A NUMERICAL MODEL OF TRANSIENT THERMAL TRANSPORT PHENOMENA IN A HIGH–TEMPERATURE SOLID–GAS REACTING SYSTEM FOR CO$_2$ CAPTURE APPLICATIONS

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ABSTRACT

A numerical model coupling transient radiative, convective, and conductive heat transfer and mass transfer to chemical kinetics of a heterogeneous solid–gas reacting system has been developed and applied to a model reaction, the decomposition of calcium carbonate into calcium oxide and carbon dioxide. The model reaction is one of two reactions involved in calcium oxide looping, a proposed thermochemical process suitable for use with concentrated solar radiation for the capture of carbon dioxide. The analyzed system is a single, porous particle in an idealized, reactor–like environment that is subjected to concentrated solar irradiation. The finite volume and explicit Euler methods are used to solve the governing equations numerically. The model predicts the time-dependent temperature distributions as well as local solid and fluid phase composition. Complete particle decomposition for the presented simulation case is reached in 35.5 s.

KEY WORDS: Solar energy, CO$_2$ capture, Porous media, Mass transfer, Heat transfer, High temperature, Numerical simulation

1. INTRODUCTION

In response to increasing anthropogenic greenhouse gas emissions and atmospheric greenhouse gas levels, carbon capture and utilization (CCU) technologies are being developed. Three categories of carbon capture are pre-combustion, oxy-combustion, and post-combustion CO$_2$ capture. In post-combustion carbon capture, fuel is consumed in its usual manner, and CO$_2$ is separated either directly from the output gas stream, where typical CO$_2$ concentrations are approximately 15%, or from the atmosphere, where CO$_2$ concentrations are of the order 100 ppm [1,2]. A proposed avenue for post-combustion carbon capture is solar thermochemical capture via calcium oxide looping [3], where CO$_2$ is chemically absorbed from a dilute source by a calcium oxide sorbent to form calcium carbonate in the exothermic, non-solar reaction,

$$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3, \quad \Delta H_{298K}^0 = -178 \text{ kJ mol}^{-1} \quad (1)$$

The calcium carbonate is thermochemically decomposed into concentrated carbon dioxide and regenerated calcium oxide in the endothermic, solar-driven reaction,

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2, \quad \Delta H_{298K}^0 = 178 \text{ kJ mol}^{-1} \quad (2)$$

In a system for calcium oxide looping, intra-particle heat transfer, mass transfer, and chemical kinetics are all important considerations. Pertinent research topics include radiation and heat transfer characteristics [4–6], interaction with high flux solar irradiation [7], chemical kinetics of both the calcination reaction [8–10] and

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carbonation reaction [11–13], intra-particle mass transfer effects on kinetics [10,14–15], and sorbent degradation [16–17]. Numerical analysis on the single particle level has been conducted considering mass transfer with chemical kinetics [10,14,18] as well as heat and mass transfer with chemical kinetics [19–21].

The rate of a heterogeneous reaction depends on chemical kinetics, mass transfer, and heat transfer. A model that accurately captures chemical kinetics, mass transfer, and heat transfer is needed to elucidate the process rate limiting factors. The knowledge of the process rate limiting factors supports the design of a reacting medium and a solar thermochemical reactor implementing the cycle (1)–(2), as well as provides guidelines for the choice of reactor operating parameters. The development of the model presented in this work is part of an effort to understand the transport processes involved in the implementation of the calcination–carbonation reaction pair for CO\(_2\) capture with concentrated solar radiation. Solar reactors for the implementation of the cycle (1)–(2) are currently being developed [22].

