Effect of surface radiative properties of a CO\(_2\) sorbent particle on its interactions with high-flux solar irradiation

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Abstract: A thermal transport phenomena model for the decomposition of a CO\(_2\) sorbent particle under concentrated solar irradiation is used to evaluate four approximate engineering models for the surface radiative properties of the particle. The radiative property models are formulated by considering the solid-phase to be opaque or semi-transparent and the size of the surface features to be either smaller or larger than the incident irradiation wavelength. Time to complete decomposition of the particle and maximum surface temperature in simulations employing the four models differ by approximately 2% and 0.5%, respectively.

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References and links
1. Introduction

Particulates undergoing chemical reactions are found in many industrial and scientific applications including thermal decomposition of natural carbonates, ignition of metallic or other solid particles, metallurgical refining, and atmospheric and aerosol sciences. Chemical sorbent particles are an important subset of reacting particulates. One such novel technology is the solar thermochemical capture of carbon dioxide (CO$_2$) via the two-step calcium oxide looping cycle [1, 2]. The high-temperature capture of CO$_2$ via solar calcium oxide looping promises high efficiencies and capture rates [3]. Concentrated CO$_2$ is a commodity with applications in the pharmaceutical, medical, environmental, food and beverage, petrochemical, oil recovery, metallurgy, and manufacturing industries [4, 5], as well as the production of synthetic transportation fuels [6]. Physical characteristics of the surface of a reacting particle can be complex, particularly with regard to the interaction of particles with high-flux solar irradiation at the particle surface. Treatment of radiative heat transfer in particulate media and the determination of surface radiative properties vary widely with application and are important considerations in many engineering applications [7].

In two-step calcium oxide looping for CO$_2$ capture, calcium carbonate (CaCO$_3$) is thermochemically decomposed into concentrated CO$_2$ and calcium oxide (CaO) sorbent in the endothermic, solar-driven calcination reaction,

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

CO$_2$ is then chemically absorbed from a dilute source by CaO to form CaCO$_3$ in the exothermic, non-solar carbonation reaction,

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

A numerical model of transient thermal transport phenomena in a solid–gas reacting particle has been developed and applied to the calcination reaction to investigate physical parameters of particle size, reaction rate, internal radiative heat transfer, and permeability, as well as operational parameters of magnitude of incident irradiation and ambient CO$_2$ concentration [8]. The thermal transport model was found to be more sensitive to heat transfer related parameters than mass transfer related parameters, but the model sensitivity to surface radiative properties was not investigated. The surface of a sorbent particle for calcium oxide looping is porous, and the porosity $\phi$ changes with time due to changing composition. The composition of the solid phase is a mixture of dense CaCO$_3$ and porous CaO, and changes due to chemical reaction.

In this work, four different phenomenological models for the surface radiative properties are presented and compared using the thermal transport model. Understanding the sensitivity of the thermal transport model to surface radiative properties is important to understanding the
interaction between sorbent particles and high-flux solar radiation, which in turn, provides input
to the design of the reacting medium and a solar reactor for calcium oxide looping CO₂ capture.

The models for surface radiative properties are formulated by considering different solid phase
opacity and feature size relative to wavelength. Development of the surface radiative property
models is motivated by the suitability and potential of using concentrated solar energy as the
process heat for driving heterogeneous thermochemical processes featuring particulate media.

2. Problem statement

A semi-transparent, porous, and non-uniform particle is subjected to high-flux solar irradiation
in an idealized environment (Fig. 1). Within the particle, local temperature, solid and fluid
phase species concentrations, porosity, and fluid conditions vary with location and in time. The
solid phase is a mixture of CaCO₃ and CaO. The fluid phase in the pore space is a mixture of
air and CO₂. The local, intrinsic chemical reaction rate depends on temperature, solid phase
composition, CO₂ 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. 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 locations within the particle undergoing chemical
reaction is captured in the heat transfer model. Conduction is modeled in both the solid and fluid
phases. Surface and volumetric radiative transfer are considered. The solid phase is radiatively
participating while the fluid phase is radiatively non-participating. Convective heat transfer
occurs between both the solid and fluid phases and the ambient surrounding fluid at the particle
surface.

