SOLAR THERMAL DISSOCIATION OF ZINC OXIDE—

REACTION KINETICS, REACTOR DESIGN, EXPERIMENTATION, AND MODELING

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presented by
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Abstract

A two-step H\textsubscript{2}O-splitting thermochemical cycle based on the Zn/ZnO redox reactions is proposed for producing solar H\textsubscript{2}; the two steps are (1) the endothermal dissociation of ZnO and (2) the exothermal hydrolysis of Zn. Several aspects of the first step of the cycle are investigated in the framework of this dissertation along with the development of a solar-driven thermogravimeter (TG) and an improved engineering design of a 10 kW solar reactor prototype.

The solar-driven TG, which enables online measurement of sample weight loss, temperature, and radiative flux, is developed to study the reaction kinetics and heat transfer for a packed-bed of ZnO particles undergoing solar thermal dissociation under conditions similar to those found in solar reactors. Isothermal runs in the temperature range 1834–2109 K were conducted and fit to a zero order Arrhenius rate law resulting in an apparent activation energy of 361 ± 53 kJ mol\textsuperscript{-1} K\textsuperscript{-1} and a frequency factor of 14.03\cdot10\textsuperscript{6} ± 2.73\cdot10\textsuperscript{6} kg m\textsuperscript{-2} s\textsuperscript{-1}. Application of L’vov’s kinetic theory yield results close to those found experimentally. A transient model of the packed-bed of ZnO particles that couples the rates of radiation, conduction, and convection heat transfer with the rate of the reaction is formulated and solved numerically using the finite volume method and the explicit Euler time integration scheme. The reaction is found to occur only in the uppermost part of the ZnO layer, which is typically of an ablation regime, characterized by the rate of radiative transfer to the endothermic reaction that proceeds faster than the rate of heat conduction to the depth of the ZnO packed-bed. The thermal transport properties of ZnO at high temperatures, namely the
extinction coefficient and the absorptivity of ZnO, are extracted by matching numerical results to those obtained experimentally.

An improved engineering design of the 10 kW solar reactor prototype for the thermal dissociation of ZnO at above 2000 K was accomplished. The reactor features a rotating cavity receiver lined with ZnO particles that are held by centrifugal force. With this arrangement, ZnO is directly exposed to concentrated solar radiation and serves simultaneously the functions of radiant absorber, chemical reactant, and thermal insulator. The multilayer cylindrical cavity is made of sintered ZnO tiles placed on top of a porous 80%Al₂O₃-20%SiO₂ insulation and reinforced by a 95%Al₂O₃-5%Y₂O₃ ceramic matrix composite, providing mechanical, chemical, and thermal stability and a diffusion barrier for product gases. The functionality of the engineering design was demonstrated in eight experimental runs where the cavity tiles were composed of ZnO tiles. The longest run exceeded four hours of operation. Operation at temperatures exceeding 2000 K was achieved during experimentation with the cavity composed of the Al₂O₃. The peak solar-to-chemical energy conversion efficiency was 3.1±0.3%. Variation of the quench gas flow rate resulted in a maximum net Zn yield of 44.9%.

A transient heat transfer model is developed for analyzing the thermal performance of the solar reactor prototype for the solar-driven dissociation of ZnO in the 1600–2136 K range. The model couples radiation, convection, and conduction heat transfer to the reaction kinetics for a shrinking domain and simulates a transient ablation regime with semi-batch feed cycles of ZnO particles. Validation is accomplished in terms of the numerically calculated and experimentally measured temperature profiles and reaction extents for a 10 kW reactor prototype tested in PSI’s high-flux solar simulator and subjected to peak solar concentration ratios exceeding 5000 suns. Scaling-up the reactor technology to 100 and 1000 kW solar thermal power input yield a maximum solar-to-chemical energy conversion efficiency of 54.5 and 61.6%, respectively, mainly as a result of higher reaction rates at higher operating
temperatures and a reduction in the conduction losses through optimization of the geometry to minimize water-cooled components.
Zusammenfassung


Das solar betriebene TG ermöglicht die Onlinemessung der Probenmassenabnahme, Probentemperatur und des Strahlungsflusses. Es wurde für die Untersuchung der Reaktionskinetik und des Strahlungsaustausches eines Festbettes aus Zinkoxidpartikeln entwickelt, die dort vergleichbaren Bedingungen wie in Solarreaktoren ausgesetzt sind. Eine isotherme Versuchsreihe wurde im Temperaturbereich von 1834 K bis 2109 K durchgeführt und durch ein Arrhenius Reaktionsmodel nullter Ordnung mit einem Frequenzfaktor von $14.03 \cdot 10^6 \pm 2.73 \cdot 10^6$ kg m$^{-2}$ s$^{-1}$ und einer scheinbaren Aktivierungsenergie von $361 \pm 53$ kJ mol$^{-1}$ K$^{-1}$ angenähert. Ähnliche Werte wurden mit L’vov’s kinetischer Theorie gefunden. Es wurde ein instationäres Model des Zinkoxidfestbettes, das die Strahlungs-, Wärmeleitungs- und Konvektionswärmestrome mit der Reaktionsrate koppelt, entwickelt und numerisch mit der finiten Volumenmethode und der expliziten Eulerintegrationsmethode gelöst. Mit diesem Modell wurde gezeigt, dass die Reaktion nur im oberen Teil der Zinkoxidschicht stattfindet, was typisch für einen Ablationsprozess ist. Dieser ist dadurch gekennzeichnet, dass die Rate des Strahlungswärmeflusses zur endothermen Reaktion grösser als die Rate des Wärmeleitungsflusses in die Tiefe des Zinkoxidbettes ist. Thermische Transportgrößen wie der Auslöschungsfaktor und das Absorptionsvermögen von ZnO bei hohen Temperaturen wurden
mittels Vergleich von numerischen und experimentellen Ergebnissen extrahiert.


Aufskalierung der Reaktortechnologie zu 100 und 1000 kW solarm-
thermischer Leistungszufuhr resultiert in maximalen Wandlungseffizienzen
von solarer zu chemischer Energie von jeweils 54.5% und 61.6%. Die hohen
Effizienzen sind hauptsächlich auf höhere Reaktionsraten bei höheren
Temperaturen und auf eine Reduktion von Wärmeleitungsverlusten durch
Optimierung der Geometrie zur Minimierung der wassergekühlten
Komponenten zurückzuführen.
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## Nomenclature

### Acronyms

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<th>Acronym</th>
<th>Description</th>
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<tr>
<td>AF</td>
<td>Annular Flow</td>
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<tr>
<td>BFE</td>
<td>Bundesamt Für Energie</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CMC</td>
<td>Ceramic Matrix Composite</td>
</tr>
<tr>
<td>CR</td>
<td>Quench Rate</td>
</tr>
<tr>
<td>ETH</td>
<td>Eidgenössische Technische Hochschule</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HFSS</td>
<td>High Flux Solar Simulator</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo ray traying</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluorethen</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institute</td>
</tr>
<tr>
<td>QF</td>
<td>Quench Flow</td>
</tr>
<tr>
<td>QZ</td>
<td>Cold Zone</td>
</tr>
<tr>
<td>RF</td>
<td>Reacting Flow</td>
</tr>
<tr>
<td>SOLZINC</td>
<td>Solar carbothermic production of Zn from ZnO</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimeter</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analyzer</td>
</tr>
<tr>
<td>WF</td>
<td>Window Flow</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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Latin Characters

\( a \)  \hspace{1cm} coefficient in Eqs. (4.13) and (4.15)
\( a \)  \hspace{1cm} stoichiometric coefficient in Eqs. (3.4)–(3.5)
\( A \)  \hspace{1cm} surface area, m\(^2\)
\( b \)  \hspace{1cm} coefficient in Eqs. (4.13) and (4.15)
\( b \)  \hspace{1cm} stoichiometric coefficient in Eqs. (3.4)–(3.5)
\( B \)  \hspace{1cm} deformation factor

\( c_p \)  \hspace{1cm} specific heat capacity, J mol\(^{-1}\) K\(^{-1}\) and J kg\(^{-1}\) K\(^{-1}\)
\( C \)  \hspace{1cm} concentration ratio, given in suns, 1 sun = 1 kW m\(^{-2}\)
\( d \)  \hspace{1cm} diameter, m
\( D \)  \hspace{1cm} diffusion coefficient, m\(^2\) s\(^{-1}\)
\( E_a \)  \hspace{1cm} activation energy, kJ mol\(^{-1}\)
\( F \)  \hspace{1cm} configuration factor
\( G \)  \hspace{1cm} grain size, m
\( h \)  \hspace{1cm} convection coefficient, W m\(^{-2}\) K\(^{-1}\)
\( I \)  \hspace{1cm} grey scale intensity
\( k \)  \hspace{1cm} thermal conductivity, W m\(^{-1}\) K\(^{-1}\)
\( k \)  \hspace{1cm} convective mass transport coefficient, m s\(^{-1}\)
\( k_B \)  \hspace{1cm} Boltzmann constant, J K\(^{-1}\)
\( k_0 \)  \hspace{1cm} pre-exponential factor, kg m\(^{-2}\) s\(^{-1}\)
\( k_0^* \)  \hspace{1cm} pre-exponential factor, kg m\(^{-3}\) s\(^{-1}\)
\( L \)  \hspace{1cm} length, m
\( m \)  \hspace{1cm} mass, kg
\( M \)  \hspace{1cm} molecular mass, kg mol\(^{-1}\)
\( n \)  \hspace{1cm} amount of substance, mol
\( n \)  \hspace{1cm} index of refraction
\( \hat{n} \)  \hspace{1cm} unit normal vector
\( N \)  \hspace{1cm} number of surface elements or finite elements
\( Nu \)  \hspace{1cm} Nusselt number
\( p \)  \hspace{1cm} porosity
\( P \) power, W
\( P \) pressure, partial pressure, (Pa)
\( Pr \) Prandtl number
\( q' \) heat flux, W m\(^{-2}\)
\( q'' \) volumetric heat sink or source, W m\(^{-3}\)
\( r \) radius, m
\( r' \) dissociation rate kg s\(^{-1}\)
\( r'' \) dissociation rate, mol m\(^{-3}\) s\(^{-1}\), kg m\(^{-3}\) s\(^{-1}\)
\( R \) universal gas constant J mol\(^{-1}\) K\(^{-1}\)
\( R \) regression coefficient
\( Ra \) Rayleigh number
\( Re \) Reynolds number
\( Sc \) Schmidt number
\( Sh \) Sherwood number
\( t \) time, s
\( T \) temperature, K
\( V \) volume, m\(^3\)
\( x \) axial position, m
\( X \) cumulative dissociation, zinc yield
\( Y \) linear shrinkage
\( z \) diffusion distance, m

**Greek letters**
\( \alpha \) specific surface area, m\(^{-1}\)
\( \alpha \) absorptance
\( \alpha \) fractional conversion
\( \beta \) mean extinction coefficient, m\(^{-1}\)
\( \gamma_{sv} \) specific surface energy, J m\(^{-2}\)
\( \delta \) parameter in Eq. (7.10)
\( \Delta H_r \) heat consumption of ZnO dissociation reaction, J mol\(^{-1}\), J kg\(^{-1}\)
\( \Delta H_r^* \) standard enthalpy of reaction
\[ \Delta S_r^e \] standard entropy of reaction
\[ \varepsilon \] emissivity
\[ \eta \] thermal energy conversion efficiency
\[ v \] kinematic viscosity, \text{m}^2 \text{s}^{-1}
\[ \rho \] density, \text{kg m}^{-3}
\[ \sigma \] Stefan–Boltzmann constant, \text{W m}^{-2} \text{K}^{-4}
\[ \tau \] transmissivity
\[ \Psi \] specific surface area, \text{m}^{-1}
\[ \omega \] angular frequency, \text{s}^{-1}
\[ \Omega \] vacancy volume, \text{m}^3

**Subscripts**

- eff effective
- f feed
- front irradiated front surface of cylinder
- i dummy index
- inn at the inner surfaces of the cavity
- k dummy index
- lateral lateral surface of cylinder
- max maximum
- min minimum
- M metal
- out at the outer surfaces of the reactor
- O oxide
- p pore, particle
- s surface
- 0 initial
1 Introduction

*Fossil fuels* such as coal, natural gas and mineral oil cover 80% of the current energy demand. The total fossil fuel resources are estimated to last for the next 400 years given the current level of energy consumption [1]. However, the global energy consumption is increasing at 2% per year and is projected to double by 2035 and to triple by 2055 [2], resulting in an even faster depletion of fossil fuels. Additionally, fossil fuel consumption contributes 56.6% of the anthropogenic greenhouse gas emissions (status 2004) [3] and most natural reserves of oil and gas are located in countries with geopolitical issues like Saudi Arabia, Iraq and Iran. Therefore, alternative, environmentally friendly, and renewable energy sources are required.

*Solar energy* has the highest potential of meeting the human energy demand due to its abundant supply and a more even distribution than any other source of renewable energy. Technologies for the utilization of solar energy comprise electricity generation by photovoltaic systems, solar thermal power stations with concentrating systems such as solar troughs and towers, and heat generation with various types of solar collectors. One of the major drawbacks of solar electricity is that it cannot be easily stored. An emerging technology that circumvents the storage problem is the generation of solar fuels directly using solar energy. The most prominent and promising solar fuel is considered to be hydrogen due to its environmental compatibility, ease of storage and distribution, and high energy content [4–9].

*Hydrogen* is presently produced from fossil fuels by catalyzed steam reforming of methane, coal gasification and partial oxidation of hydrocarbons. Currently, hydrogen is mainly used for upgrading crude oil in
refineries, the synthesis of chemical compounds such as ammonia, and as a reduction agent or as process gas in metallurgical processes [10]. Hydrogen is also being considered as an alternative energy carrier to propel airplanes and automotive vehicles [11–13] and virtually any stationary power system using fuel cells. Sustainable hydrogen can be derived from water and solar energy using electrolysis with solar electricity either from photovoltaic systems or solar thermal power systems, by photosynthetic and photoelectrochemical water splitting [14], by direct splitting of water [15, 16], and from solar thermochemical cycles.

**Solar thermochemical processes for hydrogen production** make use of concentrated solar radiation as the energy source of high-temperature process heat [17]. Several 2 and 3-step H₂O-splitting thermochemical cycles based on metal oxides redox reactions are being considered. Examined were metal redox pairs based on CeO₂/Ce₂O₃ oxides, demonstrated in a solar reactor featuring an inert gas atmosphere at \( T = 2273 \) K, \( P = 100–200 \) mbar [18]. A ZnO/MnFe₂O₄ system was demonstrated in a lab furnace at 1273 K in [19]. Mixed iron oxides containing manganese [20, 21] were tested for the production of hydrogen thermogravimetrically and those containing cobalt in a fluidized bed reactor [22]. An yttrium-stabilized, cubic zirconia material coated with iron oxide was proposed to split water in the temperature range 1273–1673 K [23, 24]. A receiver-reactor is described in [25] featuring a multi-channel ceramic honeycomb coated with an iron-oxide-based material. In the first cycle, the oxidation of the coating with steam at 1073 K produces hydrogen, followed by the regeneration of the coating at 1573 K. This system enables the completion of the reduction-hydrolysis cycle in a single solar energy converter [25]. However, the potential of the coating to absorb oxygen from steam and to release hydrogen decreased with the number of completed cycles [26]. A 100 kW reactor is currently being tested.
The disadvantage of mixed iron oxide cycles is their low molar ratio of released oxygen to the total oxygen present in the system. The major drawback of all systems using reactive coatings is their low ratio of hydrogen mass generated to support structure mass. Therefore, between the hydrogen production and coating regeneration steps, the support structure must be reheated without the release of hydrogen, resulting in a low solar-to-chemical energy conversion efficiency.

Considering the properties of the above described competing cycles, the cycle based on the ZnO/Zn redox pair is of special interest since no cyclic heating and cooling is required and a pure metal state is achieved. It consists of: (1) the solar endothermal dissociation of ZnO(s) into its elements; and (2) the non-solar exothermal steam-hydrolysis of Zn into H₂ and ZnO(s), and represented by:

1\textsuperscript{st} step (solar ZnO-decomposition): \[ 2\text{ZnO} \rightarrow \text{Zn}+0.5\text{O}_2 \] (1.1)

2\textsuperscript{nd} step (non-solar Zn-hydrolysis): \[ \text{Zn}+\text{H}_2\text{O} \rightarrow \text{ZnO}+\text{H}_2 \] (1.2)

H₂ and O₂ are derived in different steps, thereby eliminating the need for high-temperature gas separation. This cycle has been identified as a promising path for solar H₂ production from H₂O because of its potential of reaching high energy conversion efficiencies and, consequently, economic competitiveness [27, 28]. A life cycle assessment indicates a 90% reduction of greenhouse gas emissions derived from fuel cell cars driven by solar hydrogen compared to those derived from advanced fossil fuel powertrains [29].

**Review of earlier work on the ZnO/Zn cycle**—The first step of the two step ZnO/Zn water-splitting cycle was first demonstrated in a solar furnace in 1977 by Bilgen et al. [30]. Presumably, due to material problems and funding, research on this cycle was suspended for almost two decades.
Meanwhile, attention was shifted towards dissociating ZnO at lower temperatures by using solar-assisted electrochemical processes [31], solar chemical production using synthesis gas from ZnO and CH₄ [32–35], and by carbothermal reduction—experimentally demonstrated in 5 and 10 kW prototype reactors [36, 37] and in a 300 kW demonstration plant [38]. Based on this experience, a conceptual design for the scale-up to 5 MW has been performed [39].

More recently, the solar thermal ZnO dissociation was demonstrated by Lédé et al. [40] in a quartz vessel containing sintered ZnO, by Haueter et al. [41] in a rotating cavity reactor type, and by Perkins et al. [42] in an aerosol reactor type. Perkins et al. reported the O₂ measurement, which is the only clear indicator of the ongoing thermal ZnO dissociation—if Zn is recovered and no CO₂ and CO were measured during the experiment. The maximum net Zn yield was 17% [42]. However, no reliable reactor technology has been presented in literature where dissociation of ZnO occurs for longer than a few minutes with simultaneous measurement of product gases that accurately predict the recovered amount of Zn.