2. PROBLEM STATEMENT

A single, semi-transparent, porous, and non-uniform particle is subjected to high-flux solar irradiation in an idealized, reactor-like environment. The system to be analyzed consists of the solid and gas phases in the particle and is shown in Fig. 1. The thermal decomposition of calcium carbonate, Eq. (2), is selected as the model chemical reaction because of its importance for solar-driven CO\(_2\) capture via the calcium oxide looping cycle [23]. Initially, the particle is 3% porous, and the solid phase is CaCO\(_3\). As CaCO\(_3\) decomposes, the porosity increases, and the compositions of the solid and fluid phases change. The solid phase is a mixture of CaCO\(_3\) and CaO. The fluid in the pore space is a mixture of air and CO\(_2\). The physical phenomena considered in the system are chemistry, mass transfer, and heat transfer. The local chemical reaction rate varies at different locations within the particle and depends on temperature, solid phase composition, carbon dioxide concentration, and particle morphology. The solid phase composition changes due to chemistry, while the fluid phase composition is affected by chemistry, species diffusion due to concentration gradients, and bulk advection due to pressure gradients. Gas expansion and chemical reaction result in the pressure and concentration gradients that drive mass transfer in the fluid phase. Convective mass transfer occurs between the fluid in the particle pore spaces and the ambient fluid surrounding the particle. Heat transfer from the surface to the reaction site is captured in the heat transfer model. Conduction is modeled in both the solid and fluid phases. The solid phase is radiatively participating while the fluid phase is radiatively non-participating. Convective heat transfer occurs between both the solid

![Fig. 1 Reacting spherical particle](image-url)
and fluid phases at the particle surface and the ambient surrounding fluid. Chemistry, mass transfer, and heat transfer are transient and coupled.

The model is developed with the following additional assumptions: (1) the external irradiation and external heat and mass transfer convection are uniform over the particle surface; (2) the external irradiation is diffuse; (3) the particle radius does not change; (4) all pores are active and connected to the particle exterior; (5) the gas phase is radiatively nonparticipating; (6) CaCO₃ is radiatively nonscattering; (7) CaO forms as grains that are assumed to be uniform, spherical, and of radius $R_{g,CaO} = 0.472 \mu m$; (8) the solid phase initially consists of 100% CaCO₃; (9) air and CO₂ act as ideal gases; (10) the only means of fluid mass transfer is by diffusion and advection in the pore space—fluid species do not diffuse into the solid phase; (11) the surroundings are black and initially at radiative equilibrium with the particle; and (12) the solid and fluid phases are at local thermal equilibrium.

3. GOVERNING EQUATIONS

The mathematical model of the coupled heat and mass transfer and chemical kinetics is based on volume-averaged conservation equations [24–25], derived from the model developed by Keene et al. [26] for heat and mass transfer in a reacting heterogeneous cerium dioxide medium. The mathematical model consists of five coupled conservation equations: four conservation of mass equations for the four species of the system and one conservation of energy equation.

3.1 Mass conservation The volume–averaged conservation of mass equations for CaCO₃ and CaO read, respectively:

$$\frac{\partial}{\partial t} \left[ (1-\phi) \left\langle \tilde{p}_{CaCO_3} \right\rangle \right] = \left\langle r^m \right\rangle$$  (3)

$$\frac{\partial}{\partial t} \left[ (1-\phi) \left\langle \tilde{p}_{CaO} \right\rangle \right] = -\left\langle r^m \right\rangle$$  (4)

where the reaction rate term on the right-hand side is the only source or sink of each solid species.

Air is treated as a single species composed of 79% nitrogen and 21% oxygen [27]. The volume-averaged conservation of mass equations for CO₂ and air read, respectively:

$$\frac{\partial}{\partial t} \left( \phi \left\langle \tilde{p}_{CO_2} \right\rangle \right) + \nabla \cdot \left( \left\langle \tilde{p}_{CO_2} \right\rangle \left( \tilde{u}_f \right) \right) = \nabla \cdot \left( D_{CO_2,eff} \nabla \left\langle \tilde{p}_{CO_2} \right\rangle \right) + j_{CO_2} A_{phase}$$  (5)

$$\frac{\partial}{\partial t} \left( \phi \left\langle \tilde{p}_{air} \right\rangle \right) + \nabla \cdot \left( \left\langle \tilde{p}_{air} \right\rangle \left( \tilde{u}_f \right) \right) = \nabla \cdot \left( D_{air,eff} \nabla \left\langle \tilde{p}_{air} \right\rangle \right)$$  (6)

The mass source term for CO₂ is due to CO₂ produced in the chemical reaction and transported across the phase boundary. Note that there is no mass source term for the air species equation.

