Heat transfer and fluid flow analysis of a 4 kW solar thermochemical reactor for ceria redox cycling

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HIGHLIGHTS

• Splitting of H₂O and CO₂ is performed using a solar thermochemical redox cycle.
• The solar reactor features a reticulated porous ceramic foam made of CeO₂.
• A heat/mass transfer model coupling Monte-Carlo ray tracing to CFD is developed.
• Experimental validation is accomplished with a 4-kW solar reactor prototype.
• The model is applied to identify irreversibilities and improve the reactor design.

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ABSTRACT

A solar reactor consisting of a cavity-receiver containing a reticulated porous ceramic (RPC) foam made of CeO₂ is considered for effecting the splitting of H₂O and CO₂ via a thermochemical redox cycle. A transient 3D heat and mass transfer model of the reduction step is formulated and solved using Monte-Carlo ray-tracing coupled to computational fluid dynamics. Experimental validation is accomplished in terms of measured temperatures and O₂ evolution rates obtained with a solar reactor prototype tested under high-flux radiative power inputs in the range 2.8–3.8 kW and mean solar concentration ratios up to 3024 suns. Critical temperatures of up to 2250 K induced CeO₂ sublimation, which in turn affected detrimentally the solar reactor performance. The model is applied to analyze an improved geometrical design with alternative flow configuration, enabling more uniform radiative absorption and temperature distributions, and resulting in a higher solar-to-fuel energy conversion efficiency.

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1. Introduction

Solar thermochemical cycles based on metal oxide redox reactions can split CO₂ and H₂O to produce a mixture of CO and H₂ (syngas), which can be further processed to liquid hydrocarbon fuels (Steinfeld, 2005; Perkins and Weimer, 2004; Smestad and Steinfeld, 2012; Miller et al., 2013). Non-stoichiometric cerium oxide has emerged as an attractive redox active material because of its relatively high oxygen solid-state conductivity, contributing to fast redox kinetics (Chueh et al., 2012) and because of its crystallographic stability over a wide range of oxidation states (Chueh and Haile, 2010; Zinkevich et al., 2006). The two-step H₂O/CO₂-splitting solar thermochemical cycle based on oxygen-deficient ceria is represented by

High-temperature reduction:

\[ \text{CeO}_2 + \Delta H \rightarrow \text{CeO}_2 - \delta + \frac{\delta}{2} \text{O}_2 \] (1)

Low-temperature oxidation with H₂O:

\[ \text{CeO}_2 - \delta + \delta \text{H}_2 \text{O} \rightarrow \text{CeO}_2 + \delta \text{H}_2 \] (2a)

Low-temperature oxidation with CO₂:

\[ \text{CeO}_2 - \delta + \delta \text{CO}_2 \rightarrow \text{CeO}_2 + \delta \text{CO} \] (2b)

In the first, high-temperature endothermic step, ceria is thermally reduced to a non-stoichiometric state using concentrated solar energy. In the subsequent, lower temperature exothermic step, ceria is re-oxidized with H₂O and/or CO₂ to produce H₂ and/or CO, respectively. Solar reactors for effecting this cycle include cavity-receivers with rotating or stationary structures, (Lapp et al., 2013;
2. Solar reactor configuration and experimental setup

The solar reactor configuration is shown schematically in Fig. 1(a). The engineering design has been presented previously in detail (Furler et al., 2012). The main features are briefly summarized here. The solar reactor consists of a cavity-receiver with a 4 cm dia. circular aperture for the access of concentrated solar radiation. The aperture was closed by a 24 cm dia., 3 mm thick clear fused quartz disk window mounted on a frustum. A compound parabolic concentrator (CPC) (Welford and Winston, 1989) was incorporated into the aperture to further boost the solar concentration ratio\(^1\) to mean values of up to 3024 suns. The cavity contained a cylinder of reticulated porous ceramic (RPC) foam made of pure ceria composed of four 20 mm-tick, 60 mm-i.d., 100 mm-o.d. rings, and a single 20 mm-thick, 100 mm-o.d. disk. The total mass of the CeO\(_2\) cylinder was 1413 g. The cavity was insulated by a 10 mm-thick layer of CeO\(_2\) laminate surrounded by Al\(_2\)O\(_3\)-SiO\(_2\) and sheathed by an outer shell made of Inconel 600. An annular gap between RPC and insulation induced uniform radial flow across the RPC cylinder. Temperatures were measured at the outer surface of the RPC (B-type thermocouples), in the middle of the Al\(_2\)O\(_3\)-SiO\(_2\) insulation, and at the outer Inconel wall (K-type thermocouples). Argon (99.999% purity) flow rates were regulated by electronic mass flow controllers (Bronkhorst F-201C) and injected through four radial inlet ports and one axial nozzle located at the frustum close to the quartz window. Gases exited the reactor through an axial outlet port at the rear plate. The gas composition was monitored at the outlet by gas chromatography (Varian 490), supplemented by a paramagnetic alternating pressure based O\(_2\) detector (Siemens Oxymat 6). Experimentation was performed at the ETH’s high flux solar simulator (HFSS): an array of seven Xe arc lamps, close-coupled to truncated ellipsoidal reflectors, provided an external source of intense thermal radiation (mostly in the visible and IR spectra) that closely approximated the heat transfer characteristics of highly concentrating solar systems, such as solar towers and dishes (Petrasch et al., 2007). The radiative flux distribution at the aperture plane was measured optically using a calibrated CCD camera focused on a water-cooled, Al\(_2\)O\(_3\)-plasma coated Lambertian (diffusely reflecting) target. The radiative power input through the aperture \(P_{\text{radiant}}\) was obtained by integration of the radiative flux and verified with measurements using a water-calorimeter.

