Impact of mineral reactive surface area approximations on predictions of mineral dissolution rates in a CO_2 injection experiment

Elizabeth H. Mitnick[1], Lauren E. Beckingham[2], Shuo Zhang[1], Carl I. Steefel[2], Li Yang[2], Marco Voltolini[2], Alexander M. Swift[3], Jonathan Ajo-Franklin[2], David R. Cole[3], Julie M. Sheets[3], Saeko Mito[4], Ziqiu Xue[4], Donald J. DePaolo[2,1]

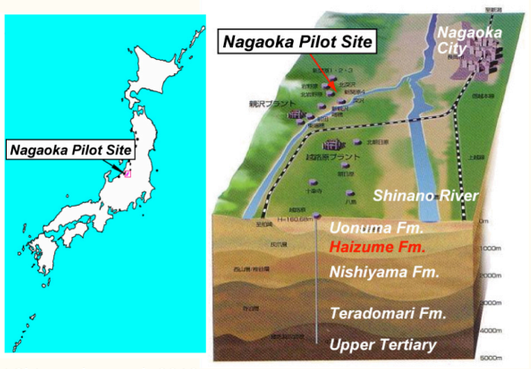
[1]University of California, Berkeley, [2]Lawrence Berkeley National Laboratory, [3]Ohio State University, [4]Research Institute of Innovative Technology for the Earth (RITE)

Abstract

Injection of supercritical CO_2 into porous reservoirs, or geologic carbon sequestration, is a promising means of reducing atmospheric CO_2 emissions. However, the rate and extent of reactions between injected fluid and surrounding geology is not well understood. Continuum-scale modeling has emerged as a tool to predict *in situ* mineral reaction rates, although a major challenge associated with this approach lies in the uncertainty associated with mineral reactive surface areas.

The present study is aimed at evaluating the impact of mineral reactive surface area approximations on predictions of reaction rates in a powder dissolution experiment. Reservoir samples from the Nagaoka pilot CO_2 injection site in Japan were reacted with CO_2-acidified brine (pCO_2 = 100 bars) in a flowthrough reactor at 50° C and the effluent chemistry from the reactor was measured. The multicomponent reactive transport code CrunchTope is used to model both steady state and time-dependent effluent chemistry as a means of evaluating classical and novel image-based approximations of surface area. Reactive surface area approximations evaluated include physical surface areas, i.e., geometric and specific, and reactive-site weighted surface areas. In the simulations, multiple pools of the major reactive phases with different grain sizes and thus specific surface area were considered. Results indicate that the use of BET-based grain-size specific mineral surface areas are the most accurate way of matching observed mineral dissolution rates in the well-stirred powder experiments, although these conclusions may not apply equally to core samples where the pore structure is intact.

Nagaoka Reservoir Rock

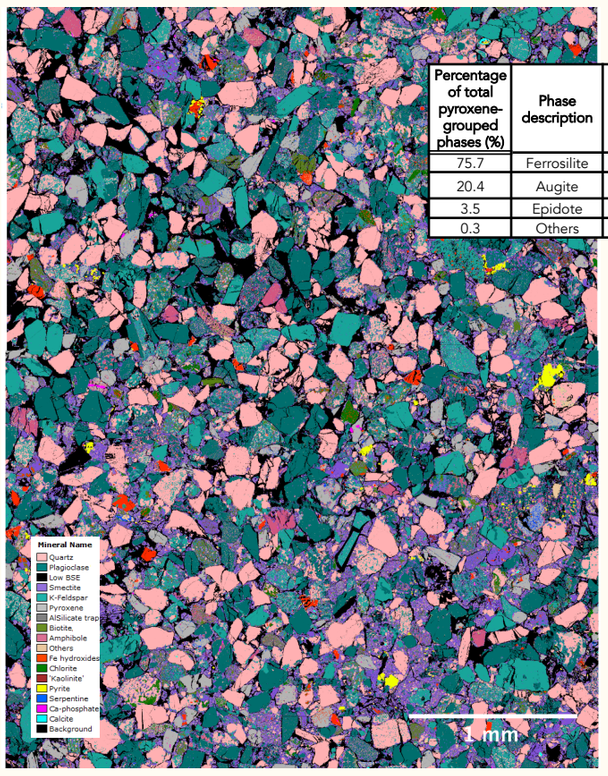


*Chiyonobu et al. 2013

Rock samples are from well cores from the CO_2 injection test site in Nagaoka, Japan.