A linear relationship between reaction extent and the initial and final porosity values is used to predict the local porosity of partially reacted solid, $\phi$ [10]:

$$\phi = \frac{\phi_f - \phi_i}{\phi_f - \phi_i}$$

where $\phi_i$ is the initial porosity, $\phi_f$ is the final porosity, and $\phi$ is the porosity at any intermediate state.
\[ \phi = \phi_{0,\text{CaCO}_3} + \left(1 - \phi_{0,\text{CaCO}_3} \right) \left[ 1 - \left( \frac{\rho_{\text{CaCO}_3}}{M_{\text{CaCO}_3}} \times \frac{M_{\text{CaO}}}{\rho_{\text{CaO}}} \right) \right] X_{\text{local}} \]  

(7)

The local and overall reaction extents, \( X_{\text{local}} \) and \( X_{\text{overall}} \) respectively, are defined as the molar fraction of solid that is CaO, locally and over the entire particle, respectively [19],

\[ X_{\text{local}} \overset{\text{def}}{=} 1 - \frac{\rho_{\text{CaCO}_3}}{\rho_{0,\text{CaCO}_3}}, \quad X_{\text{overall}} \overset{\text{def}}{=} \int_0^R 4\pi R^2 X_{\text{local}} dR \]

(8)

The reaction rate is defined as:

\[ r^{\text{def}} = -\frac{dN_{\text{CaCO}_3}}{dt} = \frac{dN_{\text{CaO}}}{dt} = \frac{dN_{\text{CO}_2}}{dt} \]

(9)

The volumetric reaction model and the reaction rate expression developed by García-Labiano et al. [10] for the calcination of Blanca limestone have been selected for use in this work. The rate expression is dependent on local morphology and \( \text{CO}_2 \) partial pressure and contains an Arrhenius type reaction rate constant. The Langmuir–Hinshelwood mechanism model with the Freundlich isotherm presented by García-Labiano et al. [10] is used to predict the dependence on \( \text{CO}_2 \) partial pressure.

The relationship between bulk fluid velocity, \( u_f \) and pressure, \( p_f \) is found by solving Darcy’s law simplification of the fluid phase conservation of momentum equation. The volume-averaged equation for momentum which yields bulk fluid velocity is:

\[ -\nabla \left( \phi \langle p_f \rangle \right) = \frac{\mu_f}{K_s} \phi \left\langle u_i \right\rangle \]

(10)

where \( \mu_f \) is the viscosity of the fluid phase and \( K \) is the permeability of the porous medium. The local fluid pressure is evaluated using the ideal gas law. The permeability of the solid is:

\[ K_s = K_{\text{CaCO}_3} (1 - X_{\text{local}}) + K_{\text{CaO}} X_{\text{local}} \]

(11)

The effective diffusivity is calculated from the gas diffusion coefficient, \( D_g \) and particle porosity [10]:

\[ D_{\text{eff}} = D_g \phi^2 \]

(12)

The gas diffusion coefficient is a combination of the binary molecular diffusivity \( D_{\text{mol}} \) and Knudsen diffusivity, \( D_K \) [10],

\[ D_g = \left( D_{\text{mol}}^{-1} + D_K^{-1} \right)^{-1} \]

(13)

The relation for binary molecular diffusivity was developed by Fuller et al. [28], and is used in this work.
Table 1 Material properties in mass conservation equations