Various computer models have been used for designing ZnO reactors. Abanades et al. [43] modeled a rotating cavity receiver with continuous feed of ZnO by employing computational fluid dynamics (CFD) for the design of a prototype reactor. Lipiński et al [44] applied the path-length Monte Carlo method to calculate radiative heat transfer in decomposing ZnO at a volume fraction of 0.1. Müller [45, 46] developed and validated a simple transient reactor model to predict the performance of a 10 kW solar chemical reactor for affecting ZnO dissociation.

The reaction kinetics of ZnO were widely studied in thermogravimetric analyzers (TGAs) by [47–53] and by Möller [54] in a solar furnace with presintered ZnO pellets. Weidenkaff et al. [55] studied the crystallization of Zn in a solar furnace and found the recombination reaction of Zn and O₂ to be
of heterogeneous nature occurring on condensed zinc as a nucleation site. Coexistence of Zn(g) and O₂ in the absence of nucleation sites is reported by Weidenkaff [56]. A detailed experimental investigation of the Zn(g) and O₂ separation in a sophisticated quench apparatus is described by Gstoehl et al. [57]. Decreasing the Zn partial pressure to ~100 Pa and quench rates >100’000 K s⁻¹ resulted in Zn yields exceeding 90% [57].

The 2\textsuperscript{nd} step of the cycle, Eq. (1.2), has been experimentally demonstrated using an aerosol-flow reactor that features in-situ formation and hydrolysis of Zn nanoparticles [58, 59], with pre-injected Zn nanoparticles [60], with particles originally produced during the SOLZINC project [61], and by oxidation of Zn(l) [62].

\textit{Thesis Outline}—This thesis was conducted in the framework of the project “Solar Thermal Production of Zinc – Final Steps Toward Scale-Up”, funded jointly by the Swiss federal Office of Energy (BFE) and Paul Scherrer Institute (PSI). The research assignment of this thesis was the development of a reliable reactor technology for affecting the dissociation of ZnO, the design of an experimental performance map, the numerical investigation of radiative heat transfer coupled with combined conduction, convection and chemical reaction rates in a packed-bed of ZnO particles, and the application of results for a numerical model of the prototype reactor.

In Chapter 2, the design of a unique solar-driven thermogravimeter is presented, which was used to study the dissociation reaction kinetics of a packed-bed of ZnO particles. This tool was also used to assess materials of construction for the solar reactor presented in Chapter 5.

Results of the kinetic study are described in Chapter 3 and are compared to published data and to values predicted by L’vov’s kinetic theory. A transient numerical model for ablative heat transfer in the shrinking packed-bed of ZnO particles undergoing thermal dissociation is shown and validated in Chapter 4 along with the derivation of thermal transport properties of ZnO.
The development of a rotary-receiver reactor that features a multilayer cavity with a similar arrangement of ZnO as in the packed-bed ZnO sample of Chapters 3 and 4 is shown in Chapter 5. Results obtained with this reactor are presented in Chapter 6.

A transient numerical model to assess the reactor technology is described and validated in Chapter 7 with experimental results obtained in the prototype reactor. The numerical model is then used to assess the reactor performance of a 100 kW and 1 MW reactor scale-up, shown in Chapter 8. Finally, Chapter 9 summarizes the work that has been conducted and gives suggestions for further research and development activities.


2 The Solar Thermogravimeter

The accurate determination of the reaction kinetics of particulate ZnO under extreme solar reactor conditions (temperatures > 2000 K and heating rates > 100 K/s) required the development of a novel solar-driven thermogravimeter that approaches the heat and mass transfer characteristics existing in solar reactors and enables on-line monitoring of the weight loss as a function of time and temperature. This chapter describes the design and fabrication of this unique apparatus and the experimental procedure.

2.1 Experimental Setup

The solar-driven thermogravimeter (solar TG) is shown schematically in Fig. 2.1.

Figure 2.1: Solar TG experimental set-up at the solar furnace. The ZnO sample is directly exposed to concentrated solar radiation, while its weight loss during the thermal decomposition is continuously monitored.
It consists of a cavity-receiver, i.e. a well-insulated cylindrical enclosure of i.d. 152 mm and length 150 mm, lined with 50 mm-thick CaO-stabilized ZrO$_2$ bricks over two layers of 36 mm-thick porous Al$_2$O$_3$. It has a 60 mm-diameter circular opening—the *aperture*—for the access of concentrated solar energy through a transparent 3 mm-thick quartz window. Inside the cavity, the ZnO sample is mounted on an Al$_2$O$_3$ rod that is suspended on a balance (Mettler Toledo; accuracy 0.01 g). With this arrangement, the ZnO sample is directly exposed to concentrated solar radiation, while its weight loss during decomposition is continuously monitored on-line.

An Ar flow, injected tangentially and radially at the aperture plane, creates an aerodynamic curtain that protects the window from condensable products and carries the gaseous products Zn(g) and O$_2$ to the outlet port at the rear of the cavity. Ar gas is also introduced into the box containing the balance to prevent back-flow of hot gases. Downstream, the Zn(g) is condensed and filtered (glass microfibre filter with pore size of 2.7 μm), and the gas composition is analyzed. Experimentation was carried out at PSI's solar furnace [63], shown in Fig. 2.2: a sun-tracking flat heliostat on-axis with a stationary primary paraboloidal concentrator. Peak solar flux concentration ratios exceeding 5000 suns (1 suns = 1 kW m$^{-2}$) can be achieved at the focal plane, enabling the sample in the solar TG to attain stagnation temperatures$^1$ above 2500 K at ultra-high heating rates faster than 1000 K/s. Solar flux intensities, regulated with a Venetian-type shutter located between the heliostat and the solar concentrator, are measured optically with a calibrated CCD camera on a water-cooled Al$_2$O$_3$-plasma coated Lambertian target. The camera also allows for sample visualization during the experimental runs.

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$^1$ The stagnation temperature is the highest temperature an ideal blackbody solar cavity-receiver is capable of achieving when solar energy is being re-radiated as fast as it is absorbed. It is given by \( (I\cdot C/\sigma)^{0.25} \), where \( I \) is normal beam insolation, \( C \) is the solar flux concentration ratio, and \( \sigma \) is the Stefan-Boltzmann constant.
Sample surface temperatures are measured with a solar-blind pyrometer that is not affected by the reflected solar irradiation because it measures in a narrow wavelength interval around 1.39 μm where solar irradiation is mostly absorbed by the atmosphere [64].

The composition of the product gases is monitored by gas chromatography (Agilent High Speed Micro GC G2890A, equipped with molecular sieve 5A and HaySep A capillary columns, detection limit = 10 ppm; sampling rate = 0.33 min⁻¹), by IR-based detectors for CO and CO₂ (Siemens Ultramat 23, detection limits = 0.2%; sampling rate = 1 s⁻¹), and by thermal conductivity-based detectors for H₂ and O₂ (Siemens Calomat 6 and Oxymat 6, accuracy = 50 ppm, sampling rate = 1 s⁻¹). The measurement of CO and CO₂ is carried out to verify that no carbothermic reduction occurs.

2.2 Sample Characterization

Two types of samples were examined; they are shown schematically in Fig. 2.3. Both were introduced in a 20 mm-i.d. 40 mm-length Al₂O₃ tube.
Figure 2.3: ZnO samples investigated: (a) sample #1, (b) sample #2. Indicated are temperature measurement locations $T_p$ (type-B thermocouple) and $T_{front}$ (solar-blind pyrometry).

Sample #1 (Fig. 2.3a) consisted of a 3.7 mm-thick sintered ZnO tile followed by a 36.3 mm-thick 80%Al$_2$O$_3$-20%SiO$_2$ porous insulation. Sample #2 (Fig. 2.3b) consisted of a 12 mm-thick packed-bed of ZnO particles, followed by a 3.7 mm-thick sintered ZnO tile and 24.3 mm-thick 80%Al$_2$O$_3$-20%SiO$_2$ porous insulation. Sample #1 was used to determine the thermal transport properties (Chapter 4); sample # 2 represented the configuration encountered in the 10 kW solar reactor (Chapter 5) and was used for the kinetic analysis (Chapter 3) and to validate a heat transfer model (Chapter 4). The total mass and mean initial porosity of the ZnO packed-bed were 6.2 g and 70%, respectively. Particle size distribution was measured by laser scattering (HORIBA LA-950 analyzer). Figure 2.4 shows the number density $f(D)$ and the respective volume density $f(D) \times D^3$ of the ZnO particles (Alpha Aesar # 11558, median particle size = 0.22 μm).
Figure 2.4: Particle size distribution functions. The dashed curve shows the number density, the solid curve shows the volume density of the ZnO packed-bed particles.

Although the relative number of big particles seems negligible, these particles significantly contribute to the total mass as shown by the volume distribution curve in Fig. 2.4. BET specific surface area (SSA), SSA = 6.23 m² g⁻¹, was measured by N₂ adsorption at 77 K (Micromeritics 3000). SEM pictures of the ZnO particles and the ZnO tile (ALPHA Ceramics, purity 99.8 wt%, bulk density 5550 kg m⁻³) are shown in Figs. 2.5a and 2.5b, respectively. The ZnO reacting particles exhibited a wurtzite-type crystal structure with no visible micro-porosity, indicating that their average porosity was due mainly to inter-particle void space. The grain size of the sintered ZnO is in the range of 2–8 μm. Grain boundaries are visible as well as an example of an embedded pore in the upper right of Fig. 2.5b.
2.3 Experimental Procedure

The cavity was first purged with Ar gas until the O₂ concentration was less than 100 ppm. With this residual O₂, the dissociation of ZnO in Ar at 1 bar total pressure is thermodynamically favorable at above 1470 K, according to the equilibrium composition calculated with the HSC code [65]. The Ar flow was maintained at 12 l_N min⁻¹ at the aperture and at 3 l_N min⁻¹ at the balance box. During a typical solar experimental run, the solar furnace’s shutter was opened to achieve the desired solar flux intensity, while the irradiated front surface of the ZnO packed-bed particles was heated to the desired temperature in less than 50 s and maintained isothermally during dissociation for at least 150 s. The duration of a single run never exceeded 720 s to avoid variations of the solar irradiation or condensation of products on the quartz window, which affect the desired isothermal conditions. No CO and CO₂ were detected during all runs, ensuring that ZnO was not reduced carbothermally. Zn re-oxidation occurred downstream but no effort was

1 l_N means liters at normal conditions; mass flow rates are calculated at 273 K and 1 bar.
undertaken to quench the products and to avoid their recombination. Figure 2.6 shows a SEM of recombined gaseous products collected in the filter downstream of the solar TG. The product particles collected in the filter exhibit a tetrapod-like structure formed by growth of ZnO crystal with wurtzite structure as a result of nucleation, condensation, and re-oxidation of Zn(g) under supersaturation [66–68].

Figure 2.6: SEM of recombined gaseous products collected in the filter.
3 ZnO Dissociation Reaction Kinetics

3.1 Introduction

Several chemical aspects of the thermal dissociation of ZnO, Eq. (1.1), were previously investigated by [70]. At 2340 K and 1 bar total pressure, $\Delta G = 0 \text{ kJ mol}^{-1}$ and $\Delta H^\circ = 395 \text{ kJ mol}^{-1}$. ZnO decomposes into its constituents rather than subliming into ZnO(g) [47, 49, 53, 71]. Values of the apparent activation energy determined by thermogravimetry in vacuum ranged from 311 to 327 kJ mol$^{-1}$ for sintered ZnO tubes, 50–100 μm layers, and single-crystals at 1136 to 1385°C [49], 356 kJ mol$^{-1}$ for ZnO spinel at 1608 to 1773 K [72], and 373 ± 6 kJ mol$^{-1}$ for ZnO particles at 1255 to 1258 K [71]. Reported values for the activation energy of dissociation in a buffer gas atmosphere were 312–376 kJ mol$^{-1}$ for ZnO particles (1 μm mean particle size) in N$_2$ at 1273 to 1823 K [48], 353 ± 26 kJ mol$^{-1}$ for ZnO particles (50 nm and 1 μm) in Ar at 1713 to 2023 K [47], and 329 kJ mol$^{-1}$ for directly irradiated pre-sintered ZnO pellets [54]. Non-stoichiometry and lattice defects were found to affect the kinetics under vacuum at 1013 and 1053 K [53]. Exploratory tests were carried out in solar furnaces with batch reactors [40, 43, 55, 73].

The 10 kW solar chemical reactor prototype described in detail in Chapter 5 features a rotating cavity-receiver lined with a packed-bed of ZnO particles. An important property of this reactor concept is that the ZnO particles are directly exposed to concentrated solar radiation and serve the functions of radiant absorbers, thermal insulators, and chemical reactants. Reaction

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1 Material from this section is published as [69]: L. O. Schunk, A. Steinfeld. Kinetics of the thermal dissociation of ZnO exposed to concentrated solar irradiation using a solar-driven thermogravimeter in the 1800–2100 K range. AIChE Journal, in press.
kinetics of the ZnO packed-bed under these conditions were not available in literature. Therefore, they were determined in the solar TG under conditions similar to those of the solar chemical prototype reactor, presented in Chapter 5, and are described in this chapter along with a comparison to published kinetic rate laws and to a theoretical model based on the Hertz–Langmuir theory.

3.2 Results

3.2.1 Experimental

Seven isothermal solar experimental runs, performed in the range 1834–2109 K, are summarized in Table 3.1. Listed are the mean effective surface temperature $T_{\text{front}}$, the mass loss of the ZnO batch $\Delta m$ during the period of evaluation of length $\Delta t$, associated mass loss rate $dm/dt$ per unit of effective (irradiated) surface area, total fractional conversion $\alpha_{\text{max}}$, and normalized linear regression coefficient of the fitted mass loss curve.

The ZnO packed-bed’s front surface temperature $T_{\text{front}}$ was determined from the measured pyrometer temperature $T_{\text{pyrometer}}$ by

$$T_{\text{front}} = (\tau_{\text{window}} \varepsilon_{\text{ZnO}})^{0.25} T_{\text{pyrometer}}$$  \hspace{1cm} (3.1)

where $\tau_{\text{window}}$ is the window transmissivity and $\varepsilon_{\text{ZnO}}$ is the emissivity of ZnO at the pyrometer’s operational wavelength, 1.39 μm. $\tau_{\text{window}} \varepsilon_{\text{ZnO}} = 0.69$ was determined using flash-assisted multi-wavelength pyrometry [74, 75]. Surface temperature fluctuations of about ±10 K were observed in several runs and ascribed to fluctuations in the solar irradiation.

The packed-bed sample of ZnO particles underwent up to 50% shrinkage during the initial 30 s due to sintering, as observed with the CCD camera.
Table 3.1: Summary of solar experimental runs: mean effective surface temperature $T_{\text{front}}$, peak solar flux concentration ratio $C_{\text{max}}$, maximum solar flux $q''_{\text{solar, max}}$ averaged over the sample’s front surface, mass loss of the ZnO batch, $\Delta m$ during the period of evaluation of length $\Delta t$, associated mass loss rate $dm/dt$ per unit of effective surface area, total fractional conversion $\alpha_{\text{max}}$, and normalized linear regression coefficient of the fitted mass loss curve.

<table>
<thead>
<tr>
<th>run #</th>
<th>$T_{\text{front}}$ (K)</th>
<th>$C_{\text{max}}$ (suns)</th>
<th>$q''_{\text{solar, max}}$ (kW m$^{-2}$)</th>
<th>$\Delta m$ (mg)</th>
<th>$\Delta t$ (s)</th>
<th>$dm/dt$ (kg m$^{-2}$ s$^{-1}$)</th>
<th>$\alpha_{\text{max}}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2109.1</td>
<td>2133</td>
<td>1662</td>
<td>380</td>
<td>140</td>
<td>0.0176</td>
<td>0.125</td>
<td>0.997</td>
</tr>
<tr>
<td>2</td>
<td>1977.8</td>
<td>1574</td>
<td>1222</td>
<td>90</td>
<td>170</td>
<td>0.0034</td>
<td>0.024</td>
<td>0.968</td>
</tr>
<tr>
<td>3</td>
<td>1889.8</td>
<td>1517</td>
<td>1177</td>
<td>80</td>
<td>250</td>
<td>0.0021</td>
<td>0.016</td>
<td>0.982</td>
</tr>
<tr>
<td>4</td>
<td>1902.1</td>
<td>1411</td>
<td>1095</td>
<td>70</td>
<td>250</td>
<td>0.0018</td>
<td>0.027</td>
<td>0.977</td>
</tr>
<tr>
<td>5</td>
<td>1833.6</td>
<td>1225</td>
<td>949</td>
<td>30</td>
<td>300</td>
<td>0.0006</td>
<td>0.010</td>
<td>0.832</td>
</tr>
<tr>
<td>6</td>
<td>2038.6</td>
<td>1837</td>
<td>1429</td>
<td>330</td>
<td>300</td>
<td>0.0071</td>
<td>0.061</td>
<td>0.998</td>
</tr>
<tr>
<td>7</td>
<td>1945.6</td>
<td>1493</td>
<td>1157</td>
<td>110</td>
<td>280</td>
<td>0.0025</td>
<td>0.021</td>
<td>0.988</td>
</tr>
</tbody>
</table>

This resulted in an overall porosity change from 70% to up to 40% before the onset of decomposition, creating a thin and dense topmost layer. The initial relative weight loss was less than 1% and may be attributed to non-stoichiometry, contraction, and lattice defects [53]. $\Delta m$ was evaluated after 75 s to bypass initiation effects by sintering and to ensure negligible surface area change and stationary surface temperature $T_{\text{front}}$. $\Delta m$ resulted from the weight loss of the batch of ZnO packed-bed particles exclusively; no reaction between ZnO and Al$_2$O$_3$ was detected. Furthermore, the ZnO tile did not contribute to $\Delta m$ since its measured temperature $T_p$ was ~250 K lower than $T_{\text{front}}$, and its surface showed no sign of dissociation after each experimental run. The rate $dm/dt$ was determined based on the final sample diameter $d = 14.0 \pm 0.5$ mm (after sintering). The sample’s density, measured by pyknometer after the run, was $5.6 \pm 0.056$ g cm$^{-3}$.