Sample depth = 1093 m

Feldspar and Pyroxene Group Mineral Compositions from QEMSCAN Analyses



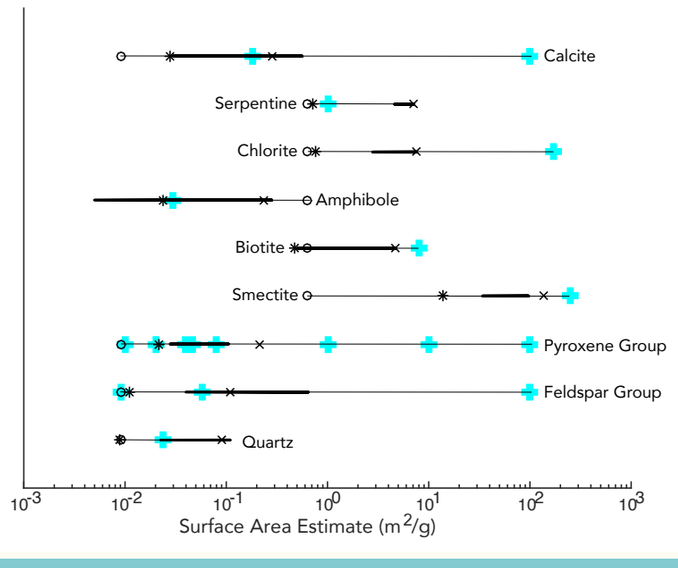
Percentage of total pyroxene-grouped phases (%)	Phase description	Ideal Composition	Composition using QEMSCAN
75.7	Ferrosilite	$FeSiO_3$	-
20.4	Augite	$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$	$(Ca_{0.98}Na_{0.02})(Mg_{0.65}Fe_{0.25}Al_{0.1})(Si_{0.96}Al_{0.04})_2O_6$
3.5	Epidote	$Ca_2(Al_2Fe^{3+})(Si_2O_7)(SiO_4)(O)(OH)$	-
0.3	Others	-	-

Percentage of total feldspar-grouped phases (%)	Phase description	Ideal Composition	Composition using QEMSCAN
6.6	Anorthite	$CaAl_2Si_2O_8$	-
59.4	Labradorite	$(Ca,Na)(Al(Al,Si)Si_2O_8)$	$(Ca_{0.62}Na_{0.38})(Al(Al_{0.62}Si_{0.38})Si_2O_8)$
28.5	Albite	$NaAlSi_3O_8$	-
5.5	Sanidine	$KAlSi_3O_8$	-

Mineral compositions in the sample determined by QEMSCAN analysis are entered into the reactive transport model's thermodynamic database.

Literature values of mineral dissolution rate constants were compiled exclusively from studies using flowthrough reactors under controlled T,P conditions.

Mineral Surface Area Approximations



We compiled a range of mineral surface area estimates to evaluate in our model, including total or specific surface area (SSA), and effective surface area (ESA) estimates.

BET SA of pure minerals, literature values (thick black line)

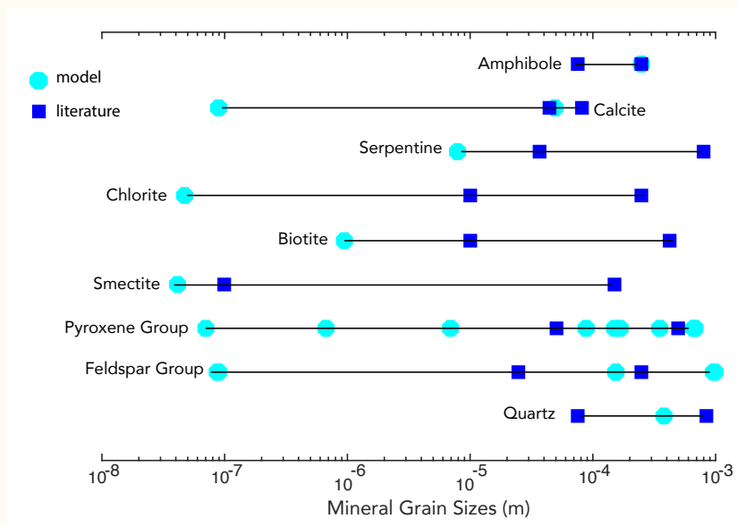
Image perimeter SSA (x)

Image perimeter SSA with scaling factor (*)

Adjusted GSA- smooth sphere ESA (o)

Model results shown in blue (+)

BET-Based Grain-Size Specific Mineral Surface Area



Literature BET grain size ranges (squares) compared with estimated grain sizes based on image analysis and model-fit SA (circles)

Assuming a spherical particle, the geometric surface area (GSA, in units of m^2/g) can be calculated as a function of particle diameters according to the following equation:

$$GSA_i = \frac{SurfaceArea_i^{total}}{mass_i} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 \rho} = \frac{3}{r\rho}$$

d = particle diameter and ρ = mineral density

$$GSA_i = \frac{6}{d\rho}$$

The geometrical surface area is related to the BET surface area (BET) through a surface roughness factor (SRF):