Fig. 1. A single particle in a reactor-like environment with non-uniform composition and
temperature under uniform direct irradiation.

The particle is initially 3% porous with solid phase composition 100% CaCO₃ and fluid phase
composition at equilibrium with the ambient. The particle is subjected to high-flux diffuse solar
irradiation uniformly distributed over the surface to approximate the conditions of a single,
rapidly rotating particle exposed directly to concentrated solar radiation. Uniform versus non-
uniform irradiation was investigated previously [9]. Radiative interactions with other particles
in a reactor for CO$_2$ capture is neglected for simplicity. The focus of the present study is to elucidate the interactions between the particle irradiation, spectral surface properties, and intra-particle transport phenomena. Incident irradiation initially goes towards particle heating until the calcination reaction temperature is reached. Calcination then proceeds until the particle is completely decomposed, and particle heating resumes.

3. Thermal transport model

A benchmark numerical model of thermal transport phenomena has been developed and applied to the calcination of a sorbent particle [8]. The model is based on volume-averaged conservation equations and consists of five coupled equations: four conservation of mass equations for the four species of the system (CaCO$_3$, CaO, CO$_2$, and air) and one conservation of energy equation. Constraint equations include a simplified conservation of momentum equation and the ideal gas equation of state.

In order to properly resolve time-dependent composition and temperature profiles within the particle during cycling, mass, momentum, and energy equations are solved. Single global conversion expressions have been developed for the calcination reaction [10, 11]. However, they have limited applicability as they are limited to specific experimental conditions and do not account for mass diffusion limitations and internal temperature gradients. Governing equations for the local solid phase composition, fluid phase composition, and temperature are included in the numerical model, because these quantities influence the local intrinsic kinetics of the calcination reaction [12, 13].

Sorbent particles considered for calcium oxide looping CO$_2$ capture range in size from the micrometers [14] to millimeters [15]. The complete calcination numerical model and the surface radiative property models have been formulated for large sorbent particles.

Conservation of mass—Solid phase

The volume-averaged conservation of mass equations for CaCO$_3$ and CaO read, respectively:

$$\frac{\partial \left[ (1-\phi) \langle \bar{\rho}_{\text{CaCO}_3} \rangle \right]}{\partial t} = \langle \bar{r}'' \rangle$$

(3)

$$\frac{\partial \left[ (1-\phi) \langle \bar{\rho}_{\text{CaO}} \rangle \right]}{\partial t} = -\langle \bar{r}'' \rangle$$

(4)

where the solid phase composition changes due to chemical reaction. As the solid phase composition changes, concomitant changes in $\phi$ are considered, but the particle radius is assumed constant.

Conservation of mass—Fluid phase

For the fluid phase, the volume-averaged conservation of mass equations for CO$_2$ and air read, respectively:

$$\frac{\partial \left( \phi \langle \bar{\rho}_{\text{CO}_2} \rangle \right)}{\partial t} + \nabla \cdot \left( \langle \bar{\rho}_{\text{CO}_2} \rangle \langle \bar{u}_f \rangle \right) = \nabla \cdot \left( D_{\text{CO}_2,\text{eff}} \nabla \langle \bar{\rho}_{\text{CO}_2} \rangle \right) + j''_{\text{CO}_2} s''_{\text{phase}}$$

(5)

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

(6)

where the molar concentrations of CO$_2$ and air change due to bulk advection, species diffusion, and for CO$_2$, chemical reaction and transport across the solid–fluid phase boundary ($j''_{\text{CO}_2} s''_{\text{phase}}$).
All pores are assumed active and connected to the particle exterior. Air is modeled as a single species composed of 79% nitrogen and 21% oxygen. Closure equations for bulk advection and diffusion are formulated using molar-averaged effective properties presented in [8].

