SOLAR-DRIVEN PYROMETALLURGICAL EXTRACTION OF ZINC VIA THE CARBOOTHERMAL REDUCTION OF PRIMARY AND SECONDARY ZnO SOURCES

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presented by

NIKOLAOS TZOUGANATOS

MSc ETH EST

born on 08.03.1988

citizen of Greece

accepted on the recommendation of

Prof. Dr. Aldo Steinfeld, examiner

Dr. Christian Wieckert, co-examiner

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Abstract

The minerals processing and extractive metallurgy industries are major consumers of electricity and high-temperature process heat, and therefore responsible for about 20% of the global fossil-fuel CO$_2$ emissions. Integration of environmentally cleaner energy sources into these industries has the potential to significantly reduce their reliance upon conventional fossil fuels and, hence, their CO$_2$ footprint. While various renewable energy sources can be employed for clean electricity generation, concentrating solar thermal technologies represent presumably the most attractive candidate for providing renewable, high-temperature heat to drive industrial processes.

This work investigates the integration of concentrated solar energy into the extractive metallurgy of zinc, a chemical element with extensive application as an anticorrosion agent for steel structures and a main constituent of metal alloys. Due to the rapid depletion of high-grade zinc ores and increasing global demand, the focus does not lie only on the primary production of zinc but also on zinc recovery from secondary sources such as zinc-bearing metallurgical waste materials. In particular, several aspects of the solar reactor technology for performing the solar-driven carbothermal reduction of primary and secondary ZnO sources are experimentally and numerically investigated.

Waelz oxide (WOX), a Zn-enriched oxidic material derived from electric arc furnace dust produced during recycling of galvanized steel, is considered as the secondary ZnO source in the current study. In the conventional industrial production of Zn, crude WOX is washed to separate off halides before being fed along with ZnS concentrates to electrolytic
plants for the production of high-grade zinc. However, the wash treatment of crude WOX generates further waste. Therefore, this work proposes and investigates novel and environmentally cleaner routes for the purification of WOX and the production of Zn using concentrated solar energy as the source of the high-temperature process heat. The solar-driven purification of WOX and its carbothermal reduction were experimentally demonstrated using a 10 kWth packed-bed solar reactor. Solar purification of crude WOX at above 1265°C reduced the amount of impurities below 0.1 wt.%, whereas carbothermal reduction of the solar-purified WOX using beech charcoal as reducing agent at temperatures between 1170°C and 1320°C yielded 90 wt.% Zn and similar production rates as those obtained with primary ZnO sources.

Besides the experimental investigation of the solar-driven carbothermal Zn production, process understanding is enhanced by a transient numerical model formulated for the 10 kWth solar reactor. It is based on a detailed heat transfer analysis that uses the incoming solar power as the driving boundary condition and couples the effects of heat conduction, convection, radiation, and chemical reaction. Model validation is accomplished by comparison with experimental data in terms of temperatures, Zn, CO, and CO₂ production rates, product yield, and solar-to-chemical conversion efficiency obtained with the solar reactor. Further, an adapted version of the numerical model is used to predict the effect of incorporating semi-continuous feeding of reactants on the process efficiency.

As the current realization of the solar reactor technology is designed for recovery of the zinc vapor generated during the solar-driven carbothermal reduction of ZnO in its solid state, remelting is required for the industrial
application of zinc as a material commodity. Considerable energy savings and increase in the process efficiency can be attained by condensing zinc vapor to liquid rather than solid. However, adaptation of the lead-splash condenser technology used in the dominating pyrometallurgical zinc production process, the Imperial Smelting Process (ISP), into a solar thermochemical plant is considered impractical owing to its mechanical complications, the continuous recirculation of large quantities of lead, and the considerably different off-gas compositions in the ISP and the solar-driven processes. An alternative zinc condenser concept involving gas bubbling through a zinc liquid bath of the off-gas evolved from the solar-driven carbothermal reduction of ZnO is thus proposed and numerically modeled for transient heat and mass transfer. Condensation of bubbles containing 53.5% of non-condensable gases yielded chemical conversions of Zn(g) to Zn(l) in the range of 95.6 – 99.8% for operation in the temperature range 500 – 650°C while conversions of Zn(g) to ZnO in the order of 10⁻⁶ were obtained, thus predicting successful suppression of Zn(g) reoxidation by CO₂ and CO.