The ZnO packed-bed surface temperature and sample weight loss as a function of time are shown in Fig. 3.1 during a representative TG run (No. 6).
Figure 3.1: Irradiated surface temperature $T_{\text{front}}$ and weight loss of the ZnO packed-bed particles as a function of time during a representative solar TG run (No. 6).

The ZnO packed-bed surface was heated to 1300 K at a rate of 150 K s$^{-1}$ once exposed to a mean solar concentration of 1400 suns, and further heated to 2038 K at a rate of 20 K s$^{-1}$. Color change from white to black was recorded by the CCD camera due presumably to non-stoichiometry at the surface [51] (formed by either preferential removal of O from the surface [49, 50] or outward diffusion of interstitial Zn [76]), which in turn resulted in a dramatic increase of the total effective absorptivity from 0.05–0.15 at room temperature [77] to about 0.9 at 2000 K [54]. Measurable weight loss was detected at above about 1825 K ($t = 30$ s) and continued at a constant rate until the shutter was closed and the run terminated. The packed bed of ZnO particles was subjected to a transient ablation regime, characterized by a rate of heat transfer—predominantly by radiation—to the top layer of the packed bed undergoing endothermic dissociation that proceeded faster than the rate of heat transfer—predominantly by conduction—to the depth of the packed bed.
$T_{\text{front}}$ and $\frac{dm}{dt}$ listed in Table 3.1 were used in the Arrhenius plot of Fig. 3.2. Applying a zero-order rate equation for linear advance of the interface in a single direction [78], the rate law is given in terms of the mass loss per unit of effective (irradiated) surface area as:

$$\frac{dm}{dt} = A k_0 e^{\frac{E_a}{RT_{\text{front}}}}$$  \hspace{1cm} (3.2)

The corresponding apparent activation energy $E_a = 361 \pm 53$ kJ mol$^{-1}$ K$^{-1}$ and frequency factor $k_0 = 14.03 \times 10^6 \pm 2.73 \times 10^6$ kg m$^{-2}$ s$^{-1}$, each at 95% confidence, were extracted by linear regression. The uncertainty bounds are mainly due to the emissivity value and the balance resolution. Note that, in contrast to conventional thermogravimetric runs, only the irradiated front surface shrinks in the solar TG, as a result of the ablative heat transfer characteristics in which the sample is subjected. A shrinking core model was not able to describe the reaction rate properly. Instead, an effective surface area $A$—the actual area of the ZnO sample exposed to the concentrated solar irradiation—was introduced in Eq. (3.2). For the $\frac{dm}{dt}$ values calculated in Table 3.1, $A$ was a circle of diameter $d = 14.0 \pm 0.5$ mm (determined after sintering), as the CCD camera showed that $A$ did not change during the thermal dissociation. The sample’s density, measured by pyknometer after the run, was $5.6 \pm 0.056$ g cm$^{-3}$.

Previous studies have identified surface diffusion as the rate-controlling step during the early stages of sintering with activation energies in the range 12.5–106 kJ mol$^{-1}$, and lattice diffusion during the intermediate and final stages of sintering at above the Tamman temperature of ZnO (~1124 K), with activation energies in the range 223–276 kJ mol$^{-1}$ [79–81].
Figure 3.2: Arrhenius plot for the rate law, Eq. (3.2).

For all runs listed in Table 3.1, the high heating rates achieved with concentrated solar radiation resulted in rapid sintering of the ZnO sample prior to any dissociation recorded by the weight loss, as expected from the higher activation energy of dissociation as compared to that of sintering. A SEM of a cross section, 3 mm behind the irradiated surface of a ZnO sample that underwent sintering and dissociation at $T_{\text{front}} = 1960$ K for 290 s is shown in Fig. 3.3. Non-interconnected pores of $0.3–0.8 \mu$m diameter are predominantly located at the grain boundaries, as previously observed during final stages of sintering at about 1650 K [81]. The dissociation of ZnO occurred mainly at the external surface exposed to concentrated solar radiation, supporting the ablation regime. Note that thermal dissociation reactions conducted under concentrated solar energy at 2000 K and above have been shown to be primarily limited by the rate at which the gaseous products diffuse from sample surface [47, 82–84]. The diffusion of gaseous products from the ZnO surface into the surrounding gas was found to be rate-controlling mechanism also at lower temperatures (1013 K) [53].
Thus, $k_0$ may strongly depend on the purge gas conditions, and can be appropriately determined as a function of the purge gas flow rate by applying L’vov theory [85], shown in the next section. In the range 1800–2100 K, the equilibrium pressure of the product gases varies by more than one order of magnitude, while $k_0$ varies by only 13% in that range and is practically insensitive to the change in the thermodynamic equilibrium conditions.

### 3.2.2 Comparison with Published Data

The value of $E_a$ is in good agreement with those found previously [47, 48, 54, 71]. Figure 3.4 shows the rate of ZnO dissociation as a function of temperature, in terms of mass loss per unit time of the experimental data listed in Table 3.1 (data points), and by applying the rate law, Eq. (3.2), derived here (solid curve). Also included are the ZnO dissociation rates calculated using the rate laws derived by Möller and Palumbo [54] and by Perkins et al. [47].
Figure 3.4: ZnO dissociation rate vs. temperature for the rate law derived in the present study (Eq. 3.2), and for those derived by Möller and Palumbo [54] and by Perkins et al. [47]. The data points correspond to the values obtained experimentally.

Note that Möller and Palumbo applied a zero-order kinetic model to presintered ZnO pellets, while Perkins et al. applied a shrinking core model to particulate ZnO,

\[
\frac{d\alpha}{dt} = k^* e^{-\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)} \left( 1 - \alpha \right)^{2/3}
\]  

(3.3)

with \( T_0 = 1895 \text{ K} \), \( E_a = 353 \pm 25.9 \text{ kJ mol}^{-1} \), and \( k^* = 3.58 \times 10^{-4} \pm 6.30 \times 10^{-5} \text{ s}^{-1} \) determined by conventional (non-solar) thermogravimetry, i.e. without direct solar irradiation. Reasonable good agreement is found between the curve of this study, obtained by on-line measurements, and that predicted by Möller and Palumbo [54], calculated from the weight loss measured after the reaction. In contrast, Perkins et al. [47] predict a reaction rate that is about one order of magnitude higher because of the fundamental differences in heat and mass transfer mechanisms and surface area per unit
masse between their experimental setup (extrapolated to an aerosol flow reactor) and the ZnO packed bed of the present study. Exposing the sample to high-flux solar irradiation provides an efficient means of radiative heat transfer directly to the reaction site. The UV portion of the incident radiation may photochemically enhance the reaction kinetics [86]. However, the high heating rates applied to the packed bed significantly alter the reacting surface by sintering. Similar ZnO sintering was observed with microwave heating at densification rates which are up to four times faster compared to low heating rates typical for laboratory thermogravimetric runs [87, 88].

3.2.3 Comparison with L’vov’s Kinetic Theory

It is possible to estimate the frequency factor from the thermodynamic properties of the materials and from the convective flow conditions by applying L’vov’s kinetic expressions [85] based on the Hertz–Knudsen–Langmuir theory for a condensing substance in an inert gas environment and in thermodynamic equilibrium. The following expressions for the Arrhenius kinetic parameters are employed:

\[ E_a = \frac{\Delta H^o_r}{a + b} \]  

\[ k_0 = \frac{M_M D_M a^{\frac{a}{a+b}} b^{\frac{b}{a+b}}}{zRT} \left( \frac{a}{a^{\frac{a}{a+b}} b^{\frac{b}{a+b}}} \right) e^{\frac{\Delta S^o_r - R(a+b)}{R(a+b)}} \]  

where \( D \) is the binary diffusion coefficient of oxygen (O) or metal (M) in the buffer gas, \( M_M \) the molecular mass of the solid, \( a \) and \( b \) are the stoichiometric coefficients of metal and oxygen in the starting oxide, respectively, \( T \) is the temperature of decomposition, \( \Delta H^o_r \) and \( \Delta S^o_r \) are the standard entropy and enthalpy of reaction, respectively, and \( R \) is the ideal gas constant. \( z \) is the diffusion distance to the buffer gas location where the concentration of the
substance drops to zero, which approaches the free molecular path length of the product gases for decomposition into vacuum [85]. For ZnO decomposition in an Ar buffer gas atmosphere, the convective mass transport coefficient is introduced [89], \( k = D/z \), and calculated using a correlation for a flow normal to a disk [90]:

\[
\text{Sh} = \frac{kd_{\text{cylinder}}}{D} = \frac{8}{\sqrt{2\pi}} \left( \frac{d_{\text{aperture}}}{d_{\text{cylinder}}} \right)^{1/2} \left( \frac{\text{Re} \, \text{Sc} \, d_{\text{aperture}}}{4L_{\text{front-aperture}}} - \frac{d_{\text{cylinder}}}{d_{\text{aperture}}} \right)^{1/2}
\]

(3.6)

The characteristic lengths for the Sherwood (Sh), Reynolds (Re), Schmidt (Sc) numbers are based on the cylinder diameter \( d_{\text{cylinder}} \), aperture diameter \( d_{\text{aperture}} \), and the distance between the cylinder front surface and aperture \( L_{\text{front-ap}} \). At 2000 K and for \( L_{\text{front-aperture}} = 0.05 \) m, \( d_{\text{aperture}} = 0.06 \) m, \( d_{\text{cylinder}} = 0.007 \) m, \( \text{Re} = 22.1 \), \( D_{\text{Zn-Ar}} = 535.7 \times 10^{-6} \) m\(^2\) s\(^{-1}\) [91], and \( \text{Sc} = 0.63 \), Eq. (3.6) yields \( \text{Sh} = 18.56 \), \( k = 0.70 \) m s\(^{-1}\), and \( z = 771 \times 10^{-6} \) m. Further applying Eq. (3.5) for \( D_{\text{O-Ar}} = 962.4 \times 10^{-6} \) m\(^2\) s\(^{-1}\) [92], \( \Delta H_{\text{r}} = 712.3 \) kJ mol\(^{-1}\), and \( \Delta S_{\text{r}} = 272.4 \) J mol\(^{-1}\) K\(^{-1}\) at 2000 K, it yields \( k_0 = 5.99 \times 10^6 \) kg m\(^{-2}\) s\(^{-1}\), which is of the same order of magnitude as the experimentally determined value. Discrepancies may be attributed to turbulences in the Ar flow from its injection position at the quartz window across the aperture to the ZnO sample surface, and buoyancy effects at the hot ZnO sample surface. Equations (3.5) and (3.6) may be used to evaluate \( k_0 \) at buffer gas flow conditions different to those observed in the present study. Since Sh scales with the square root of the flow velocity, the reaction kinetics can be enhanced by increasing the flow velocity across the ZnO surface. Using Eq. (3.4), \( E_a = 356 \) kJ mol\(^{-1}\), which compares well with the value experimentally determined.

Operating conditions were typical of an ablation regime controlled by the rate of radiative heat transfer to the first layers of ZnO undergoing endothermic dissociation, as shown in the next Chapter. The ZnO
dissociation reaction occurred in the topmost layers at the highest temperatures, as radiative transfer to the exposed (effective) surface proceeded at a faster rate than heat conduction across the packed-bed.

3.3 Conclusion

An experimental investigation was carried out using a novel solar-driven thermogravimeter for the determination of the ZnO dissociation kinetics under direct high-flux solar irradiation in a solar furnace. Experimental data was fitted to a zero-order Arrhenius rate law, yielding an apparent activation energy that is in close agreement with the theoretical value obtained by applying L’vov’s kinetic expressions along with a correlation for convective mass transport across the ZnO packed-bed surface. Sintering was observed prior to ZnO dissociation. The packed bed of ZnO particles was subjected to an ablation regime characterized by a rate of radiative heat transfer to the top layer of ZnO packed bed undergoing endothermic dissociation that proceeded faster than the rate of conductive heat transfer to the depth of the packed bed.
4  Ablative Heat Transfer in the Packed-Bed of ZnO

The fundamental understanding of the heat and mass transfer phenomena occurring in the packed-bed of reacting ZnO particles required the extension of the previous kinetic analysis to an energy/mass transport model of a packed-bed reactor that couples the rates of radiation, conduction, and convection heat transfer with the rate of the reaction. The experimental data obtained with the solar-driven thermogravimeter, presented in Chapter 3, and additional experimental runs with sample #1, shown in Chapter 2.2, were used for the determination of the thermal transport properties of the packed-bed of ZnO particles and for validating the packed-bed reactor model.

4.1 Heat Transfer Model

The schematic of the domain of the heat transfer model for sample #2 is depicted in Fig. 4.1. The packed-bed of ZnO particles is represented by \( N = 100 \) initially equally-spaced shrinking differential volumes, the ZnO tile and the insulation by \( N = 20 \), and \( N = 30 \) non-shrinking differential volumes, respectively.

\[ \]

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\( ^1 \) Material from this chapter is published as [93]: L. O. Schunk, W. Lipiński, A. Steinfeld. Ablative heat transfer in a shrinking packed-bed of ZnO undergoing thermal dissociation. AIChE Journal, in press.
Figure 4.1: Schematic of the domain of sample #2. The packed-bed of ZnO particles is equally divided into 100 shrinking differential volumes, the ZnO tile and the insulation by 20 and 30 non-shrinking volumes, respectively.

**Mass conservation** – The transient mass conservation equation is given by:

\[
\frac{dn_{ZnO}}{dV \, dt} = r^m
\]  

(4.1)

where \(dV\) is a differential volume of ZnO shrinking with time as the sample undergoes sintering and thermal dissociation. The ZnO dissociation rate is modeled by applying a zero-order Arrhenius-type rate law,

\[
r^m = -\frac{k^*}{M_{ZnO}} \, e^{-\frac{E_a}{RT}}
\]  

(4.2)

where \(k^* = \alpha k_0\) with the specific surface area \(\alpha\). The kinetic parameters \(E_a = 361 \text{ kJ mol}^{-1}\) \(k_0 = 14.03 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}\) were determined using the solar TG for ZnO samples directly irradiated in a solar furnace, as shown in Chapter 3.

**Energy conservation** – The transient pseudo 1-D energy conservation equation is given by:

\[
\rho c_p \frac{\partial T}{\partial t} = \nabla (k_{\text{eff}} \nabla T) + q^m_{\text{radiative}} - \Psi(t) \varepsilon_{\text{internal}} \sigma (T^4 - T_{\text{cavity}}^4) + q^m_{\text{chemistry}}
\]  

(4.3)
where $\Psi(t)$ is the lateral surface area to volume ratio of the cylindrical sample and $q''''_{\text{radiative}}$ arises from absorption and from emission of inner volumes, which are exposed to incident solar energy during the sintering process,

$$q''''_{\text{radiative}} = \frac{A}{V} \left[ \alpha_s q''_{\text{solar}} - \sigma \epsilon \left( T^4 - T_{\text{cavity}}^4 \right) \right] \quad (4.4)$$

$q''_{\text{solar}}$ is the incident solar flux and $A$ represents the irradiated surface area between incremental volumes of different diameter. $q''''_{\text{chemistry}}$ is the volumetric heat sink rate due to the endothermic ZnO dissociation given by the product of the reaction rate and enthalpy change $\Delta H_r$ in J mol$^{-1}$ [65],

$$q''''_{\text{chemistry}} = r'''' \Delta H_r (T)$$

$$= r'''' \left( 4.851 \times 10^5 - 13.13 T - 2.164 \times 10^{-3} T^2 \right) \quad (4.5)$$

The boundary conditions at the directly irradiated surface, $x = L(t)$ and at the back surface, $x = 0$ and initial conditions for Eq. (4.3) are given in Eqs. (4.6–4.8), respectively, as:

$$k_{\text{eff}} \frac{\partial T}{\partial x} = h_{\text{front}} \left( T_{\text{gas}} - T \right) + \epsilon \sigma \left( T_{\text{cavity}}^4 - T^4 \right) + \alpha_s q''_{\text{solar}} \quad (4.6)$$

$$k_{\text{eff}} \frac{\partial T}{\partial x} = \epsilon \sigma \left( T^4 - T_{\text{cavity}}^4 \right) \quad (4.7)$$

$$T(x, t = 0) = T_0 \quad (4.8)$$

The effective thermal conductivity is given by the sum of the conductive and radiative contributions:

$$k_{\text{eff}} = k_{\text{conductive}} + k_{\text{radiative}} \quad (4.9)$$

For the optically-thick packed-bed, the Rosseland diffusion approximation [94] is applied:
The thermal conductivity of the porous packed-bed of ZnO particles, is given by [95]

\[ k_{\text{radiative}} = 16n^2/(3\beta) \sigma T^3 \]  

\[ (4.10) \]

where the porosity \( p \) of the batch is calculated in the following section and the deformation factor for spherical particles is given by [95] \( B = 1.25(1 - p/p_n)^{1/3} \). \( k_{\text{ZnO}} \) decreases from 27 to 6 W m\(^{-1}\) K\(^{-1}\) in the interval 295–973 K for hot-pressed ZnO particles [96], while decreases from 37 to 4 W m\(^{-1}\) K\(^{-1}\) in the interval 295–1273°K for fully sintered ZnO [97]. The latter results are used in this study to approximate \( k_{\text{ZnO}} \) by an exponential fit,

\[ k_{\text{ZnO}}(T) = 59.145 e^{-2 \times 10^{-3} T} \]

The spectral emissivity of ZnO is assumed constant over the entire spectral and temperature ranges considered in the present study, and equal to 0.69 as measured at 1.39 \( \mu \)m and 2000 K [74]. The absorptivity on the other hand is assumed to increase with temperature (see Section 4.2). The convective heat transfer coefficient \( h_{\text{front}} \) is obtained by employing the Nu correlation for a circular disc exposed to a perpendicular fluid flow [90],

\[ Nu = \frac{8}{\sqrt{2\pi}} \left( \frac{2d_{\text{aperture}}}{d_{\text{cylinder}}} \right)^{1/2} \left( \frac{d_{\text{aperture}} \Re \Pr}{4L_{\text{front-aperture}}} - \frac{2d_{\text{cylinder}}}{d_{\text{aperture}}} \right)^{1/2} \]

\[ (4.12) \]
The characteristic lengths for Nu and Re are based on the cylinder diameter $d_{\text{cylinder}}$, aperture diameter $d_{\text{aperture}}$, and the distance between the cylinder front surface and aperture $L_{\text{front-aperture}}$. The bulk gas temperature $T_{\text{gas}}$ is taken to be equal the measured mean cavity temperature $T_{\text{cavity}}$. Convective heat transfer at the lateral and back surfaces is assumed negligible as compared to radiative heat transfer between these surfaces and the cavity walls, and hence omitted from the analysis. The variation of heat capacities and thermal conductivities of the insulation materials are incorporated as a function of temperature [98, 99]. The finite volume method and the explicit Euler time integration scheme are applied for solving Eqs. (4.1) and (4.3), which are integrated over shrinking circular disc elements $\Delta V$ and over a finite time step $\Delta t$. The rates of shrinking in the radial and axial directions are determined independently for each finite volume based on the rates of sintering and ZnO-dissociation, as elaborated in the next section.