**Conservation of momentum**

Darcy’s law simplification of the conservation of momentum equation is used to determine the fluid velocity in the pore space. Darcy’s law simplification is used for its simplicity and appropriateness, because fluid velocities are low enough to maintain laminar flow at all times and locations within the particle.

\[-\nabla \left( \phi \langle p f \rangle f \right) = \frac{\mu f}{K} \phi \langle \vec{u} f \rangle \tag{7}\]

where \(p_f\) is the local fluid pressure, \(\mu_f\) is the viscosity of the fluid, \(K\) is the permeability of the porous solid, and \(\langle \vec{u} f \rangle\) is the superficial fluid velocity. The local fluid pressure is evaluated using the ideal gas equation as the total fluid pressure remains low at all times and locations within the particle.

**Conservation of energy**

The solid and fluid phases are assumed to be at local thermal equilibrium, yielding one conservation of energy equation for the system,

\[\frac{\partial \langle \bar{\rho} \rangle}{\partial t} + \nabla \cdot \left( \langle \bar{\rho} f \rangle f \langle \bar{h} f \rangle f \langle \vec{u} f \rangle \right) = \nabla \cdot \left( \langle \bar{h}_{CO_2} \rangle f D_{CO_2,eff} \vec{\nabla} \langle \bar{\rho}_{CO_2} \rangle f \right)\]

\[+ \nabla \cdot \left( \langle \bar{h}_{air} \rangle f D_{air,eff} \vec{\nabla} \langle \bar{\rho}_{air} \rangle f \right) + \nabla \cdot (k_{eff} \nabla \langle T \rangle) - \langle \nabla \cdot \vec{q}_{rad} \rangle \tag{8}\]

where latent heat changes due to bulk fluid advection, fluid species diffusion, conduction, and radiative heat transfer within the particle. Property relations for enthalpy and equations for effective conductivity and radiative heat flux, used in Eq. (8), are given in [8].

**Boundary and initial 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,

\[\frac{\partial \langle \bar{\rho}_{CaCO_3} \rangle_s}{\partial r} \bigg|_{r=0} = \frac{\partial \langle \bar{\rho}_{CaCO_3} \rangle_s}{\partial r} \bigg|_{r=r_p} = 0 \tag{9}\]

\[\frac{\partial \langle \bar{\rho}_{CaO} \rangle_s}{\partial r} \bigg|_{r=0} = \frac{\partial \langle \bar{\rho}_{CaO} \rangle_s}{\partial r} \bigg|_{r=r_p} = 0 \tag{10}\]

\[\frac{\partial \langle \bar{\rho}_{CO_2} \rangle f}{\partial r} \bigg|_{r=0} = 0 \tag{11}\]

\[\left[ \langle \bar{\rho}_{CO_2} \rangle f \vec{u} f - D_{CO_2,eff} \frac{\partial \langle \bar{\rho}_{CO_2} \rangle f}{\partial r} \right] \bigg|_{r=r_p} = h_{m,eff} \left( \langle \bar{\rho}_{CO_2} \rangle f \bigg|_{r=r_p} - \bar{\rho}_{CaCO_2} \right) \tag{12}\]
\[
\frac{\partial \langle \rho_{\text{air}} \rangle_t}{\partial r} \bigg|_{r=0} = 0
\]  
\[
\left[ \langle \rho_{\text{air}} \rangle_t u_t - D_{\text{air,eff}} \frac{\partial \langle \rho_{\text{air}} \rangle_t}{\partial r} \right] \bigg|_{r=r_p} = \left. h_{\text{m,eff}} \right( \langle \rho_{\text{air}} \rangle_t \bigg|_{r=r_p} - \bar{\rho}_{\text{w,air}} \right)
\]  
(13)

