering $Mg(OH)_2$ carbonation in slurry phase is relatively rapid (Botha and Strydom, 2001; Park et al., 2003), the reaction mechanism likely proceeds through a different pathway when H_2O is involved. Highly hydrated environments may even eliminate the occurence of the heterogeneous carbonation reaction (Zhao et al., 2010). Thus, this study aimed to investigate the effect of H_2O on the reaction pathways of $Mg(OH)_2$ carbonation in high pressure gas–solid experiments and a slurry phase experiment through systematic solid product analyses.

2. Experimental

2.1. Sample preparation

Reagent-grade $Mg(OH)_2$ (Acros Organics) was used throughout the carbonation experiments. The particle size distribution was obtained through the laser diffraction measurement (LS^{TM} 13 320 MW, Beckman Coulter, Inc.). All $Mg(OH)_2$ particles were under 150 μm with the majority under 50 μm. $Mg(OH)_2$ particles had a surface area of 6.93 $m^2\,g^{-1}$, and the majority of pores were under 5 nm in diameter (NOVA-win 2002 BET analyzer, Quantachrome Corporation). A thin layer of $Mg(OH)_2$ was coated on glass slides to minimize mass transfer limitations within bulk powder during reaction. The layer was prepared by adding ~5 mL of a 0.1 g mL^{-1} $Mg(OH)_2$ aqueous suspension to the slide and excess water was evaporated in an oven at 353 K overnight.

2.2. Low pressure carbonation of $Mg(OH)_2$

A Setaram SETSYS thermogravimetric analyzer (TGA) was used to perform atmospheric pressure carbonation experiments while allowing for continuous monitoring of reaction progress, in terms of mass change, and precise control of reaction temperature and gaseous environment composition. 30–50 mg samples of $Mg(OH)_2$ were loaded into alumina crucibles for each TGA run.

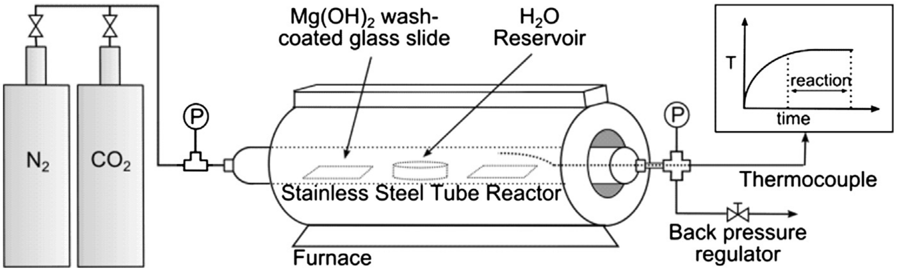

Fig. 1. Schematic diagram of high temperature and pressure experimental setup.