A typical experimental run consisted of two consecutive stages: (1) the solar reactor was pre-heated for 30 min at a radiative power input \(P_{\text{radiant}} = 0.8\) kW; (2) the radiative power input was increased to 2.8, 3.4, or 3.8 kW to initiate thermal reduction. The corresponding mean solar concentration ratios over the aperture were 2228, 2706, and 3024. During both stages, the Ar flow rate was kept constant at 1.8 L min\(^{-1}\) (SLPM; mass flow rate calculated at 273.15 K and 101.325 Pa) through the side inlets (uniformly distributed over the four radial inlets) and 0.2 L min\(^{-1}\) through the reactor front.

3. Heat and mass transfer analysis

Fig. 1(b) shows a schematic representation of the individual computational domains (fluid, solid, and porous) of the model. The reactor cavity, reactor front, gas-gap, inlets, and outlet are modeled as fluid domains, assumed to be a non-participating media for radiation. Laminar flow conditions (Re<150 in all domains, (Seguin et al., 1998)) and ideal gas mixtures are assumed. The Al\(_2\)O\(_3\)-SiO\(_2\) insulation, ceria laminate, and the Inconel reactor shell are modeled as solid domains. The reactive ceria RPC is modeled as a homogeneous and radiative participating two-phase porous domain.

Governing equations — The continuity, species conservation, momentum, and energy conservation equations in the fluid domains are given respectively by

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0
\]  

(3)

\[
\frac{\partial (\rho Y_1)}{\partial t} + \nabla \cdot (\rho Y_1 \mathbf{U}) = 0
\]  

(4)

\[
\frac{\partial (\rho Y_2)}{\partial t} + \nabla \cdot (\rho Y_2 \mathbf{U}) = -\nabla p + \nabla \cdot \left( \nabla \mathbf{U} + \frac{2}{3} \nabla (\nabla \cdot \mathbf{U}) \right) + \mathbf{S}_{\text{M buoy}}
\]  

(5)

\[
\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho h \mathbf{U}) = \nabla \cdot (\mathbf{K} \nabla T)
\]  

(6)

where \(\rho\) is the density, \(\mathbf{U}\) is the velocity vector, \(Y_i\) the concentration of \(O_2\) in the gas mixture, \(\mu\) is the dynamic viscosity, \(\mathbf{K}\) is the identity matrix, \(\mathbf{S}_{\text{M buoy}}\) is an external momentum source accounting for buoyancy, \(h\) is the enthalpy, and, \(k\) is the thermal conductivity of the gas mixture. Gas diffusion is neglected in Eqs. (4) and (6) because \(R_e > 1\), thus advective mass transport is dominant compared to mass diffusion. Gas flows are modeled as Ar–O\(_2\) mixtures of variable composition, determined by solving Eq. (4). Kinetic energy and viscous dissipation are neglected in Eq. (6) because \(U<1\) m s\(^{-1}\) and \(Br<1\).

Due to the absence of flows, the energy conservation equation in the solid domains is simplified to

\[
\frac{\partial (\rho h)}{\partial t} = \nabla \cdot (\mathbf{K} \nabla T)
\]  

(7)

The governing equations for the fluid phase of the RPC porous domain are as follows:

\[
\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho \mathbf{K} \cdot \mathbf{U}) = S_{C O_2}
\]  

(8)

\[
\frac{\partial (\rho Y_1)}{\partial t} + \nabla \cdot (\rho Y_1 \mathbf{U}) = S_{C O_2}
\]  

(9)

\[
\frac{\partial (\rho h \mathbf{U})}{\partial t} + \nabla \cdot (\rho h \mathbf{U} \cdot \mathbf{U}) = -\nabla p + \nabla \cdot \left( \mu \mathbf{K} \mathbf{U} + \frac{2}{3} \nabla (\nabla \cdot \mathbf{U}) \right) + \mathbf{S}_{\text{M buoy}} + \mathbf{S}_{\text{M porous}}
\]  

(10)

\(^1\) The solar concentration ratio, \(C\), is defined as solar radiative power intercepted by the aperture. \(C\) is expressed in units of “suns” when normalized to 1 kW m\(^{-2}\).
\[
\frac{\partial (\varepsilon \rho h)}{\partial t} + \nabla \cdot (\overline{\kappa} \cdot T) = \nabla \cdot (kVT) + S_{\text{E, solar}} + \dot{V}_q + \dot{Q}_{\text{fs}}
\]  