One of the major disadvantages of this solar reactor technology is the presence of a quartz window used to protect the reactor components against oxidation in the ambient atmosphere. It is a fragile and troublesome component that is not easy to keep uncontaminated by particle depositions and condensable gases evolving in the reaction chamber. Elimination of the quartz window would overcome one of the most significant hurdles toward commercialization. The last part of this work presents the actions taken toward this direction and encompasses the engineering design, fabrication, and successful experimental demonstration of a windowless packed-bed
solar reactor. The reactor design was aided by a numerical model that couples Monte Carlo ray tracing, thermal, and structural analyses. Different geometrical configurations made of carbon-fiber-reinforced SiC ceramic matrix composites or monolithic SSiC were experimentally tested for their suitability as solar absorbers in terms of their thermal behavior, structural stability, and oxidation resistance in air. Their chemical resistance to Zn(g), CO, and CO₂ was investigated by conducting carbothermal ZnO reduction experiments at temperatures above 1200°C. Peak Zn(g) production rates of 0.05 mol/min were obtained, leading to peak solar-to-chemical energy conversion efficiency up to 15%.
Zusammenfassung

Die Mineralverarbeitungs- und Metallindustrien weisen einen hohen Strom- und Hochtemperatur-Prozesswärme-Verbrauch auf, und sind somit verantwortlich für etwa 20% der weltweiten CO₂-Emissionen. Integration von umweltfreundlicheren Energieträgern in diese Industrien hat das Potenzial, ihre Abhängigkeit von fossilen Brennstoffen und ihren CO₂-Fußabdruck deutlich zu verringern. Für die umweltfreundliche Stromerzeugung können unterschiedliche erneuerbare Energieträger eingesetzt werden. Hingegen sind solarthermische Kraftwerke vermutlich die attraktivste Technologie zur Bereitstellung erneuerbarer Hochtemperatur-Prozesswärme.


In der vorliegenden Studie wird als sekundärer Zinkvorstoff Wälzoxid (WOX) benutzt. Wälzoxid ist ein hoch zinkhaltiges oxidisches
Zusammenfassung


Außer der experimentellen Untersuchung der solaren karbothermischen Produktion von Zn wird das Prozessverständnis durch die Formulierung eines instationären, numerischen Modells für den 10 kW\textsubscript{th} Solarreaktor verbessert. Dieses basiert sich auf einer detaillierten Wärmeübertragungsanalyse, die die eintreffende Solarenergie als Randbedingung benutzt und die Effekte der Wärmeleitung, Konvektion, thermischen Strahlung und chemischen Reaktion berücksichtigt. Die Modellvalidierung wird durch Vergleich mit in dem Solarreaktor erhaltenen experimentellen Temperatur-, Produktionsraten-, Produktausbeute- und Prozesseffizienzdaten durch-
geführt. Weiterhin wird eine angepasste Version des numerischen Modells eingesetzt, um die Wirkung semikontinuierlich zugeführter Ausgangsstoffe auf die Prozesseffizienz vorherzusagen.

