Supplementary Information (SI)

Analysis of Thermochemical Energy Storage in Metal Carbonates: Characterizing Cycling-Induced Degradation

Michael J. Adams[a], Tae Kyu Kim[a], Samuel Pennell[b], Judith Vidal[b], Akanksha K. Menon[a,b †]

[a] George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

[b] National Renewable Energy Laboratory, Golden, CO 80401, USA

[†] Corresponding author email: akanksha.menon@me.gatech.edu

Pellet Fabrication and Initial Characterization

A cold sintering fabrication method, utilizing a dissolution-precipitation mechanism based on the enhanced solubility of calcium carbonate in water under high pressures, was used to form densified pellets.[1, 2] Pellets were fabricated from calcium carbonate powder (99% purity, Thermo Scientific), which was first sieved to particle diameters less than 300 μm (intraparticle diffusion resistance impedes carbonation above this size).[3] A mixture of 1.2 g of calcium carbonate powder and 120 μL of deionized water was loaded into a 20 mm die set and compressed at a pressure of 255 MPa for 30 minutes under ambient temperature (22°C). Subsequently, pressed pellets were dried in a convection oven at 80°C for 24 hours. The dry pellet density was obtained by measuring its mass and dimensions (thickness = 1.75 ± 0.02 mm). The calculated density is 2.16 ± 0.03 g/cm^3, which is 80% of the theoretical density (2.71 g/cm^3). The pellet was then diced into wedge-shaped samples of ~40 mg each; all samples in this work were from the same pellet to ensure constant thickness and density.

Initial TGA characterization was performed with one long reaction cycle, comprising a 30-minute calcination and a 75-minute carbonation reaction. Temperature, DSC, and sample mass were recorded continuously at a sampling rate of 300 points/minute. The instrument was calibrated using the melting point and enthalpy of melting of various metals, including In, Sn, Bi, Zn, Al, Ag, and Au. Blank experiments were performed to subtract disturbances caused by changes in temperature and gas flow. The mass data was converted into the molar conversion ratio, X. While this method is based on mass uptake data from TGA, we note that the conversion ratio is directly proportional to storage capacity by the reaction enthalpy of the TCM. The storage capacity based on DSC is challenging due to a mismatch in the energy density of the sample and the calibration materials. Also, the DSC signal is also more sensitive to changes in temperature than TGA, requiring additional equilibration time before the reaction onset for accurate measurements. Therefore, the conversion ratio based on TGA is the preferred metric.

Time Constant Analysis - Calcination

Characterization begins with fully carbonated samples, or a conversion ratio equal to one. Samples begin to emit CO_2 as they are heated to the calcination temperature, at which point they decompose spontaneously, and the conversion ratio exponentially decays to zero. The rate of thermal decomposition in metal carbonates has been widely studied as a first-order reaction, with Arrhenius dependence on temperature and linear dependence on the partial pressure $p(CO_2)$. Therefore, the conversion ratio during calcination is expected to follow first-order exponential decay with time. Although the calcination reaction in this work

was performed in an inert environment, self-generation of CO_2 and mass transfer limitations in consolidated form factors (*e.g.,* pellets) significantly slow the reaction rate, resulting in variations in measured Arrhenius parameters and gas pressure dependence.[4, 5] Therefore, the effective reaction rate is unique to the form factor in addition to temperature and gas pressure, requiring empirical fitting. For this, the decomposition reaction was analyzed during the initial "long" cycle comprising a 30-min calcination and 75-min carbonation. During calcination, the sample was heated to 850°C in an environment of ultra-high purity argon (99.999%). The reaction extent during calcination is reported in terms of conversion ratio based on the sample mass, which was sampled at 300 points/min. The calcination data can then be fitted as a simple first-order exponential, $X = X_o \exp(-t/\tau)$, where τ is the time constant and 3τ is the 95% completion threshold. Note that the initial conversion ratio for the fitting is less than one due to the loss of CO_2 prior to the spontaneous reaction. The data and fitting function are shown in Figure S1, resulting in a calcination reaction period of ~ 10-min. We note that this time constant is not an evaluation of the reaction kinetics due to significant diffusion limitations in the sample; instead, it is used to obtain a standardized cutoff time for the reaction.

