A Shrinking Core Model for Steam Hydration of CaO-Based Sorbents Cycled for CO₂ Capture: Supplementary Information

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Nomenclature

C	Molar concentration	mol/m³
D_e	Effective diffusivity within pores	m²/s
D_g	Gas-phase diffusivity	m²/s
D_K	Knudsen diffusivity	m²/s
d_p	Particle diameter	m
d_{pore}	Pore diameter	m
k_A	First order rate constant for the reaction of CaO with steam	m/s
k_B	Boltzmann constant	J/K
k_g	Mass transfer coefficient	m/s
M	Molar mass	g/mol

N	Number of cycles	
n	Number of moles	mol
p	Pressure	Pa
R	Universal gas constant	J/mol/K
Re	Reynolds number	
r	Radius	m
S_V	Specific, BET, surface area, expressed in m^2/m^3	m^2/m^3
Sc	Schmidt number	
Sh	Sherwood number	
T	Temperature	K
t	Time	s
U	Fluid velocity	m/s
U_{mf}	Minimum fluidisation velocity	m/s
W	Molar flux	$mol/m^2/s$
X	Mole fraction	
$X_{Ca(OH)_2}$	Conversion to $Ca(OH)_2$	
ΔH_r^θ	Enthalpy of reaction under standard conditions	kJ/mol
ε_x	Porosity of species x	
λ	Mean free path	m
μ_g	Fluid viscosity	kg/m/s
ρ_g	Gas density	kg/m^3
ρ_x	Density of species x	kg/m^3
σ	Collision diameter	m
τ_{pore}	Pore tortuosity	
Ω	Collision integral	

	Subscripts for C, r, X	
c/C	At the core of the particle – CaO/Ca(OH)$_2$ interface	
s/S	At the surface of particles	
B	In the bulk phase (not applicable to r)	
E	At equilibrium (not applicable to r)	

1 Bulk Diffusivity and Mass Transfer Coefficients

The gas-phase diffusivity (D_g) was calculated from Chapman-Enskog theory (see Table 1), using Eq. 1, taken from Cussler [1] and adapted for SI units, where T is the temperature of hydration, M_x the molar mass of species x and p the bulk pressure.

$$D_g = \frac{5.96 \times 10^{-24} T^{3/2} \left(1/M_{\text{H}_2\text{O}} + 1/M_{\text{N}_2}\right)^{1/2}}{p\sigma_{12}^2 \Omega} \qquad \qquad Eq.\ 1$$

The collision diameter (σ_{12}) was calculated as the arithmetic mean of the two species, $\sigma_{12} = 0.5(\sigma_{\text{H}_2\text{O}} + \sigma_{\text{N}_2})$, and the collision integral (Ω) was calculated as $\Omega = f(k_\text{B}T/\varepsilon_{12})$ using a correlation provided by Cussler [1], where k_B is the Boltzmann constant and the energy of interaction (ε_{12}) was calculated as the geometric mean of the two species, $\varepsilon_{12} = \left(\varepsilon_{\text{CO}_2}\varepsilon_{\text{N}_2}\right)^{1/2}$. All collision diameters and energies of interaction were provided by Cussler [1]. The Sherwood Number (Sh) for this work has been estimated (see Table 1) using a correlation from Perry and Green [2], $\text{Sh} = 0.91 Re_p^{0.49} Sc^{0.33}$, which is dependent on the Reynolds (Re) and Schmidt (Sc) Numbers, defined by $\text{Re}_\text{p} = U d_\text{p} \rho_\text{g}/\mu_\text{g}$ and $\text{Sc} = \mu_\text{g}/\rho_\text{g} D_\text{g}$ respectively. The fluid viscosities (μ_g) and densities (ρ_g) were obtained from the NIST Chemistry Webbook [3] and the fluid velocity (U) was calculated for the

temperatures of interest (473, 573 and 673 K) using a cold (293 K) inlet flow-rate of 100 cm^3/s and an internal diameter of the TGA furnace of 17 mm. An estimate of the mass transfer coefficient (k_g) was calculated (see Table 1) for the temperatures of interest from the Sherwood Number, gas-phase diffusivity and the particle diameter (d_p), as $k_g = D_g \text{Sh}/d_p$.