Da die aktuelle Festbett-Solarreaktortechnologie die Zink-Gewinnung aus dem im Reaktor entstehenden Zinkdampf in festem Zustand vorsieht, ist das Umschmelzen von Zink für seine industrielle Anwendung als Materialrohstoff erforderlich. Eine erhebliche Energieeinsparung und Erhöhung der Prozesseffizienz können durch Umwandlung von Zinkdampf in die flüssige statt in die feste Phase erreicht werden. Jedoch ist die Anwendung des in dem dominierenden pyrometallurgischen Zinkherstellungsverfahren (Imperial-Smelting-Verfahren) angewandten Sprühkondensators in einem solarbetriebenen Prozess aufgrund seiner mechanischen Komplikation, der kontinuierlichen Rezirkulation von großen Bleimengen, und der deutlich unterschiedlichen Gaszusammensetzung in dem Imperial-Smelting- und dem Solarverfahren nicht als sinnvoll angesehen. Deshalb wird ein alternatives Zinkkondensatorkonzept vorgeschlagen und numerisch modelliert, welches das Durchleiten des im Reaktor entstehenden Abgasstoms durch ein flüssiges Zinkbad vorsieht. Kondensation aus Blasen mit einem 53.5%igen Gehalt an nicht-kondensierbaren Gasen im Temperaturbereich zwischen 500°C und 650°C ergab einen 95.6%igen bis 99.8%igen chemischen Umsatz von Zn(g) zu Zn(l), während der Umsatz von Zn(g) zu ZnO eine Größenordnung von 10⁻⁶ aufwies. Demnach hat das Modell unter diesen Betriebsbedingungen eine erfolgreiche Unterdrückung der Zn(g) Reoxidation mit CO₂ und CO vorhergesagt.
Einer der Hauptnachteile der angewandten Solarreaktortechnologie ist die Verwendung eines Quarzfensters, das die Reaktorkomponenten vor Oxidation durch die Umgebungsatmosphäre schützt. Es ist eine fragile und störende Komponente, die man nur schwer vor Partikelabscheidungen und kondensierbaren Reaktionsgasen schützen kann. Die Vermeidung des Quarzfensters würde eine der wichtigsten Hürden zur Kommerzialisierung der Technologie überwinden. Der letzte Teil der vorliegenden Arbeit stellt die in diese Richtung ergriffenen Massnahmen vor und umfasst Design, Konstruktion, Fertigung, und erfolgreiche experimentelle Demonstration eines fensterlosen Festbett-Solarreaktors. Das Reaktor-Design wurde durch ein numerisches Modell unterstützt, das ein Monte Carlo Ray-tracing, eine thermische, und eine strukturelle Analyse koppelt. Unterschiedliche geometrische Konfigurationen aus kohlefaser verstärkten Siliciumkarbid-Keramikmatrixverbundwerkstoffen oder aus monolithischem SSiC wurden auf ihre Eignung als Solarabsorberkörper in Bezug auf ihr thermisches Verhalten, strukturelle Stabilität und Oxidationsbeständigkeit in Luft experimentell geprüft. Ihre chemische Beständigkeit in Zn (g), CO und CO\textsubscript{2} wurde durch die Durchführung von Versuchen zur karbothermischen Reduktion von Zinkoxid bei Temperaturen über 1200°C untersucht. Eine maximale Zn(g)-Produktionsrate von 0.05 mol/min wurde erhalten, welche einem solarchemischen Umsatzwirkungsgrad von 15% entspricht.
Acknowledgements

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<tr>
<td>$c_p$</td>
<td>specific heat capacity</td>
<td>$J \cdot kg^{-1} \cdot K^{-1}$</td>
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<td>D</td>
<td>diameter</td>
<td>$m$</td>
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<tr>
<td>g</td>
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<td>$J \cdot mol^{-1}$</td>
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<td>enthalpy of reaction</td>
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</tr>
<tr>
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<td>standard enthalpy of reaction</td>
<td>$J \cdot mol^{-1}$</td>
</tr>
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<td>k</td>
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<td>( = 8.314 J·mol$^{-1}$·K$^{-1}$)</td>
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<tr>
<td>Sₜ</td>
<td>heat source/sink</td>
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<tr>
<td>SC</td>
<td>enthalpy loss associated with changes in the SiC walls grid size</td>
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<tr>
<td>t</td>
<td>time</td>
<td>s, or min</td>
</tr>
<tr>
<td>Δt*</td>
<td>optimal time step</td>
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<tr>
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<td>uₜₐₐ₀</td>
<td>relative velocity of bubbles to liquid</td>
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<td>superficial velocity</td>
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<td>y</td>
<td>mass fraction</td>
<td>kg·kg⁻¹</td>
</tr>
<tr>
<td>z</td>
<td>axial coordinate</td>
<td>m</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>stoichiometric C:ZnO molar ratio</td>
<td>mol C·(mol ZnO)⁻¹</td>
</tr>
<tr>
<td>α</td>
<td>thermal diffusivity</td>
<td>m²·s⁻¹</td>
</tr>
<tr>
<td>δ</td>
<td>Kronecker delta function</td>
<td>-</td>
</tr>
<tr>
<td>ε</td>
<td>emissivity</td>
<td>-</td>
</tr>
<tr>
<td>εᵥ</td>
<td>bed void fraction</td>
<td>-</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity</td>
<td>Pa·s</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity</td>
<td>$m^2·s^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>kg·$m^{-3}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
<td>W·$m^{-2}·K^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($=5.67·10^{-8}$ W·$m^{-2}·K^{-4}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>stress</td>
<td>MPa</td>
</tr>
<tr>
<td>$\tau_{TOL}$</td>
<td>prescribed local error tolerance</td>
<td>-</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>volume fraction</td>
<td>$m^3·m^{-3}$</td>
</tr>
</tbody>
</table>

