Transient heat and mass transfer analysis in a porous ceria structure of a novel solar redox reactor

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Abstract

Thermal transport processes are numerically analyzed for a porous ceria structure undergoing reduction in a novel redox reactor for solar thermochemical fuel production. The cylindrical reactor cavity is formed by an array of annular reactive elements comprising the porous ceria monolith integrated with gas inlet and outlet channels. Two configurations are considered, with the reactor cavity consisting of 10 and 20 reactive elements, respectively. Temperature dependent boundary heat fluxes are obtained on the irradiated cavity wall by solving for the surface radiative exchange using the net radiation method coupled to the heat and mass transfer model of the reactive element. Predicted oxygen production rates are in the range 40–60 $\mu\text{mol s}^{-1}$ for the geometries considered. After an initial rise, the average temperature of the reactive element levels off at 1660 and 1680 K for the two geometries, respectively. For the chosen reduction reaction rate model, oxygen release continues after the temperature has leveled off which indicates that the oxygen release reaction is limited by chemical kinetics and/or mass transfer rather than by the heating rate. For a fixed total mass of ceria, the peak oxygen release rate is doubled for the cavity with 20 reactive elements due to lower local oxygen partial pressure.

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1 Introduction

Two-step solar thermochemical metal oxide redox cycles have been identified as promising pathways for solar fuel production [1,2]. The oxidation of a partially or fully reduced metal oxide is utilized to split water and CO₂ into syngas, a mixture of H₂ and CO, according to:
endothermic reduction step:

exothermic fuel production step:

or

where M stands for a metal, δ_{red} and δ_{ox} are the oxygen non-stoichiometries of the metal oxide at the end of the reduction and oxidation steps, respectively, and $\Delta\delta = \delta_{\text{red}} - \delta_{\text{ox}}$ is the change in oxygen non-stoichiometry during the cycle. The net effect is the splitting of H₂O and CO₂:

or

Several metal oxides have been proposed to realize the cycle (1)–(2), including ferrites [3–5], zinc oxide [6–11], ceria [12–16], and mixed metal oxides [17–20]. Above 1273 K, ceria can reach substantial oxygen non-stoichiometries of up to $\delta = 0.25$ completely within the fluorite crystal structure, without melting or phase change [14,21]. In addition, ceria has shown the potential of maintaining open architectures even after repeated heating to approx. 1773 K [22], which allows for the employment of highly porous reactive ceria structures in high-temperature solar reactors. Conducting the process steps (1) and (2) at different temperatures is thermodynamically favorable [23], but introduces irreversibilities due to the periodic heating and cooling of the ceria [24]. While isothermal operation of the cycle avoids these heat losses, it requires different oxygen partial pressures for the two steps to drive fuel production. This constraint necessitates high sweep gas flow rates or low total pressure in the reaction chamber [25–28] to achieve high process efficiency.

Numerous reactor designs have been proposed with a porous morphology for the solid reactive material to split H_2O and CO_2 in a single reactor. Cylindrical porous ceria structures of different morphologies (porous monolith, reticulate porous ceramic, felt) are used in the reactors presented in [22,29–31], with gases flowing radially through the porous material. The reactor tested at Sandia National Laboratories uses counter-rotating disks which serve as a support of the reactive material (ferrite or ceria) and as solid–solid heat regenerators [32]. A similar reactor concept, developed at the University of Minnesota, uses two concentric counter-rotating cylinders, with the outer cylinder consisting of porous ceria, while the inner cylinder is non-porous and inert and serves as the heat regenerator [33,34]. A particle-based reactor consisting of two separate reaction chambers for reduction and fuel production has been presented by Ermanoski et al. [26].

Numerical heat and mass transfer models of solar thermochemical systems are developed to aid reactor design and optimization, and to gain a more fundamental understanding of transport phenomena in environments with high-flux irradiation. These models can be broadly divided into two categories according to their scope [35]: (i) models of a generic modeling domain representative of a section or part of a solar reactor, focusing on the detailed analysis of the different heat and mass transfer mechanisms occurring in the system, and (ii) models that aim at capturing the heat and mass transfer in an actual solar reactor. For ceria-based reactor designs, the existing transport models focus on two-temperature cycles. Lapp et al. [36] present a three-dimensional heat transfer analysis pertinent to reactor design, precluding the effects of flow field and transients in chemical reactions. The transient model developed by Keene et al. in [37,38] uses an axisymmetric porous bed to investigate the effects of medium morphology and chemical kinetics on transport processes. Transient, three-dimensional analyses of heat and mass transfer coupled to chemical kinetics of ceria-based redox reactions in reactor-type geometries are absent in the literature.

In the present study, a computational fluid dynamic (CFD) model is developed to simulate transient heat and mass transfer in a reactive element of the novel reactor proposed by Lipiński et al. [39] for the thermochemical splitting of CO_2 and/or H_2O via redox cycling of ceria for an isothermal mode of operation. The proposed design is amenable to operation in batch or continuous mode with the unique feature of simultaneous solid-state heat recovery and directed gas delivery and removal to and from the redox material, respectively, which eliminates the mixing of the sweep gas and oxidizer gas streams. The focus is on the analysis of the reduction reaction (1)—the crucial step of the solar-driven cycle, coupling solar irradiation and heterogeneous chemistry—to elucidate the coupled thermal transport phenomena and chemical

kinetics. At present, the oxidation kinetics of ceria at high temperatures, $T > 1673$ K, is not available in the literature, and thus not included in this study. The model is applied to two exemplary reactive element geometries to simulate batch mode reduction. The model takes into account the temperature dependent heat fluxes on the cavity walls of the reactor. The interactions between the various transport processes and their influence on chemical performance—oxygen release rate and reduction extent—are presented for the two geometries considered.