For the conservation of energy equation:

\[
\frac{\partial \langle T \rangle_t}{\partial r} \bigg|_{r=0} = 0
\]  
\[
k_{\text{eff}} \frac{\partial \langle T \rangle_t}{\partial r} \bigg|_{r=r_p} = h_{\text{eff}} \left( T_\infty - \langle T \rangle_t \bigg|_{r=r_p} \right) + \alpha_{\text{eff,solar}} q''_{\text{solar}} + \alpha_{\text{eff,w}} \sigma T_\infty^4 - \varepsilon_{\text{eff,p}} \sigma \left( \langle T \rangle_t \bigg|_{r=r_p} \right)^4
\]  
(16)

where the effective surface radiative properties are all evaluated for the particle surface. \( \alpha_{\text{eff,solar}} \) is evaluated for incident irradiation with the spectral distribution of a blackbody at \( T = 5777 \text{K} \); \( \alpha_{\text{eff,w}} \) is evaluated for incident irradiation with the spectral distribution of a blackbody at \( T_\infty \); and \( \varepsilon_{\text{eff,p}} \) is evaluated for emitted irradiation with the spectral distribution of a blackbody at \( \langle T \rangle_t \bigg|_{r=r_p} \).

The initial conditions are:

- For Eq. (3)
  \[
  \langle \rho_{\text{CaCO}_3} \rangle |_{t=0} = \frac{\rho_{\text{CaCO}_3}}{M_{\text{CaCO}_3}}
  \]  
  (17)

- For Eq. (4)
  \[
  \langle \rho_{\text{CaO}} \rangle |_{t=0} = 0
  \]  
  (18)

- For Eq. (5)
  \[
  \langle \rho_{\text{CO}_2} \rangle |_{t=0} = \bar{\rho}_{\text{w,CO}_2} = \bar{y}_{\text{w,CO}_2} \left( \frac{p_0}{RT} \right)
  \]  
  (19)

- For Eq. (6)
  \[
  \langle \rho_{\text{air}} \rangle |_{t=0} = \bar{\rho}_{\text{w,air}} = (1 - \bar{y}_{\text{w,CO}_2}) \left( \frac{p_0}{RT} \right)
  \]  
  (20)

Initially, the solid and fluid phases are isothermal at an initial temperature \( T_0 \). Thus, the initial condition for Eq. (8) reads:

\[
\langle T \rangle |_{t=0} = T_0
\]  
(21)

The governing equations are solved numerically in space and time by employing the 1-D finite volume method and the explicit Euler time-integration scheme. Material properties used for the system and numerical solution methods are given in [8]. The particle has a radius \( r_p = 2.5 \text{mm} \). The magnitude of the incident flux is \( q''_{\text{solar}} = 1 \text{ MW m}^{-2} \). The baseline simulation parameter set is shown in Table 1. The model predicts transient heat and mass fluxes, temperature distributions, and extent of the calcination reaction within the particle. The extent of the calcination reaction, referred to as the reaction extent, describes the solid phase composition and is defined as \( X = 1 - N_{\text{CaCO}_3}/N_{0,\text{CaCO}_3} \), where \( N_{\text{CaCO}_3} \) and \( N_{0,\text{CaCO}_3} \) are the local and initial amount of substance of \( \text{CaCO}_3 \), respectively.
Table 1. Baseline simulation parameter set.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\infty, CO_2}$</td>
<td>0.99</td>
<td>—</td>
</tr>
<tr>
<td>$p_0$</td>
<td>101,325</td>
<td>Pa</td>
</tr>
<tr>
<td>$q''_{\text{solar}}$</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>

4. Surface radiative property models

Four models for surface radiative properties are formulated by considering (a) the surface of the solid phase to be either non-absorbing or absorbing and (b) the size of the surface features to be either smaller or larger than the incident wave length. If the surface features are predominantly smaller than the incident wavelength, the effective medium (EM) assumption is used. If the surface features are predominantly larger than the incident wavelength, the optically discrete medium (ODM) assumption is used. The models are outlined in Table 2.

Table 2. Surface radiative property models.