(11)

where \( \varepsilon \) is the volume porosity, \( \overline{\kappa} \) is the isotropic porosity tensor, \( S_{\text{E, O}_2} \) the \( \text{O}_2 \) mass source accounting for oxygen evolution during thermal reduction, \( S_{\text{fl, porous}} \) a momentum source accounting for viscous losses and inertial drag forces imposed by the porous structure on the fluid according to the Düupit–Forchheimer law, \( S_{\text{fl}} \) accounts for incoming absorbed solar radiation from the HiSS, and \( \dot{V}_q \) is the radiative source term accounting for radiation exchange. The energy conservation equations of fluid and solid are coupled via the source term \( \dot{Q}_{\text{fs}} = h_{b} \cdot A_{\text{b}}(T_{\text{c}} - T_{\text{fl}}) \), where \( h_{b} \) is the interphasic heat transfer coefficient, \( A_{\text{b}} \) is the fluid–solid area density, and \( T_{\text{c}} \) and \( T_{\text{fl}} \) are the temperatures of the solid and fluid, respectively. Thermal equilibrium between both phases \((T_c = T_{\text{fl}})\) is enforced by setting \( h_{b} \) artificially high \((10,000 \text{ W m}^{-1} \text{ K}^{-1})\), which is reasonable in this case, as \( P_{\text{em}} < 1 \), thus thermal diffusion is dominant over advection.

The governing equation for the solid phase of the RPC porous domain is:

\[
\frac{\partial (1 - \varepsilon) \rho h}{\partial t} = \nabla \cdot (\overline{\kappa} \cdot \overline{\kappa} \cdot \overline{\nabla} T) + S_{\text{E, reaction}} + \dot{Q}_{\text{sf}}
\]  

(12)

where \( S_{\text{E, reaction}} \) is the energy sink accounting for the endothermicity of the CeO\(_2\) reduction reaction.

The RPC is modeled as participating media. The radiative transfer equation for an isotropic, gray, absorbing-emitting-scattering participating media is given by

\[
dl(T, \mathbf{s}) = -\beta I(T, \mathbf{s}) + \sigma \int I(\tau, \mathbf{s}')d\omega'
\]  

(13)

where \( \tau \) is the position vector, \( \mathbf{s} \) is the direction vector, \( s \) is the path length, \( \beta, \sigma \) and \( \alpha \) are the extinction, absorption, and scattering coefficients, respectively, \( I \) is the radiation intensity depending on position \( r \) and direction \( s \), \( h_b \) is the blackbody radiation intensity depending on the local temperature \( T \), and \( \omega \) is the solid angle. The radiation source term in Eq. (11) is given by

\[
\dot{V}_q = \alpha \left( 4\pi h_b - \int_{4\pi} I d\omega' \right)
\]  

(14)

Material properties—Material properties are listed in Table 1. Heat capacities \( (c_p) \) of CeO\(_2\) and Al\(_2\)O\(_3\)-SiO\(_2\) insulation have been measured by differential scanning calorimetry (DSC) using a Netsch DSC 404 C Pegasus in the temperature range 470–1100 K and 470–1400 K, respectively. The thermal conductivity \( (k) \) of CeO\(_2\) laminate was measured in the temperature range of 300–973 K by laser flash analysis using a Netsch Laserflash-analysier LFA 457. The thermal conductivity of the Al\(_2\)O\(_3\)-SiO\(_2\) insulation was taken from the manufacturer (Zircar Zirconia, Inc., 2014). The effective heat and mass transfer properties of the RPC structure have been determined by direct numerical pore-level simulation on the exact RPC geometry obtained by computer tomography (Suter et al., 2014; Haussener et al., 2010; Petrasch et al., 2008). The effective extinction coefficient of the RPC was determined by pore-level MC on its 3-D tomographic scans (Suter et al., 2014; Haussener et al., 2010). The scattering and absorption coefficients were calculated from \( \sigma = \rho_s \cdot \beta \) and \( \alpha = (1 - \rho_s) \cdot \beta \), where \( \rho_s \) is the surface total reflectance weighted by the Planck blackbody spectral emission in a temperature range 300–2500 K. \( \rho_s \) of partially reduced ceria at \( \delta = 0.035 \) was measured with an integrating sphere using a monochromatic collimated beam of light emitted by a Xe-arc in a spectral range 300–1600 nm under three different incident angles (8°, 40°, and 60°). The thermal conductivity of CeO\(_2\), the optical properties of the Al\(_2\)O\(_3\)-SiO\(_2\) insulation, polished aluminum frustum and CPC were taken from the literature (Touloukian and Dewitt, 1972; Touloukian, 1967; Siegel and Howell, 2002). The quartz window is modeled as a partially transparent thin disc with \( \varepsilon_{\text{g}} = 0.94 \) and \( \rho_s = 0.06 \).

Boundary conditions and source terms—The boundary conditions and source terms are schematically indicated in Fig. 1(b). The radiative power input delivered by the HiSS and absorbed within the cavity-receiver was determined by MC ray tracing, yielding the energy sources \( S_{\text{E, solar}} \) to the CFD code. At the outer reactor shell, natural convective heat transfer was modeled using Nusselt correlations for vertical flat surfaces (Churchill and Chu, 1975) and for horizontal cylinders (Churchill and Chu, 1975). The water-cooled CPC and frustum were assumed to be at 293 K. 0.45 L min\(^{-1}\) of \text{Ar} containing an \text{O}_2 mass fraction of \( 1 \times 10^{-5} \) was injected at \( T = 293 \) K normally to the inlet surface through each of the four radial inlet ports. 0.2 L min\(^{-1}\) of Ar flow with \( P_{\text{O}_2} = 1 \times 10^{-5} \text{ atm} \) was injected at \( T = 293 \) K axially and uniformly distributed over the window surface. A the outlet, \( P_{\text{relative}} = 0 \) Pa. The reduction of nonstoichiometric ceria was modeled based on thermodynamic equilibrium, as previous work has shown that the overall kinetics were controlled by heat transfer (Furler et al., 2012). Experimental data by Panlener et al. (1975) was fitted according to the procedure described by Schewe and Steinfeld (2012) and Ermanoski et al. (2013) yielding the following expressions of nonstoichiometry \( \delta \) and reaction enthalpy \( \Delta H \) as a function of temperature and \( P_{\text{O}_2} \):