2 Problem statement

The solar reactor concept is shown in Figure 1. The reactor consists of an array of adjacent annular reactive ceria elements that form a cylinder. The reactive elements are contained in an insulated cylindrical solar cavity. Concentrated solar radiation enters the cavity through the aperture at the reactor front and is absorbed on the inner surfaces of the reactive elements. The radiation incident at the aperture is assumed to be axisymmetric with a diffuse angular distribution subtending a cone half-angle of 90° to approximate the distribution of radiation exiting a compound parabolic concentrator. A batch process is modeled with all the reactive elements undergoing thermal reduction in the presence of concentrated sunlight. Prior to the reduction step, on-sun oxidation is assumed to proceed in the reactive elements until chemical equilibrium is attained. For a batch process with uniform incident source, the modeling domain reduces to a single reactive element due to rotational symmetry.

A schematic of a single reactive element is shown in Figure 2. It consists of highly porous ($\sim 65\%$) ceria with micrometer-sized pores. The fabrication procedure for such porous ceria monoliths is elaborated in [22], and numerical predictions of their macroscopic transport properties are reported by Haussener and Steinfeld in [40]. The elements are sealed with a thin

layer of impermeable and opaque coating. Such high-temperature ceramic sealings have been proposed for applications in hypersonic engine components and gas turbines [41] and ceramic microreactors [42]. Gases are distributed and collected from the porous ceria through hollow cylindrical inlet and outlet zones inside the reactive element, referred to as inlet and outlet channels, respectively .

Figure 1. Reactor concept for solar thermochemical CO₂ splitting: (a) axial cross-section, and (b) radial cross-section [39]. The numbered surfaces are: (#0) aperture, (#1) inner surface of the reactive element assembly, (#2) front wall, and (#3) back wall.

Figure 2. Cross-section of the reactive element showing the sealed porous ceria structure with embedded gas channels.

The porous ceria structure is assumed to be homogenous, isotropic, and with constant porosity and specific surface area. High-purity N_2 sweep gas enters the reactive element through the inlet channel at a fixed temperature, mass flow rate and composition, and is forced to flow through the porous ceria structure. A mixture of sweep gas and oxygen exits the reactive element through the outlet channel. Local thermal equilibrium is assumed between the fluid and solid phases as justified by the negligible temperature differences between the two phases observed by Keene et al. [43]. The porous ceria is an optically-thick radiatively participating medium based on numerical predictions and experimental measurements [40,44]. In the latter studies, strong spectral behavior of radiative coefficients was shown at ambient temperature. Here, we model the medium as grey for simplicity, with the radiative properties assumed to be representative for calculations of the total radiative fluxes. Simplifying assumptions are made to capture radiative heat exchange in the reactor cavity to determine boundary heat fluxes on the reactive elements. The aperture, surface #0 in Figure 1, is modeled as cold and black with an explicit flux of incident concentrated solar radiation. The front and back walls of the cavity, surfaces #2 and #3 in Figure 1, are modeled as diffuse and gray. The lateral cavity wall formed by the reactive elements, surface #1 in Figure 1, is discretized into ten axial diffuse and gray rings. The boundary heat flux at the inner surface of the reactive element is determined by iteratively calculating the radiative heat exchange inside the cavity using the net radiation method [45]. The convective loss from the cavity is neglected in this study—a limiting situation with a stagnant fluid inside the cavity that can be approached by employing a down-facing vertically oriented reactor cavity [46]. For a horizontal cavity at a uniform temperature of 1773 K, we estimate up to 15% heat losses due to natural convection using the correlations for heat losses through a side-facing aperture [47]. Adiabatic boundary conditions are imposed for the front and back walls of

the cavity and the outer surface of the reactive element. The latter assumption, introduced in this study for simplicity, corresponds to an upper limit in the predicted temperatures as conduction losses through cylindrical walls of solar thermochemical reactors typically account for 15–30% of the solar power input. Buoyancy, hydrodynamic dispersion, viscous dissipation and thermal expansion effects are omitted from consideration.

3 Heat and mass transfer model

The governing equations for heat and mass transfer in porous ceria subjected to a sweep gas flow and undergoing a heterogeneous gas–solid chemical reaction have been derived by Keene et al. [43] by applying volume-averaging techniques [48] and by using the Darcy’s law in lieu of the momentum equation. In the present model, the governing equation for momentum transport is formulated using the extended Darcy–Brinkman–Forchheimer model.

3.1 Mass conservation

With the assumed constant porosity, ϕ , of the medium, the mass conservation equation for the solid phase is formulated as:

$$(1-\phi)\frac{\partial\langle\rho_s\rangle^s}{\partial t} = -\dot{m}_{\text{sf},\text{O}_2}'' a_{\text{sf}} \quad (4)$$

where the source term, $\dot{m}_{\text{sf},\text{O}_2}'' a_{\text{sf}}$, is the volumetric interphase mass transfer rate of oxygen between solid and fluid phase. The intrinsic average density of the solid phase, $\langle\rho_s\rangle^s$, decreases with time as it releases oxygen during the thermal reduction process. For a constant control volume, the density of the solid phase can be expressed as a function of the non-stoichiometry:

$$\langle\rho_s\rangle^s = \rho_{\text{CeO}_2} \left(1 - \langle\delta_s\rangle^s \frac{M_{\text{O}_2}}{2M_{\text{CeO}_2}} \right) \quad (5)$$

where ρ_{CeO_2} is assumed constant and equal to 7220 kg m^{-3} [37,38].