<table>
<thead>
<tr>
<th>Effective medium</th>
<th>Optically discrete medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-absorbing</td>
<td>Model 1: EM, $k = 0$</td>
</tr>
<tr>
<td>Absorbing</td>
<td>Model 3: EM, $k \neq 0$</td>
</tr>
</tbody>
</table>

The thermal transport model requires the effective absorptance $\alpha_{\text{eff}}$ and emittance $\varepsilon_{\text{eff}}$ of the particle surface in Eq. (16) to describe radiative heat transfer at the particle surface. These effective properties are a mixture of the individual properties of the two solid phase species and the fluid in the pore space. Refractive indices of the constituents of the particle surface are used to evaluate reflectance, which is then used to evaluate absorptance and emittance. The computational approaches for evaluating effective absorptance and emittance for models assuming EM and ODM are shown in Fig. 2. The computational approach for models assuming the solid phase to be opaque or transmitting is the same, therefore Fig. 2(a) applies to Models 1 and 3, assuming EM, and Fig. 2(b) applies to Models 2 and 4, assuming ODM. The fluid in the pore space is treated as perfectly transparent and non-refracting in all models.

In Models 1 and 3 shown in Fig. 2(a), refractive indices for each surface constituent are converted to dielectric functions, then combined using the local reaction extent and the porosity of the surface to yield an effective dielectric function. The effective dielectric function is converted to an effective refractive index, $n_{\text{eff}} = n_{\text{eff}} + ik_{\text{eff}} = f\left(\varepsilon_{\text{eff}}, \varepsilon'_{\text{eff}}\right)$. The effective refractive index is used with the Fresnel equations to evaluate the effective spectral, directional–hemispherical reflectance $p_{\lambda,\text{eff}}$. The dielectric function and refractive index are related by [16]:

\[
\varepsilon' = n^2 - k^2 \\
\varepsilon'' = 2nk
\]  \hspace{1cm} (22)

\[
n^2 = \frac{1}{2}\left(\varepsilon' + \sqrt{\varepsilon'^2 + 4\varepsilon''^2}\right) \\
k^2 = \frac{1}{2}\left(-\varepsilon' + \sqrt{\varepsilon'^2 + 4\varepsilon''^2}\right)
\]  \hspace{1cm} (23)
Equations (22) and (23) are used for species and effective quantities. After evaluating the surface constituent dielectric functions, the effective dielectric function is:

\[
\begin{align*}
\varepsilon'_\text{eff} &= (1 - \phi_{\text{surface}}) \left[ (1 - X_{\text{surface}}) \varepsilon'_{\text{CaCO}_3} + X_{\text{surface}} \varepsilon'_{\text{CaO}} \right] + \phi_{\text{surface}} \varepsilon'_{\text{fluid}} \\
\varepsilon''_\text{eff} &= (1 - \phi_{\text{surface}}) \left[ (1 - X_{\text{surface}}) \varepsilon''_{\text{CaCO}_3} + X_{\text{surface}} \varepsilon''_{\text{CaO}} \right] + \phi_{\text{surface}} \varepsilon''_{\text{fluid}}
\end{align*}
\]  

(24)

where \(X_{\text{surface}}\) and \(\phi_{\text{surface}}\) are related by:

\[
\phi_{\text{surface}} = \phi_0 \text{CaCO}_3 + (1 - \phi_0 \text{CaCO}_3) \left[ 1 - \left( \frac{\rho_{\text{CaCO}_3}}{M_{\text{CaCO}_3}} \times \frac{\bar{M}_{\text{CaO}}}{\rho_{\text{CaO}}} \right) \right] X_{\text{surface}}
\]  

(25)

where \(\phi_0 \text{CaCO}_3 = 0.03\) is the initial porosity of unreacted \(\text{CaCO}_3\); \(\rho_{\text{CaCO}_3}\) and \(\rho_{\text{CaO}}\) are the true densities of non-porous \(\text{CaCO}_3\) and \(\text{CaO}\), respectively; and \(\bar{M}_{\text{CaCO}_3}\) and \(\bar{M}_{\text{CaO}}\) are the molar masses of \(\text{CaCO}_3\) and \(\text{CaO}\), respectively.