\[
\log(\delta) = a_1 + a_2 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2}) + a_3 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^2 + a_4 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^{1.5} + a_5 \cdot T + a_6 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2}) + a_7 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^2 + a_8 \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^{1.5} + a_9 \cdot T + a_{10} \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^{2.5} + a_{11} \cdot T + a_{12} \cdot \log(P_{\text{O}_2}/P_{\text{O}_2})^{3.0}
\]  

(15)

\[
\Delta H = b_1 + b_2 \cdot \delta^{0.5}
\]  

(16)

The fitting parameters are listed in Table 2.
HFSS: (a) measured with a calibrated CCD camera on a Lambertian target; (b) simulated by MC, and (c) measured and simulated along the vertical and horizontal axes. The mean relative difference between the measured and simulated values over the aperture size was 2.9%.

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂ RPC</td>
<td>Density (kg m⁻³)</td>
<td>7220</td>
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</tr>
<tr>
<td></td>
<td>Porosity (%)</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total CeO₂ mass [g]</td>
<td>1413</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permeability (m²)</td>
<td>4.63376×10⁻⁸</td>
<td></td>
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<tr>
<td></td>
<td>Disrupt-Forchheimer coefficient (m⁻¹)</td>
<td>1616.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity solid (W m⁻³ K⁻¹)</td>
<td>(17.8004–0.02402×T+0.0000112032×T²–1.7×10⁻⁸×T³)</td>
<td>280–2000K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7.9799+0.00483184×T–9.3197×10⁻⁸×T²+2.8×10⁻⁸×T³)</td>
<td>Suter et al., 2014; Touloukian, 1967</td>
</tr>
<tr>
<td></td>
<td>Specific extinction coefficient (J kg⁻¹ K⁻¹)</td>
<td>–0.0001271×T²+0.2697656×T+299.8695684</td>
<td>280–1100K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>444.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exinction coefficient (m⁻¹)</td>
<td>497.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>497.8</td>
<td>Suter et al., 2014</td>
</tr>
<tr>
<td></td>
<td>Surface reflectance (at λ=0.035)</td>
<td>–3×10⁻³×T+0.2866</td>
<td>300–2500</td>
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<td></td>
<td>Absorption coefficient CeO₂₅₅⁵ (m⁻¹)</td>
<td>(1–(–0.00006×T+0.411))×497.8</td>
<td>300–2500</td>
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<td></td>
<td>Scattering coefficient CeO₂₅₅⁵ (m⁻¹)</td>
<td>(–0.00006×T+0.411)×497.8</td>
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<td>Fluid–solid heat transfer coefficient (W m⁻² K⁻¹)</td>
<td>10000</td>
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<td>Fluid–solid area density (m⁻¹)</td>
<td>952</td>
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<tr>
<td>Al₂O₃–SiO₂ insulation</td>
<td>Density (kg m⁻³)</td>
<td>560.65</td>
<td>Zircar Zirconia, 2014</td>
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<td></td>
<td>Specific heat capacity (J kg⁻¹ K⁻¹)</td>
<td>4×10⁻⁷×T²–1.1797×10⁻³×T²+1.5987289×T+477.6995948</td>
<td>≤1480K</td>
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<td></td>
<td></td>
<td>1118.44</td>
<td>&gt;1480K</td>
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<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>0.00012926×T+0.019654</td>
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<td></td>
<td>Hemispherical total emittance</td>
<td>0.28</td>
<td>Zircar Zirconia, Inc., 2014</td>
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<td>CeO₂ laminate</td>
<td>Density (kg m⁻³)</td>
<td>504.4</td>
<td>Touloukian and Dewitt, 1972</td>
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<td></td>
<td>Specific heat capacity (J kg⁻¹ K⁻¹)</td>
<td>–0.0001271×T²+0.2697656×T+299.8695684</td>
<td>280–1100K</td>
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<td>444.27</td>
<td>&gt;1100K</td>
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<tr>
<td></td>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>2.2×10⁻⁷×T²+2.8387×10⁻⁴×T+0.1767688</td>
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<td></td>
<td>Hemispherical total emittance</td>
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<td>Inconel 600</td>
<td>Density (kg m⁻³)</td>
<td>8470</td>
<td>Special Metal Corporation, 2014</td>
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<td></td>
<td>Specific heat capacity (J kg⁻¹ K⁻¹)</td>
<td>0.2827×T+327.29</td>
<td>123–1173</td>
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<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>0.0158×T+10.169</td>
<td>123–1073</td>
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<tr>
<td>Argon</td>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>2.35332617×10⁻¹³×T⁰–1.289997670118×10⁻⁸×T³+4.83701613785442×10⁻⁵×T</td>
<td>290–2400</td>
</tr>
<tr>
<td></td>
<td>Dynamic viscosity (kg m⁻¹ s⁻¹)</td>
<td>3.51928×10⁻¹⁵×T²–2.0456156372×10⁻¹¹×T⁰+6.8496118733571×10⁻⁸×T+4.20667800364964×10⁻⁶</td>
<td>290–2400</td>
</tr>
</tbody>
</table>