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{CaCO}_3}$</td>
<td>2730</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\rho_{\text{CaO}}$</td>
<td>3350</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\phi_{\text{CaCO}_3}$</td>
<td>0.03</td>
<td>–</td>
<td>[10]</td>
</tr>
<tr>
<td>$\phi_{\text{CaO}}$</td>
<td>0.56</td>
<td>–</td>
<td>[10]</td>
</tr>
<tr>
<td>$\mu_{\text{CO}_2}$</td>
<td>$1.2 \times 10^6 + 5 \times 10^8 T - 1.1 \times 10^{11} T^2$</td>
<td>N s m$^{-2}$</td>
<td>[29]</td>
</tr>
<tr>
<td>$\mu_{\text{N}_2}$</td>
<td>$4.5 \times 10^7 + 6.4 \times 10^8 T - 2.7 \times 10^{11} T^2 + 5.4 \times 10^{15} T^3$</td>
<td>N s m$^{-2}$</td>
<td>[30]</td>
</tr>
<tr>
<td>$\mu_{\text{O}_2}$</td>
<td>$-4.9 \times 10^7 + 8.1 \times 10^8 T - 4.0 \times 10^{11} T^2 + 1.0 \times 10^{14} T^3$</td>
<td>N s m$^{-2}$</td>
<td>[30]</td>
</tr>
<tr>
<td>$K_{\text{CaCO}_3}$</td>
<td>$4.5 \times 10^{-14}$</td>
<td>m$^2$</td>
<td>[25]</td>
</tr>
<tr>
<td>$K_{\text{CaO}}$</td>
<td>$4.37 \times 10^{-13}$</td>
<td>m$^2$</td>
<td>[31]</td>
</tr>
</tbody>
</table>

3.2 Energy conservation The three modes of heat transfer—radiation, conduction, and convection—are included in the analysis. Conduction is considered in the solid and fluid phases. In the fluid phase, heat is advected by bulk fluid motion and diffuses with species motion. Convective heat transfer occurs at the boundary between both phases and ambient conditions. Radiative transfer within the particle is analyzed, as well as radiation incident on the particle surface interacting with both phases. The volume-averaged conservation of energy equation is:

$$
\frac{\partial}{\partial t} \left( \langle \rho \rangle \langle \bar{E} \rangle \right) + \nabla \cdot \left( \langle \rho \rangle \langle \bar{u} \rangle \langle \bar{E} \rangle \right) = \nabla \cdot \left( \langle \bar{E}_{\text{CO}_2} \rangle \langle D_{\text{CO}_2,\text{eff}} \rangle \langle \bar{E}_{\text{CO}_2} \rangle \right) 
$$

$$
+ \nabla \cdot \left( \langle \bar{E}_{\text{air}} \rangle \langle D_{\text{air,eff}} \rangle \langle \bar{E}_{\text{air}} \rangle \right) + \nabla \cdot (k_{\text{eff}} \nabla \langle T \rangle) - \langle \nabla \cdot \bar{q}_{\text{rad}} \rangle
$$

(14)

The total effective conductivity is the sum of the weighted phase conductivities.

$$
k_{\text{eff}} = (1 - \phi) \left[ \frac{\langle \bar{E}_{\text{CO}_2} \rangle \langle k_{\text{CO}_2} \rangle + \langle \bar{E}_{\text{CaO}} \rangle \langle k_{\text{CaO}} \rangle}{\langle \bar{E}_{\text{CO}_2} \rangle + \langle \bar{E}_{\text{CaO}} \rangle} \right] + \phi \left[ \frac{\langle \bar{E}_{\text{CO}_2} \rangle \langle k_{\text{CO}_2} \rangle + \langle \bar{E}_{\text{air}} \rangle \langle k_{\text{air}} \rangle}{\langle \bar{E}_{\text{CO}_2} \rangle + \langle \bar{E}_{\text{air}} \rangle} \right]
$$

(15)

The Rosseland diffusion approximation is used to model radiative heat transfer within the particle [32]. The radiative conductivity, $k_{\text{rad}}$ is a function of refractive index of the host medium, temperature, and the Rosseland-mean extinction coefficient, $\beta_R$ [32].