In Models 2 and 4 shown in Fig. 2(b), refractive indices for \(\text{CaCO}_3\) and \(\text{CaO}\) are used directly in the Fresnel equations to evaluate the spectral, directional–hemispherical reflectance \(\rho'_\lambda\text{eff}\) for \(\text{CaCO}_3\) and \(\text{CaO}\) separately. \(\rho'_\lambda\text{CaCO}_3\) and \(\rho'_\lambda\text{CaO}\) are then combined using the local reaction extent and porosity of the surface to yield \(\rho'_\lambda\text{eff}\).

\[
\rho'_\lambda\text{eff} = (1 - \phi_{\text{surface}}) \left[ (1 - X_{\text{surface}}) \rho'_\lambda\text{CaCO}_3 + X_{\text{surface}} \rho'_\lambda\text{CaO} \right] + \phi_{\text{surface}} \rho'_\lambda\text{fluid}
\]  

(26)

In all models, \(\rho'_\lambda\text{eff}\) is averaged over all directions to evaluate the spectral, hemispherical reflectance \(\rho_\lambda\text{eff}\).

\[
\rho_\lambda\text{eff} = \frac{1}{\pi} \int_0^{\pi} \rho'_\lambda\text{eff} \cos \theta \, d\Omega
\]  

(27)
Fig. 3. Complex refractive indices for CaCO$_3$ and CaO (a) real and imaginary parts and (b) magnified view of the imaginary part in the visible wavelength range.

The total effective absorptance $\alpha_{\text{eff}}$ and emittance $\varepsilon_{\text{eff}}$ are calculated from the total effective reflectance $\rho_{\text{eff}}$ by averaging $\rho_{\lambda, \text{eff}}$ over the appropriate incident or emitted spectra,

$$
\alpha_{\text{eff}}(T_{\text{src}}) = \frac{\int_{\lambda=0}^{\infty} (1 - \rho_{\lambda, \text{eff}}) E_{b\lambda}(T_{\text{src}}) d\lambda}{\sigma T_{\text{src}}^4}
$$

$$
\varepsilon_{\text{eff}}(T_{\text{src}}) = \frac{\int_{\lambda=0}^{\infty} (1 - \rho_{\lambda, \text{eff}}) E_{b\lambda}(T_{\text{src}}) d\lambda}{\sigma T_{\text{src}}^4}
$$

The Fresnel equations are [17]:

$$
p_{i}^2 = \frac{1}{2} \left[ \sqrt{(n_i^2 - k_i^2 - n_{i\perp}^2 \sin^2 \theta)^2 + 4n_i^2k_i^2} - (n_i^2 - k_i^2 - n_{i\perp}^2 \sin^2 \theta) \right]
$$

$$
q_{i}^2 = \frac{1}{2} \left[ \sqrt{(n_i^2 - k_i^2 - n_{i\parallel}^2 \sin^2 \theta)^2 + 4n_i^2k_i^2} - (n_i^2 - k_i^2 - n_{i\parallel}^2 \sin^2 \theta) \right]
$$

$$
\rho_{i,\lambda,\perp} = \frac{(n_i \cos \theta - p_i)^2 + q_i^2}{(n_i \cos \theta)^2 + q_i^2}, \quad \rho_{i,\lambda,\parallel} = \frac{(p_i - n_i \sin \theta \tan \theta)^2 + q_i^2}{(p_i + n_i \sin \theta \tan \theta)^2 + q_i^2} \rho_{i,\lambda,\perp}
$$

$$
\rho_{i,\lambda} = \frac{\rho_{i,\lambda,\perp} + \rho_{i,\lambda,\parallel}}{2}
$$

where $n_i$ is the refractive index of the fluid surrounding the particle, and $i = \text{CaCO}_3$ or $\text{CaO}$ for Models 1 and 3 and $i = \text{eff}$ for Models 2 and 4.

The real parts of the refractive index $n$ for CaCO$_3$ and CaO are taken from [18, 19] and [19], respectively. The imaginary parts of the refractive index $k$ for CaCO$_3$ and CaO are taken from [18, 20] and [19, 21], respectively. Refractive indices versus wavelength for CaCO$_3$ and CaO are shown in Fig. 3. Mathematical expressions are used to approximate refractive index experimental data resulting in the discontinuity of curves shown in Fig. 3.