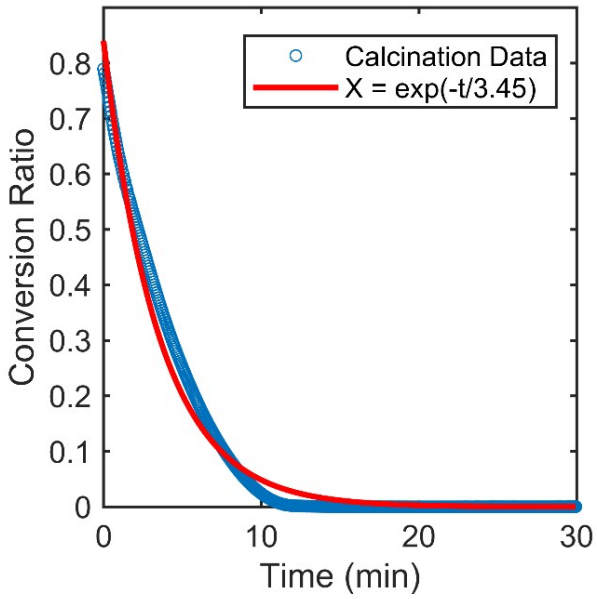

Figure S1: Fitting time constant analysis to calcination data (pellet sample).

Rate Model Analysis - Carbonation

The carbonation reaction was analyzed using the general rate model established for spherical grains.[6] The instantaneous reaction rate, $\frac{dX}{dt}$ comprises two terms proportional to the fraction of unreacted CaO surface area (δ) and $CaCO_3$ product layer surface area $(1-\delta)$, governing the kinetic-limited and ionic diffusion-limited regimes during the carbonation reaction, as shown in Equation 1. The unreacted surface area (δ) can be calculated by integrating Equation 2. These equations predict the conversion at a given time after the onset of carbonation in terms of the initial surface area S_0 and porosity ε_0 of the reactant and its kinetic parameters. The primary fitting parameters are the reaction rate constant k_s, surface diffusion coefficient D_s, and model function β containing the product layer diffusion coefficient.[6] The ratio of chemical

reaction rate to surface diffusion rate is K_s, which can also be defined as the product of the Damköhler number and molar volume. The initial surface area S_0 and porosity ε_0 of the reactant are typically measured by mercury porosimetry, but they are left as additional fitting parameters herein.[3, 7] The equations also contain geometric functions κ_s, g_D, and p_D defined in Equations 3-5.[6] The remaining variables are known: C is the CO_2 gas concentration in mol/m^3, C_e is the equilibrium gas concentration, and Z is the ratio of molar volumes of the product to the reactant. The equilibrium gas concentration is defined in Equation 6.[8]

$$\frac{dX}{dt} = \frac{k_s S_0}{1-\varepsilon_0}\kappa_s(C-C_e) \times \left[\frac{\delta}{1+K_s(C-C_e)} + \frac{1-\delta}{g_D + \beta(C-C_e)p_D}\right] \#(1)$$

$$\frac{d\delta}{dt} = -\frac{k_s Z}{D_s} \times \frac{C-C_e}{1+K_s(C-C_e)}\delta \#(2)$$

$$\kappa_s(X) = (1-X)^{2/3} \#(3)$$

$$g_D(X) = \frac{(1-X)^{2/3}}{[1+(Z/(1-\delta)-1)X]^{2/3}} \#(4)$$

$$p_D = \frac{3(1-X)^{2/3}}{[1+(Z/(1-\delta)-1)X]^{2/3}} \times \left\{[1+(Z/(1-\delta)-1)X]^{2/3} - (1-X)^{2/3}\right\} \#(5)$$

$$C_e = \frac{1.826 \times 10^{12}}{8.314T}\exp\left(-\frac{19680}{T}\right) \#(6)$$

The time-dependent Equations 1-5 are solved implicitly over the same duration as the experimental data using a log-spaced time step to capture rapid changes during kinetic reaction period. The initial values for X and δ are zero and one, respectively. Initial guesses and ranges for the fitting parameters were informed by similar empirical fits by Li.[6] A custom MATLAB function was scripted to iterate this process to solve for the optimal fitting parameters that minimize the Euclidean norm of the difference between the experimental and calculated conversion ratio vectors. Figure S2 compares the conversion ratio data during carbonation to the model-calculated values. The resulting microstructural parameters, $S_0 = 4.0 \times 10^7\ m^2/m^3$ and $\varepsilon = 0.50$, are in good agreement with reported values for CaO formed by thermal decomposition of CaCO3 in similar reaction conditions.[3] The resulting kinetic parameters are $k_s = 1.8 \times 10^{-11}\ m^4/mol/s$, $D_s = 3.2 \times 10^{-8}\ m/s$, $D_p = 1.11 \times 10^{-16}\ m^2/s$.