The continuity equation for the fluid phase is:

$$\frac{\partial}{\partial t} \left(\phi \langle \rho_f \rangle^f \right) + \nabla \cdot \left(\langle \rho_f \rangle^f \langle \bar{\mathbf{u}}_f \rangle \right) = \dot{m}_{\text{sf}, \text{O}_2}'' a_{\text{sf}} \quad (6)$$

The conservation equation for species i of the fluid phase takes into account the accumulation of species i in the control volume, convective and diffusive mass transport, and species production by chemical reactions:

$$\frac{\partial}{\partial t} \left(\phi \langle \rho_f \rangle^f \langle Y_i \rangle^f \right) + \nabla \cdot \left(\langle \rho_f \rangle^f \langle \bar{\mathbf{u}}_f \rangle \langle Y_i \rangle^f \right) = \nabla \cdot \left(D_{i, \text{eff}} \langle \rho_f \rangle^f \nabla \langle Y_i \rangle^f \right) + \dot{m}_{\text{sf}, \text{O}_2}'' a_{\text{sf}} \quad (7)$$

Using the ideal gas law for a multi-component mixture, the thermodynamic equation of state for the fluid phase can be written as:

$$\langle p_f \rangle^f = \sum_i \frac{\langle Y_i \rangle^f}{M_i} \langle \rho_f \rangle^f \bar{R} \langle T \rangle \quad (8)$$

The closure equation to determine the interfacial oxygen mass transfer, $\dot{m}_{\text{sf}, \text{O}_2}''$, was derived by

Keene et al. [43]:

$$\dot{m}_{\text{sf}, \text{O}_2}'' = k_r \frac{M_{\text{O}_2}}{2} \left(\langle \delta_s \rangle^s \right)^3 \left[\exp \left(\frac{1}{2} \frac{\Delta \bar{h}_{\text{O}_2}^0 - \langle T_s \rangle^s \Delta \bar{s}_{\text{O}_2}^0}{\bar{R} \langle T_s \rangle^s} \right) - \left(\frac{\langle p_{\text{O}_2} \rangle^f}{p_{\text{ref}}} \right)^{1/2} \right] \quad (9)$$

This expression has been derived assuming doubly ionized oxygen vacancies in the ceria, and by applying crystal site conservation, electroneutrality, and the law of mass action. The thermodynamic functions of standard oxidation enthalpy $\Delta \bar{h}_{\text{O}_2}^0$ and entropy $\Delta \bar{s}_{\text{O}_2}^0$ for an infinitesimal change in non-stoichiometry δ_s of ceria have been found to be independent of

temperature, and measured values have been reported as a function of δ_s in the range of $0.001 < \delta_s < 0.27$ [23]. k_r is the morphology-dependent reaction rate parameter and is arbitrarily chosen as $1 \text{ mol}_{\text{O}_2} \text{ m}^{-2}$ in this analysis.

3.2 Momentum conservation

A wide range of flows through porous media can be modeled using semi-heuristic momentum equations known as the Darcy–Brinkman–Forchheimer model, developed by Vafai and Tien [49]. Applied to the present problem, they yield:

$$\frac{1}{\phi} \frac{\partial}{\partial t} \langle \rho_f \bar{\mathbf{u}}_f \rangle + \frac{1}{\phi^2} \langle \bar{\mathbf{u}}_f \rangle \cdot \nabla \langle \rho_f \bar{\mathbf{u}}_f \rangle = -\nabla \langle p \rangle^f + \frac{\mu}{\phi} \nabla^2 \langle \bar{\mathbf{u}}_f \rangle - \frac{\mu}{K} \langle \bar{\mathbf{u}}_f \rangle - \rho_f F_{\text{DF}} \left| \langle \bar{\mathbf{u}}_f \rangle \right| \langle \bar{\mathbf{u}}_f \rangle \quad (10)$$

The first two terms on the left-hand side of equation (10) represent the flow development terms and predict entrance length effects. The terms on the right hand side represent fluid phase pressure gradient, bulk viscous shear stress due to the presence of a rigid bounding surface or a free-fluid porous medium interface, Darcy pressure drop, and inertial pressure losses, respectively.

3.3 Energy conservation

The overall energy equation is formulated as [50]:

$$\begin{aligned} \frac{\partial}{\partial t} \left((1-\phi) \langle \rho_s \rangle^s \langle h_s \rangle^s + \phi \langle \rho_f \rangle^f \langle h_f \rangle^f \right) + \nabla \cdot \left(\langle \rho_f \rangle^f \langle \bar{\mathbf{u}}_f \rangle \sum_{i=1}^N \langle Y_i \rangle^f \langle h_i \rangle^f \right) \\ = \nabla \cdot (k_{\text{eff}} \nabla \langle T \rangle) + \nabla \cdot \left(\langle \rho_f \rangle^f \sum_i \langle h_i \rangle^f D_{i,\text{eff}} \nabla \langle Y_i \rangle^f \right) - \langle \nabla \cdot \bar{\mathbf{q}}_{\text{rad}} \rangle - \frac{\dot{m}_{\text{sf},\text{O}_2}'' a_{\text{sf}}}{M_{\text{O}_2}} \bar{h}_{\text{red}} \end{aligned} \quad (11)$$