Effective absorptance of the particle surface varies with surface composition, while effective emittance may vary with both surface composition and temperature. Figure 4 shows $\alpha_{\text{eff}}$ and $\varepsilon_{\text{eff}}$
versus the surface reaction extent. For the non-absorbing models (Models 1 and 2), $\alpha_{\text{eff}} = \varepsilon_{\text{eff}}$ because the real components of the refractive index for all species do not vary with wavelength and are therefore not a function of temperature. Model 1 predicts the highest values for $\alpha_{\text{eff}}$ and $\varepsilon_{\text{eff}}$. The change in $\alpha_{\text{eff}}$ and $\varepsilon_{\text{eff}}$ with reaction extent is 6% and 4% for Models 1 and 2, respectively. For the absorbing models (Models 3 and 4), surface temperature and composition both influence $\varepsilon_{\text{eff}}$, but composition has the stronger influence. Model 4 predicts the lowest values for $\alpha_{\text{eff}}$ and $\varepsilon_{\text{eff}}$. The change in $\alpha_{\text{eff}}$ with reaction extent is 5% and 2% for Models 3 and 4, respectively. The change in $\varepsilon_{\text{eff}}$ with reaction extent for $T = 800$K is 6% and 3% for Models 3 and 4, respectively.

5. Results

Radiative property models are compared based on time to complete conversion of the particle when the overall reaction extent $X_{\text{overall}} = 1$, time to complete conversion of the particle surface when the local reaction extent $X_{\text{surface}} = 1$, and the maximum achieved surface temperature. Overall reaction extent and the local reaction extent at the particle surface are shown versus time in Fig. 5. The particle in the simulation employing Model 1 reaches complete conversion at $t = 32.1$s. Models 2 and 3 reach complete conversion at $t = 32.4$s and $t = 32.3$s, respectively. Model 4 reaches complete conversion in the longest amount of time, $t = 32.6$s. Time to complete particle conversion increases with decreasing surface radiative properties. Similarly, the particle surfaces in the simulations employing Model 1, 2, and 3 reach complete conversion at $t = 3.4$s, and Model 4 reaches complete conversion at $t = 3.5$s.

Surface temperature versus time is shown in Fig. 6. The maximum temperature of the particle occurs at the surface at end of the 40s simulation. The maximum surface temperature achieved using Models 1 and 2 is 1975K and 1972K, respectively. The maximum surface temperatures achieve using Models 3 and 4 are 1971K and 1965K, respectively.

Simulations employing EM models exhibit higher predicted effective surface radiative properties, but non-absorbing models yield the highest maximum surface temperatures. Model 4 yields the lowest effective properties resulting in the less radiation absorption, longest time to complete conversion, and lowest maximum surface temperature.
Fig. 5. Reaction extent versus time for the baseline case for (a) the entire particle and (b) the particle surface.

Fig. 6. Surface temperature versus time.

6. Summary
Four phenomenological models for the surface radiative properties of a reacting sorbent particle are applied to a 2.5 mm radius particle of CaCO$_3$ subjected to 1 MW m$^{-2}$ solar irradiation. Comparing time to complete particle conversion and maximum surface temperature from simulations employing the four models, the largest change in time to complete conversion between models is less than 2%, and the largest change in maximum achieved surface temperature between models is 0.5%.

Model 1 predicts the highest effective surface radiative properties, while Model 4 predicts the lowest. EM models predict higher effective properties than ODM models, and non-absorbing models predict higher effective properties than absorbing models. Models 1 and 4 show the upper and lower bounds for surface radiative properties for the system considered. Pore size diameters can be in the range $\sim 0.01$ µm to 0.5 µm, and CaO grain diameters are $\sim 1$ µm, thus
depending on the wavelength band, the sorbent particle surface will exhibit both optically
discrete and effective medium behavior. Future work will include development of a spectral
mixed surface property model. Refractive index data, SEM imaging, and other surface evaluating
techniques should be used to support selection of the appropriate surface property model.