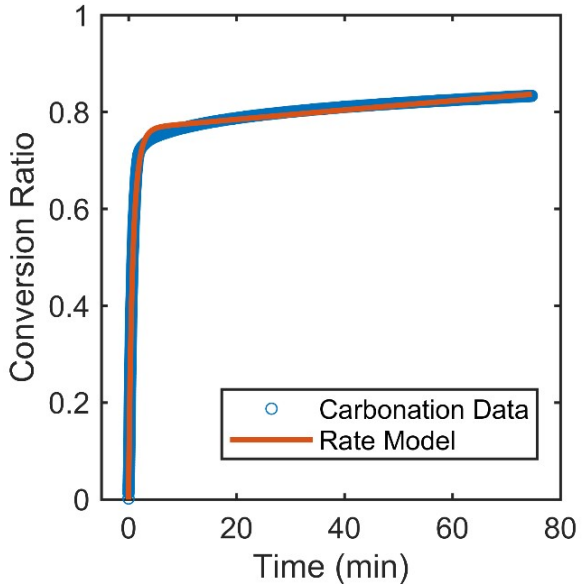

Figure S2: Fitting rate model to carbonation data (pellet sample).

Ultimately, δ exhibits exponential decay with time, which can be described by a first-order exponential fit and time constant. Again, 3τ corresponds to 95% completion, and we refer to this duration as the Kinetic Completion Time. The result for $\delta(t)$ is shown in Figure S3 below, resulting in a completion time of about 3 minutes. The conversion ratio at this threshold is the Kinetic Conversion Ratio, X_k, which is used in this study to compare carbonation extent across different cycle conditions.

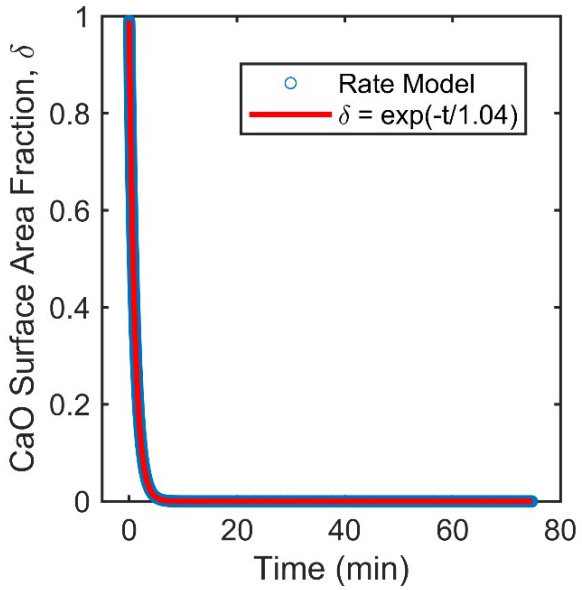

Figure S3: Time constant analysis of surface area function, δ. A time constant of 1.04 corresponds to a kinetic completion time of about 3 minutes.

Comparing Total and Kinetic Conversion in Pellets

To quantify degradation under cycling, a baseline experiment was performed with "long" reaction times comprising 30-min calcination and 75-min carbonation segments (consistent with the initial characterization described in Methods). The total conversion ratio (including both kinetic and diffusion regimes) over 16 cycles is shown in Figure S4, which decreases from 83% to 22% due to cycling-induced degradation. Importantly, this translates to a reduction in thermal storage capacity of the TCM as the conversion ratio is a direct measure of residual storage capacity.