Numerical Solution—The MC simulations were performed using the in-house code VEGAS (Petrasch, 2010) with 10¹⁰ rays. The CFD simulations were performed with ANSYS CFX 14.0. The discrete transfer radiation model was applied to solve Eq. (13), (Lockwood and Shah, 1981; Ansys Inc., 2012) which was transformed into a set of transport equations for I and solved for discrete solid angles along s. The governing equations are discretized both in space (284,411–3,277,176 tetrahedras) and time (time step=2 s) and solved on the individual control volumes by the finite-volume method with a first order upwind and second order backward Euler scheme. Simulations were performed on the central high-performance cluster Brutus of ETH Zurich.

4. Experimental validation

The MC simulation of the HFSS was experimentally validated with measurements of the radiative flux distribution at the focal plane. Fig. 2 shows the radiative flux distribution for all seven Xe-arcs of the HFSS: (a) measured with a calibrated CCD camera on a Lambertian target; (b) simulated by MC, and (c) measured and simulated along the vertical and horizontal axes. The mean relative difference between the measured and simulated values over the aperture size was 2.9% with a standard deviation of 0.045 MW m⁻². Deviations are attributed to non-ideal ellipsoidal geometry and misalignment.

Experimental validation of the solar reactor model was accomplished by comparing its numerical outputs to experimental data obtained with the prototype solar reactor tested at the HFSS for a set of three experimental runs with P_solar=2.8, 3.4, and 3.8 kW. A summary of the operating conditions is presented in Table 3 (Furler et al., 2012). Fig. 3(a)–(c) shows the experimental data (dashed curves) and numerically calculated (solid curves) temperatures at locations T_B1, T_B2, T_K1, T_K2, and T_K3 (positions indicated in Fig. 4) as a function of time for three runs with P_solar=2.8, 3.4, and 3.8 kW. Also shown are the measured (dashed curves) and simulated (solid curve) O₂ evolution curves at the outlet of the reactor as a function of time. The temperature of the ceria RPC rose rapidly with increasing P_solar, from the initial 1015 K (average of T_B1 and T_B2) after pre-heating at 0.8 kW to 1800 K at 2.8 kW, 1855 K at 3.4 kW, and 1899 K at 3.8 kW. Additionally,
as $P_{solar}$ increased from 2.8 to 3.8 kW, both the peak and average heating rates increased from $127$ K min$^{-1}$/36 K min$^{-1}$ to $163$ K min$^{-1}$/56 K min$^{-1}$. As expected, higher heating rates and temperatures lead to higher $O_2$ peak rates and higher total $O_2$ evolution. This trend is captured by the reactor model which predicts a peak temperature (average of $T_{fl,1}$ and $T_{fl,2}$) and a total $O_2$ evolution of $1793$ K and $1.33$ ml g$^{-1}$ CeO$_2$ for $2.8$ kW, $1837$ K and $1.73$ ml g$^{-1}$ CeO$_2$ for $3.4$ kW, and $1869$ K And $1.93$ ml g$^{-1}$ CeO$_2$ for $3.8$ kW, respectively. The temperature agreement between simulation and experiment is reasonably good at all locations for the experimental runs.

Discrepancies are attributed to uncertainties in the positioning of the thermocouples and to the extrapolation of measured material properties to higher temperatures, such as the case for $k$ of CeO$_2$ laminate and Al$_2$O$_3$–SiO$_2$ insulation. Good matching is also obtained between measured and simulated $O_2$ evolution rates, especially in the cases of $2.8$ kW and $3.4$ kW, considering the uncertainties with thermodynamic data at above $1773$ K.

The solar-to-fuel energy conversion efficiency is defined as follows:

$$\eta_{solar\rightarrow fuel} = \frac{\Delta H_{fuel} \int r_{fuel} dt}{\int P_{solar} dt + \int \dot{E}_{inert} dt}$$

(17)

where $r_{fuel}$ is the molar rate of fuel production, $\Delta H_{fuel}$ is the heating value of the fuel, $P_{solar}$ is the solar radiative power input, $r_{inert}$ is the flow rate of the inert gas, and $\dot{E}_{inert}$ is the energy required to separate the inert gas (assumed 20 kJ mol$^{-1}$ inert gas) (Haering 2008).

Assuming stoichiometric fuel production ($r_{fuel}=2r_{O_2}$) according to Eq. (2b) and accounting for $15$ min of pre-heating, the experimentally determined values of efficiency were: $\eta_{solar\rightarrow fuel} = 1.16\%$, $1.42\%$, and $1.73\%$ for $2.8$ kW, $3.4$ kW, and $3.8$ kW, respectively. These are slightly higher than the numerically simulated values: $\eta_{solar\rightarrow fuel} = 1.06\%$, $1.39\%$, and $1.55\%$ for $2.8$ kW, $3.4$ kW, and $3.8$ kW, respectively, attributed to the slight under-prediction of the total $O_2$ yield. Note that the sensible heat of solids and gases was not recovered during the experimental runs.