The electromagnetic wave theory [32], Mie theory [33], and the transport approximation [34] are used to evaluate the spectral absorption coefficient, $\kappa$, and the spectral scattering coefficient, $\sigma_s$. For simplicity, it is assumed that CaO grains are uniform in size and distribution and that they scatter radiation independently. The real parts of the refractive index for calcium carbonate and calcium oxide are taken from [7,35] and [35], respectively. The imaginary parts of the refractive index for calcium carbonate and calcium oxide are taken from [7,36] and [19,35], respectively. The spectral extinction coefficient is used directly with the gray-band approximation to obtain the radiative conductivity using the Rosseland diffusion approximation [32].
Table 2 Properties in energy conservation equation

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{\text{CaCO}_3}$</td>
<td>$1.1 \times 10^2 T + 1.1 \times 10^2 T^2 + 2.6 \times 10^6 T^{-1} - 1.3 \times 10^6$</td>
<td>J mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$h_{\text{CaO}}$</td>
<td>$50.4 T + 2.1 \times 10^3 T^2 + 8.5 \times 10^5 T^{-1} - 6.5 \times 10^5$</td>
<td>J mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$h_{\text{CO}_2}$</td>
<td>$51.1 T + 2.2 \times 10^3 T^2 + 1.5 \times 10^6 T^{-1} - 4.1 \times 10^5$</td>
<td>J mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$h_{\text{N}<em>2}$ and $h</em>{\text{O}_2}$</td>
<td>Linearly interpolated from tabulated data</td>
<td>J mol$^{-1}$</td>
<td>[27]</td>
</tr>
<tr>
<td>$r_{\text{p, CaCO}_3}$</td>
<td>$1.1 \times 10^2 T + 2.2 \times 10^2 T - 2.6 \times 10^6 T^{-1} - 1.3 \times 10^6$</td>
<td>J mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$r_{\text{p, CaO}}$</td>
<td>$50.4 + 4.2 \times 10^3 T - 8.5 \times 10^5 T - 6.5 \times 10^5$</td>
<td>J mol$^{-1}$</td>
<td>[37]</td>
</tr>
<tr>
<td>$r_{\text{p, CO}_2}$</td>
<td>$51.1 + 4.4 \times 10^3 T - 1.5 \times 10^6 T - 4.1 \times 10^5$</td>
<td>J mol$^{-1}$</td>
<td>[37]</td>
</tr>
<tr>
<td>$k_{\text{CaCO}_3}$</td>
<td>$(1.073 \times 10^3)(77 + T)^{-1} + 0.13$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[38]</td>
</tr>
<tr>
<td>$k_{\text{CaO}}$</td>
<td>0.6</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[19]</td>
</tr>
<tr>
<td>$k_{\text{CO}_2}$</td>
<td>$-6.1 \times 10^3 + 7.5 \times 10^5 T + 9.5 \times 10^9 T^2 - 1.1 \times 10^{11} T^3$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[29]</td>
</tr>
<tr>
<td>$k_{\text{N}_2}$</td>
<td>$-2.3 \times 10^4 + 1.0 \times 10^4 T - 6.0 \times 10^8 T^2 + 2.2 \times 10^{11} T^3$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[39]</td>
</tr>
<tr>
<td>$k_{\text{O}_2}$</td>
<td>$1.6 \times 10^4 + 9.4 \times 10^5 T - 2.8 \times 10^8 T^2 + 5.2 \times 10^{12} T^3$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[39]</td>
</tr>
</tbody>
</table>

3.3 Boundary conditions Two boundary conditions—one at the particle surface and one at the particle center—are required for each of the five conservation equations. The solid phase species do not move in space so the mass fluxes at the center and surface are zero. The mass flux at the center of the particle for all species is zero due to symmetry. For the fluid species, the boundary condition at the surface is a mixed condition defined by advection and diffusion at the particle surface and convective mass transfer away from the particle surface. Thus,

\[
\left. \frac{\partial \langle \rho_{\text{CaCO}_3} \rangle}{\partial r} \right|_{R=0} = 0
\]  \hspace{1cm} (16)

\[
\left. \frac{\partial \langle \rho_{\text{CaO}} \rangle}{\partial r} \right|_{R=0} = 0
\]  \hspace{1cm} (17)