Table 1 Calculated values of gas phase diffusivities, Sherwood Numbers and mass transfer coefficients at the temperatures of investigation

Temperature of hydration [K]	473	573	673
Gas phase diffusivity [m^2/s]	5.15x10^{-5}	7.30x10^{-5}	9.73x10^{-5}
Sherwood Number	1.78	1.64	1.53
Mass transfer coefficient [m/s]	0.154	0.201	0.249

The mass transfer coefficient can be used to calculate the flux of H$_2$O at the surface of the particle (W_{H_2O,r_s}), with knowledge of the molar bulk and surface concentrations of H$_2$O (C_B and C_S respectively), using Eq. 2. Assuming a perfect gas and knowledge of the overall molar concentration (C), the mole fractions of H$_2$O can be calculated from $C_x = CX_x$.

$$W_{H_2O,r_s} = -k_g(C_B - C_S) = -k_g C(X_B - X_S) \qquad \text{Eq. 2}$$

2   Intra-Particle Diffusivity

The mechanism of diffusion through the particle has to be established, in order to calculate the intra-particle diffusivity. To establish whether Knudsen diffusion contributes, the mean free path of molecules has to be compared to the average pore diameter; Knudsen diffusion occurs when molecules collide with pore walls more frequently than with other molecules. The mean free path (λ) was calculated, using $\lambda = 1/\sqrt{2}\pi\sigma_{H_2O}C$, as 208, 252 and 296 nm for 473, 573 and 673 K respectively. The pore size distribution of the Ca(OH)$_2$ product layer through which the steam diffuses to react with the CaO was not directly measured. Therefore, it was calculated indirectly,

using data obtained for porosity (obtained from mercury porosimetry measurements, < 360 μm) and average pore diameter (as obtained from nitrogen adsorption studies) for the cycled CaO. First, the porosity of Ca(OH)$_2$ was calculated from a mass balance of CaO and Ca(OH)$_2$, assuming no change in particle/layer size (see Eq. 3). Then, the average pore size was calculated, assuming a constant pore length (see Eq. 4), i.e., constant growth along the length of the pore. Experimental data for CaO and calculated data for Ca(OH)$_2$ are presented in Table 2.

$$\varepsilon_{\text{Ca(OH)}_2} = 1 - \frac{\rho_{\text{CaO}} M_{\text{Ca(OH)}_2} (1 - \varepsilon_{\text{CaO}})}{\rho_{\text{Ca(OH)}_2} M_{\text{CaO}}} \qquad\qquad Eq.\ 3$$

$$d_{\text{pore,Ca(OH)}_2} = \frac{d_{\text{pore,CaO}} \varepsilon_{\text{Ca(OH)}_2}}{\varepsilon_{\text{CaO}}} \qquad\qquad Eq.\ 4$$

Table 2 Experimental data for CaO and calculated data for Ca(OH)$_2$

Cycle number	CaO porosity	CaO average pore diameter [nm]	Ca(OH)$_2$ porosity	Ca(OH)$_2$ average pore diameter [nm]
0	0.685	25.6	0.372	13.9
2	0.597	34.2	0.196	11.2
6	0.566	36.0	0.134	8.6
13	0.553	34.0	0.109	6.7

The pore diameter is therefore smaller than the mean free path length (7-14 nm vs. 210-300 nm). The Knudsen Numbers (λ/d_{pore}) are between 15 and 45 – depending on extent of cycling and temperature of hydration, which are within the range in where Knudsen diffusion is expected. The Knudsen diffusivity (D_{K}) was calculated according to Eq. 5 (see

Table 3), using the molar mass of H$_2$O [1]. Then, the effective diffusivity (D_e) through the pores was derived according to Eq. 6 using the conventional expression for resistances in series [4] combined with a term to account for porosity and pore tortuosity [1] (see

Table 3). The pore tortuosity (τ_{pore}), which is a factor to account for the non-linear nature of pores, was taken as 3 [1]. This is a typical value suggested, in absence of experimental data, by Cussler [1].

$$D_K = \frac{1}{3} d_{\text{pore}} \left(\frac{2RT}{\pi M_{H_2O}} \right)^{1/2} \qquad\qquad Eq.\ 5$$

$$D_e = \frac{\varepsilon_{\text{Ca(OH)}_2}}{\tau_{\text{pore}}} \left(\frac{1}{D_g} + \frac{1}{D_K} \right)^{-1} \qquad\qquad Eq.\ 6$$