The first two terms on the left-hand side represent the change in enthalpy of the solid and fluid phases and the third term describes the advection of enthalpy in the fluid phase. The volume-

averaged medium temperature, $\langle T \rangle$, is represented below as T for brevity. Since the maximum change of the specific heat capacity of ceria due to changes in the non-stoichiometry within the range of 0–0.2 is only 2% [51], h_s is treated as a function of temperature only. The right-hand side of equation (11) includes enthalpy transfer associated with heat conduction, mass diffusion, radiation, and interphase enthalpy transfer due to chemical reaction, where:

$$\bar{h}_{\text{red}} = -\frac{1}{2} \int_0^{\delta} \Delta \bar{h}_{\text{O}_2}(\delta^*) d\delta^* \quad (12)$$

The gas phase is treated as radiatively non-participating and the radiative source term, $\nabla \cdot \bar{\mathbf{q}}_{\text{rad}}''$, that appears in the energy equation is modeled using the Rosseland diffusion approximation [52]:

$$\langle \nabla \cdot \bar{\mathbf{q}}_{\text{rad}}'' \rangle = \nabla \cdot (-k_R \nabla T) \quad (13)$$

with:

$$k_R = \frac{16n^2\sigma T^3}{3\beta_m} \quad (14)$$

where β_m is the Rosseland mean extinction coefficient [53], and n is the real part of the refractive index of the host medium. Even though the Rosseland diffusion approximation leads to errors in the predicted radiative flux at the medium boundaries [54], it is well suited for the considered morphology with optical thickness of 550. For the pore size and porosities considered in this study, the gas phase is assumed to be the host medium, and thus $n \approx 1$.

3.4 Initial and boundary conditions

Initial conditions—The flow field, temperature distribution, and non-stoichiometry distribution within the reactive element are initialized with the steady-state solution obtained at the end of the oxidation step, equation (2), when no further reaction between solid and fluid is

taking place, i.e. $d\langle\delta_s\rangle^s/dt=0$. The initial O_2 partial pressure distribution is set equal to the equilibrium partial pressure, $p_{O_2,ox}$, due to partial thermal dissociation of CO_2 , which is a function of local gas temperature and pressure. The initial non-stoichiometry distribution is the equilibrium non-stoichiometry, which is a function of temperature and O_2 partial pressure as given by thermodynamic data in [55]. The initial oxygen mass fraction within the reactive element is determined by $p_{O_2,ox}$ and assuming that the gas composition switches instantaneously from $O_2 + CO_2 + CO$ during oxidation to $O_2 + N_2$ when sweep gas starts flowing through the reactive element.

Boundary conditions—The boundary conditions applied at the surfaces of the reactive element are summarized in

Table 1. At the inlet, the upstream value for the mass flow rate of the gas normal to the inlet plane, $\dot{m}_{inlet}$, the oxygen mass fraction, $Y_{O_2,inlet}$, and the gas temperature $T_{f,inlet}$ are specified. The upstream mass and heat diffusion are taken into account at the inlet. At the outlet, the gases leave at atmospheric pressure and the zero-gradient boundary condition is imposed for the other field variables. On all sealed surfaces the no-slip boundary condition is enforced. All sealed surfaces of the reactive element are modeled to be adiabatic, except for the inner cylindrical surface, which is irradiated with concentrated solar radiation. The boundary heat flux at the inner surface is determined by iteratively calculating the net radiative heat exchange in the cavity using the net radiation method with view factors calculated using the Monte Carlo ray-tracing method [45]. The aperture (surface #0 in Figure 1) is mapped as the surface element $i = 0$. Surface #1 is discretized into $N = 10$ axial rings, $i = 1, \dots, N$. The front and back walls (surfaces #2 and #3 in Figure 1) are mapped as $i = N+1$ and $i = N+2$, respectively. This leads to a system of $N+3$

equations for the $N+1$ unknown surface heat fluxes for the aperture and the reactive element rings, $q''_i, i=0, \dots, N$, and the temperatures of the front and back walls, T_{N+1} and T_{N+2} , respectively.[†]

$$\frac{q''_i}{\epsilon_i} - \sum_{j=0}^{N+2} \left(\frac{1}{\epsilon_i} - 1 \right) F_{i-j} q''_j + H_{oi} = E_{bi} - \sum_{j=0}^{N+2} F_{i-j} E_{bj}, \quad i = 0, \dots, N+2, \quad (15)$$

where F_{i-j} denotes the view factor from surface i to surface j , and H_{oi} is the solar radiative flux incident on surface i and is calculated from the solar flux at the aperture, H_o , as:

$$H_{oi} = \frac{A_0}{A_i} F_{0-i} H_o \quad (16)$$

For the axial rings, the surface temperature is calculated by averaging over all faces of the surface mesh that are within the ring and the average temperature is used to determine E_{bi} .

Table 1. Boundary conditions.