**Sintering** — is assumed to be isotropic and following three idealized, sequential stages [100, 101]. Transitions from the initial to the intermediate and final stages occur at relative densities $\rho/\rho_p = 0.65$ and 0.95, respectively [102]. In each stage, lattice diffusion from the grain boundary is assumed to be the controlling mechanism with suppressed grain growth, as observed experimentally for microwave-sintered ZnO samples subjected to heating rates comparable to those in this study [87]. Grains are assumed to have tetrakaidecahedral shape. In the initial stage, the density and the relative linear shrinkage $Y = (L - L_0)/L_0$ (where $L$ is either $x$ or $d$) are obtained from [102]:

$$\rho = \rho_0 (1 + Y)^{-3}, \quad Y = \left( \frac{80 \pi D \gamma_{sv} \Omega}{2^b (G / 2)^a k_B T} \right)^{2/b}, \quad (4.13)$$

where $G = 14 \ \mu m$ is the grain size, $\gamma_{sv} = 1 \ \text{J m}^{-2}$ [81] is the specific surface energy of ZnO, $k_B$ is the Boltzmann constant, and $\Omega = 2.4 \times 10^{-29} \ \text{m}^3$ [81] is
the vacancy volume of ZnO. \(D\) in m\(^2\) s\(^{-1}\) is the diffusion coefficient, obtained by fitting to a lattice diffusion model [80],

\[
D = 1.72 \cdot \exp\left(-\frac{276 \pm 13 \text{kJ} \cdot \text{mol}^{-1}}{RT}\right).
\]  

(4.14)

In the intermediate and final stages, the density variation due to sintering is obtained from [102]:

\[
\frac{1}{\rho} \frac{d\rho}{dt} = 40 \left(\frac{D \Omega}{G^a k_B T}\right) \left(b \gamma_{sv} \right) \frac{r_p}{r_p}
\]  

(4.15)

Coefficients \(a\) and \(b\) of Eqs. (4.13) and (4.15) are listed in Table 4.1. \(r_p\) is the mean pore size approximated by \(r_p \approx 0.1967 \sqrt{p G}\) [102].

Table 4.1: Coefficients \(a\) and \(b\) in Eqs. (4.13) and (4.15) for initial, intermediate, and final stages of the sintering model [102].

<table>
<thead>
<tr>
<th>Initial stage</th>
<th>Intermediate stage</th>
<th>Final stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>(b)</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

The linear shrinkage in the intermediate and final stages is due to the combined sintering and mass change due to the chemical reaction. Thus,

\[
\frac{dx}{dt} = \frac{x dd}{dt} = \frac{4\Delta V \left(\frac{d\rho}{dt} - r''M\right)}{3\rho \pi d^2}
\]

(4.16)

where \(\Delta V\) is the size of a finite volume.
4.2 Results

4.2.1 Radiative Properties

A selected solar experimental run is performed with sample #1 (presented in Chapter 2.2) to determine the extinction coefficient $\beta$ and the surface absorptance $\alpha_s$ for dense ZnO by fitting the numerically calculated temperatures to those experimentally measured. In this specific run, dissociation is neglected because temperatures were kept below 1810 K and the final measured reaction extent was only 0.65%. $\beta$ is assumed to be constant. $\alpha_s$ is assumed to be proportional to the values of the mean grey scale intensity of the irradiated surface, measured online with the CCD camera,

$$\alpha_s = \alpha_{s,\text{min}} + \left[ I_{\text{max}} - I(t) \right] \frac{\alpha_{s,\text{max}} - \alpha_{s,\text{min}}}{I_{\text{max}} - I_{\text{min}}}.$$  \hspace{1cm} (4.17)

The sample is exposed to a step-wise increasing solar flux $q_{\text{solar}}'$ ranging from 0.16 to 0.90 MW m$^{-2}$, as shown in Fig. 4.2. The measured and computed temperatures $T_{\text{front}}$ and $T_p$ are also shown in Fig. 4.2. Best fit was obtained for $\beta = 1900$ m$^{-1}$, $\alpha_{s,\text{min}} = 0.15$, and $\alpha_{s,\text{max}} = 0.95$. The values of $\alpha_{s,\text{min}}$ and $\alpha_{s,\text{max}}$ are consistent with previous reports at 295 and 2000 K, respectively [54, 103]. The value of $\beta$ is lower than that for a mixture of ZnO and C at room temperature [104], most likely due the different composition and temperatures, along with the uncertainty of $k_{\text{ZnO}}$. The extinction coefficient of the porous packed-bed is computed as [105]:

$$\beta_{\text{porous}} = (1-p) \beta$$  \hspace{1cm} (4.18)
Figure 4.2: Experimentally measured incident solar flux, experimentally measured and numerically calculated temperatures on the irradiated front surface $T_{\text{front}}$, and behind the ZnO tile $T_p$, as a function of time for sample #1.

Finally, $k_{\text{eff}}$, defined in Eq. (4.9), in $\text{W m}^{-1}\text{K}^{-1}$ is represented for $p = 0$ and $T \geq 1200$ K by:

$$k_{\text{eff}}(T) = \frac{59.145 e^{-2 \times 10^{-3} T} + 3.02 \times 10^{-10} T^3}{k_{\text{conductive}} + k_{\text{radiative}}}$$  \hspace{1cm} (4.19)

### 4.2.2 Temperatures and Chemical Conversion

Seven solar experimental runs with sample #2 were carried out as presented in Chapter 3; their operational conditions are listed in Table 3.1. The specific surface area $a = 840 \text{ m}^{-1}$ was iteratively found by fitting experimentally measured and numerically calculated dissociation rates for all 7 runs, as shown in the Arrhenius-type plot of Fig. 4.3.
Figure 4.3: Arrhenius plot for the experimentally measured and numerically calculated reaction rates. The solar run numbers are indicated by labels adjacent to the data points.

Measured and calculated temperatures and weight loss for runs No. 2 and 3 are shown as a function of time in Figs. 4.4 and 4.5, respectively. The sample was subjected to a stepwise increasing solar flux with $q'_{\text{solar,max}} = 1.22$ MW m$^{-2}$, whereas maximum solar flux $q''_{\text{solar,max}} = 1.17$ MW m$^{-2}$ was applied during run No. 3 at $t = 0$ s. The agreement for $T_{\text{front}}$ is reasonable well for both runs. The sudden increase for run No. 2 at $t = 362$ s is due to an increase in $q''_{\text{solar}}$ from 0.64 to 1.21 MW m$^{-2}$, while the sudden decrease for run No. 3 at $t = 416$ s is due to the termination of the run and interruption of $q''_{\text{solar}}$. Discrepancy between measured and calculated $T_p$ is observed during the initial stages, attributed to an overestimation of the sintering rate, which in turn resulted in an overestimation of $k_{\text{eff}}$ and, consequently, faster heating of the packed-bed of ZnO particles. On the other hand, the model is able to predict with good accuracy the weight loss, occurring at $T_{\text{front}} > 1000$ K.
Figure 4.4: Experimentally measured and numerically calculated temperatures on the irradiated front surface $T_{\text{front}}$, and behind the ZnO tile $T_p$, and weight loss as a function of time for run No. 2.

Figure 4.5: Experimentally measured and numerically calculated temperatures on the irradiated front surface $T_{\text{front}}$, and behind the ZnO tile $T_p$, and weight loss as a function of time for run No. 3.
Figure 4.6: Modeled temperature profiles across the ZnO packed-bed of ZnO particles at times $t = 10, 20, 30, 40, 50, 70, 100$ and $400$ s for run No. 3.

The temperature profiles across the packed bed of ZnO particles are shown in Fig. 4.6 for run No. 3. The parameter is the reaction time, $t = 10–400$ s. Shrinking due to sintering and dissociation is clearly observed. The front surface retraces from its axial position $x = 0.04$ m to $0.037$ m in the first $100$ s due mainly to shrinkage, and afterwards due mainly to dissociation as $T_{\text{front}}$ exceeds $1878$ K. The advance of sintering is also manifested by the change of $k_{\text{eff}}$ and the temperature gradients across the packed-bed: Evidently, as sintering progresses and the bed shrinks, $p$ decreases and $k_{\text{eff}}$ increases, resulting in low $\Delta T$ across the bed.

The local dissociation rates across the packed-bed for run No. 3 are shown in Fig. 4.7, along with the cumulative dissociation, defined as:

$$X(x,t) = \frac{\int_0^t d^2r'' dx}{\int_0^t d^2r'' dx}$$

(4.20)
Figure 4.7: Modeled dissociation rate and cumulative dissociation across the ZnO packed-bed at $t = 100, 200,$ and $400$ s for run No. 3.

The parameter is the reaction time, $t = 100, 200, 300,$ and $400$ s. As expected, the maximum dissociation rate $r_{\text{max}}^{\prime \prime \prime}$ is found at the front layer exposed to direct solar irradiation, where the temperature is the highest. However, it decreases rapidly towards the inner layers as a result of the Arrhenius dependency. $r_{\text{max}}^{\prime \prime \prime}$ increases from $1.08$ kg m$^{-3}$ s$^{-1}$ at $t = 100$ s to $2.55$ kg m$^{-3}$ s$^{-1}$ at $t = 400$ s as the temperature of the entire packed-bed increases. Interestingly, $X$ rapidly drops in the first few millimeters since most of the dissociation reaction occurs there. For example, at $t = 100$s, $92\%$ of the reaction occurs within an active layer of $2$ mm thickness. The active layer thickness increases with time and temperature: at $t = 400$ s, $90\%$ of the reaction occurs within the first $4$ mm of the sample. Thus, the packed-bed is subjected to an ablation regime controlled by the rate of heat transfer by radiation to the endothermic reaction. The active layer corresponds approximately to the thickness of the ablated surface region of the sample, which contains small cracks, needles, and ridges.
Figure 4.8: SEM of the product sample after the solar run No. 3 for: (a) a layer near the irradiated surface, and (b) layer in the vicinity of the ZnO tile at $x = 0.029$ m. The sample was prepared by breaking-up the sample along a crack that resulted from rapid sintering of ZnO.

SEM images of the product sample after the solar run No. 3 are shown in Fig. 4.8 for: a) a layer near the irradiated surface, and b) a layer in the vicinity of the ZnO tile at $x = 0.029$ m. The irradiated surface exhibits pores and cracks, suggesting that product gases Zn(g) and O$_2$ can escape through these cracks and ridges, bypassing the limitation imposed by diffusion through small pores at the dense regions of the bed. The deeper layer is fully sintered and is characterized by grain sizes in the range 5–30 μm.

4.3 Conclusions

A pseudo 1-D transient numerical model has been developed for simulating an irradiated packed-bed of ZnO particles undergoing sintering and thermal dissociation. The governing mass and energy conservation equations that couple the radiative, conductive, and convective heat transfer to the kinetic rate of the dissociation reaction were formulated and solved numerically by the finite volume method using the explicit time integration scheme. The thermal transport properties, namely the extinction coefficient, the surface
absorptivity, and the effective thermal conductivity were obtained by fitting measured and calculated temperatures for a selected run without reaction. The ZnO dissociation reaction occurred in the topmost layers at the highest temperatures which is typical of an ablation regime, as radiative transfer to the endothermic reaction proceeded at a faster rate than conduction across the packed-bed.
5 Solar Reactor Development

For the first solar step, the proposed chemical reactor concept is based on a rotating cavity receiver lined with ZnO particles that are held by centrifugal force and directly exposed to high-flux irradiation \[41\]. With this arrangement, ZnO serves simultaneously as radiant absorber, chemical reactant, and thermal insulator. A 10 kW reactor prototype was fabricated and tested in PSI’s solar furnace by first effecting the carbothermal reduction of ZnO in the range of 1400–1800 K \[36\]. However, at the higher temperatures required for the ZnO dissociation (>2000 K), mechanical stability problems were encountered with the Hf/HfO\(_2\)-based cavity as a result of the heating and cooling cycles and operation in an oxidizing atmosphere \[107\]. In this chapter, an improved reactor design is presented that eliminates the material related problems.

5.1 Reactor Design

A schematic of the 10 kW solar reactor configuration is depicted in Fig. 5.1. Its main component is a 160 mm diameter rotating cylindrical cavity (1) composed of fully sintered ZnO tiles glued on top of porous 80\%Al\(_2\)O\(_3\)-20\%SiO\(_2\) insulation (2) with a ceramic adhesive of the same composition. Dimensions of the solar reactor prototype are listed in Table 5.1.

---

Figure 5.1: Schematic of the solar chemical reactor configuration: (1), rotating cavity lined with sintered ZnO tiles; (2), 80%Al₂O₃-20%SiO₂ insulation; (3), 95%Al₂O₃-5%Y₂O₃ CMC; (4), alumina fibers; (5), Al reactor shell; (6), aperture; (7), quartz window; (8), dynamic feeder; (9), conical frustum; and (10), rotary joint.

Figure 5.2: Reactor’s cavity made from ZnO tiles (1) and 80%Al₂O₃-20%SiO₂ insulation (2). Not seen here are the ZnO tiles on the lateral back and front walls. The cavity’s inner diameter is 160 mm.
Table 5.1: Main geometric parameters of the 10 kW solar reactor prototype.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10 kW reactor prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture diameter, mm</td>
<td>60</td>
</tr>
<tr>
<td>Window diameter, mm</td>
<td>240</td>
</tr>
<tr>
<td>Cavity diameter, mm</td>
<td>160</td>
</tr>
<tr>
<td>Cavity length, mm</td>
<td>230</td>
</tr>
<tr>
<td>Cavity exit diameter, mm</td>
<td>80</td>
</tr>
<tr>
<td>Insulation thickness, mm</td>
<td>120</td>
</tr>
<tr>
<td>Mantle thickness, mm (Al)</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5.2 shows the arrangement of the 32 ZnO tiles and the Al₂O₃ insulation on the cavity walls. The ZnO tiles are resistant to thermal shocks, partly due to their relatively high thermal conductivity: 37 W m⁻¹ K⁻¹ at room temperature and decreasing to 4 W m⁻¹ K⁻¹ at 1273 K. They serve primarily as thermal shock absorber and, to a lower extent, as thermal insulator. The maximum allowable temperature at the interface between tiles and insulation is the eutectic phase temperature of the system ZnO-Al₂O₃-SiO₂ [108], around 1930 K, as determined in separate tests using the solar TG with samples directly exposed to concentrated solar radiation [109]. The ZnO tiles were replaced in the second experimental campaign (Chapter 6.2) by Al₂O₃ tiles because they exhibit a maximum allowable temperature ~2000 K [108] and showed good thermal shock resistance, as determined in material tests with the solar TG. The outermost cavity layer (3) is made of 1.5 mm thick 95%Al₂O₃-5%Y₂O₃ CMC, which provides both mechanical stability and a diffusion barrier for product gases. The volume between the CMC and the aluminum reactor shell (5) is packed with insulating alumina fibers (4). Concentrated solar radiation enters the cavity through a 3 mm thick quartz window (7), which is mounted on a water-cooled aluminum ring and integrated to the front face of the cavity via a conical frustum (9) that contains a 60 mm diameter aperture (6). The reactor has a dynamic feeder (8).
that extends and contracts within the cavity, and enables to evenly spread out a layer of ZnO particles of desired thickness along the entire cavity. The rotational movement along the horizontal axis generates a centripetal acceleration that forces the ZnO particles to cover the cavity wall, thereby creating an efficient use of the cavity space for radiation heat transfer to the reaction site. The feeder tip is protected from the hot cavity by a cap made of dense Al₂O₃, compound to a disk of alumina insulation, all packed into a 1 mm thick layer of alumina CMC.

Inert gas (Ar) is injected through nozzles located around the frustum, creating an aerodynamic curtain that protects the window from condensable Zn(g). The inert gas carries the gaseous products Zn(g) and O₂ to the exit of the cavity and flows along the annular gap between the water-cooled feeder (8) and a water-cooled rotating cylinder wall, referred to as the “quench unit.” The cold walls and the injection of cold Ar promote the rapid quench of Zn(g) to Zn(s). The feeder can be retracted and scraped clean from deposited solids.

5.2 CFD Design of the Aerodynamic Window Protection

Condensation of gaseous products and deposition of aerosols on the window may deteriorate its transmissivity, resulting in lower reactor efficiency and eventually leading to the destruction of the window. CFD was employed to determine Ar nozzle locations and orientations for optimum flow configuration of the aerodynamic window protection.

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1 CFD simulations presented in this chapter have been performed within the framework of [110]: P. Leu. Untersuchung einer Tornado-Gasführung im Zirrus Solarreaktor mit CFD. Master Thesis, ETH Zürich, 2006.

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Figure 5.3: (a) Velocity in m s\(^{-1}\), (b) temperature in K, (c) and Zn(g) mole fraction fields in the central cross section of the reactor for the best flow configuration.