Table 3 Calculated Knudsen and effective diffusivity for hydration temperatures and cycling extents investigated

Cycle Number	Knudsen diffusivity [m²/s]			Effective diffusivity [m²/s]		
	at 473 K	at 573 K	at 673 K	at 473 K	at 573 K	at 673 K
0	3.45×10^{-6}	3.80×10^{-6}	4.11×10^{-6}	4.00×10^{-7}	4.47×10^{-7}	4.89×10^{-7}
2	2.79×10^{-6}	3.08×10^{-6}	3.33×10^{-6}	1.73×10^{-7}	1.93×10^{-7}	2.11×10^{-7}
6	2.13×10^{-6}	2.34×10^{-6}	2.54×10^{-6}	9.16×10^{-8}	1.02×10^{-7}	1.11×10^{-7}
13	1.66×10^{-6}	1.83×10^{-6}	1.98×10^{-6}	5.84×10^{-8}	6.48×10^{-8}	7.05×10^{-8}

3   Mass Transfer through the Product Layer

A mass balance on the flux of H_2O (W_{H_2O}) between r and Δr in the product layer, assuming quasi-steady state conditions, results in Eq. 7 [5].

$$\frac{d\left(W_{H_2O,r} r^2 \right)}{dr} = 0 \qquad\qquad Eq.\ 7$$

The constitutive equation (or Fick's Law) for a constant molar concentration is given by Eq. 8 [6], where the first term refers to convective flux, the second to diffusive flux, and species A and B are the diffusing and counter-diffusing gases respectively. For the hydration of lime, species A is H_2O and there is no counter-diffusing gas; therefore Eq. 8 rearranges to become Eq. 9.

$$W_{\text{Ar}} = (W_{\text{Ar}} + W_{\text{Br}})X_{\text{A}} - CD_e \frac{dX_{\text{A}}}{dr}$$

Eq. 8

$$W_{\text{H}_2\text{O,r}} = \frac{-CD_e}{\left(1 - X_{\text{H}_2\text{O,r}}\right)} \frac{dX_{\text{H}_2\text{O,r}}}{dr}$$

Eq. 9

Combining Eq. 7 and Eq. 9 gives Eq. 10.

$$\frac{d}{dr}\left(\frac{-CD_e r^2}{(1 - X_{\text{H}_2\text{O,r}})} \frac{dX_{\text{H}_2\text{O,r}}}{dr}\right) = 0$$

Eq. 10

To solve for $X_{\text{H}_2\text{O,r}}$ in this Eq. 10, the boundary conditions must be applied: at the first boundary

condition (BC1) $r = r_{\text{S}}$ and $X_{\text{H}_2\text{O,r}} = X_{\text{S}}$, and at the second (BC2) $r = r_{\text{C}}$ and $X_{\text{H}_2\text{O,r}} = X_{\text{C}}$.

$$X_{\text{H}_2\text{O}} = 1 - (1 - X_{\text{C}})\left[\frac{(1 - X_{\text{S}})}{(1 - X_{\text{C}})}\right]^{\left(\frac{1}{r} - \frac{1}{r_{\text{C}}}\right)/\left(\frac{1}{r_{\text{S}}} - \frac{1}{r_{\text{C}}}\right)}$$

Eq. 11

$X_{\text{H}_2\text{O}}$ from Eq. 11 is then differentiated with respect to r to give Eq. 12.

$$\frac{dX_{\text{H}_2\text{O}}}{dr} = \frac{(1 - X_{\text{C}})\left[\frac{(1 - X_{\text{S}})}{(1 - X_{\text{C}})}\right]^{\left(\frac{1}{r} - \frac{1}{r_{\text{C}}}\right)/\left(\frac{1}{r_{\text{S}}} - \frac{1}{r_{\text{C}}}\right)} \ln\left[\frac{(1 - X_{\text{S}})}{(1 - X_{\text{C}})}\right]}{r^2\left(\frac{1}{r_{\text{S}}} - \frac{1}{r_{\text{C}}}\right)}$$

Eq. 12

Substituting Eq. 11 and Eq. 12 into Eq. 9 gives Eq. 13, the equation for molar flux through the

product layer.