Surface	Boundary conditions
Inlet	$\dot{m} _{\text{inlet}} = \dot{m}_{\text{inlet}}; Y_{\text{O}_2} _{\text{inlet}} = Y_{\text{O}_2, \text{inlet}}; T_{\text{f}} _{\text{inlet}} = T_{\text{f, inlet}}$
Outlet	$\langle p_{\text{f}} \rangle^{\text{f}} = p_{\text{atm}}; \frac{\partial \langle Y_{\text{O}_2} \rangle^{\text{f}}}{\partial n} = 0; \frac{\partial T}{\partial n} = 0$
Inner cylindrical surface	$\vec{\mathbf{u}}_{\text{f}} \cdot \hat{\mathbf{n}} = 0; \frac{\partial \langle Y_{\text{O}_2} \rangle^{\text{f}}}{\partial n} = 0; k_{\text{w}} \frac{\partial \langle T \rangle}{\partial n} = q''_{\text{rad, RE}}$
All other surfaces	$\vec{\mathbf{u}}_{\text{f}} \cdot \hat{\mathbf{n}} = 0; \frac{\partial \langle Y_{\text{O}_2} \rangle^{\text{f}}}{\partial n} = 0; \frac{\partial \langle T \rangle}{\partial n} = 0$

[†] The net radiation method and view factor reciprocity relations assume that all elements $i = 1, \dots, N+2$ are characterized by uniform temperature, properties, incident and outgoing intensity. These assumptions are not strictly satisfied in the present study as axial and circumferential variations are observed in the results of the simulations of the reactive element (see section Results).

3.5 Thermophysical properties

The temperature dependent thermophysical material properties of viscosity and thermal conductivity for the gases are adopted from [56]. The specific heat capacity values for ceria and the gases are obtained from [57]. For bulk ceria, the temperature dependent thermal conductivity values are found in Chekhovskoy and Stavrovsky 1969 [58]. The mass diffusion coefficient of the individual gas species is calculated by using kinetic theory for rigid spheres [59]. The intrinsic viscosity and thermal conductivity for the gas mixture is calculated using mole fractions as a weighting function for the pure species values.

3.6 Macroscopic effective transport properties of porous ceria

The effective transport properties that appear in the volume-averaged transport equations depend on the intrinsic transport properties and the pore-scale morphology of the material. The properties of the macroporous ceria used in this analysis were determined via pore-level simulations [40]. The values are listed in Table 2.

Table 2. Morphological and effective heat and mass transport properties of porous ceria, determined via pore-level simulations [40].

Parameter	Morphology dependence	Value	Unit
ϕ	—	0.65	—
a_{sf}	$f(d_p, \phi)$	6.5×10^5	m^{-1}
K	$f(d_p, \phi)$	2.4×10^{-11}	m^2
F_{DF}	$f(d_p, \phi)$	1.6×10^5	m^{-1}
β_λ	$\beta_\lambda(\phi, d_p, n)$	5.5×10^4	m^{-1}

$k_{\text{stag,eff}}$	$f(k_s, k_f, \phi, a)$	$k_s \left[a \left(\frac{k_f/k_s}{\phi(1-k_f/k_s) + k_f/k_s} \right) \dots \right. \\ \left. + (1-a)(\phi k_f/k_s + 1 - \phi) \right]; a = 0.5$	$\text{W m}^{-1} \text{K}^{-1}$
$D_{i,\text{eff}}$	$f(D_i, \phi, \text{Tortuosity})$	ϕD_i	$\text{m}^2 \text{s}^{-1}$

3.7 Parameters

The simulation parameters are listed in Table 3. The parameters N_{RE} , r_{outer} , t_{RE} and d_{ch} (Figure 2) are selected as the set of independent (prescribed) geometry parameters. The length, L , of the reactive element is calculated based on the selection of the independent geometry parameters and the specified mass of ceria in the reactor. Two cases are simulated with $N_{\text{RE}} = 10$ and $N_{\text{RE}} = 20$ reactive elements, referred to as geometry G₁ and G₂, respectively. The length of the reactive element in G₂ is made 20% greater than G₁, with all other geometric parameters unaltered (see Table 3), to retain the same mass of ceria in both geometries. The sealing is assumed to be diffuse-gray with an emissivity of 0.7. The existing literature for the optical properties of metal oxides suggests a trend of increasing emissivity with increasing temperature, especially in the infrared spectrum [45,60]. The total mass of ceria in the reactor and the gas flow rate through the reactive element have been selected based on a thermodynamic analysis of the process [25]. The inlet gas flow rates for the two geometries are scaled with respect to the mass of the reactive material, i.e. the sweep gas flow rate per unit mass of ceria in the reactive element is retained constant ($50.5 \mu\text{mol s}^{-1} \text{g}_{\text{ceria}}^{-1}$) for both cases [25]. The gases enter the reactive element at 1500 K, corresponding to a gas-phase heat recovery effectiveness of 80% with an O₂ partial pressure of 10 ppm. The solar cavity receives a solar power input of 2500 W at a concentration ratio of $C = 2600$ at the aperture.

Table 3. Reactor parameters for the two cases with $N_{\text{RE}} = 10$ and $N_{\text{RE}} = 20$ reactive elements; G_1 and G_2 refer to the two geometries investigated.