**Subscripts**

- b: bubble
- b: bulk
- bed: packed bed
- cond: condensation
- cond: thermal conduction
- conv: thermal convection
- e: externally supplied
- eff: effective
- f: feedstock
- g: gas phase
- i: incident
- i, j: cell indices
- i, j, k: surface segment indices
- i, j, k: chemical species indices
l leaving to surroundings
l liquid phase
o outgoing
s solid phase
v vapor
∞ bulk liquid

Superscripts

eq at thermodynamic equilibrium

Acronyms

CCD charge-coupled device
CMC ceramic matrix composite
CPC compound parabolic concentrator
EAF electric arc furnace
FE finite element
FV finite volume
GC gas chromatography
GHG greenhouse gas
HFSS High-Flux Solar Simulator
ISF Imperial Smelting furnace
LC lower cavity
MC Monte Carlo
RHS right-hand side
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SP</td>
<td>separation plate</td>
</tr>
<tr>
<td>tpd</td>
<td>tons per day</td>
</tr>
<tr>
<td>UC</td>
<td>upper cavity</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>W-N</td>
<td>Wheaton-Najarian</td>
</tr>
<tr>
<td>WOX</td>
<td>Waelz oxide</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Global extraction of material resources

The global extraction of material resources exhibited a 60% increase between 1980 and 2008 [1], largely driven by the rapid world population growth and rising per capita material consumption in the developing world, and is projected to further rise by 85% until 2030 [2]. Although global material extraction has been increasing overall, growth rates vary among the various material categories. Particularly, fossil fuels and biomass extraction increased by 82% and 61% over the last 35 years, whereas the demand for industrial minerals and metals has expanded rapidly by 240% and 183%, respectively, over the same period of time. Thus, the share of the two latter categories in the total raw material extraction has been constantly increasing and is currently just below 60% [3].

The minerals processing and extractive metallurgical industries are major consumers of fossil-fuel-derived electricity and process heat and, consequently, the largest source of anthropogenic greenhouse gas (GHG) emissions in the industrial sector. In absolute terms, extraction of cement, steel, aluminum, zinc, lead and copper release a cumulative annual amount of ~ 5240 Mt CO₂-eq, corresponding to about 20% of the global fossil-fuel CO₂ emissions [4]. Thus, meeting the rapidly growing demand for industrial minerals and metals, while reducing the GHG emissions from this sector in order to comply with the current climate change regulations, poses a severe
challenge for sustainable materials management. While technological advancements are constantly contributing to this direction by reducing the quantity of materials required to serve economic functions in society, the environmental impact of materials extraction and processing can be further decreased by pursuing material recycling strategies. Besides reducing the amount of waste produced and eliminating the need for mining new unexploited ores, the use of recycled raw materials has the potential to produce significant energy savings in the production of minerals and metals and, hence, reduce the annual GHG emissions from this sector by 200 Mt CO$_2$-eq [5]. In particular, the energy intensity of metal production processes can be reduced by 60 – 95% depending on the metal and the number of recycles when using scrap metals instead of raw materials as feedstock [6].

Further reduction in the amount of GHGs generated by the minerals processing and extractive metallurgy industries can be obtained by integrating environmentally cleaner energy sources into these industries to reduce their reliance on fossil fuels. Apart from environmental drivers, economic incentives toward this direction are often provided by changes in governmental policies. The introduction of a $23-per-ton-CO_2$ carbon tax into the Australian economy has been identified to induce an increase in the production costs of common minerals and metals by 2 – 19% depending on the energy intensity of the process [7].