5. Modelling results and discussion

Incoming thermal radiation—Fig. 5 shows the radiative flux distribution at $P_{solar}=3.8$ kW that is: (a) impinging on the exposed ceria RPC surface; (b) absorbed on the exposed top Al$_2$O$_3$–SiO$_2$ insulation; and (c) absorbed on the water-cooled cooper-ring (part of reactor front), as determined by MC. Both axial and radial non-uniformity is observed. The front parts of the RPC and the Al$_2$O$_3$–SiO$_2$ insulation are more strongly irradiated than locations towards the rear end because of the large rim angle of the HFSS ($>45^\circ$) combined with the optical design of the CPC (outlet angle $=90^\circ$) which directs the incoming radiation mostly onto areas close to the reactor front. This resulted in an average radiative flux of $122$ kW m$^{-2}$ on the RPC side walls and $250$ kW m$^{-2}$ on the RPC back plate compared to peak $690$ kW m$^{-2}$ at locations close to the reactor front. The radial non-uniformity in flux distribution is attributed to partial misalignment of the Xe-arcs. In total, $2.3$ kW of radiative power ($60.5\%$ of $P_{solar}$) is volumetrically absorbed within the RPC structure.

The Al$_2$O$_3$–SiO$_2$ insulation receives an average and peak radiative flux of $210$ and $393$ kW m$^{-2}$, respectively, resulting in
0.93 kW (24.5% of $P_{\text{solar}}$) absorbed radiative power. The water-cooled copper ring which is placed directly after the CPC absorbs 0.19 kW (5% of $P_{\text{solar}}$).

Temperature distribution and flow analysis—Fig. 6(a) shows the temperature distribution and normalized velocity vectors of the flow field in the vertical cross-section of the solar reactor after 30 min pre-heating with $P_{\text{solar}}=0.8$ kW and 16 min reduction with $P_{\text{solar}}=3.8$ kW. The $O_2$ concentration at peak $O_2$ evolution is depicted in Fig. 6(b). As expected, locations exposed to high radiative fluxes exhibit higher temperatures. The model predicts a peak and average ceria temperature of 2258 K and 1915 K, respectively. The highest temperature is achieved close to the reactor front where the RPC is exposed to a radiative flux exceeding 650 kW m$^{-2}$. Such high temperatures are undesired as it causes ceria sublimation and mechanical failure of the RPC structure, as experimentally observed (Furler et al., 2012; Furler et al., 2012). Due to the very high ceria temperatures, the $O_2$ concentration reaches a peak value of 17% at these locations. The temperature difference across the RPC is 145 K on average. For the $Al_2O_3$–$SiO_2$ insulation, the model predicts temperatures above 2200 K at certain locations close to the aperture, which exceeds the melting temperature (2143 K) as experimentally verified. The contact surface of the $Al_2O_3$–$SiO_2$ and $CeO_2$ laminate is maintained below 1700 K to prevent undesired side reactions (Mizuno et al., 1975). The mean gas temperature in the cavity and at the outlet are 1798 K and 1767 K, respectively. In the reactor front, the mean gas temperature is only 488 K due to the injected flows
at $T = 293$ K and the water-cooled surfaces. Free convection is dominating the flow pattern, causing internal circulations and forcing the radially incoming gases to flow into the reactor front. This situation has a detrimental effect on $\eta_{\text{solar}} = \text{C}_0 / \text{C}_0$ because O$_2$ is not efficiently purged from the reactor, limiting the ceria reduction according to Eq. (1). Furthermore, ceria vapor derived by sublimation of the overheated RPC is carried out by the gas flow and condenses on the water-cooled specular CPC, lowering its reflectivity and consequently the radiative power input through the aperture by up to 15%, as experimentally observed (Furler et al., 2012).

These gas circulations can be avoided by increasing the purge gas flow and reversing the flow direction. Fig. 7 shows a contour plot of the velocity and normalized velocity vectors of the flow field in the vertical cross section for $P_{\text{solar}} = 2.8$ kW and an Ar flow rate of 12.5 L min$^{-1}$ provided tangentially through 6 nozzles around the window circumference. The flow direction is reversed by operating the radial openings as additional outlets instead of inlets. For simplicity, the reduction chemistry is omitted. The tangential injection of Ar causes a swirl flow pattern preventing back flow of gases from the cavity into the reactor front, thus depositions of sublimated CeO$_2$ at the CPC surface. In contrast, providing the Ar flow radially or axially did not prevent the back flow of gases below Ar flow rates of 15 L min$^{-1}$.