Fitting the general rate model to the carbonation reaction in the first cycle results in a kinetic completion time of about 3 min. The corresponding kinetic conversion ratio for the baseline experiment is shown in Figure S4 – interestingly, this represents 88% of the total conversion in the first cycle, even though it represents only 3 min out of the full 75 min carbonation period. The kinetic conversion also shows a similar degradation trend as the overall conversion, which suggests that degradation primarily occurs in this regime of the two-stage carbonation reaction. Over 16 cycles, the kinetic conversion decays from 88% to 74% of the total conversion which is attributed to the loss of reactant surface area.[9] The reaction rate constant k_s is inversely proportional to specific surface area, while the diffusion constants remain unchanged. Therefore, the Damköhler number analogue, K_s, increases and the reaction rate dX/dt during the kinetic-limited period decreases with cycle count as described by Equation 1.

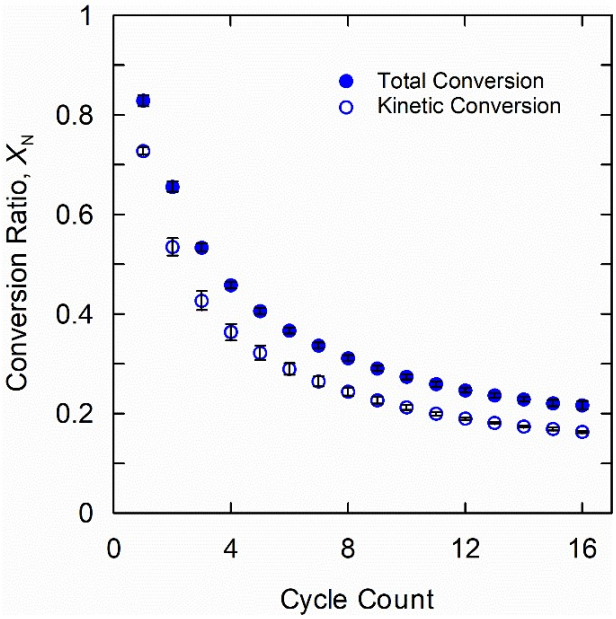

Figure S4: Conversion Ratio for long cycles, comprising 30-min calcination and 75-min carbonation segments. The total conversion and kinetic conversion from the same experiment are analyzed. Total conversion is based on the full 75-min carbonation whereas kinetic conversion is based on the kinetic completion time of 3 min. The symbols and error bars represent the mean and standard deviation across three samples.

Comparing Pellet and Powder Samples

In addition to comparative analysis between samples with different cycle duration, this methodology allows for comparison of TCMs across various form factors. Powder samples at the mg-scale are expected to have minimal gas diffusion resistance. Densified materials such as pellets are expected to have significant diffusion resistance. This methodology enables characterization of both transport-limited and transport-unlimited regimes, enabling thorough evaluation of material degradation across multiple reaction phases.

Comparative analysis between powder and pellet samples was conducted through a 15-cycle TGA/DSC experiment. A TGA crucible containing calcium carbonate powder (height-matched to pellet samples) underwent identical calcination-carbonation cycles (30-minute calcination, 30-minute carbonation). End-of-cycle conversion revealed similar conversion ratios across form factors over this reaction period, as shown in Figure S5.

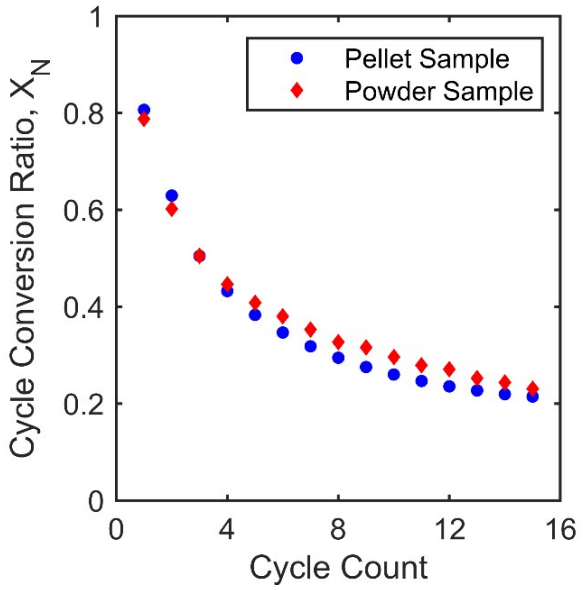

Figure S5: Total (end-of-cycle) conversion of powder and densified form factors after 30-minute calcination and 75-minute carbonation cycles.