1.2 Potential of concentrated solar energy

On the road to a sustainable energy use in these industries, solar energy is an attractive candidate since it is essentially inexhaustible while its
utilization is ecologically benign. However, the dilute nature of solar radiation, as best indicated by the maximum energy flux ($\sim 1 \text{ kW} \cdot \text{m}^{-2}$) reaching the earth’s surface, limits the efficiency at which solar energy can be utilized. Concentration of solar radiation incident on a large area of land onto a smaller area by the use of parabolic mirrors-reflectors and subsequent collection of the concentrated solar energy by a receiver overcomes this problem and enables conversion of sunlight to process heat.

Potential applications of concentrated solar thermal technologies in the minerals processing and extractive metallurgical industries include:

- utilization of solar-generated electricity in the ore mining, minerals processing and metal extraction processes
- provision of low- and moderate-temperature process heat to gases and liquids used at all stages of minerals and metals extraction and processing
- provision of high-temperature process heat for driving thermal and thermochemical processes

Transition from fossil-fuel- to solar-generated electricity in the Australian minerals and metallurgical processing industries has been identified to have the greatest potential to reduce GHG emissions out of all the potential applications of solar thermal technologies [7], owing mainly to the high share of electricity-intensive hydrometallurgical processes in the Australian extractive metallurgy and also to the high amounts of electricity consumed by all other processes involved between ore mining and metal production. Indeed, about 68% of the GHG emissions released along the whole bauxite-to-aluminum process chain in Australia are attributed to electricity production, while the major component thereof ($\sim 87\%$)
corresponds to the energy-intensive electrolytic reduction of $\text{Al}_2\text{O}_3$ to Al [7]. Thus, shifting the electricity generation from fossil fuel-based power plants to renewable energy sources will result in a noteworthy reduction of the energy-related CO$_2$ emissions. Concentrated solar power systems represent a mature and well-established technology, proven at commercial scale in existing power plants in operation for more than 30 years [8], and are therefore not within the scope of the present study.

Heat delivery to fluids used in mining, minerals and metallurgical processing represents another application of concentrated solar thermal systems, which however is expected to have a relatively low influence on the total amount of GHG emissions as it accounts for a rather small share of the total energy use in these industries.

On the contrary, since minerals processing and pyrometallurgical methods for the extraction of metals are major consumers of high-temperature process heat and, consequently, an important contributor to the total GHG emissions, the carbon footprint of these processes can be reduced considerably by providing the high-temperature process heat by a cleaner energy source like concentrated solar radiation [9].

1.3 Solar-driven minerals and metallurgical processing

Thermal and thermochemical processes with great potential for replacing fossil-fuel-derived process heat by concentrated solar thermal energy encompass: a) processing of industrial minerals, b) extraction of metals from their ores, c) recycling of scrap metals and metallurgical waste materials.
1.3.1 Solar-driven processing of industrial minerals

Due to the extensive application of cement in the construction industry and the severe GHG emissions from the cement manufacture, accounting for about 8% of the global GHG releases [4], integration of concentrated solar thermal technologies into the cement production has attracted considerable attention. The most energy-intensive step in the cement manufacturing process is the thermal decomposition of limestone (CaCO₃) to lime (CaO) and proceeds in preheater-kiln calcining systems at temperatures up to 1450°C. It is responsible for about 90% of the total GHG emissions in the cement industry; 35 – 40% thereof is generated by fossil fuel combustion in the kiln and 60 – 65% is chemically released during the decomposition reaction:

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$  \hspace{1cm} (1.1)

Replacing fossil-fuel-derived process heat with concentrated solar radiation to drive the highly-endothermic reaction has the potential to generate 20% GHG savings in the lime manufacturing industry. The solar-driven thermal decomposition of limestone has been previously proposed and experimentally demonstrated in a 10 kWₘₜ solar multitube rotary kiln tested at the Paul Scherrer Institute’s solar furnace [10]. The solar kiln consists of a tilted rotating cylindrical cavity-receiver containing 16 solar absorber tubes made of recrystallized silicon carbide (ReSiC). Solar radiation gets absorbed on the outer surface of the tubes, into which 1 – 5 mm limestone particles were fed at a rate of 2 – 8 kg/h and calcined at temperatures between 930°C and 1130°C. High-purity lime with a degree of calcination up to 98% was produced. Peak lime production rates of 4 kg/h were obtained, leading to a
reactor efficiency of about 35% [11]. An economic evaluation estimated that the production cost of solar lime for a 20–25 MWth solar plant would exceed by 2–3 times the selling price of the conventional product [12]. However, with trends toward lower investment costs for concentrated solar thermal plants, solar-driven decomposition of CaCO3 is expected to become an economically viable path in the future.

