Chemical Engineering Journal 324 (2017) 397–413

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Kinetics of flue gas CO_2 mineralization processes using partially dehydroxylated lizardite

Subrahmaniam Hariharan, Marco Mazzotti *

ETH Zurich, Institute of Process Engineering, Sonneggstrasse 3, CH-8092 Zurich, Switzerland

HIGHLIGHTS

- Passivation behavior of amorphous silica is quantitatively described.
- Single- and two-step semi-continuous mineralization set-up is built.
- The kinetic models can quantitatively predict the mineralization performances.

ARTICLE INFO

Article history:
Received 3 March 2017
Received in revised form 5 May 2017
Accepted 6 May 2017
Available online 11 May 2017

Keywords:
CO_2 mineralization
Lizardite
Kinetics
Dehydroxylation
Hydromagnesite

ABSTRACT

A systematic approach to characterize and to predict the CO_2 mineralization performances of partially dehydroxylated lizardite particles at low temperatures ($\leqslant 90\,^{\circ}C$) and at low CO_2 partial pressures ($\leqslant 1$ bar) was developed in this study. The dissolution kinetics of partially dehydroxylated lizardite particles was accurately described, and the passivating effect of amorphous silica precipitation on the dissolving particles was quantitatively measured. The passivation by amorphous silica was found to inhibit the Mg release rates, and the inhibitory effect was stronger at 60 °C than at 30 °C. An empirical correction to the dissolution rates was found to be sufficient to describe this inhibitory effect. A well controlled, semi-continuous experimental set-up that could run both single- and two-step CO_2 mineralization experiments was built, and the empirical correction together with the kinetic models that describe the various events that occur during a CO_2 mineralization process were quantitatively validated. The presence of NaCl or $NaHCO_3$ did neither reduce the passivation behavior of amorphous silica nor enhance the CO_2 mineralization performances significantly at these operating conditions.

1. Introduction

The climate goal of the Paris Agreement adopted during COP21 in December 2015 is to hold "the increase in the global average temperature to well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above pre-industrial levels" [1]. In order to achieve this objective, technical mitigation solutions such as carbon capture and storage (CCS) are imperative [2]. In a conventional CCS operation, CO_2 is captured from a point source, compressed and transported in order to be stored underground in a suitable geological formation. Under circumstances where geological storage of CO_2 is infeasible, alternative technologies for the permanent storage of CO_2 are necessary. Mineral carbonation or CO_2 mineralization is one such alternative that offers an unquestionably permanent storage of CO_2 in a chemically stable carbonate form [3]. The natural analogue of this CO_2 mineralization process is called silicate weathering where calcium (Ca) and magnesium (Mg) bearing rocks (the source mineral) react with atmospheric carbon dioxide to form carbonate rocks at geological time scales [3].

In order to speed up the kinetics of this process, ex situ CO_2 mineralization was proposed where the source mineral is reacted with a higher concentration of CO_2 in a reactor. The huge abundance of serpentine, a magnesium silicate, makes it an attractive feedstock for large scale mineralization of CO_2. Global estimates for accessible serpentine reserves are expected to significantly exceed the total Mg requirement to neutralize the CO_2 from all worldwide coal resources (which is estimated at 10 000 Gt) [4]. However, the rates of extraction of Mg from serpentine under lean operating conditions is extremely slow. In order to have fast dissolution rates for serpentine in an aqueous medium, the use of additives in the mineralization process is necessary [5,6]. Alternatively, natural serpentine particles when heated to a high temperature ($> 600\,^{\circ}C$) undergo dehydroxylation, which results in destruction of crystal lattice, formation of forsterite grains, and the generation

---

* Corresponding author.
E-mail address: marco.mazzotti@ipe.mavt.ethz.ch (M. Mazzotti).