\[
\left. \frac{\partial \langle \rho_{\text{CO}_2} \rangle}{\partial r} \right|_{R=0} = 0
\]  \hspace{1cm} (18)

\[
\left. \langle \rho_{\text{CO}_2} \rangle t - D_{\text{CO}_2, \text{eff}} \frac{\partial \langle \rho_{\text{CO}_2} \rangle}{\partial r} \right|_{R=R_p} = h_{\text{direct}} \left( \langle \rho_{\text{CO}_2} \rangle \right|_{R=R_p} - \langle \rho_{\text{CO}_2} \rangle_{R=0} \right)
\]  \hspace{1cm} (19)
For the conservation of energy equation:

$$\frac{\partial (\bar{\rho} v)}{\partial r} \bigg|_{r=R} = 0$$

(20)

$$\left[ \bar{v} \right] \left[ \frac{\partial (\bar{\rho} v)}{\partial r} \right] \bigg|_{r=R} = h_{\text{in,eff}} \left[ \frac{\partial (\bar{\rho} v)}{\partial r} \right] \bigg|_{r=R} - \bar{\rho}_{\text{v,CO}_2}$$

(21)

For the conservation of energy equation:

$$\frac{\partial (\bar{T})}{\partial r} \bigg|_{r=0} = 0$$

(22)

$$k_{\text{eff}} \frac{\partial (\bar{T})}{\partial r} \bigg|_{r=R} = h_{\text{eff}} \left( T_c - \bar{T} \right)_{R=R} + \alpha_{\text{eff}} q_{\text{v,eff,\omega}} - \varepsilon_{\text{eff}} \sigma \left[ \left( \bar{T} \right)_{R=R} \right]^4 - T_w^4$$

(23)

The surface mass transfer coefficient is found from the correlation for convective mass transfer for a sphere in a flow as reported in [40]:

$$Sh_d = 2 + 0.6 \text{Re}_d^{0.5} \text{Sc}^{1/3}$$

(24)

The surface heat transfer coefficient is found from the correlation for surface convective heat transfer proposed by Whitaker [41] for flow past a single particle,

$$\text{Nu}_d = 2 + \left( 0.4 \text{Re}_\infty^{1/2} + 0.06 \text{Re}_\infty^{7/3} \right) \text{Pr}_\infty^{0.4} \left( \frac{\mu_\infty}{\mu_{\infty, R=R}} \right)^{1/4}$$

(25)

The total effective absorptivity, $\alpha_{\text{eff}}$ and emissivity, $\varepsilon_{\text{eff}}$ are calculated from the total reflectivity, $\rho_{\alpha, \text{eff}}$. The heterogeneous solid features at the particle surface are assumed much larger than the incident wavelength, so the medium is treated as optically discrete. Fresnel equations are first used to evaluate the spectral, directional–hemispherical reflectivity of CaCO$_3$ and CaO at the particle surface, $\rho_{\alpha, \text{CaCO}_3}$ and $\rho_{\alpha, \text{CaO}}$, respectively. The reflectivity of the fluid in the pore space, $\rho_{\alpha, f}$ is assumed to be zero. These values are combined to yield the surface medium's effective spectral, directional–hemispherical reflectivity, accounting for the local reaction extent and porosity,

$$\rho_{\alpha, \text{eff}} = (1-\phi) \left[ (1-X_{\text{local}}) \rho_{\alpha, \text{CaCO}_3} + X_{\text{local}} \rho_{\alpha, \text{CaO}} \right] + \phi \rho_{\alpha, f}$$

(26)

The spectral, directional–hemispherical reflectivity is averaged over all directions to evaluate the spectral, hemispherical reflectivity, $\rho_{\alpha, \text{eff}}$. The spectral, hemispherical reflectivity is averaged over the incident or emitted spectrum to yield the total absorptivity or emissivity, respectively.