Energy Flows—Fig. 8 shows the instantaneous energy balance as a function of time for the reduction stage performed with $P_{\text{solar}} = 3.8$ kW. Indicated is the heat consumed by the endothermic reaction, the sensible heat content of reactor components, and the heat losses by conduction, convection, and radiation (reflected and re-emitted). Heating of the reactor components (reactor shell, Al$_2$O$_3$–SiO$_2$ insulation, CeO$_2$ laminate, CeO$_2$ RPC) consumed 31% of $P_{\text{solar}}$ on average, but account for 17% of $P_{\text{solar}}$ at the end of reduction ($t = 46$ min). Conductive losses to the water-cooled front and through the insulated walls were significant and accounted for 16% of $P_{\text{solar}}$ on average, but account for 17% of $P_{\text{solar}}$ at the end of reduction ($t = 46$ min). Radiative losses, the dominant source of irreversibility, increased considerably with reduction time due to the increasing cavity temperature and accounted for 48% of $P_{\text{solar}}$ on average and 57% of $P_{\text{solar}}$ peak. Sensible heat loss by the out-flowing gas (Ar/O$_2$ mixture) and convection losses at the window and water-cooled surfaces were less significant and amounted to 1% each. The remaining fraction of energy, about

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**Fig. 6.** (a) Normalized velocity vectors and temperature distribution in the vertical cross-section after 30 min pre-heating with $P_{\text{solar}} = 0.8$ kW and 16 min reduction with $P_{\text{solar}} = 3.8$ kW and (b) Normalized velocity vectors and O$_2$-concentration in the vertical cross-section of the cavity-receiver at peak O$_2$-evolution ($t = 38$ min) at $P_{\text{solar}} = 3.8$ kW.
2.9% of $P_{solar}$ was consumed by the endothermic reduction of CeO$_2$.

There is room for optimization of the aperture’s size to maximize the absorption of $P_{solar}$ and minimize re-radiation losses (Steinfeld and Schubnell, 1993). The cavity's ability to capture $P_{solar}$ is given by the apparent absorptivity, $\alpha_{apparent}$, defined as the fraction of radiative flux across the aperture that is absorbed by the cavity walls. $\alpha_{apparent}$, determined by MC, is only 0.85 because of 10% reflection losses escaping through the aperture and 5% absorption losses on water-cooled surfaces inside the cavity. Selective coatings for quartz windows with high transmissivity can be reduced by using thermal insulation materials with lower specific heat capacities. Further, minimizing $\Delta T$ between the reduction and oxidation steps of the cyclic process can eliminate this energy penalty. Conduction losses can be obviously reduced by improving the insulation and by avoiding the heat bridges created by water-cooled surfaces, but the Al-made CPC and frustum require active cooling because of the exposure to radiative fluxes exceeding 2000 W/m$^2$. Alternative cooling fluids (e.g., oil) should be assessed to minimize $\Delta T$ between the hot cavity and actively cooled reactor front. Operation under vacuum pressures could further reduce heat losses to the surroundings, reduce usage of purge gas, and achieve lower O$_2$ partial pressures (Ermanoski et al., 2013). The radiative properties of the ceria RPC, especially the optical thickness, can be optimized for efficient radiative penetration and absorption by adjusting the pore size and porosity (Suter et al., 2014).

To increase $\eta_{solar-fuel}$, an alternative solar reactor design depicted in Fig. 9 is proposed. The cavity has a conical shape to enable a more uniform distribution of absorbed incoming radiation and to avoid hot spots. A $\theta_i-\theta_o$ secondary concentrator (Rabl and Winston, 1976) with acceptance angle $\theta_i=45^\circ$ and exit angle $\theta_o=60^\circ$ is incorporated to reduce the aperture diameter to 3.5 cm, boost the solar concentration ratio, and prevent direct high-flux irradiation of the insulation close to the aperture. This element is actively cooled but maintained at $T=573$ K to lower conduction losses. The ceria mass loading is increased to 2500 g to enhance the solar concentration ratio, and prevent direct high-flux irradiation of the insulation close to the aperture. This element is actively cooled but maintained at $T=573$ K to lower conduction losses.

Fig. 11 shows the temperature distribution (a) and the O$_2$ concentration (b) along with the normalized velocity vectors of the flow field in the vertical cross-section of the solar reactor at the end of the reduction step ($t=40$ min) and at peak O$_2$ evolution ($t=20$ min) performed at $P_{solar}=2.0$ kW, respectively. The conical cavity design coupled to the $\theta_i-\theta_o$ secondary concentrator results in...
a more homogeneous temperature distribution within the RPC, on average 52 K across the structure, and prevents hot spots and melting of the $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ insulation. The tangential injection of purge gas close to the window circumference at flow rates $\dot{V}_{\text{min}}/C_0$ induces a swirl flow which prevents backflow of gases into the reactor front and thereby $\text{CeO}_2$ depositions on the secondary concentrator, consistent with the results of Fig. 7.

Furthermore, it also hinders $\text{O}_2$ from circulating into the reactor front which enhances purging. This can be seen in Fig. 11(b) which shows a clear difference in $\text{O}_2$ concentration between the reactor front and the reactor cavity. Assuming stoichiometric oxidation with $\text{CO}_2$ ($r_{\text{CO}_2}=2r_{\text{O}_2}$), the new solar reactor design reaches $\eta_\text{solar-to-fuel}=5.4\%$ (without heat recovery).