ANSYS CFX [111] code was used to solve the governing three-dimensional Navier–Stokes equations for simulating the flow patterns akin to the natural tornado phenomenon [112]. The quadratic Reynolds shear stress turbulence model was applied because it best copes with turbulence effects of rotational flows [113]. Modes of heat transfer considered were convection and conduction. Radiative transfer was omitted for simplification since the emphasis was on obtaining the fluid flow field in the proximity of the window. The boundary wall temperatures applied correspond to the
experimentally measured values. The window, frustum, and cavity temperatures were set to 900 K, 900 K, and 2000 K, respectively. The rate of ZnO dissociation into Zn(g) and O₂ at 2000 K was set to 0.17 g s⁻¹ [107]. The flow configuration leading to the lowest concentration of Zn(g) close to the window was obtained by injecting Ar gas through 12 nozzles of 2.5 mm diameter in the radial direction at a plane next to the window and through 6 nozzles of 1.7 mm diameter at an angle of 45 deg with respect to the radial direction at the aperture plane. The Ar mass flow rate through each nozzle was 0.032 g s⁻¹ at the window and was 0.02 g s⁻¹ at the aperture. Figure 5.3 shows (a) the velocity, (b) temperature, and (c) Zn(g) mole fraction fields in the central cross section of the reactor for the best flow configuration.

Due to the frustum shape of the reactor’s front part, eddy flow patterns formed close to the window. These eddies did not extend beyond the aperture and, therefore, did not carry products by convection from the cavity compartment to the window. However, further increase of the Ar flow rate resulted in the breakdown of the vortex flow pattern in the frustum’s region, leading to backflow from the cavity toward the window. Preheated Ar gas entered the reactor at 900 K; a mixture of Ar and product gases Zn(g) and O₂ exited the reactor at 1350 K. The gas temperature increase resulted from convective heat transfer between fluid and cavity walls and from the generation of Zn(g) and O₂ at 2000 K. The Zn(g) mole fraction was in the range of $7 \times 10^{-6} – 18 \times 10^{-6}$ at the plane located 4 mm from the window and was in the range of 0.01–0.66 inside the cavity.
5.3 Experimental Setup

Experimentation was carried out at PSI’s high-flux solar simulator (HFSS) [114], shown in Fig. 5.4.

Figure 5.4: Schematic of the optical layout of the PSI’s high flux solar simulator (HFSS), comprising 10 high-pressure xenon arc lamps, each close-coupled to a truncated ellipsoidal reflector (left) [114], and photograph (right). Main visible features are the 10 xenon arcs with their truncated ellipsoidal reflectors, and a calorimeter-reactor.

This research facility comprises an array of ten 15 kW_e high-pressure xenon arcs, each close coupled with truncated ellipsoidal specular reflectors of common focus. It provides an external source of intense thermal radiation (radiative power >50 kW, power flux >10,000 suns) that closely approximates the heat transfer characteristics of highly concentrating solar systems, such as solar towers and solar furnaces; yet, it enables experimental work under controlled steady and unsteady conditions for reproducible measurements and model validation. The experimental setup of the 10 kW reactor prototype with peripherals is schematically shown in Fig. 5.5.
Figure 5.5: Experimental setup of the solar reactor and peripherals at PSI’s HFSS.

Power fluxes incident on the reactor were measured optically with a calibrated CCD camera on a water-cooled Al₂O₃-plasma coated Lambertian target. Radiative power input into the reactor was calculated by numerically integrating the radiative flux over the reactor’s aperture and accounting for the window’s mean transmissivity of 93%. Temperatures at various locations of the back side of the ZnO tiles were measured with Type-B thermocouples. The temperature measured halfway along the back side of the ZnO tiles is referred to as the “cavity temperature.” Pyrometry was not applied because of the intense reflected radiation over a wide spectrum. Ar gas flow rates were controlled using electronic flow meters (Bronkhorst HI-TEC). The outlet product gas flow rate was measured with an electronic flow meter (Bronkhorst LOW-ΔP flow). The composition of the product gases was monitored by gas chromatography (GC) (Agilent High Speed Micro GC G2890A, equipped with molecular sieve 5A and HaySep A capillary columns), by IR-based detectors for CO and CO₂ (Siemens Ultramat 23), and by thermal conductivity-based detector for O₂ (Siemens Calomat 6 and Oxymat 6). The GC has a 10 ppm detection limit at a sampling rate of
0.33 min⁻¹. The IR detector has a 0.2% detection limit at a sampling rate of 1 s⁻¹. The conductivity-based detector has a 50 ppm detection limit at a sampling rate of 1 s⁻¹. Solid particles were collected downstream in a polytetrafluorethen (PTFE) filter with a pore size of 0.2 μm, and analyzed after termination of each experiment by X-ray diffraction (XRD, Philips Xpert, Fe Kα, λ = 1.93740 Å). The presence of CO and CO₂ was monitored to ensure that ZnO was not reduced carbothermally.
6 Solar Reactor Experimentation

In the previous chapter, a reactor design was presented which allowed experimental operation up to 1930 K, measured behind the ZnO cavity tiles. The focus of the experimental study presented in Chapter is the demonstration of the reactor concept, i.e. reliable operation and the measurement of O\(_2\) as the main indicator of the ongoing ZnO dissociation reaction. The experimental campaign using ZnO cavity tiles is presented in Section 6.1, the campaign with Al\(_2\)O\(_3\) cavity tiles in Section 6.2. The focus of the latter campaign lay in closing the Zn mass and gas balance of ZnO→Zn+0.5O\(_2\) reaction, determining the solar-to-chemical energy conversion efficiency and investigating the quenching of Zn(g) and O\(_2\) to avoid recombination. The quench section was slightly modified to allow variation of quench flow rates and cooling rates [115].

6.1 ZnO Cavity\(^1\)

Table 6.1 summarizes the experimental conditions. The radiation power input through the reactor’s aperture was in the range of 1.6–9.9 kW. The peak solar flux concentration ratio was 5880 suns; the maximum mean solar flux concentration ratio through the aperture was 3490 suns. The Ar mass flow rate needed to keep the window clean and carry the gaseous products was in the 0.32–0.49 g s\(^{-1}\) range. The Ar mass flow rate for quenching the product gases was in the 0.68–0.95 g s\(^{-1}\) range. The semi-continuous feeding of ZnO ranged from 120 g to 410 g during a feeding cycle of typically 50 s.

Eight experimental runs were carried out with one to nine feed cycles at cavity temperatures in the range 1807–1907 K (measured behind the ZnO tiles). The total experimental time was 23 h. A typical experiment consisted of three phases: (1) heating, (2) feeding and ZnO dissociation, and (3) cooling. Firstly, the reactor’s cavity was slowly heated to 1600 K within approximately 1 h by stepwise ignition of four arcs of the HFSS and delivering up to 6 kW through the reactor’s aperture. During this heating phase, the cavity temperature was not allowed to exceed 1630 K in order to prevent the unprotected irradiated ZnO tiles from dissociating. The predicted ZnO dissociation rate according to Eq. (3.2) at 1630 K is only $0.437 \times 10^{-3} \text{ g s}^{-1}$ which is prohibitively low. In the second phase, the screw feeder was extended into the cavity and ZnO particles were spread uniformly on the rotating cavity walls. To avoid overheating of the feeder’s cap, the power input from the HFSS was interrupted briefly ($\sim 50$ s) during the feeding cycle. Afterward, six arcs were ignited and the cavity temperature was maintained in the range of 1807–1907 K. In five experimental runs, the feed cycle was repeated. In the third phase, the HFSS was shut down and the reactor underwent cooling while maintaining the Ar flow.
<table>
<thead>
<tr>
<th>run No.</th>
<th># feed cycles</th>
<th>Total ZnO fed (g)</th>
<th>Max. mean radiative flux (kW m⁻²)</th>
<th>Max. power input (kW)</th>
<th>Duration 2nd phase (min)</th>
<th>Max. cavity temperature⁷ (K)</th>
<th>Max. O₂ release (mol s⁻¹ 10⁻⁶)</th>
<th>Solid products recovered downstream (g)</th>
<th>Zn content in filtered particles (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.4</td>
<td>25</td>
<td>1807</td>
<td>12.8</td>
<td>16.4 ± 1.4</td>
<td>18.5 ± 7</td>
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<td>18</td>
<td>1893</td>
<td>22.2</td>
<td>12.1 ± 0.1</td>
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<td>3300</td>
<td>9.3</td>
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<td>1862</td>
<td>27.0</td>
<td>22.5 ± 3.3</td>
<td>41.7 ± 7</td>
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<td>19.1</td>
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<td>33.8 ± 7</td>
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<td>9.6</td>
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<td>1861</td>
<td>18.8</td>
<td>41.5 ± 20.8</td>
<td>25.4 ± 7</td>
</tr>
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<td>6</td>
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<td>9.0</td>
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<td>17.4</td>
<td>59.5 ± 6.8</td>
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<td>9.9</td>
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<td>1882</td>
<td>14.1</td>
<td>148.4 ± 28.8</td>
<td>36.1 ± 7</td>
</tr>
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<td>8</td>
<td>9</td>
<td>1180</td>
<td>3330</td>
<td>9.4</td>
<td>241</td>
<td>1880</td>
<td>10.8</td>
<td>224.2 ± 49.5</td>
<td>26.7 ± 7</td>
</tr>
</tbody>
</table>

⁷Measured behind the ZnO tile
Figure 6.1 shows the radiative power input, cavity temperature, and O_2 molar flow rate during a representative experimental run (run No. 1) with a single feed cycle. When the cavity temperature reached 1580 K, 284 g of ZnO were fed during 40 s, while the cavity temperature dropped by 150 K due to the short interruption of the power input and the addition of fresh ZnO particles. Immediately afterward, the radiative power input was reestablished to a level of 7 kW for 1460 s. A stationary cavity temperature of 1807 K was reached 1200 s after feeding.

Figure 6.1: Radiative power input, cavity temperature, and O_2 molar flow rate in the product gases measured during experimental run No. 1, with one feed cycle of 284 g ZnO.

The O_2 base level in the reactor before feeding was 100 ppm (3.5×10^{-6} mol s^{-1}) and was attributed to air trapped in the insulating material, as corroborated by the GC’s N_2 measurement. This base level never exceeded 100 ppm in all experimental runs. The O_2 level dropped shortly after feeding as a result of CO_2 formation by oxidation of carbon impurities contained in
The amount of carbon per 100 g ZnO was in the 0.044–0.066 g range and, therefore, considered negligible.

The O₂ molar flow rate, the main indicator of the ongoing ZnO dissociation reaction, increased when the cavity temperature reached 1500 K, peaked to $12.8 \times 10^{-6}$ mol s⁻¹ at 1798 K, and dropped to the base level when the HFSS was shut off. Note that a substantial portion of the O₂ formed by ZnO dissociation recombined with Zn(g), as determined by a ZnO mass balance. As previously observed in laboratory experiments with a temperature-gradient tubular furnace [56], rapid cooling of the gaseous products along the length of the quench unit led to supersaturation and nucleation of Zn vapor and subsequent partial reoxidation of condensed Zn. Primary modes of particle growth were condensation and coalescence [107]. The particles mainly deposited on the water-cooled surfaces along the annular gap of the quench unit and in the filter downstream of the reactor.

The key design concept of the rotary reactor is that the layer of ZnO particles in the rotary reactor achieves three beneficial functions. Firstly, as a radiant absorber it eliminates the need to transport high temperature process heat through the reactor walls. Second, as the chemical reactant, it benefits from the reaction favorable high temperatures directly at the reaction site. Finally, the layer acts as a thermal insulator which reduces the thermal load on the sintered ZnO tiles and ceramic insulation that line the cavity.

The reactor is operated in the so-called “ablation” mode, where the rate of heat transfer—predominantly by radiation—to the thin layer of ZnO particles undergoing endothermic dissociation proceeds faster than the rate of heat transfer—predominantly by conduction—through the cavity walls. Thus, the outer layers remain colder than the irradiated inner layers. This ablation mode is especially noticeable in Fig. 6.2 for run No. 3, in which the ZnO dissociation reached its maximum rate—indicated by the peak O₂ rate of $27 \times 10^{-6}$ mol s⁻¹—earlier than the cavity temperature attained its stationary.
value of 1850 K. In this run, 398 g of ZnO were fed, creating a thicker layer than that of run No. 1, and the radiative power input was 9 kW. As the layer of ZnO particles undergoes shrinkage due to the dissociation reaction, a new feed cycle is required to ensure that the ZnO tiles are not exposed to the direct high-flux irradiation. Otherwise, the tiles and the ceramic insulation might exceed their maximum allowable temperature. Multiple feed cycles were investigated in runs 4–8.

Figure 6.3 shows the radiative power input, cavity temperature, and O₂ molar flow rate in the product gases measured during experimental run No. 4. Two feed cycles of 158 g of ZnO each were performed in this run.

Figure 6.2: Radiation power input, cavity temperature, and O₂ molar flow rate in the product gases measured during experimental run No. 3, with one feed cycle of 398 g ZnO.
Figure 6.3: Radiative power, cavity temperature, and O\textsubscript{2} molar flow rate in the product gases measured during experimental run No. 4, with two feed cycles of 158 g ZnO each.

The power input was shortly interrupted during each feed cycle, resulting in 180 K temperature drop and, consequently, an interruption of the dissociation reaction, as indicated by the drop of the O\textsubscript{2} molar flow rate to the base level. Once the radiative power was reestablished, ZnO dissociation proceeded as indicated by the increase in the O\textsubscript{2} concentration. After the second feed cycle, the O\textsubscript{2} molar flow rate peaked at \(19.1 \times 10^{-6}\) mol s\(^{-1}\) at 1835 K, and then decreased as ZnO particles were consumed. Along the length of the quench unit, Zn(g) and O\textsubscript{2} partly recombined and deposited on the quench unit (specifically, between the cavity’s lateral back wall and the injection location of cold Ar). The formation of ZnO particles promoted further recombination, resulting in clogging and a further decrease in the O\textsubscript{2} molar flow rate. Clogging may be eliminated by shortening the hot quench section [116].

Figure 6.4 shows the radiative power input, cavity temperature, and O\textsubscript{2} molar flow rate in the product gases measured during experimental run No. 6. Five feed cycles of 120 g of ZnO each were performed in this run.
Figure 6.4: Radiative power input, cavity temperature, and O\textsubscript{2} molar flow rate in the product gases measured during experimental run No. 6, with five feed cycles of 120 g ZnO each.

Analogous to run No. 4, the power input was shortly interrupted during each feed cycle, resulting in a 75 K temperature drop and, consequently, an interruption of the dissociation reaction, as indicated by the drop of the O\textsubscript{2} molar flow rate to the base level for less than 1 min. After the first feed cycle, the O\textsubscript{2} molar flow rate peaked to $17.4 \times 10^{-6}$ mol s\(^{-1}\) at 1805 K, and then decreased due to partial clogging at the exit. The second through fifth feed cycles were conducted at cavity temperatures in the range of 1880–1907 K.

Figures 6.5 and 6.6 show the radiative power input, cavity temperature, and O\textsubscript{2} molar flow rate in the product gases measured during experimental run Nos. 7 and 8, respectively. The heating phases lasted 1.5 h and 1.1 h, respectively. Fresh ZnO particles were fed every 25–40 min. Seven feed cycles of 133 g of ZnO each were performed in run No. 7; nine feed cycles of 131 g of ZnO each were performed in run No. 8. The maximum O\textsubscript{2} molar flow rate was $14.1 \times 10^{-6}$ mol s\(^{-1}\) and $10.8 \times 10^{-6}$ mol s\(^{-1}\), respectively.
Figure 6.5: Radiative power input, cavity temperature, and O_2 molar flow rate in the product gases measured during experimental run No. 7, with seven feed cycles of 133 g ZnO each.

Figure 6.6: Radiative power input, cavity temperature, and O_2 molar flow rate in the product gases measured during experimental run No. 8, with nine feed cycles of 131 g ZnO each.
The second phase of both runs exceeded 4 h. In contrast to run No. 6 (Fig. 6.4), the level of O₂ did not decrease from cycle to cycle because deposits on the quench unit were mechanically removed to prevent partial clogging. However, it resulted in temporary oscillations in the O₂ molar flow rate.

The amount of solid products recovered downstream of the cavity’s exit (at the quench unit and filter) is listed in Table 6.1 for each run. It represented, on the average, 13% of the total ZnO fed; the rest accumulated inside the cavity and formed a layer on top of the tiles. The Zn content of the particles collected in the filter far downstream is listed in Table 6.1. A maximum was 41.7 mol% and was found for run No. 3. The result correlates well with the amount of O₂ measured at the outlet. In contrast, no correlation was found between the cavity temperatures (measured behind the ZnO tiles) and the oxygen evolution because of varying thickness of ZnO layer—which in turn affected the temperature—and varying reoxidation extents of Zn—which in turn affected the O₂ concentration. As described in the next section, part of the continued reactor development work is aimed at optimizing the quench unit configuration to avoid Zn reoxidation.
6.2 Al₂O₃ Cavity

6.2.1 Main Performance Indicators

A set of 15 experimental runs were performed with the 10 kW prototype reactor composed of Al₂O₃ cavity tiles. Experimental conditions and performance indicators are listed in Table 6.2. Main parameters were the Ar flow rate across the reactor’s window and aperture (WF) and the quench flow rates (QF) along with the maximum radiation power input. The number of feed cycles was varied between one and three. The feeder was located far downstream of the cavity exit during run No. 5, thus, forming a tubular reactor exit, in order to avoid clogging of the outlet section. The maximum power input was set between 9.1 kW and 11.6 kW in order to obtain the desired cavity temperatures in the range 1757–2001 K. The duration of the second phase was between 50 min and 90 min. WF and QF were in the range 7–28 lₙ min⁻¹ and 30–90 lₙ min⁻¹, respectively. The maximum Zn content of the quenched products $X_{Zn,QS}$ was 44.9% for run No. 13, the maximum Zn content of the filtered products was 51.1% as determined by dissolution of the products in HCl with the measurement of evolved H₂ [115].