The specific values of the physical parameters simulating high-flux solar irradiation and a gas flow, reactor-like environment are given in Table 3.
### Table 3 Baseline physical parameters for reactor-like environment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{y}_{v,CO_2}$</td>
<td>0.99</td>
<td>–</td>
</tr>
<tr>
<td>$p_0$</td>
<td>101,325</td>
<td>Pa</td>
</tr>
<tr>
<td>$q^*_{solar}$</td>
<td>1</td>
<td>MW m⁻²</td>
</tr>
<tr>
<td>$T_0$</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>$T_w$</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>$\varepsilon_w$</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>$T_{\infty}$</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>$u_{\infty}$</td>
<td>0.09</td>
<td>m s⁻¹</td>
</tr>
</tbody>
</table>

#### 3.4 Initial Conditions

The initial conditions are:

- For Eq. (3)

$$\left\langle \bar{\rho}_{CaCO_3} \right\rangle \mid_{t=0} = \frac{\rho_{CaCO_3}}{M_{CaCO_3}} \quad (27)$$

- For Eq. (4)

$$\left\langle \bar{\rho}_{CaO} \right\rangle \mid_{t=0} = 0 \quad (28)$$

- For Eq. (5)

$$\left\langle \bar{\rho}_{CO_2} \right\rangle \mid_{t=0} = \bar{\rho}_{v,CO_2} \quad (29)$$

- For Eq. (6)

$$\left\langle \bar{\rho}_{air} \right\rangle \mid_{t=0} = \bar{\rho}_{v,air} \quad (30)$$

Initially, the solid and fluid phases are isothermal at an initial temperature $T_0$. Thus, the initial condition for Eq. (14) reads:

$$\left\langle T \right\rangle \mid_{t=0} = T_0 \quad (31)$$

The numerical solution is obtained by employing the 1D finite volume method and the explicit Euler time integration scheme. The spatial domain is discretized into spherical shell volume elements with the constant thickness, $\Delta r$. The time domain is discretized into equal time intervals of length $\Delta t$. The governing equations are integrated over a finite volume, $V_i$ and a time step, $\Delta t$, yielding the discrete equation forms.

The discrete equations are solved using a Fortran 90 code developed specifically for this application. Table 4 summarizes the numerical solution parameters.
Table 4 Baseline numerical solution parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0025</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta r$</td>
<td>8.3x10^{-5}</td>
<td>M</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>2.5x10^{-6}</td>
<td>M</td>
</tr>
</tbody>
</table>

4. RESULTS

The parameters listed in Tables 3 and 4 are referred to in the following text as the baseline simulation parameter set. The model is employed to study thermochemical characteristics of the model calcination system.

Figures 2 and 3 show the results of the baseline simulation. Temperature profiles as a function of time are shown in Fig. 2a for the particle surface, the particle center, and midway between. Initially, the temperature increases in all three locations until the onset of the chemical reaction at the surface. Once the surface of the particle starts reacting, the heating rate of the surface slows and remains slower until the reaction stops, at which time, the particle surface resumes heating.

![Fig. 2](image)

(a) Local temperature versus time for select locations and (b) local temperature profiles in the particle for selected times

The temperature at the interior locations remains nearly constant as the outer portions of the particle react. The chemical reaction stops when the particle is completely converted, and the temperature at the center begins to increase again and approaches the surface temperature. The maximum temperature of 1879 K is observed after 40 s of simulation time at the particle surface.

Temperature profiles within the particle for different times are shown in Fig. 2b. The temperature profiles within the particle show a distinct transition point between reacted and unreacted areas of the particle in the curves for $t = 5$, 10, and 30 s. The distinct transition location indicates the reaction zone. The temperature of the reaction zone is fairly constant throughout the simulation and falls between approximately 1150 K and 1250 K. These temperatures are of the same order as calcination temperatures determined by thermodynamic analysis [42]. After the onset of chemical reaction, the temperature of the unreacted particle interior is also fairly isothermal at the same temperature as the reaction zone. The reacted portion of the particle is not isothermal and shows strong temperature gradients from the particle surface to the reaction front.
Figure 3a shows overall particle conversion versus time for the baseline simulation. In the initial part of the simulation, all irradiation goes towards heating the particle and the particle does not react. The particle begins to react at \( t = 1.7 \) s when the surface temperature reaches \( T = 1200 \) K. The reaction progresses through the particle until overall particle conversion is achieved at \( t = 35.5 \) s.