The feasibility of using concentrated solar radiation as the source of the high-temperature process heat was experimentally investigated also for the glass manufacture. Heat treatment of pure silica, ternary simple-soda-lime-silica (SLS) glass batch and industrial SLS pellets at temperatures close to 1400°C resulted in complete conversion of the raw materials to X-ray amorphous glasses [13].

Other processes with great potential for integration of solar thermal energy include the production of metal oxides by calcination of their respective carbonates or hydroxides. Magnesium oxide is a likely candidate since it is produced at high temperatures (700 – 2000°C) according to:

\[
\begin{align*}
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2 \\
\text{Mg(OH)}_2 & \rightarrow \text{MgO} + \text{H}_2
\end{align*}
\]

(1.2)  
(1.3)

The amount of high-temperature heat required to drive the process is directly dependent on the specific calcination temperature, which is determined by the desired level of reactivity of the MgO product. Alternatively, solar energy can be employed in the production of alumina (Al2O3) via the decomposition of aluminium hydroxide (Al(OH)3):

\[
2 \text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O}
\]

(1.4)
Conventionally, aluminium hydroxide is converted to anhydrous alumina in rotary kilns and fluid flash calciners at temperatures above 1000°C, and fossil-fuel-derived process heat represents more than 90% of the energy consumption. Thus, a hybrid solar-fossil-fuel-powered rotary kiln allowing for round-the-clock operation has the potential to generate GHG savings up to 30 – 35% in alumina production processes [7].

1.3.2 Solar production of metals

The substantial amounts of high-temperature process heat consumed in smelting processes reveal the great potential of concentrated solar thermal technologies for integration into the field of metal production. Solar-driven production of metals can proceed via the thermal dissociation of metal sulfides (Eq. 1.5) as well as via the thermal dissociation (Eq. 1.6) or the carbothermal reduction (Eq. 1.7) of metal oxides:

$$M_xS_y \rightarrow xM + yS \quad (1.5)$$

$$M_xO_y \rightarrow xM + \frac{y}{2}O_2 \quad (1.6)$$

$$M_xO_y + y C \rightarrow xM + y CO \quad (1.7)$$

where $M$, $M_xS_y$, and $M_xO_y$ denote the metal, metal sulfide and metal oxide, respectively.

The solar-driven production of metals directly from their respective metal sulfides has been proposed with an aim to replacing both processes involved in the conventional metal extraction, roasting and smelting, by an environmentally cleaner metal production route that would substantially reduce the $SO_2$ and $CO_2$ emissions. The technical feasibility of the solar
thermal extraction of zinc and copper from ZnS and Cu$_2$S, respectively, was experimentally investigated in a tube furnace interfaced to a quench unit under inert atmospheres. At temperatures up to 1800 K no metallic Zn was detected presumably due to recombination of Zn(g) with S$_2$(g) in the quench unit. On the contrary, direct thermal extraction of Cu from Cu$_2$S appears to be a promising route since metallic Cu was produced at temperatures as low as 1323 K while recombination of Cu(l) and S$_2$(g) does not represent a major problem since separation will occur naturally during the process [14].