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¹ The investigation of Zn(g) and O₂ quenching presented in this section has been performed within the framework of: C. Suter. Development and experimental investigation of a quench unit for a solar thermal rotary reactor. Master Thesis, ETH Zürich, 2008 [107].
<table>
<thead>
<tr>
<th>run No.</th>
<th># feed cycles</th>
<th>Total ZnO fed (g)</th>
<th>Max. power input (kW)</th>
<th>Duration 2nd phase (min)</th>
<th>Max. cavity temperature (K)</th>
<th>WF (l min⁻¹)</th>
<th>QF (l min⁻¹)</th>
<th>Solid products recovered downstream (g)</th>
<th>Zn content of quenched products (mol%)</th>
<th>Zn content in filtered particles (mol%)</th>
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<td>1</td>
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<td>184</td>
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<td>1887</td>
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<td>23.3</td>
<td>41.4 ± 0.8</td>
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<td>1785</td>
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<td>21.2</td>
<td>29.7 ± 0.6</td>
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<td>72</td>
<td>1878</td>
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<td>49.8 ± 3.8</td>
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<td>0</td>
<td>9.1</td>
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<td>1801</td>
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<td>90</td>
<td>30.5 ± 0.2</td>
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<td>34.0 ± 0.7</td>
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<td>44.9</td>
<td>51.1 ± 1.0</td>
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<td>68</td>
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<td>60</td>
<td>120.3 ± 11.8</td>
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<td>16.7 ± 0.3</td>
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<td>118.7 ± 15.2</td>
<td>8.9</td>
<td>16.8 ± 0.3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Measured behind the Al₂O₃ tiles; <sup>b</sup>feeder was located far downstream the cavity exit
### 6.2.2 Gas and Zn Mass Balance

The closure of the Zn mass and the gas balance is accomplished by comparing the amount of Zn recovered after the run $m_{\text{Zn,HCl}}$ with the amount of Zn effectively quenched during the run $m_{\text{Zn,gas}}$, which is predicted by integration of the measured mass flow rates of $O_2$, $CO$, $CO_2$, and $H_2$, according to:

$$m_{\text{Zn,gas}} = M_{\text{ZnO}} \int_{t=0}^{t} \left( 2\dot{n}_{O_2} + 2\dot{n}_{CO_2} + \dot{n}_{CO} - \dot{n}_{H_2} \right) dt \quad (6.1)$$

Note that $\dot{n}_{H_2}$ is assumed to be formed via the hydrolysis reaction of Zn and moisture trapped in the reactor’s insulation and, hence, reduces the amount of $m_{\text{Zn,gas}}$. The amount of Zn lost by this reaction was found to increase with increasing temperatures and was attributed to the higher water vapor release from the insulation material. During run No. 15, 64% of originally quenched Zn was lost via the hydrolysis reaction. The measurement of CO and $CO_2$ resulted from the carbothermal reduction of ZnO with carbon impurities in the feed stock. The carbothermal reduction of ZnO accounted for not more than 20% of the recovered Zn.

The closure of the Zn mass and gas balance is exemplary shown for run Nos. 1 and 4, which featured $QF = 60$ and 30 l min$^{-1}$, respectively. Figure 6.7 shows the radiative power input, cavity temperature, and $O_2$ molar flow rate for these two runs as a function of time. The feeding of ZnO and application of solar power was analogous to the runs described in Section 6.1. The $O_2$ molar flow rate was significantly higher during run No. 1 compared to run No. 4 as shown in Fig. 6.7 a and b, respectively. The higher $QF$ of run No. 1 compared to run No. 4 resulted in lower partial Zn pressure, and, thus, promoted the quenching of Zn(g) and $O_2$ [57], as corroborated by the $O_2$ measurement.
Figure 6.7: Radiative power input, cavity temperature, and O₂ molar flow rate in the product gases measured during (a) experimental run No. 1, and (b) run No. 4.
Figure 6.8: Predicted amount of Zn according to Eq. 6.1 (gas analysis) and recovered amount of Zn (HCl method) after: (a) run No. 1 and (b) run No. 4. Note that the amount of Zn lost by the hydrolysis reaction is added to the recovered amount of Zn in order to facilitate comparison.

Figure 6.8 shows the amount of Zn predicted according to Eq. 6.1 (gas analysis) and the recovered amount of Zn (HCl method) for run No. 1 and No. 4. 9.7±1.5 g Zn was predicted and recovered after run No. 1 compared to 3.3±0.7 g after run No. 4 due to the higher O₂ molar flow rate of run No. 1. Note that the amount of Zn lost by the hydrolysis reaction is added to the second column in Fig. 6.8 to facilitate the comparison of the Zn mass and gas balance. The agreement of the Zn gas and mass balance is found by comparing the height of the first and second column of Fig. 6.8, respectively. Agreement was found for all 15 runs within measurement uncertainty of the gas analysis.

6.2.3 Solar-to-Chemical Energy Conversion Efficiency

The solar-to-chemical energy conversion efficiency \( \eta_i \) per feed cycle is defined as
where \( t_{f,i} \) is the time at the beginning of a feed cycle, and \( t_{f,i+1} \) its termination. The summation in Eq. (6.2) takes into account the non-uniform temperature distribution along the cavity length. The cavity is divided into three segments, represented by the temperature \( T_{c,j} \), measured behind the cavity tiles at the front, half way along the cavity length (referred to as cavity temperature in previous section), and at the back. The heat consumption of the endothermic ZnO dissociation reaction in J kg\(^{-1}\) is given by [65]:

\[
\Delta H_i(T) = 5.96 \times 10^6 - 161.32T - 2.66 \times 10^{-2}T^2
\]  

(6.3)

\( \eta_1 \) of the first feed cycle of all 15 runs is shown in Fig. 6.9a as a function of the mean cavity temperature \( T_{c,\text{mean}} \), which was in the range 1627–1806 K.
Significant scattering of data points is observed, which is attributed to the different experimental conditions. At higher $T_{c,\text{mean}}$, during the second and third feed cycle, $\eta_{2,3}$ shows lower scatter as shown in Fig. 6.9b. $\eta_{2,3}$ increases with $T_{c,\text{mean}}$ up to $3.1\pm0.3\%$ at $T_{c,\text{mean}} = 1911$ K and then decreases to $2.3\pm0.2\%$ at $T_{c,\text{mean}} = 1937$ K (rightmost data point, run No. 15). This decrease is due to the formation of Al$_2$ZnO$_4$ from ZnO and the Al$_2$O$_3$ cavity tiles as corroborated by XRD measurements. The reaction ZnO + Al$_2$O$_3$ → Al$_2$ZnO$_4$ is thermodynamically favorable at temperatures ~2000 K [108]. Since the amount of ZnO feedstock was not sufficient during run No. 15, not enough ZnO was available for driving the dissociation reaction, and, thus, resulted in a low value of $\eta_2$. No ZnO was left in the cavity after the run and 0.68 mol Al$_2$ZnO$_4$ formed as determined by an overall ZnO mass balance. Yet, it remains to be investigated if the reaction still proceeds with used tiles at temperatures comparable to those of run No. 15.

6.2.4 Influence of Zn Partial Pressure on Zinc Yield

The Zn partial pressure in the quench section (QS) of the prototype reactor $P_{\text{Zn,QS}}$ as a function of the amount of recovered ZnO $n_{\text{exp,QS}}$ and total Ar flow $n_{\text{Ar in WF+QF}}$, defined as

$$P_{\text{Zn,QS}} = P_0 \frac{n_{\text{exp,QS}}}{1.5n_{\text{exp,QS}} + n_{\text{Ar in WF+QF}}}$$

(6.4)

was varied during run Nos. 1–15 by setting $T_c$ and, hence, the dissociation rate, and by adjusting the total flow WF + QF. Figure 6.10 shows the Zn yield $X_{\text{Zn,QS}}$ in the quench section as a function of $P_{\text{Zn,QS}}$ for the 15 experimental runs. $X_{\text{Zn,QS}}$ is found to increase with decreasing $P_{\text{Zn,QS}}$. Two distinct regions of $X_{\text{Zn,QS}}$ are observed in Fig. 6.10. Almost constant Zn yield $X_{\text{Zn,QS}} \sim 14\%$ is found for $P_{\text{Zn,QS}}$ in the range 370–600 Pa. Hence, the quench device is inefficient at these Zn partial pressures. For $P_{\text{Zn,QS}} < 370$ Pa, $X_{\text{Zn,QS}}$ increases approximately linearly with decreasing $P_{\text{Zn,QS}}$. 67
Increasing $X_{Zn,QS}$ with decreasing $P_{Zn,QS}$ is also found in a setup that features a sophisticated quench device as shown in Section 6.3, however is contrary to results published in [55]. This contradiction is attributed to the different setup, to the absence of high cooling rates (CR), and to the lack of analyses of product gases in the experimental study of [55], implying the inability of excluding the carbothermal reduction of ZnO as a possible reaction mechanism.

6.2.5 Particle Analysis

Figure 6.11 shows the fraction of particles recovered in the filter unit for all 15 runs as a function of the total Ar flow $WF + QF$. The fraction of particles recovered in the filter is found to increase with increasing $WF + QF$. Significant scattering of data points is observed, which is attributed to partial clogging of the cavity exit.
Figure 6.11: Fraction of particles recovered in the filter unit for run Nos. 1–15 as a function of the total Ar flow WF + QF.

Other particles were deposited primarily on the water-cooled surfaces of the quench section and inside the flexible tube that connects the quench section to the filter unit. These particles had to be removed mechanically after each run.

The particle size distributions of recovered products are affected by the quench rate and partial pressures. The quench flow rate QF influences the residence time of products in the control-volume (composed of the quench section and the flexible tube, which connects the reactor with the filter unit) from the cavity exit to the filter unit. Note that WF is small compared to QF and, therefore, is not considered here. Presumably, higher QF results in higher quench rates, and, thus, to smaller particles in the quench section. Higher QF also results in a shorter residence time of quenched products. Since particle growth by mechanisms of coagulation and coalescence depends on residence time, smaller particles are expected to be found in the filter unit for runs with high OF.
Figure 6.12: Volume density distribution of particles collected in the filter unit after run Nos. 4 (30 l min$^{-1}$), and 13 (90 l min$^{-1}$).

Figure 6.12 shows the particle volume density distribution curves as a function of QF for run No. 4 (QF = 30 l min$^{-1}$, $P_{Zn,QS} = 416.5$ Pa) and No. 13 (QF = 90 l min$^{-1}$, $P_{Zn,QS} = 42.3$ Pa). The first peak at $D \sim 0.3$ μm of run No. 13 is higher and shifted towards a smaller particle size compared to run No. 4. The second peak at $D \sim 10$ μm is smaller than that of run No. 4. However, the third peak of run No. 13 at $D \sim 100$ μm is higher, which is presumably due to more particles being removed and transported to the filter unit by the Ar flow from the location of clogging (at the cavity exit); there, large particles are formed by continuous condensation and re-oxidation of Zn(g) under supersaturated conditions. It is recommended that further studies of particle growth should be conducted in the solar TG (presented in Chapter 2) where experimental conditions like reaction rates, Zn partial pressures, and quench flow rates can be easily set. Furthermore, clogging—the main source of uncertainty—can be avoided in the solar TG as demonstrated by using a sophisticated quench device [57], see also Section 6.3.
SEM images of deposits recovered in the filter unit after run No. 13 are presented in Fig. 6.13. The pictures show that the particles are round and prismatic with sizes of 50–200 nm, similar to those observed previously in a temperature-gradient tube furnace by [56]. Presumably, the round particles were obtained from homogeneous nucleation of Zn with subsequent solidification of zinc droplets, while the prismatic-shaped particles were obtained by direct transition from the gas to solid phase. The deposits also contain parts of large tetrapod-like ZnO structures, which were also found at the cavity exit where clogging occurred. These particles were presumably carried by the Ar flow to the filter unit. SEM images of deposits recovered in the filter unit after run No. 4 are shown in Fig. 6.14. Particles exhibit mostly prismatic shape. A minor number of round Zn particles are observed, which correspond to a low Zn content of 6.3% (see Table 6.2) as measured by dissolution in HCl.

Figure 6.13: SEM images of particles collected in the filter unit after run No. 13. The zinc content was 51.1%. Magnification (a) 20’000×; (b) 100’000×
Figure 6.14: SEM images of particles collected in the filter unit after run No. 4. The zinc content was 6.3%. Magnification (a) 50’000×; (b) 150’000×

6.3 Quenching Apparatus for Zn(g) and O₂

Rapid cooling for avoiding the recombination of Zn vapor and O₂ derived from the solar thermal dissociation of ZnO was investigated using the solar TG described in Chapter 3, coupled to a quenching apparatus. A scheme of the quench apparatus is depicted in Fig. 6.15. It features hot, transition, and cold zones. The hot and transition zones have been realized by a set of three Al₂O₃ concentric tubes. In the hot zone, the Zn(g)/O₂ flow mixture diluted in Ar that exits the solar TG (denoted RF: Reacting Flow) enters the quenching unit. RF’s mass flow rate was set to 8 l N/min⁻¹; its temperature was \( T_{RF} > 1800 \text{ K} \). In the transition zone, the RF is surrounded by an annular Ar flow (denoted AF: Annular Flow) for suppressing diffusion of RF to the walls. Zinc droplet formation was avoided by maintaining the AF’s temperature at \( T_{RF}=870 \text{ K} \), about 50 K higher than the Zn saturation temperature for the given experimental conditions.

---

Figure 6.15: Schematic of the quench apparatus illustrating the three temperature zones.

Mixing between RF and AF is minimized by selecting the tube diameters (i.d. = 15 mm in the hot zone and i.d. = 20 mm in the transition zone) and the AF’s mass flow rate (set to 10.5 lN min⁻¹) to keep velocities in the laminar flow regime. The cold zone consists of a water-cooled stainless steel tube containing a port for the injection of cold Ar (denoted QF: Quench Flow). QF’s temperature was \( T_{QF} = 298 \text{ K} \); its mass flow rate was set to 27 lN min⁻¹ to ensure that the mixture reached a temperature below the Zn melting point (693 K).

Inside the cavity of the solar TG, a ZnO sample was mounted on an Al₂O₃ rod that was suspended on the balance. The sample consisted of a pressed and sintered ZnO tile. A SEM of the material is shown in Fig. 2.5b. This setup allowed retracting the ZnO tile into the insulation to avoid premature dissociation during preheating of the cavity. At the beginning of an experimental run, the ZnO tile was located inside the insulation. The reactor was then heated to the desired temperature and maintained under isothermal conditions before the ZnO sample was lifted up to 40 mm into the hot cavity. Sixteen solar experimental runs were performed for cavity temperatures in the range 1821–2050 K. Two geometrical configurations for the hot zone were examined: the length of the innermost ceramic tube was either 24 mm
as shown in Fig. 6.15 or shortened to 12 mm. About 3 g ZnO was dissociated in every run. The dissociation rate $\dot{m}_{ZnO}$ was in the range $1.8–15.3$ mg s$^{-1}$, which results in molar Ar/Zn dilutions for the cold zone in the range of 170–1500. The Zn partial pressure $P_{Zn,CZ}$ varied in the range 67–604 Pa, as a result of the injection of AF + QF. Particles formed were collected downstream in a glass microfiber filter with pore size of $2.7\,\mu m$ and analyzed after termination of each experiment by X-ray diffraction (XRD). Figure 6.16 shows the net Zn yield $X_{\text{particles}}$ defined as the Zn content of particles collected downstream of QF injection as a function of $P_{Zn,CZ}$. The vertical dashed line indicates $P_{Zn,CZ}$ corresponding to the triple point (22 Pa), below which Zn(g) can be condensed without passing through a liquid phase. The zinc yield was in the range 58–94% for $P_{Zn,CZ} < 200$ Pa and decreased to 40–76% for higher zinc partial pressures. The estimated cooling rate evaluated along streamlines is indicated next to each data point.

![Figure 6.16: Zinc yield of products collected after the quench versus zinc partial pressure in the cold zone (CZ) for both geometrical configurations. Labels indicate cooling rates.](image-url)
Those obtained at the design operating conditions with a cooling rate of 77,000 K s\(^{-1}\) are enclosed by the dashed curve.

### 6.4 Conclusion

A set of eight experimental runs at PSI’s HFSS with an improved 10 kW solar reactor prototype for the thermal dissociation of ZnO(s) was performed. The rotating cavity was made of multilayer ceramics, with the innermost layer composed of ZnO particles held by centrifugal force on top of sintered ZnO tiles glued onto porous ceramic insulation. All reactor components worked well for 23 h of testing at maximum temperatures in the range of 1807–1907 K, measured behind the ZnO tiles. The material of construction of the cavity fulfilled the severe requirements of the reaction. The ZnO tiles showed no signs of mechanical failure and did not require replacement. The window aerodynamic protection performed well; Zn condensation was observed but did not prevent the continuation of the runs. The reactor was operated in transient “ablation” mode with semi-continuous feed cycles of ZnO particles.

A set of 15 experimental runs at PSI’s HFSS with the 10 kW solar reactor prototype for the thermal dissociation of ZnO(s) was performed using Al\(_2\)O\(_3\) cavity tiles. The tiles worked well for temperatures up to 2000 K and were mechanically and chemically superior to the ZnO tiles. The Zn balance was closed for all runs by comparing the recovered amount of Zn with that predicted Zn from the integration of mass flow rates of the product gases. The solar-to-chemical energy conversion efficiency increased with increasing temperature. An increased Zn yield was found with decreasing Zn partial pressures in the quench section. As Zn partial pressures exceeded 370 Pa, little influence was found on the Zn yield. The fraction of particles recovered in the filter unit increased with increasing quench flows, along with a decrease of particle size. SEM images of recovered particles show prismatic
and tetrapod-like ZnO structures and round Zn particles. Runs with a 3-zone quench apparatus that was mounted at the outlet of the solar TG and featured an annular Ar flow to suppress Zn(g) diffusion and subsequent oxidation at the walls resulted in Zn yields exceeding 90%.

Further work is aimed at incorporating the 3-zone quench apparatus into the solar chemical prototype reactor to avoid Zn/O₂ recombination.
7 Numerical Reactor Model and Validation

Chemical reactors based on the concept of direct irradiation require matching the rate of heat transfer to the rate of the chemical reaction. Modeling such an interaction is needed for assessing the performance of different designs and for optimizing the reactor design for maximum solar-to-chemical energy conversion efficiency [118]. A heat transfer model was initially formulated for a simplified reactor geometry, neglecting the semi-batch feeding mode of operation and the shrinkage of the ZnO layer [45]. These simplifications limited its applicability for the optimization and scale-up of the reactor technology, since matching the rate of heat transfer to the rate of the chemical reaction is needed for maximizing its energy conversion efficiency. In this chapter, the reactor model is expanded to consider the exact 3D geometry of the cavity and its material properties, the actual semi-batch feeding mode of ZnO particles, and the fact that the packed-bed layer of ZnO particles lining the cavity shrinks as the reaction progresses. Further, the more accurate kinetic rate law derived in Chapter 3 for directly irradiated ZnO samples is incorporated into the model. Validation is accomplished by comparing the numerically calculated and experimentally measured temperatures and reaction extents for the 10 kW reactor prototype described in Chapter 5. The model is then applied to optimize the reactor design and to analyze the thermal performance of 100 and 1000 kW scaled-up reactors in Chapter 8.