Name	Symbol	Value		Units
		G_1	G_2	
Number of reactive elements	N_{RE}	10	20	
Outer radius of reactive element	r_{outer}	100		mm
Thickness of reactive element	t_{RE}	10		mm
Radius of cavity	r_{cav}	90		mm
Gas channel diameter	d_{ch}	5		mm
Length of reactive element	L	350	420	mm
Emissivity of sealing	ε	0.7		
Mass of ceria in reactor	m_{ceria}	4.6		kg
Inlet mass flow rate	$\dot{m}_{\text{f,inlet}}$	0.65	0.325	g s^{-1}
Inlet gas temperature	$T_{\text{f,inlet}}$	1500		K
Inlet O_2 concentration in sweep gas	$X_{\text{O}_2,\text{inlet}}$	10^{-5}		
Incident solar radiation	$\dot{Q}_{\text{solar}}$	2500		W
Solar concentration ratio	C	2600		suns

3.8 Numerical implementation

The transport equations (4), (6), (7), (10) and (11) are solved using the finite volume method on an unstructured, hexagonal dominant mesh with approximately 10^5 cells by employing ANSYS Fluent 14.0.1 [50]. A first-order Euler implicit scheme is used for time integration with

a time step of 0.01 s. The SIMPLE algorithm is used to couple the pressure and the velocity fields, with second order upwinding for the advection terms in the momentum and energy equations. The non-stoichiometry in the solid phase is computed with a user-defined scalar transport equation [61]. The source terms for mass, momentum, and energy have been linearized appropriately to enforce the positivity criterion [62]. The temperature-dependent wall heat flux boundary condition on surface 1 (Figure 1) presents a challenge for the numerical solution, especially in the transient case. Due to the T^4 -dependence of the net radiative flux, the energy equations are under-relaxed by a factor of 0.95. The mesh is partitioned using the Metis method over eight nodes and verified to ensure load balancing. The governing equations are solved with the globally scaled residual values for convergence set as 10^{-8} for continuity, momentum, and species transport equations, 10^{-12} for the energy equation, and 10^{-12} for the user-defined scalar transport equation that calculates the non-stoichiometry. The transient simulations are performed using high-performance computing resources, $8 \times$ Intel Xeon X5690 (4.1 GHz, 12 GB) core.

4 Results

4.1 Steady-state results

Steady-state flow of oxidizer through the reactive element in the absence of chemical reactions is first simulated to establish the flow field, temperature, and non-stoichiometry distributions in the reactive element at the beginning of the reduction step. Figure 3 shows contours of steady-state pressure temperature, and non-stoichiometry in several axial cross-sections along the length of the reactive element for both geometries G_1 and G_2 . The flow arrangement in the reactive element with the embedded gas channels results in a uniform spatial distribution of pressure along the length (axial direction) of the reactive element as shown in

Figures 3a and 3b. The gases flow through the porous medium in circumferential direction (inlet to outlet), resulting in a large pressure drop across the reactive element due to the large flow resistance imposed by the micrometer-sized features of the porous medium. The regions between gas channel and interface to the adjacent reactive element exhibit nearly no gas flow. An excessive pressure drop is undesired because of high power requirements for pumping the fluid through the reactive element and potential disintegration of the porous structure due to large tensile stresses. Doubling the number of reactive elements, N_{RE} , decreases the pressure drop from 3 to 0.7 atm. When N_{RE} is doubled, the gas flow rate and the length of the flow path through the reactive element are both reduced by a factor of two, which results in the four-fold reduction in pressure drop between inlet and outlet. The gas temperature increases as it flows from the inlet to the outlet channel through the porous ceria. The temperature also increases along the length of the reactive element due to heating in the inlet channel. Figure 3c and 3d depict that the temperature of the reactive element varies from 1500 K near the gas inlet to about 1900 K on the inner wall surface for both geometries. The shorter flow length in G_2 results in higher uniformity of velocity, pressure and temperature than in G_1 . The axial variation of average (circumferentially and radially averaged) temperatures is 1618–1676 K for G_1 and 1626–1797 K for G_2 . At any axial plane, the peak ceria temperature is located on surface #1 between outlet channel and interface to the adjacent reactive element as this region is exposed to very low gas flow. The maximum temperature of 1915 K attained in G_1 is slightly higher than G_2 (1896 K) due to the higher incident flux on G_1 . The equilibrium oxygen partial pressure due to the thermal dissociation of CO_2 depends strongly on the gas temperature and only weakly on the pressure, and therefore increases along the circumferential (flow) direction at any axial plane, as shown in Figures 3e and 3f. Despite the increase in oxygen partial pressure in the flow direction, the

steady-state non-stoichiometry of ceria increases due to increasing temperature as shown in Figures 3g and 3h. G_2 exhibits greater uniformity in the distribution of local non-stoichiometry and higher circumferentially and radially averaged non-stoichiometry (0.01–0.0254) as compared to G_1 (0.008–0.013).

Figure 4 shows the axial variations of temperature and net heat flux on surface #1, where $z/L=0$ is the axial plane of the gas inlet/outlet and $z/L=1$ is the plane adjacent to the reactor aperture. The net heat flux results from absorption and reflection of the incident radiation and radiation emission on surface #1. The temperature of surface #1 is circumferentially averaged at various axial locations and the net heat flux distribution is determined using equation (15). For both geometries, the average wall temperature increases with increasing z/L as the gases heat up through the inlet channel (Figure 3). The circumferentially-averaged wall temperatures are higher for G_2 in comparison with G_1 due to the shorter flow path. Along the z -direction, increasing reradiation losses due to increasing surface temperature result in decreasing net heat flux (see Figure 4b). Higher heat fluxes are observed in G_1 than G_2 due to lower average surface temperatures and smaller cavity aspect ratio (r_{cav}/L). At steady-state, G_1 and G_2 receive a net power input of 195 W and 96 W through surface #1, and hence 1950 W and 1920 W are transferred to the inner cylindrical wall of the reactor, respectively. The rest of the 2.5 kW_{th} input power is lost due to reradiation and reflection from the cavity.