In Fig. 3b, local particle conversion versus time is shown for three locations. The rate of conversion varies between the three shown locations. While all locations reach complete conversion within seconds from the local onset of the chemical reaction, the particle surface and the particle interior (\( R/R_p = 1.0 \) and \( R/R_p = 0.0 \), respectively) react more quickly, while midway between (\( R/R_p = 0.5 \)), the particle reacts comparatively more slowly.

![Figure 3](image1.png)

**Fig. 3** (a) Overall reaction extent versus time and (b) local reaction extent versus time for selected locations within the particle

Figure 4 compares the local volumetric reaction rate for the three particle locations. The fastest reaction rate, \(-76050 \text{ mol s}^{-1}\text{m}^{-3}\), is seen at the particle center. This is more than 3 times faster than the highest reaction rate observed at the particle surface and more than 7 times faster than the highest reaction rate seen midway between, \(-23399 \text{ mol s}^{-1}\text{m}^{-3}\) and \(-10720 \text{ mol s}^{-1}\text{m}^{-3}\), respectively. The reaction rates at the surface and the center are faster than the reaction rate midway between because those locations experience higher rates of heating from the onset of the chemical reaction and therefore faster kinetics.

![Figure 4](image2.png)

**Fig. 4** Local reaction rate versus time for selected locations within the particle
5. CONCLUSIONS

A numerical model coupling chemical kinetics of thermochemical decomposition, mass transfer, and heat transfer has been developed for a heterogeneous reacting particle. The thermochemical decomposition of CaCO$_3$ was selected as the model chemical reaction because of its application in solar CO$_2$ capture via the calcium oxide based carbonation–calcination cycle. The model predicts, with previously unreported detail, the interactions of the coupled transient physical phenomena at the intra-particle level.

Onset of chemical reaction occurs at the particle surface at 1.7 s when the surface temperature is 1200 K. Overall particle conversion is reached after 35.5 s. A distinct reaction front moving through the particle is observed. The distinction in temperature gradients at the reaction front between the reacted and unreacted portions of the particle is pronounced and suggests the reaction is heat transfer limited for the conditions considered in this work.

The numerical solution utilizes the explicit Euler method for time integration. The time step required for stability with this method is sufficiently small to produce meaningful results for this study, but simulations are computationally costly. The computational costs of extending this model to a group of particles, as in a reactor, can be prohibitively high. The evaluation of radiative conductivity is the most computationally expensive component.

The future work will use the model to investigate reactor operating conditions. It will also include the addition of carbonation kinetics to the model in order to simulation the complete reaction loop. Because full carbonation of each particle is desired, it is expected that the mass transfer of CO$_2$ through the outer layer of calcium carbonate will be an important reactive medium design concern.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{A}$</td>
<td>specific surface area ($m^2$ m$^{-3}$)</td>
</tr>
<tr>
<td>$i$</td>
<td>spatial index ($-$)</td>
</tr>
<tr>
<td>$j^*$</td>
<td>molar flux (mol m$^{-2}$)</td>
</tr>
<tr>
<td>$K$</td>
<td>permeability (m$^2$)</td>
</tr>
<tr>
<td>$r^w$</td>
<td>volumetric reaction rate (mol m$^{-3}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$X$</td>
<td>reaction extent ($-$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>porosity ($-$)</td>
</tr>
</tbody>
</table>

Subscripts

- $d$: diameter
- eff: effective
- f: fluid
- g: gas
- K: Knudsen

Superscripts

- f: fluid
- s: solid
- ' : directional
- $\infty$: free stream
- $\bar{\lambda}$: spectral
- $\bar{\phi}$: hemispherical

REFERENCES