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1 Material from this chapter has been submitted for publication as [117]: L. O. Schunk, W. Lipiński, A. Steinfeld. Heat transfer analysis of a solar receiver-reactor for the thermal dissociation of ZnO—Experimental validation at 10 kW and scale-up to 1 MW. Chemical Engineering Journal, submitted 2008.
7.1 Heat Transfer Model

A transient thermal model is formulated for the prototype reactor described in detail in Chapter 5. Dimensions are listed in Table 5.1. Figure 7.1 shows the reactor’s cross-section with locations of temperature measurements.

Figure 7.1: Cross section of the solar chemical reactor. Indicated are the locations of temperature measurements with type-B (B) and type-K (K) thermocouples.

The model couples radiative, conductive, and convective heat transfer with the endothermic dissociation of ZnO. The unsteady-state energy conservation equation is given by:

\[ \rho c_p \frac{\partial T}{\partial t} = \nabla (k \nabla T) + q_{\text{chemistry}} \]  

(7.1)

\( q_{\text{chemistry}} \) is the volumetric heat sink rate due to the endothermic dissociation of ZnO,

\[ q_{\text{chemistry}} = -r \Delta H_r(T) \]  

(7.2)
where the enthalpy change of the reaction is given by Eq. (6.3) and the reaction rate is modeled by applying the zero-order Arrhenius-type rate law

\[ r^m = k_0^* e^{\frac{-E_a}{RT}} \]  

(7.3)

with \( E_a = 361 \text{ kJ mol}^{-1} \) experimentally determined in Section 3.2.1 for directly irradiated ZnO samples. The frequency factor, \( k_0^* = 2.81 \times 10^9 \text{ kg m}^{-3} \text{ s}^{-1} \), has been adjusted to fit the rates obtained in the solar reactor, as they were affected by convective mass transport at the ZnO surface. The boundary conditions at the internal and external surfaces and initial conditions for Eq. (7.1) are given in Eqs. (7.4–7.6), respectively, as:

\[ k_{\text{eff}} \nabla T \cdot \hat{n} = h_{\text{inn}} (T - T_{\text{gas}}) + q_{\text{radiative}} \]  

(7.4)

\[ k_{\text{eff}} \nabla T \cdot \hat{n} = h_{\text{out}} (T_{\text{ambient}} - T) + \varepsilon \sigma (T_{\text{ambient}}^4 - T^4) \]  

(7.5)

\[ T(x, r, t = 0) = T_0 \]  

(7.6)

The effective thermal conductivity of ZnO is given by Eqs. (4.9)–(4.10) where the mean attenuation \( \beta = 1900 \text{ m}^{-1} \) was determined in Section 4.2.1. The thermal conductivity of porous ZnO \( k_{\text{conductive}} \) as a function of porosity \( p \) is given by Eq. (4.11). The porosity \( p \) is assumed zero for the 10 kW reactor and varied in the range 0–0.5 for scaling-up to 100 and 1000 kW in Chapter 8. The convective heat transfer coefficients \( h_{\text{inn}}, h_{\text{out}}, \) and \( h_{\text{out,window}} \) at the inner surfaces of the cavity, external walls of the Al-mantle, and window, respectively, were determined by CFD simulations [111] and using the correlations [119–121]:

\[ \text{Nu}_{\text{out}} = 0.318 \left( \frac{\omega d^2}{2\nu} \right)^{0.571} \]  

(7.7)
\[
\text{Nu}_{\text{out,window}} = \left( 0.825 + \frac{0.387 \text{Ra}^{1/6}}{1 + (0.492 / \text{Pr})^{9/16}} \right)^2 + 1.855 \left( \frac{\omega d^2}{2 \nu} \right)^{0.4} \tag{7.8}
\]

\( h_{\text{in}} \) varied in the range 100–780 W m\(^{-2}\). \( h_{\text{out}} = 6.17 \) W m\(^{-2}\) and \( h_{\text{out,window}} = 23 \) W m\(^{-2}\) for an angular velocity \( \omega = 11.1 \) s\(^{-1}\) and characteristic lengths \( d = 0.4 \) m (outer diameter), and \( d = 0.24 \) m (window diameter), respectively.

Radiative exchange in the cavity is modeled by assuming independent transfer of the incident directional solar radiation and the radiation emitted diffusely by the cavity walls. The net heat source to element \( A_i \) arising from the solar radiation, \( q_{\text{solar},i} \), is modeled by applying Monte Carlo ray tracing method (MC), which accounts for the complete exchange process of the solar radiation between all reactor elements. The MC simulation setup composed of all internal reactor surfaces along with the HFSS ellipsoidal reflector surfaces is shown in Fig. 7.2 for the optical characteristics of the HFSS facility [114, 122]. The total radiation power \( P_{\text{solar}} \) and, hence, \( q_{\text{solar}}' \) is calibrated by the total radiation power measured calorimetrically through the aperture opening behind the quartz window and the directional dependence is calibrated by the radiation flux distribution measured with the CCD camera across the aperture plane as displayed in Fig. 7.3.

The radiosity method (enclosure theory) [94] is applied to obtain the net radiative flux \( q_{\text{walls}}'' \) arising from radiation emitted by the cavity walls. The corresponding system of equations is given by:

\[
q_{\text{radiative},i} = q_{\text{walls},i}'' - q_{\text{solar},i}''
\tag{7.9}
\]

\[
\sum_{i=1}^{N} \left( \frac{\delta_{ki}}{\epsilon_i} - F_{k-i} \frac{1-\epsilon_i}{\epsilon_i} \right) q_{\text{walls},i}'' = \sum_{i=1}^{N} (\delta_{ki} - F_{k-i}) \sigma T_i^4 \tag{7.10}
\]

where \( \delta_{ki} = 1 \) when \( k = i \) and \( \delta_{ki} = 0 \) when \( k \neq i \). The configuration factors \( F_{k-i} \) are calculated by MC with \( 10^8 \) rays emitted from each inner surface.
Figure 7.2: Simulation setup composed of the HFFS ellipsoidal reflectors and the prototype reactor used to determine the distribution of the net heat flux arising from solar radiation. Not shown are the xenon arcs.

Figure 7.3: Measured and calculated radiation flux across the aperture plain as a function of position for 10 arcs of the high flux solar simulator (HFSS).
Eq. (7.10) is solved iteratively for $N = 92$ by matrix inversion using the Gauss–Seidel numerical algorithm. Eq. (7.1), (7.9), and (7.10) are solved simultaneously. Since the radiative properties of the cavity walls are time independent, MC is executed only once, at the beginning of the solution procedure. The water-cooled components (Al-front shield, aperture, and quench section) are modeled as solids at 297 K. The frustum and cavity surfaces are assumed grey-diffuse surfaces. The window is treated as perfectly transparent for incident solar radiation and as opaque grey-diffuse for IR radiation emitted by the inner surfaces of the cavity. The finite volume method and the explicit Euler time integration scheme are applied to solve the integrated form of Eq. (7.1) over a finite time step $\Delta t$ and over shrinking annular elements $\Delta V$. As the reaction progresses at a rate $r_i''$ and the ZnO layers shrink, the thickness $\Delta r$ of a finite ZnO annular element with outer radius $r_2$ varies according to:

$$\Delta r = r_2 - \left( \frac{1}{\pi \rho} \sum_{i=1}^{N_{\text{feed}}} \Delta m_i - r_i'' \Delta V_i \Delta t \right).$$

Finally, the cyclic batch-feeding of ZnO particles is modeled by adding finite volumes to the numerical domain. The baseline parameters used in the numerical simulation are listed in Appendix A1.

### 7.2 Model Validation

A set of four experimental runs with 3 (see Table 6.2, run No. 3), 5, 7, and 9 (see Table 6.1, run Nos. 6, 7, and 8) consecutive feed cycles was used to validate the reactor model. These runs consisted of three phases: (1) heating, (2) feeding and dissociation, and (3) cooling. Firstly, the reactor’s cavity was heated to 1600 K within approximately 1 hour by igniting stepwise the arcs of the HFSS and delivering from 1.6 kW to 5.7 kW through the reactor’s aperture. During this heating phase, the cavity temperature was not allowed
to exceed 1630 K in order to prevent the unprotected irradiated ZnO tiles from dissociating, as described in Chapter 6.1. In the second phase, the screw-feeder was extended into the cavity and ZnO particles were spread uniformly over the rotating cavity walls. To avoid overheating of the feeder’s cap, the power input $P_{\text{solar}}$ from the HFSS was interrupted briefly (~50 s) during the feeding. Afterwards, radiative power was re-established and further increased up to 10 kW while the irradiated cavity temperature $T_{\text{ZnO-surface}}$ was maintained in the range 1840–1980 K. The batch feed cycles were repeated. In the third phase, the HFSS was shut down and the reactor underwent cooling while keeping the Ar flow.

Figures 7.4 a, b, c, and d show the experimentally measured (solid curves) and numerically calculated (dashed curves) temperatures at locations $T_{B,1}$, $T_{B,2}$, $T_{K,1}$, and $T_{K,2}$ for the four runs with 3, 5, 7, and 9 consecutive feed cycles, respectively. Also indicated are the measured power input and the calculated dissociation rate of ZnO. The arrows on top of the figure point out to the times when the batch feeding of ZnO took place. The temperature agreement is reasonably good at all location for all 4 runs. As expected, temperatures dropped during ZnO-feeding due to the interruption of $P_{\text{solar}}$ and the addition of fresh ZnO particles. Discrepancies are attributed to slow and partial mixing of hot residual and cold fresh particles (not modeled). Note that pyrometry could not be applied to measure the ZnO surface temperature, $T_{\text{ZnO-surface}}$, because of the intense reflected radiation over a wide spectrum. The calculated value, typically 30 K above $T_{B,1}$, compares well with that measured in a solar furnace where a solar-blind pyrometer could be used [46]. The reaction rate increased as $T_{\text{ZnO-surface}}$ exceeded 1700 K, dropped to zero during ZnO-feeding, and climbed up to 40 mg s$^{-1}$ as $P_{\text{solar}}$ was resumed and the temperature levels re-established. The maximum power input was 9.9 kW, which corresponds to a peak solar concentration ratio of 5600 suns and a mean of 3490 suns over the aperture.
Figure 7.4. Experimentally measured (solid curves) and numerically calculated (dashed curves) temperatures halfway along the reactor cavity at locations $T_{B,1}$, $T_{B,2}$, $T_{K,1}$, $T_{K,2}$ (see locations in Fig. 7.1), measured radiation power input $P_{\text{solar}}$, and numerically calculated ZnO-dissociation rate as a function of time for the experimental runs with (a) 3, (b) 5, (c) 7, and (d) 9 feed cycles. The top arrows point out to the times when the batch feeding of ZnO took place.
Table 7.1 lists the experimentally measured mass of ZnO dissociated during the complete run and the numerically calculated mass that is obtained by integrating the dissociation rate of ZnO for the 4 runs shown in Figs. 7.4 a-d.

Table 7.1: Amount of ZnO dissociated during experimental runs with 3, 5, 7, and 9 feed cycles and the corresponding amount obtained by integrating the calculated ZnO dissociation rate.

<table>
<thead>
<tr>
<th># feed cycles</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 (run 3, Table 6.2)</td>
<td>68.5 ± 5.2</td>
<td>63.9</td>
</tr>
<tr>
<td>5 (run 6, Table 6.1)</td>
<td>59.5 ± 6.8</td>
<td>54.0</td>
</tr>
<tr>
<td>7 (run 7, Table 6.1)</td>
<td>148.4 ± 28.8</td>
<td>223.3</td>
</tr>
<tr>
<td>9 (run 8, Table 6.1)</td>
<td>224.2 ± 49.5</td>
<td>197.1</td>
</tr>
</tbody>
</table>

Reasonable good agreement in the mass balance is found for all 4 runs. The model is able to corroborate the experimental observation that the ZnO dissociation reaction occurred in the topmost layers at the highest temperatures, which is typical of an ablation regime as radiative heat transfer to the endothermic reaction proceeded at a faster rate than heat conduction across the packed-bed.

7.3 Energy Balance for the 9-Feed Cycle Run

Figure 7.5 shows the instantaneous energy balance as a function of time for the run with 9 feed cycles, corresponding to Fig. 7.4d. Indicated is the heat consumed by the endothermic reaction (including the sensible heat of dissociated ZnO), the sensible heat of reactor components, and the heat losses by conduction, convection, and re-radiation. Heating the reactor materials consumes 13.1% of $P_{\text{solar}}$ as listed in Table 7.2. Conductive losses to the water-cooled front shield, aperture, and quench amount to 46.7% of $P_{\text{solar}}$. 
Figure 7.5. Instantaneous energy balance of the experimental run with 9 feed-cycles. Indicated is the heat consumed by the endothermic reaction (including the sensible heat of dissociated ZnO), the sensible heat of reactor components, and the heat losses by conduction, convection, and re-radiation.

Table 7.2: Energy balance of the 9-feed cycle run with the prototype reactor with $P_{\text{polar}} = P_{\text{polar, measured}}$, and $P_{\text{polar}} = 1.2 \times P_{\text{polar, measured}}$ ($P_{\text{polar, measured}}$ is the radiative power measured during the run with 9 feed cycles).

<table>
<thead>
<tr>
<th>Prototype reactor</th>
<th>$P_{\text{polar}}$</th>
<th>$P_{\text{polar, measured}}$</th>
<th>$1.2 \times P_{\text{polar, measured}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>1.1%</td>
<td>2.9%</td>
<td></td>
</tr>
<tr>
<td>$r_{\text{mean}}$ (g h$^{-1}$)</td>
<td>49</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>Re-radiation</td>
<td>30.2%</td>
<td>33.1%</td>
<td></td>
</tr>
<tr>
<td>Sensible Heat</td>
<td>13.1%</td>
<td>11.3%</td>
<td></td>
</tr>
<tr>
<td>Conduction</td>
<td>46.7%</td>
<td>44.5%</td>
<td></td>
</tr>
<tr>
<td>Convection</td>
<td>8.9%</td>
<td>8.2%</td>
<td></td>
</tr>
</tbody>
</table>

Radiative losses through the aperture and annular exit amount to 18.7 and 11.5% of $P_{\text{polar}}$, respectively. Convective losses from the reactor mantle
amounts to 8.9% of $P_{\text{solar}}$. The solar-to-chemical energy conversion efficiency is defined as:

$$
\eta = \frac{r \left[ \Delta H_r(T) + \int_0^T c_{p,ZnO} dT \right]}{P_{\text{solar}}}
$$

(7.12)

$\eta$ was only 1.1% when integrated over the complete run of Fig. 7.5. The highest value obtained experimentally was $\eta = 3.1\%$ for $P_{\text{solar}} = 11.1\ kW$, as higher operating temperatures were reached and, consequently, higher reaction rates were induced. A calculated increase of only 20% in $P_{\text{solar,measured}}$ ($P_{\text{solar,measured}}$ is the radiative power measured during the run with 9 feed cycles and is taken as the reference power input in subsequent sections) translated to an increase of 216% in the reaction rate and to $\eta = 2.9\%$ as listed in Table 7.2. Nevertheless, substantial conduction heat losses to the water-cooled components remained the major source of inefficiency (46.7% of $P_{\text{solar}}$) for the 10 kW prototype reactor.

### 7.4 Optimized prototype reactor geometry

Conduction losses to the water-cooled quench unit and radiative losses through the annular were identified as the main reason for the low values of $\eta$. In this section, the performance of an optimized design of the prototype reactor is analyzed. The optimized design is obtained by downsizing the cavity exit from $d_{\text{exit}} = 80\ mm$ to $d_{\text{exit}} = 30\ mm$ and by removing the exit’s water-cooling. The new cavity exit basically exhibits the geometry of the solar TG’s exit ($d_{\text{exit,solar TG}} = 25\ mm$). The diameter of the screw-type feeder system is reduced from 50 to 20 mm.

Parametric runs with $P_{\text{solar}}$ in the order of $0.7–1.15 \times P_{\text{solar,measured}}$ were calculated to obtain $\eta$ as a function of the maximum ZnO surface temperature $T_{\text{ZnO-surface}}$. Figure 7.6 shows $\eta$ as a function of $T_{\text{ZnO-surface}}$. 
Figure 7.6: Solar-to-chemical conversion efficiency for the non-optimized and for the optimized reactor prototype design as a function of the maximum ZnO surface temperature. The data points obtained with the reference power input ($P_{\text{solar,measured}}$) are indicated with dotted circles.

As expected, $\eta$ is found to strongly increase with increasing $T_{\text{ZnO-surface}}$ since the reaction rate increases exponentially with $T_{\text{ZnO-surface}}$. $T_{\text{ZnO-surface}}$ increases from 1919.1 K for the non-optimized reactor prototype (Section 7.3) to 2117.2 K for the optimized reactor prototype with baseline power input. $\eta$ increases from 1.1% to 17.0%, which is due to a reduction of conduction losses from 46.7% to 22.1% of $P_{\text{solar}}$ and a reduction of re-radiation losses through the cavity exit from 11.5% to 4.4% of $P_{\text{solar}}$. Figure 7.6 also indicates that a relatively small increase in the operation temperature can have an important effect in the efficiency. For example, an increase of only 100 K from 2000 to 2100 K results in an increase of $\eta$ by 115% from 7% to 15%. When $T_{\text{ZnO-surface}} > 2100$ K, the increase in $\eta$ decreases because re-radiation losses scale according to $T^4$. Presumably, $\eta$ decreases as $T_{\text{ZnO-surface}} > 2300$ K.
7.5 Conclusion

A transient heat transfer model has been formulated to simulate a solar cavity-receiver lined with a shrinking layer of ZnO particles that are directly exposed to concentrated solar radiation and undergo thermal dissociation. The radiosity and Monte Carlo methods are applied to obtain the distribution of net radiative fluxes, and the finite volume method with the explicit Euler time integration scheme were applied to solve the unsteady energy conservation equation that links conductive, convective, and radiative heat transfer to the rate of the reaction. Experimental validation was accomplished with a 10 kW prototype in terms of temperatures and reaction extents for 4 experimental runs with multiple feed cycles. The ZnO dissociation reaction occurred in the topmost layers which is typical of an ablation regime, as radiative transfer to the endothermic reaction proceeded at a faster rate than heat conduction across the ZnO layer and insulation. The solar-to-chemical conversion efficiency of the prototype reactor is increased from 1.1% to 17% by optimizing its geometry of the outlet section, primarily due to a decrease of conduction losses.
8 Reactor Scale-up

The numerical model, which was presented and validated in the previous chapter, is employed to simulate the thermal performance of a reactor scale-up to 100 kW and 1 MW radiation power and to assess the energy partitioning. It is expected that the thermal energy conversion efficiency increases significantly in the 100 kW and 1 MW reactors, since their heat losses by conduction can be decreased significantly by optimization of water-cooled reactor components.