The superior performance compared to the cylindrical cavity is attributed to lower radiation and conduction losses (on average 57% lower), to a more uniform temperature distribution within the reactor cavity (av. $\Delta T_{\text{cross RPC}}$ cylindrical reactor $=145$ K, conical reactor $=52$ K), to more effective purging of $\text{O}_2$ from the cavity by the Ar flow (av. $\dot{V}_{\text{O}_2}$ at peak $\text{O}_2$-evolution: cylindrical reactor $=0.0999$ atm, conical reactor $=0.0185$ atm), and to a higher mass loading of ceria ($m_{\text{cylindrical}}=1413$ g, $m_{\text{conical}}=2500$ g). Further increase of $\eta_\text{solar-to-fuel}$ to 6.4% is feasible by recovering the sensible heat of gases and solids during the temperature swing between reduction and oxidation steps.

6. Summary and conclusions

We have presented a dynamic numerical model of a high-temperature solar reactor that couples Monte-Carlo ray-tracing to computational fluid dynamics. Experimental validation of the model was accomplished by comparing temperatures and $\text{O}_2$ evolution rates at the reactor outlets for a redox cycles with $P_{\text{solar}}=2\text{ kW}$ during reduction and $P_{\text{solar}}=0\text{ kW}$ during oxidation.

![Fig. 9. Schematic of the conical solar reactor configuration.](image-url)

![Fig. 10. Numerically calculated average temperatures of the ceria RPC, $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ insulation, and reactor shell and (bottom) numerically calculated $\text{O}_2$ evolution rate at the reactor outlets for a redox cycles with $P_{\text{solar}}=2\text{ kW}$ during reduction and $P_{\text{solar}}=0\text{ kW}$ during oxidation.](image-url)

![Fig. 11. (a) Normalized velocity vectors and temperature distribution in the vertical cross-section of the cavity-receiver at the end of the reduction step ($t=40$ min) performed with $P_{\text{solar}}=2.0$ kW and (b) normalized velocity vectors and $\text{O}_2$-concentration in the vertical cross-section at peak $\text{O}_2$-evolution ($t=20$ min).](image-url)
of absorbed incoming radiation and reached peak values of 2250 K at highly exposed regions close to the aperture. Such high temperatures induce ceria sublimation and cause local melting of the Al2O3–SiO2 insulation. Further complication arose from the buoyancy-driven natural convection flow carrying CeO2 (g) towards the actively-cooled reactor front where it eventually condensed, thereby reducing the CPC’s surface reflectance and consequently the radiative power input through the aperture. Increasing the purge gas flow rate and reversing the flow direction by providing the gas tangentially through 6 nozzles close to the window circumference is found to prevent the backflow of gas to the reactor front. An alternative reactor design featuring a conical cavity shape coupled to θi − θ0, secondary concentrator enabled a more uniform distribution of absorbed incoming radiation and prevented hot spots on the insulation. Lower radiation/conduction losses, higher ceria mass loading, and effective purging of evolved O2 resulted in ηsolar-to-fuel of 5.4% (without heat recovery). Further increase of ηsolar-to-fuel to 6.4% is feasible by recovering the sensible heat of gases and solids during the temperature swing between reduction and oxidation steps. Other improvements include the use of selective coatings for quartz windows, RPC with optimized pore size and porosity, and operation under pressure-swing isothermal conditions.

### Nomenclature

#### Symbols

- \( A_{fl} \): fluid–solid area density (m⁻¹)
- \( a_i \): fitting parameter
- \( b_i \): fitting parameter
- \( C \): solar concentration ratio
- \( c_p \): heat capacity (J mol⁻¹ K⁻¹)
- \( E_{	ext{inert}} \): energy for inert gas separation from the air (J mol⁻¹)
- \( h \): enthalpy (J kg⁻¹)
- \( \dot{h} \): convective heat transfer coefficient (W m⁻² K⁻¹)
- \( \Delta H_{	ext{fuel}} \): interphaseal heat transfer coefficient (W m⁻² K⁻¹)
- \( \Delta H \): reaction enthalpy (J mol⁻¹)
- \( I \): radiation intensity (W m⁻²)
- \( l_b \): blackbody radiation emission intensity (W m⁻²)
- \( f \): identity matrix
- \( \rho \): density (kg m⁻³)
- \( \rho_s \): surface total reflectance
- \( \tau_s \): transmittance
- \( \omega \): solid angle (deg)

#### Greek symbols

- \( \alpha \): absorption coefficient (m⁻¹)
- \( \alpha_{\text{apparent}} \): apparent cavity absorptance
- \( \beta \): extinction coefficient (m⁻¹)
- \( \sigma \): scattering coefficient (m⁻¹)
- \( \delta \): nonstoichiometry
- \( \varepsilon \): porosity
- \( \varepsilon_s \): surface emittance
- \( \mu \): dynamic viscosity (kg m⁻¹ s⁻¹)
- \( \rho \): density (kg m⁻³)
- \( \rho_s \): surface total reflectance

#### Dimensionless Groups

- \( Br \): Birkman number
- \( Pe \): Péclet number
- \( Pe_{\text{mass}} \): Péclet number for mass transport
- \( Pe_{\text{th}} \): Péclet number for heat transfer
- \( Re \): Reynolds number

#### Abbreviations

- CCD: charge-coupled device
- CFD: computational fluid dynamics
- CPC: compound parabolic concentrator
- ETH: Swiss Federal Institute of Technology
- GC: gas chromatography
- HFSS: High-Flux Solar Simulator
- MC: Monte-Carlo method
- RPC: reticulated porous ceramic
- SLPM: standard liters per minute at 273.15 K and 1 atm

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### References