(a)

(b)

(c)

(d)

Figure 3. Steady-state pressure (Pa), temperature (K), equilibrium oxygen partial pressure (Pa) and ceria non-stoichiometry distributions inside the reactive element, for geometry G_1 (a, c, e, g) and geometry G_2 (b, d, f, h); gases enter and exit the reactive element at the top as indicated in 3a.

Figure 4. (a) Temperature and (b) net heat flux distributions on the inner surface of the reactor (surface #1) as functions of normalized axial coordinate (averaged circumferentially); gases enter and exit the reactive element at $z/L = 0$.

4.2 Transient results

The transient thermal reduction step has been simulated over a time period of 600 s for both geometries. Within the chosen simulation time period, we observe that the field variables of interest, especially the rate of O_2 production, reach monotonic trends with time. The average temperature, non-stoichiometry, and O_2 release rates in the reactive element are useful quantities to compare the performance of the two geometries. The temperature is a key driving force for the oxygen release from the solid, as the equilibrium non-stoichiometry of ceria increases exponentially with temperature [23]. From Figure 5a it is observed that for both geometries, the temperature rises after the onset of reduction as the thermal capacitance (ρc_p) of CO_2 is 1.5 times greater than N_2 at 1773 K. The average temperature is higher in G_2 (1675–1683 K) than in G_1 (1636–1661 K) due to the higher temperature uniformity in G_2 . The temperature rise is steeper for G_1 over the first 400 s due to the low oxygen production rate (Figure 5c) and the corresponding decrease in the energy consumed by the endothermic reduction step. The higher

temperatures and lower oxygen partial pressures due to the decreased total pressure (Figure 3), obtained for G_2 result in higher ceria non-stoichiometries as depicted in Figure 5b. The rate of change in non-stoichiometry is only slightly higher for G_2 than for G_1 ($3.6 \times 10^{-6} \text{ s}^{-1}$ versus $3 \times 10^{-6} \text{ s}^{-1}$), indicating that the assumed reaction rate expression results in very slow release of O_2 . As the temperature increases slowly in G_2 , the accumulation of oxygen in the reactive element causes the O_2 release rate to decrease with time. In contrast, the faster temperature rise in G_1 results in increasing oxygen release rates between 50 and 390 s. The rate begins to drop only after 400 s as the temperature levels off. Despite the asymptotic behavior of the temperature for both geometries, the oxygen release rate only slowly decreases with time, indicating that, for the chosen reaction rate parameters, the chemical process is limited by surface kinetics and mass transport. Figure 5d shows the fraction of the net power transferred to the reactive element, $\dot{Q}_{\text{chem}}/\dot{Q}_{\text{wall}}$, that is used to drive the endothermic chemical reduction of ceria, and the remainder is used to heat the material. The curves follow the trends observed in Figure 5c for the O_2 release rate because the heat absorption by the chemical reactions is proportional to the reaction rate, but independent of temperature and only weakly dependent on non-stoichiometry.

(a)

(b)

Figure. 5 Transient evolution of average temperature (a), non-stoichiometry (b), O₂ release rate (c), and fraction of the net power transferred to the reactive element that is used for chemical reduction in the reactive element (d) (averaging is performed over the volume of the reactive element).

From the point of view of the reactor design, the gas flow rates, the durations of the reduction and oxidation steps, and the mode of operation have to be optimized for maximum reactor efficiency. Analysis of this aspect is beyond the scope of this work. However, the simulation results allow for the evaluation of the time-averaged rate of O₂ production for the entire reactor for a batch reduction process. Assuming that the O₂ production rate is equal in all reactive elements in the reactor, the time-averaged rate of O₂ production by the reactor is calculated as:

$$\bar{R}_{\text{O}_2} = \frac{V_{\text{RE}} N_{\text{RE}} \int_0^{t_{\text{red}}} \dot{m}_{\text{sf},\text{O}_2}'' a_{\text{sf}} dt}{t_{\text{red}}} \quad (17)$$

where t_{red} is the time period for the reduction step and V_{RE} is the bulk volume of one reactive element. Figure 6a shows that for short reduction times ($t_{\text{red}} < 200$ s), the time-averaged O_2 production rate is at least 50% higher for G_2 than for G_1 . For longer reduction times, the curves for G_1 and G_2 approach each other ($\sim 1.4 \times 10^{-6} \text{ kg s}^{-1}$).

The change in non-stoichiometry in the reactive element over the reduction step is a direct measure of the amount of O_2 removed from the ceria lattice. The average non-stoichiometry in the reactive element after the reduction time t_{red} can be calculated from the time-averaged O_2 release rate, $\bar{R}_{\text{O}_2}$, as:

$$\delta_{\text{avg}} = \frac{2\bar{R}_{\text{O}_2}t_{\text{red}}/M_{\text{O}_2}}{m_{\text{ceria,reactor}}/M_{\text{CeO}_2}} \quad (18)$$

As a result of the higher temperatures which result in higher O_2 release rates, G_2 is reduced to a larger extent than G_1 for any reduction time, t_{red} , as shown in Figure 6b. For $t_{\text{red}} = 600$ s, δ_{avg} is 20% higher for G_2 than for G_1 . The larger extent of reduction in G_2 is anticipated to result in higher fuel production rates in the subsequent oxidation step.

Figure 4. (a) Time-averaged O₂ production rate and (b) extent of reduction for the entire reactor as functions of the duration of the thermal reduction step.