http://dx.doi.org/10.1016/j.cej.2017.05.040
1385-8947/

Nomenclature

β	exponent in the description of the surface area of a porous shell [–]
$\dot{j}$	particle dosing rate [min^{-1}]
μ_j	stoichiometric index for Mg during the dissolution of silicate species j [–]
ρ_c	crystal density of hydromagnesite [$\mathrm{g\,m}^{-3}$]
ρ_s	solution density [$\mathrm{kg\,m}^{-3}$]
σ_j	stoichiometric index for Si during the dissolution of silicate species j [–]
a_{sp}^{BET}	specific surface area of the PSD measured by BET method [$\mathrm{m}^2\,\mathrm{g}^{-1}$]
a_{sp}^{shell}	specific surface area of the porous shell [$\mathrm{m}^2\,\mathrm{g}^{-1}$]
c	concentration of aqueous solute [$\mathrm{mol\,kg}^{-1}$]
d_{32}	Sauter mean diameter [m]
D_j^{core}	dissolution rate of silicate species j from the core of the particle [$\mathrm{mol\,min}^{-1}$]
D_j^{shell}	dissolution rate of silicate species j from the shell of the particle [$\mathrm{mol\,min}^{-1}$]
$f(L)$	particle size distribution [m^{-1}]
f_{CO_2}	fugacity of CO_2 [bar]
F_{in}	molar flow rate of the gas entering the reactor [$\mathrm{mol\,min}^{-1}$]
F_{MT}	molar flow rate of the gas absorbed into the solution [$\mathrm{mol\,min}^{-1}$]
F_{out}	molar flow rate of the gas exiting the reactor [$\mathrm{mol\,min}^{-1}$]
$f_j^{core}\left(m_j^{core}\right)$	particle size distribution for species j in the core of the particle [mol^{-1}]
$f_j^{shell}\left(m_j^{shell}\right)$	particle size distribution for species j in the shell of the particle [mol^{-1}]
G	growth rate [$\mathrm{m\,min}^{-1}$]
J	particle dosing rate [$\mathrm{mg\,min}^{-1}$]
j	index for a silicate species in a particle [–]
k_{Si}	lumped rate constant for the precipitation of amorphous silica [$\mathrm{mol\,min}^{-1}$]
k_{MT}	lumped mass transfer coefficient [$\mathrm{m}^3\,\mathrm{min}^{-1}$]
K_{sp}	solubility product [–]
k_v	volume shape factor [–]
L	characteristic length of hydromagnesite particle [m]
M	molar mass [$\mathrm{g\,mol}^{-1}$]
m_w	mass of water in the reactor [kg]
m_j^{core}	moles of silicate species j present in the core of the particle [mol]
m_j^{shell}	moles of silicate species j present in the shell of the particle [mol]
N_{Mg}	total number of moles of a Mg remaining in the entire PSD of dissolving PDL particles [mol]
N_{Si}	total number of moles of a Si remaining in the entire PSD of dissolving PDL particles [mol]
P	total pressure [bar]
p_{CO_2}	partial pressure of CO_2 [bar]
Q	flow rate of solvent [$\mathrm{kg\,min}^{-1}$]
R_{CO_2}	mass of CO_2 captured per unit mass of PDL particles [$gCO_2/gPDL$]
R_{Hy}	overall precipitation rate of hydromagnesite [$\mathrm{mol\,min}^{-1}$]
R_{Si}	overall precipitation rate of amorphous silica [$\mathrm{mol\,min}^{-1}$]
r_j	specific dissolution rate for a silicate species j [$\mathrm{mol\,m}^{-2}\,\mathrm{min}^{-1}$]
S_j	saturation index of silicate species j [–]
S_j^{core}	time varying reactive surface area of a silicate species j in the core of a particle [m^2]
S_j^{shell}	time varying reactive surface area of a silicate species j in the shell of a particle [m^2]
T	temperature [K]
t	time [min]
t_J	dosing period [min]
$V_{g,m}$	molar volume of gas phase [$\mathrm{L\,mol}^{-1}$]
V_g	volume of gas phase [L]
w	mass of serpentine added to the reactor [mg]
$y_{CO_2,in}$	CO_2 composition of the gas entering the reactor [–]
$y_{CO_2,out}$	CO_2 composition of the gas exiting the reactor [–]
y_{CO_2}	mole fraction of CO_2 in the reactor gas phase [–]
y_{H_2O}	mole fraction of H_2O in the reactor gas phase [–]
y_{N_2}	mole fraction of N_2 in the reactor gas phase [–]

Acronyms

CCS	carbon capture and storage
COP21	21st yearly session of the Conference of the Parties
MFC	mass flow controller
MFM	mass flow meter
MS	mass spectrometer
PBE	population balance equation
PDL	partially dehydroxylated lizardite
PEEK	polyether ether ketone
PID	piping and instrumentation diagram
PSD	particle size distribution
PTFE	polytetrafluoroethylene

of pores that result in an increased reactive surface area for dissolution [7]. The ability to carbonate thermally activated serpentine at both low and high temperatures/ CO_2 partial pressures has been demonstrated in literature [8,9].

The dissolution of any silicate mineral is inhibited by several kinetic phenomena. This makes the accurate estimation of these phenomena extremely important in order to engineer solutions that overcome most of these limitations. In this regard, there have been several studies in literature that have performed detailed investigations on the dissolution kinetics of various silicate minerals and on the precipitation kinetics of carbonates. However, to the best of our knowledge, none of these kinetic models has been successfully extended in order to quantitatively predict the dynamics of an ex situ CO_2 mineralization process. The ability of the kinetic models to predict the performance of mineralization experiments is essential before these models can be used to design optimal processes.

In our earlier studies [10–12], we have described the complete dissolution kinetics of partially dehydroxlated lizardite (PDL) particles of a narrow and well defined 20–63 μm particle size fraction at low temperatures ($30\,^\circ C \leqslant T \leqslant 90\,^\circ C$) and under flue gas atmosphere (CO_2 partial pressure, p_{CO_2}, below 1 atm). We have developed a kinetic model that accounted for the effect of pH, the inhibition of silicate dissolution rates by Mg^{2+} ions, and the reducing chemical affinity for the dissolving species as they approach their corresponding solubility equilibrium. All experiments in our earlier studies were conducted in a well controlled reaction setting, where the precipitation of secondary phases was carefully avoided. However, the precipitation of amorphous silica and/or magnesium