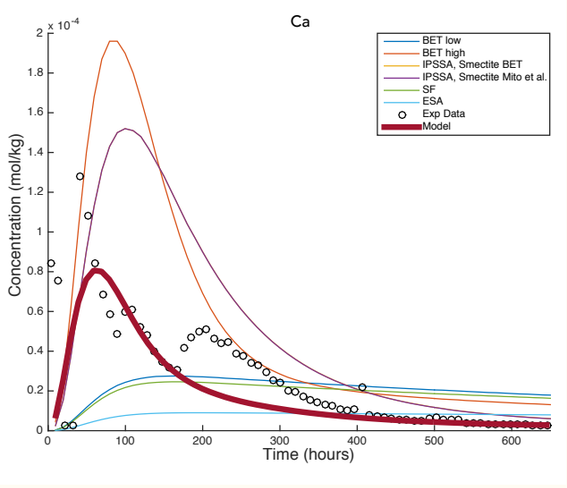
$$BET = GSA * SRF$$

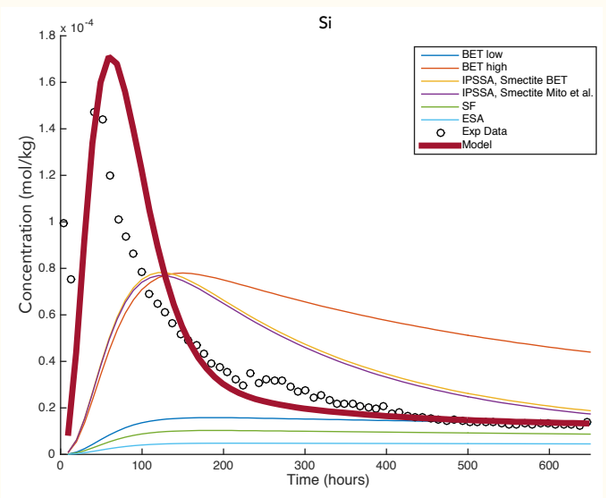
Evaluating Mineral Surface Area Approximations Using CrunchTope

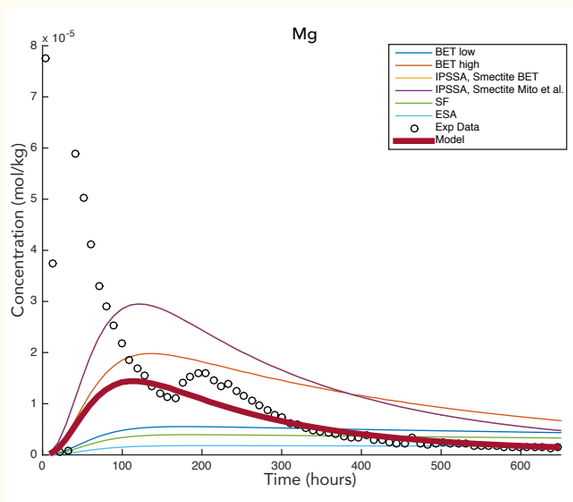
How does Crunch handle surface area inputs?

1. SSA (m^2/g) x molar weight of mineral (g/mol)
2. Divide by molar volume (mol/m^3) → m^2 mineral/m^3 mineral.
3. Multiply by volume fraction (m^3 mineral/m^3 porous media), → m^2 mineral/m^3 media.
4. This value *A* gets used in rate equation (TST).

$$r = kA\left[1-\left(\frac{Q}{K}\right)^M\right]^n$$







Summary of findings

Advanced surface area estimates do not consistently over- or under-predict effluent concentrations of major cations.

Only simulations with image-based and high literature BET SA approximations approach time-dependent dissolution behavior.

Best model fits to powder dissolution experiment data are attained with BET-based grain size specific formulations of surface area.

To determine if these estimates are the best approximations of surface area overall, they need to be tested on material with intact pore structure.

References

Stillings & Brantley 1995. Geochim. et Cosmochim. Act., 59, 1483-1496.; White & Peterson 1990. in Melchior et al. 1990, ACS Symposium, ACS. Washington, D.C.; Chiyonobu et al. 2013. Energy Proc., 37, 3546-3553.; Oelkers et al., 1994, **Geochim. et Cosmochim. Act., 58, 2011-2024; Gudbrandsson et al., 2014. Geochim. et Cosmochim. Act., 139, 154-172.; Tester et al., 1994, Geochim. et Cosmochim. Act., 58, 2407-2420.**

Acknowledgements

This work was supported as part of the Center for Nanoscale Control of Geologic CO_2 (NCGC) , an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.