$$W_{\text{H}_2\text{O,r}} = \frac{-CD_e \ln\left[\frac{(1 - X_{\text{S}})}{(1 - X_{\text{C}})}\right]}{r^2\left(\frac{1}{r_{\text{S}}} - \frac{1}{r_{\text{C}}}\right)}$$

Eq. 13

4   Mass Balance on Ca(OH)₂ Formation during Reaction

A balance on the number of moles of CaO at time t ($n_{\text{CaO,t}}$) is given by Eq. 14. Noting that (i) the

rate of production of Ca(OH)₂ is the negative rate of production of CaO and (ii) the rate of production

of Ca(OH)₂ is also the negative rate of production of H₂O, the rate of production of Ca(OH)₂ is given

by Eq. 15. From this, Eq. 16 for the rate of change of the core radius can be derived.

$$n_{\text{CaO,t}} = \frac{4\pi r_{\text{c,t}}^3 \rho_{\text{CaO}}(1 - \varepsilon_{\text{CaO}})}{3M_{\text{CaO}}} \qquad \textit{Eq. 14}$$

$$\frac{-dn_{Ca(OH)_2}}{dt} = \frac{dn_{CaO}}{dt} = \frac{d\left(\frac{4\pi r_{\text{c}}^3 \rho_{\text{CaO}}(1 - \varepsilon_{\text{CaO}})}{3M_{\text{CaO}}}\right)}{dt} = \frac{dn_{H_2O}}{dt} = 4\pi r_{\text{C}}^2 W_{\text{H}_2\text{O},r_c} \qquad \textit{Eq. 15}$$

$$\frac{dr_{\text{C}}}{dt} = \frac{M_{\text{CaO}} W_{\text{H}_2\text{O},r_c}}{\rho_{\text{CaO}}(1 - \varepsilon_{\text{CaO}})} \qquad \textit{Eq. 16}$$

A constant external diameter of particles has been assumed; therefore, r_{C} can be related to the

conversion to Ca(OH)₂ ($X_{\text{Ca(OH)}_2}$) within the particles according to Eq. 17.

$$X_{\text{Ca(OH)}_2} = 1 - \left(\frac{r_{\text{c}}}{r_{\text{s}}}\right)^3 \qquad \textit{Eq. 17}$$

By differentiating $X_{\text{Ca(OH)}_2}$ in Eq. 17 with respect to r_{C} and multiplying by dr_{c}/dt in Eq. 16 (i.e., by

applying the chain rule), and substituting for $r_{\text{c}}/r_{\text{s}}$, Eq. 18 can be derived. This gives a relationship

between experimentally derived rates of reaction and the flux of H₂O at the interface of the core and

the product layer.

$$\frac{dX_{\text{Ca(OH)}_2}}{dt} = \frac{-3}{r_{\text{s}}}\left(1 - X_{\text{Ca(OH)}_2}\right)^{2/3} \frac{M_{\text{CaO}} W_{\text{H}_2\text{O},r_c}}{\rho_{\text{CaO}}(1 - \varepsilon_{\text{CaO}})} \qquad \textit{Eq. 18}$$

5   First Order Kinetics of Reaction

First order reaction kinetics is assumed and therefore the rate of formation of Ca(OH)$_2$ is given in Eq. 19, where k_A is the first order rate constant per unit surface area, S_V is the BET surface area per unit volume (using data presented in Table 1 [see full paper], expressed in m^2/m^3, calculated from $S_V = S_{BET}\rho_{CaO}(1 - \varepsilon_{CaO})$) and X_C and X_E are the mole fraction of H$_2$O at the core and the mole fraction associated with the equilibrium partial pressure of H$_2$O over Ca(OH)$_2$ at the temperature of hydration respectively. $(X_C - X_E)$ is chosen as the effective mole fraction of H$_2$O driving the reaction; note that the reaction will cease if $X_C = X_E$.

$$\frac{d(n_{Ca(OH)_2})}{dt} = \frac{4\pi r_c^3 S_V}{3} k_A C(X_C - X_E) \qquad \text{Eq. 19}$$

The molar rate of reaction of Ca(OH)$_2$ is related to the flux of H$_2$O at the interface of the core and the product layer using Eq. 20; it therefore follows that the flux of H$_2$O at the interface can be presented by Eq. 21.