5 Summary and Conclusions

A three-dimensional, CFD model has been developed to simulate transient thermal reduction in an annular, porous ceria cylinder during batch operation. The influence of the number of reactive elements constituting the reactor cavity on the temperature and pressure distributions in the reactive element and on the rate of oxygen production and the extent of reduction is studied. The temperature-dependent net wall heat flux distribution on the reactive element is obtained by incorporating surface–surface radiative heat transfer in the reactor cavity enclosure. Steady-state simulations initialize all field variables (temperature, pressure, non-stoichiometry, oxygen mass fraction), assuming that all reactive elements in the reactor are oxidized on-sun to completion prior to the start of the transient reduction step.

The gas channel configuration in the porous structure enables uniform circumferential flow through the element from the inlet to the outlet. The temperatures for both the gas and solid phases increase from the back wall of the reactor cavity, where the gas inlets/outlets are located, to the aperture. Strong spatial variations are observed for all field variables along the flow direction. For the case of 10 elements in the reactor cavity, a high pressure drop of 3 atm is observed across the reactive element, which is detrimental to both the material utilization and structural integrity of the reactive element. The cavity configuration with 20 reactive elements exhibits lower pressure drop, higher temperature uniformity and increased oxygen production rates. Two factors result in the higher rate of O₂ release in G₂ than in G₁: higher average temperatures and lower oxygen partial pressures. The observed molar rates (time-averaged) of

O₂ production by the entire reactor are in the range of 40–70 $\mu\text{mol s}^{-1}$. For the assumed rate expression for the reduction reaction, it can be inferred that the thermal reduction process is limited by mass transfer and inherent surface kinetics rather than by heat transfer.

The model makes substantial assumptions about the reaction mechanism for oxygen release and uptake in ceria and the morphology dependent reaction rate parameter in the rate expression. However, the relative trends in hydrodynamic, thermal and chemical performance for the considered geometries are expected to be similar to model predictions. Future work will employ the computational framework developed in this study to simulate a complete reduction–oxidation cycle, perform parametric variations of design variables and experimentally validate the present model using solar reactor prototypes.

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Nomenclature

A	area, m^2
A_0	aperture area, m^2
a_{sf}	solid–fluid interface area per unit bulk volume, m^{-1}
C	solar concentration ratio
D	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
d_{ch}	channel diameter, m
d_{p}	pore diameter, m
E_{b}	blackbody emissive power, W m^{-2}
F	view factor
F_{DF}	Forchheimer or inertial drag coefficient, m^{-1}
f	function
H_{o}	externally incident solar radiative flux, W m^{-2}
h	specific enthalpy including sensible and formation components, J kg^{-1}
$\bar{h}_{\text{red}}$	average enthalpy of reduction, J mol^{-1}
i	index
j	index
K	permeability, m^2
k	thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
k_{r}	kinetic rate constant, $\text{kmol m}^{-2} \text{s}^{-1}$
k_{R}	radiative conductivity, $\text{W m}^{-1} \text{K}^{-1}$

L	length of reactive element, m
M	molecular weight, kg kmol ⁻¹
m	mass, kg
$\dot{m}$	mass flow rate, kg s ⁻¹
$\dot{m}_{\text{sf}}''$	interphase mass flux between solid and fluid, kg m ⁻² s ⁻¹
N	number
n	refractive index
p	pressure, Pa
$\dot{Q}$	power, W
$\dot{Q}_{\text{solar}}$	concentrated solar power input to the reactor, W
q''	heat flux, W m ⁻²
$\bar{R}$	universal gas constant, J kmol ⁻¹ K ⁻¹
$\bar{R}_{\text{O}_2}$	average O ₂ release rate, kg s ⁻¹
r	radius, m
T	temperature, K
t	time, s
t_{RE}	thickness of reactive element, m
$\mathbf{u}$	velocity, m s ⁻¹
V	volume, m ³
X	mole fraction
x	Cartesian coordinate

Y	mass fraction
y	stoichiometric coefficient; Cartesian coordinate
z	Cartesian coordinate

Greek Letters

β	extinction coefficient, m^{-1}
$\Delta \bar{h}_{\text{O}_2}^0$	standard oxidation enthalpy, J mol^{-1}
$\Delta \bar{s}_{\text{O}_2}^0$	standard oxidation entropy, $\text{J mol}^{-1} \text{K}^{-1}$
$\Delta \delta$	change in non-stoichiometry
δ	non-stoichiometry
δ^*	dummy variable
ε	total hemispherical emissivity
ε_{hex}	heat exchanger effectiveness
μ	dynamic viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
ϕ	porosity
ρ	density, kg m^{-3}
σ	Stefan–Boltzmann constant, $\text{W m}^{-2} \text{K}^{-4}$

Subscripts

amb	ambient
atm	atmospheric
avg	average
cav	cavity
chem	chemistry

eff	effective
f	fluid
<i>i</i>	index
m	mean
outer	outer radius
ox	oxidation
RE	reactive element
rad	radiative
red	reduction
ref	reference
s	solid
sf	solid-fluid in porous medium
stag	stagnation
w	wall

Abbreviations

G	geometry
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Other symbols

$\langle \rangle$	superficial average
$\langle \rangle^f$	intrinsic average over fluid phase
$\langle \rangle^s$	intrinsic average over solid phase

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Transient heat and mass transfer analysis in a porous ceria structure of a novel solar redox
reactor

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