8.1 Reactor Size at 100 and 1000 kW and Assumptions

The reactor model is employed to predict the thermal performance of scaled-up reactors during two typical consecutive days of operation for a nominal power input $P_{\text{solar,nominal}} = 100$ and 1000 kW. Dimensions are listed in Table 8.1. The aperture size is set for an average solar concentration ratio of 3500 suns. $q_{\text{solar}}$ is assumed to be uniformly distributed over the inner surfaces of the cavity. Feeding a new batch of ZnO particles takes place once the ZnO-layer thickness has decreased by 60%. Two consecutive sunny days are simulated to investigate the reactor dynamics during start-up and shut-down: $P_{\text{solar}}$ is increased linearly from zero to $P_{\text{solar,nominal}}$ within the first hour, held constant for 8 h, set to zero for 15 h, and then repeated to simulate the operation on the second day. Variation of $\rho$ in the range 0–0.5 and of $\beta$ in the range 1900–7850 m$^{-1}$ [93, 104] account for the uncertainties of the values.

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1 Material from this chapter has been submitted for publication as [117]: L. O. Schunk, W. Lipiński, A. Steinfeld. Heat transfer analysis of a solar receiver-reactor for the thermal dissociation of ZnO—Experimental validation at 10 kW and scale-up to 1 MW. Chemical Engineering Journal, submitted 2008.
assigned to these two properties of the ZnO-layer. Baseline values used are $p = 0.5$ and $\beta = 7850 \text{ m}^{-1}$. The extinction coefficient of the porous ZnO is $\beta_{\text{porous}} = (1-p)\beta$ [105].

Table 8.1: Main geometric parameters of the reactor scale-up to 100 kW and 1 MW.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>100 kW</th>
<th>1 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture diameter, mm</td>
<td>190</td>
<td>600</td>
</tr>
<tr>
<td>Window diameter, mm</td>
<td>370</td>
<td>790</td>
</tr>
<tr>
<td>Cavity diameter, mm</td>
<td>500</td>
<td>1600</td>
</tr>
<tr>
<td>Cavity length, mm</td>
<td>750</td>
<td>2400</td>
</tr>
<tr>
<td>Cavity exit diameter, mm</td>
<td>80</td>
<td>260</td>
</tr>
<tr>
<td>Insulation thickness, mm</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Mantle thickness, mm (steel)</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

8.2 Performance of the 100 and 1000 kW Reactors

The solar power input, reaction rate, and ZnO surface temperature are shown as a function of time for the first day of operation in Figs. 8.1 a and b of the 100 and 1000 kW reactors, respectively. Heating from ambient to $T_{\text{ZnO-surface}} = 2000 \text{ K}$ takes about 1 h for both reactors. Twelve and 14 feed cycles of 20 and 200 kg ZnO each are performed for the 100 and 1000 kW reactors, respectively. For the 100 kW reactor, the reaction rate increases from 3.4 g s$^{-1}$ at $t = 1 \text{ h}$ to 10.5 g s$^{-1}$ by $T_{\text{ZnO-surface}} = 2126 \text{ K}$ towards the end first day. For the 1000 kW reactor, the reaction rate increases from 43.0 g s$^{-1}$ at $t = 1 \text{ h}$ to 116.9 g s$^{-1}$ by $T_{\text{ZnO-surface}} = 2136 \text{ K}$ towards the end of the first day. As already observed in the 10 kW prototype, the reaction rate drops to zero during ZnO feeding as a result of the drop in $T_{\text{ZnO-surface}}$. 

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Figure 8.1. Solar power input, ZnO surface temperature halfway along the reactor cavity, and ZnO-dissociation rate as a function of time for the first day of operation at $P_{\text{solar,nominal}} = 100$ kW (a) and 1000 kW (b).
Figure 8.2. Temperature contour plot (in K) of the 100 kW reactor (a) at \( t = 7 \) h on the first day of operation, and (b) at \( t = 24 \) h just before operation on the second day.

Temperature distributions after 7 h and 24 h are shown in Figs. 8.2 a and b, respectively for the 100 kW reactor. Temperatures are uniform along the cavity length after 7 h (max. \( T_{ZnO-surface} = 2126 \) K) and decrease across the insulating material and close to the water-cooled aperture and quench. During the 15 h reactor cool-down, temperatures in the reactor insulating material are in the range 400–800 K as shown in Fig. 8.2b.

Figures 8.3 a and b show power input, reaction rate, and ZnO surface temperature as a function of time for the second day of operation.
Figure 8.3. Solar power input, ZnO surface temperature halfway along the reactor cavity, and ZnO-dissociation rate as a function of time for the second day of operation at $P_{solar,nominal} = 100$ kW (a) and 1000 kW (b).
Heating to $T_{\text{ZnO-surface}} = 2000$ K on the second day is reduced to about 0.4 h for both reactors since a significant amount of heat is stored in the reactor materials. Thirteen and 14 feed cycles of 20 and 200 kg ZnO each are performed for the 100 and 1000 kW reactors, respectively. The reaction rate is slightly higher compared to the first day of operation and increases from 4.2 g s$^{-1}$ and 63.4 g s$^{-1}$ at $t = 0.4$ h to 10.6 g s$^{-1}$ and 117.9 g s$^{-1}$ towards the end of the second day while $T_{\text{ZnO-surface}}$ increases by about 100 K to 2127 K and 2139 K for the 100 and 1000 kW reactors, respectively.

Figure 8.4 shows $\eta$, calculated by integration over the first day, as a function of $\beta$ and $p$. $\eta$ is 50.0% for the baseline values and is practically insensitive to the variation of $\beta$ from 1900 to 7850 m$^{-1}$, with a slight increase due to the lower $k_{\text{radiative}}$. In contrast, $\eta$ decreases relatively by 15% when $p$ is varied from 0.5 to 0, due to a decrease in $k_{\text{conductive}}$ and in the volume of reacting ZnO.

![Figure 8.4](image)

Figure 8.4. Solar-to-chemical energy conversion efficiency of the 100 kW reactor as a function of $\beta$ for $p = 0$, 0.25, and 0.5 for the first day of operation.
Table 8.2 lists the energy balances for the 100, and 1000 kW reactors. $\eta$ increases from 50.0% and 55.9% on the first day of operation to 54.5% and 61.6% for the second day of operation for the 100 kW and 1000 kW reactors, respectively. The increase of $\eta$ from the first to the second day is due to the heat stored in the reactor materials, which reduces the amount of $P_{\text{solar}}$ needed for reheating. Therefore, the time for heating is reduced to 0.4 h on the second day since $T_{\text{ZnO-surface}} = 800 \text{ K}$ after 15 h of reactor cooling. The major sources of irreversibility are those derived from heat losses by re-radiation through the aperture, which, to some extent, can be reduced by increasing the incident solar radiative flux and, consequently, reducing the aperture size.

Table 8.2: Energy balance for the 100 and 1000 kW scaled-up reactors for the first and second day of operation for $p = 0.5$, $\beta = 7850 \text{ m}^{-1}$.

<table>
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<tr>
<th></th>
<th>100 kW</th>
<th></th>
<th>1000 kW</th>
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<tr>
<td></td>
<td>1st day</td>
<td>2nd day</td>
<td>1st day</td>
<td>2nd day</td>
</tr>
<tr>
<td>$\eta$</td>
<td>50.0%</td>
<td>54.5%</td>
<td>55.9%</td>
<td>61.6%</td>
</tr>
<tr>
<td>$r_{\text{mean}}$ (kg h$^{-1}$)</td>
<td>25.2</td>
<td>29.2</td>
<td>282.5</td>
<td>330.8</td>
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<tr>
<td>Re-radiation</td>
<td>17.5%</td>
<td>17.3%</td>
<td>17.6%</td>
<td>17.3%</td>
</tr>
<tr>
<td>Sensible Heat</td>
<td>20.5%</td>
<td>14.4%</td>
<td>19.8%</td>
<td>13.2%</td>
</tr>
<tr>
<td>Conduction</td>
<td>6.6%</td>
<td>7.0%</td>
<td>2.5%</td>
<td>2.7%</td>
</tr>
<tr>
<td>Convection</td>
<td>5.4%</td>
<td>6.8%</td>
<td>3.9%</td>
<td>5.2%</td>
</tr>
</tbody>
</table>

The incorporation of secondary non-imaging concentrators, e.g. compound parabolic concentrators [123] has the potential of boosting the solar concentration ratio by a factor of $1/\sin^2 \alpha$, where $\alpha$ denotes the rim angle of the incoming solar radiation. The sensible heat of the hot products Zn(g) and O$_2$ exiting the reactor is lost during the quenching for avoiding their recombination [57]. Alternatively, electrothermal methods for in-situ separation of Zn(g) and O$_2$ at high temperatures may allow partial recovery of the sensible heat in separate streams [124]. The significantly higher value
of $\eta$ predicted for the 100 and 1000 kW reactors as compared to that measured for the 10 kW reactor is primarily due to higher $T_{ZnO-surface}$ (higher by about 200 K) and, consequently, significantly higher reaction rates, and to a reduction of the conduction losses through optimization of the geometry to minimize water-cooled components.

The influence of $T_{ZnO-surface}$ on the energy conversion efficiency was examined for the first day of operation by varying $P_{solar,nominal}$ in the range 50–100 kW and 500–1000 kW for the 100 and 1000 kW reactors, respectively. $\eta$ is plotted as a function of $T_{ZnO-surface}$ in Fig. 8.5. For the 100 kW reactor, $\eta$ increases from 23% to 50.0% as $P_{solar}$ increases from 50 to 100 kW and $T_{ZnO-surface}$ from 1994 to 2126 K. An increase of $T_{ZnO-surface}$ by about 100 K to 2094 K results in a remarkable increase of $\eta$ by 21% to 44%. A similar conclusion is obtained for the 1000 kW reactor as shown in Fig. 8.5.

![Figure 8.5](image_url)

Figure 8.5: $\eta$ as a function of $T_{ZnO-surface}$ for the 100 and 1000 kW reactors. Variation of $T_{ZnO-surface}$ is obtained by varying $P_{solar,nominal}$ in the range 50–100 kW and 500–1000 kW.
The solar-to-chemical energy conversion efficiency exceeds 23% for both reactors at 50% of the nominal power input resulting in $T_{\text{ZnO-surface}} \sim 2000 \, \text{K}$. Therefore, it can be concluded that the reactors can still operate efficiently when the available radiation power differs from the nominal power, for example if the insolation is reduced due to haze or clouds.

### 8.3 Conclusion

Scaling up the reactor to 100 and 1000 kW nominal solar power input has the potential of reaching maximum solar-to-chemical conversion efficiencies exceeding 60%, mainly as a result of higher reaction rates at higher operating temperatures and a reduction in the conduction losses through optimization of the geometry to minimize water-cooled components. Negligible influence of the attenuation coefficient on the conversion efficiency was found whereas a decrease of ZnO-porosity from 0.5 to 0 lowered the conversion efficiency relatively by 15%. An increase of $\eta$ from the first to the second day of operation was observed due to heat stored in the reactor materials. An increase of $T_{\text{ZnO-surface}}$ by about 100 K to 2094 K for the 100 kW reactor results in a remarkable increase of the solar-to-chemical energy conversion efficiency by 21% from 23% to 44%.
9 Summary and Outlook

Several aspects of the dissociation of ZnO were investigated in this thesis along with the development of a reliable 10 kW prototype reactor for affecting the solar thermal ZnO dissociation. Firstly, a solar-driven thermogravimeter, in which a packed-bed of ZnO particles is directly exposed to concentrated solar radiation while its weight loss is continuously monitored, was developed and applied to measure the thermal dissociation rate in a setup closely approximating the heat and mass transfer characteristics of solar reactors.

Isothermal thermogravimetric runs were performed in the range 1834–2109 K and fitted to a zero-order Arrhenius rate law with apparent activation energy $361 \pm 53 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and frequency factor $14.03 \times 10^6 \pm 2.73 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$. Application of L’vov’s kinetic expression for solid decomposition along with a convective mass transport correlation yielded kinetic parameters in close agreement with those derived from experimental data.

A transient heat transfer model was formulated for the shrinking packed-bed of reacting ZnO particles exposed to concentrated solar irradiation. The model combines conduction, convection, and radiation heat transfer with simultaneous sintering and reaction kinetics. Validation is accomplished in terms of temperatures and dissociation rates experimentally measured during the kinetic study with ZnO packed-bed samples subjected to peak solar flux concentration ratios in the range 1225–2133 suns. The packed-bed was subjected to an ablation regime controlled by the rate of radiative heat transfer to the first layers of ZnO undergoing endothermic dissociation.
Then, an improved engineering design of a solar chemical reactor for the thermal dissociation of ZnO at above 2000 K was developed. It features a rotating cavity-receiver lined with a packed-bed of ZnO particles that are held by centrifugal force. With this arrangement, ZnO is directly exposed to concentrated solar radiation and serves simultaneously the functions of radiant absorber, chemical reactant, and thermal insulator. The multi-layer cylindrical cavity is made of either sintered ZnO or Al₂O₃ tiles placed on top of a porous 80%Al₂O₃-20%SiO₂ insulation and reinforced by a 95%Al₂O₃-5%Y₂O₃ ceramic matrix composite, providing mechanical, chemical, and thermal stability and a diffusion barrier for product gases. 3D CFD was employed to determine the optimal flow configuration for an aerodynamic protection of the quartz window against condensable Zn(g).

Experimentation was carried out at PSI’s high flux solar simulator with a 10 kW reactor prototype subjected to mean radiative heat fluxes over the aperture exceeding 3000 suns (peak 5880 suns). The reactor was operated in a transient ablation mode with semi-continuous feed cycles of ZnO particles, characterized by a rate of heat transfer—predominantly by radiation—to the layer of ZnO particles undergoing endothermic dissociation that proceeded faster than the rate of heat transfer—predominantly by conduction—through the cavity walls. Two experimental campaigns were conducted. ZnO cavity tiles were used in the first campaign where the reliable reactor operation and the measurement of O₂ were demonstrated. The longest run exceeded four hours of operation. The Zn mass and gas balance was closed for each run of the second campaign where Al₂O₃ tiles were used which allowed reactor operation up to 2000 K tile temperature. The maximum solar-to-chemical energy conversion efficiency was 3.1±0.3%. The net Zn yield increased with decreasing Zn partial pressure in the quench section. The maximum was 44% at 42 Pa Zn partial pressure. Zn yield exceeding 90% were obtained with a sophisticated quench device, which was tested in the solar TG.
A transient numerical model of the 10 kW reactor was formulated which matches the rate of radiative heat transfer to the rate of conduction, convection, and the rate of chemical reaction. Validation of the model was obtained by comparing measured and calculated temperature profiles and reaction extends of four experimental runs with 3, 5, 7, and 9 feed cycles.

Assessing the partitioning of incident radiation power showed that most losses occur by conduction to water-cooled components. The solar-to-chemical energy conversion efficiency was only 1.1% for the run with 9 feed cycles, however, increased to 2.9% by increasing the incident solar radiation by 20% and increased to 17.0% by decreasing the size of the cavity exit of the prototype reactor. A further reduction of water-cooled components relative to the cavity size can be accomplished by scaling-up the reactor technology to 100 kW and 1000 kW. The solar-to-chemical energy efficiency was found to exceed 60% for the 1000 kW reactor and showed a minor dependence on the mean extinction coefficient, whereas a decrease of ZnO-porosity from 0.5 to 0 lowered the conversion efficiency relatively by 15%.

Ongoing work is aimed at increasing the prototype reactor efficiency and the net zinc yield in order to prepare the reactor technology for a scale-up to 100 kW, planned in 2010. The solar-to-chemical energy conversion efficiency of the prototype reactor could be increased by downsizing its outlet section as shown by model calculations, and by increasing the temperature of the ZnO packed-bed. An increase of only 100 K from 2000 to 2100 K results in an increase of the solar-to-chemical energy conversion efficiency by 115% from 7% to 15%. An additional recommendation for avoiding Zn reoxidation and, consequently increasing the Zn yield, would be to implement the 3-zone quench device that was successfully tested in the solar TG.

The reactor model may be further extended to account for the directional distribution of concentrated solar radiation power from solar towers and
actual sunshine data of the site of operation to assess the reactor performance on a yearly basis.
Literature Cited


[37] T. Osinga, U. Frommherz, A. Steinfeld, C. Wieckert. Experimental Investigation of the Solar Carbothermic Reduction of ZnO Using a


[86] M. Gunze, W. Hirschwald, E. Thull. Der Einfluss einer intensiven Sauerstoffbehandlung auf die thermische, chemische und


[99] Rath Group, www.rath-group.com, product #: Kerform KVS 1800/400


[114] J. Petrasch, P. Coray, A. Meier, M. Brack, P. Haberling, D. Wuillemin, A. Steinfeld. A Novel 50 kW 11,000 suns High-Flux Solar Simulator


[125] ALPHA CERAMICS, www.alpha-ceramics.de
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<td>$293 \leq T \leq 810$</td>
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<td>W m$^{-1}$ K$^{-1}$</td>
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Curriculum Vitae

Name Lothar Schunk
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