$$W_{H_2O,r_c} = \frac{-1}{4\pi r_c^2} \frac{d(n_{Ca(OH)_2})}{dt} \qquad \text{Eq. 20}$$

$$W_{H_2O,r_c} = \frac{-r_c S_V}{3} k_A C(X_C - X_E) \qquad \text{Eq. 21}$$

6   Application of the Shrinking Core model

The application of the model proceeded as follows:

6.1   Fundamental Equations

To recap, the fundamental equations are: (i) Eq. 2 for mass transfer of H$_2$O to the particle surface; (ii) Eq. 13 for mass transfer of H$_2$O through the product layer; (iii) Eq. 21 for mass transfer of H$_2$O to

form $Ca(OH)_2$ by reaction; and (iv) Eq. 18 relating mass transfer of H_2O at the interface of the core and the product layer to experimental data.

6.2 Analysis of Molar Flux through the Product Layer at its Boundaries

Considering the molar flux of H_2O at the particle surface, where $r = r_S$, Eq. 22 can be derived. Note that r_C/r_S is related to the conversion to $Ca(OH)_2$ according to Eq. 17.

$$W_{H_2O,r_s} = \frac{-CD_e \ln\left[\frac{(1-X_S)}{(1-X_C)}\right]}{r^2\left(\frac{1}{r_S} - \frac{1}{r_C}\right)}\Bigg|_{r=r_s} = \frac{-CD_e \ln\left[\frac{(1-X_S)}{(1-X_C)}\right]}{r_S\left(1 - \frac{1}{r_C/r_S}\right)} \qquad \text{Eq. 22}$$

Considering the molar flux of H_2O at the interface of the CaO core and $Ca(OH)_2$ product layer, where $r = r_c$, Eq. 23 can be derived.

$$W_{H_2O,r_c} = \frac{-CD_e \ln\left[\frac{(1-X_S)}{(1-X_C)}\right]}{r^2\left(\frac{1}{r_S} - \frac{1}{r_C}\right)}\Bigg|_{r=r_c} = \frac{-CD_e \ln\left[\frac{(1-X_S)}{(1-X_C)}\right]}{r_S\left(\left(\frac{r_C}{r_S}\right)^2 - \frac{r_C}{r_S}\right)} \qquad \text{Eq. 23}$$

6.3 Finding Solutions for the SCM

A solution for k_A was found for each set of experimental conditions separately (i.e., for each hydration temperature and number of cycles before hydration). Initially, 41 data points were taken from each experiment at *equal conversion increments* for conversions to $Ca(OH)_2$ of between 0.05 and either 0.95, if full conversion was achieved, or the final conversion at t = 1080 s. Subsequently, X_S and X_C were calculated using the two equations Eq. 24 and Eq. 25 for all data points, using values of $dX_{Ca(OH)_2}/dt$ and $X_{Ca(OH)_2}$ (used to calculate r_C/r_S with Eq. 17) determined experimentally. X_S and X_C could not be calculated analytically and, therefore, were established numerically using a

script written in Matlab. Eq. 24 was obtained by substituting Eq. 23 into Eq. 18, while Eq. 25

considers the core of the particles and was derived by equating Eq. 2 and Eq. 22.

$$\frac{dX_{Ca(OH)_2}}{dt} = 3\left(1 - X_{Ca(OH)_2}\right)^{2/3} \frac{M_{CaO}}{\rho_{CaO}(1 - \varepsilon_{CaO})} \frac{C\,D_e \ln\left[\frac{(1 - X_S)}{(1 - X_C)}\right]}{r_S^2\left(\left(\frac{r_C}{r_S}\right)^2 - \frac{r_C}{r_S}\right)} \qquad Eq.\ 24$$

$$-k_G(X_B - X_S) = \frac{-D_e \ln\left[\frac{(1 - X_S)}{(1 - X_C)}\right]}{r_S\left(1 - \frac{1}{(r_C/r_S)}\right)} \qquad Eq.\ 25$$

Then, k_A was calculated for each experiment from Eq. 21 by a least squares method across all data

points using a script written in Matlab. In this way, a value of k_A was established for each set of

experimental conditions. The values of k_A obtained were then used to obtain projected idealised

model results for X_S, X_C and $X_{Ca(OH)_2}$ as a function of time.

7   References

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