Appling the rate model analysis to carbonation reactions in the powder sample resulted in the following fitting parameters: $S_0 = 3.8 \times 10^7\ m^2/m^3$ $\varepsilon = 0.47$, $k_s = 2.1 \times 10^{-10}\ m^4/mol/s$, $D_s = 3.0 \times 10^{-8}\ m/s$, and $D_p = 5.0 \times 10^{-16}\ m^2/s$. The reactant surface area function, δ, decays much faster in the powder than the densified material, and the kinetic completion time is 16.5 seconds. With this information, we can compare the kinetic conversion ratio, X_k, of the powder to the densified form factor in Figure S6. In this case, we observe that the material has consistent kinetic conversion ratio regardless of form factor. The cold sintering fabrication had no adverse effect on the conversion ratio, and therefore storage capacity, of the material. The density of the material may be tuned as needed to optimize reaction rate and duration of the kinetic period, which is the primary change in the material.

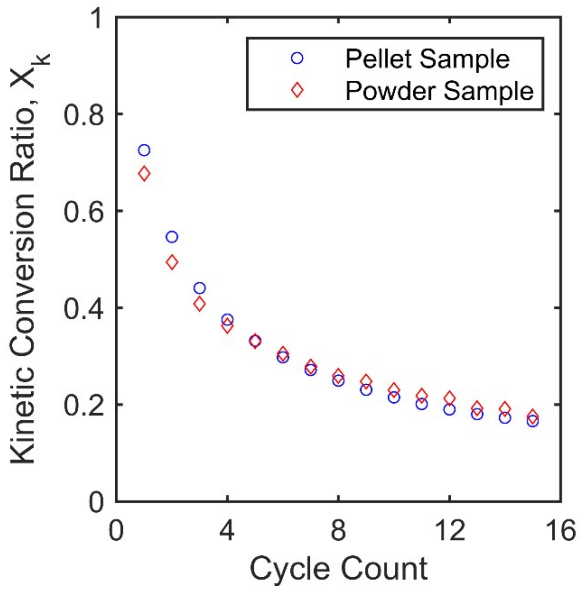

Figure S6: Kinetic conversion ratio of powder and densified form factors at the kinetic completion time of 17 seconds and 3 minutes, respectively.

References

1. Yamaguchi, K. and S. Hashimoto, *Mechanism of densification of calcium carbonate by cold sintering process.* Journal of the European Ceramic Society, 2022. **42**(13): p. 6048-6055.
2. Cao, M., et al., *Dense and strong calcite ceramics prepared by room-temperature cold sintering based on high-pressure-enhanced solubility.* Journal of the American Ceramic Society, 2023. **106**(3): p. 1668-1680.
3. Grasa, G., et al., *Application of the random pore model to the carbonation cyclic reaction.* AIChE Journal, 2009. **55**(5): p. 1246-1255.
4. Hotta, M., et al., *Kinetic Parameterization of the Effects of Atmospheric and Self-Generated Carbon Dioxide on the Thermal Decomposition of Calcium Carbonate.* The Journal of Physical Chemistry C, 2022. **126**(18): p. 7880-7895.
5. Sanchez-Rodriguez, D., et al., *Kinetic analysis of reversible solid-gas reactions in films: application to the decomposition of CaCO$$_3$$and BaCO$$_3$$carbonates.* Journal of Thermal Analysis and Calorimetry, 2024.
6. Li, Z., *General rate equation theory for gas–solid reaction kinetics and its application to CaO carbonation.* Chemical Engineering Science, 2020. **227**: p. 115902.
7. Bhatia, S.K. and D.D. Perlmutter, *A random pore model for fluid-solid reactions: I. Isothermal, kinetic control.* AIChE Journal, 1980. **26**(3): p. 379-386.
8. Hu, N. and A.W. Scaroni, *Calcination of pulverized limestone particles under furnace injection conditions.* Fuel, 1996. **75**(2): p. 177-186.
9. Abanades, J.C. and D. Alvarez, *Conversion Limits in the Reaction of CO2 with Lime.* Energy & Fuels, 2003. **17**(2): p. 308-315.