Thermal dissociation of common metal oxides is thermodynamically favored at very high temperatures (> 3050 K) [15], thus posing very severe challenges on the solar reactor materials. From this perspective, the relatively low onset temperature (2340 K) of the ZnO dissociation reaction at a total pressure of 1 bar makes this metal oxide the most attractive candidate for a solar-driven dissociation process. The onset temperature of the reaction can be lowered further by using inert gas to dilute the gaseous products and consequently shift the thermodynamic equilibrium. Experimental investigations on the solar-driven ZnO dissociation were previously performed using various solar reactor concepts including entrained flows [16], packed beds [17], gravity-fed moving bed [18], and rotary cavity receivers [19], [20]. Concerning the rotary cavity receiver-reactor concept, the experimental demonstration [20] and numerical modeling [21] of a 10 kW$_{th}$ directly-irradiated solar reactor prototype was followed by a pilot-scale demonstration of a 100 kW$_{th}$ solar thermochemical plant [22] experimentally tested in the solar furnace of PROMES-CNRS (Odeillo, France). During reactor operation, a layer of ZnO particles was directly exposed to concentrated solar radiation and reached temperatures up to
1936 K. Despite obtaining relatively high dissociation rates (3.4 g/min), the molar purity of Zn in the products ranged only between 12% and 49% due to partial reoxidation of Zn(g) with O$_2$ in the off-gas stream. The reversion reaction represents a major limitation of this process and its extent depends substantially on the amount of inert gas (Ar) injected at the reactor outlet for rapid quenching and dilution of the gaseous products [22], [23].

Except for the thermal dissociation of ZnO, solar process heat is not sufficient for driving reaction (1.6) [15]. Therefore, some amount of high-quality energy in the form of work is required to shift metal formation to lower temperatures. This can be supplied in the form of chemical energy by introducing a carbonaceous reducing agent to carbothermally reduce the respective metal oxide according to Eq. (1.7). Temperatures required to drive such a process can be lowered further by decreasing the total pressure of the system [24]. Despite introducing a CO$_2$ emitting source into the process, significant emissions savings can still be attained vis-à-vis conventional smelting processes, in which carbonaceous material is used not only as a reducing agent but also as the primary source of process heat. The production of common metals via the solar carbothermal reduction route has been investigated using various solar reactor concepts and reducing agents.

The solar carbothermal reduction of alumina (Al$_2$O$_3$) was experimentally investigated under vacuum conditions at Paul Scherrer Institute’s high flux solar simulator [25]. The total pressure in the solar reactor was maintained between 3.5 – 12 mbar to lower the onset temperature of Al vapor formation. Experiments were carried out using Al$_2$O$_3$ and bio-charcoal at Al$_2$O$_3$:C molar ratios of 1:3 and temperatures in the range of 1300 – 2000 K. Aluminum contents of 4 – 19 wt.% were
attained in the products at temperatures between 1660 K and 2000 K. Alumina was also present in the products and its formation was attributed to the reversion reaction of Al(g) with CO in the off-gas stream. A major shortcoming of this process is the high-complexity of the Al₂O₃ – C system, which led to the formation of undesired byproducts (Al₄C₃, Al₄O₄C) in the crucible [26].

Experimental tests were performed in the same reactor configuration to investigate the technical feasibility of a solar-driven carbothermal Si production process under vacuum conditions [27]. Mixtures of SiO₂ and beech charcoal at SiO₂:C molar ratios of 1:1, 1:2 and 1:4 were introduced into the solar reactor and directly exposed to concentrated solar radiation. At a total pressure of ~ 3 mbar and temperatures between 1997 K and 2263 K, products with Si purity of 66.1 – 79.2 wt.% were obtained. Apart from Si, Si-O compounds and SiC were detected in the condensed gaseous products and the crucible, respectively. The vacuum carbothermal reduction of silica was investigated also in Paul Scherrer Institute’s 1 kWₑ imaging furnace [28] at slightly higher total pressures (7 mbar) and temperatures up to 1800 K [29]. At SiO₂:C molar ratios of 1:1, 1:1.5 and 1:2, Si purities in the range of 41.9 – 55.3 wt.% were attained and similar intermediate products (SiO, SiO₂, SiC) were detected in the condensed gases and the crucible. The presence of SiO₂ in the condensed products was attributed to the disproportionation reaction of the metastable SiO(g) to solid Si and SiO₂ in the off-gas stream. Experimental runs carried out at higher pressure (1 bar) in a solar thermogravimeter at Paul Scherrer Institute’s solar furnace [10] required considerably higher temperatures (2075 – 2312 K) to yield similar Si purities (36.1 – 45.9 wt.%) [29].
Introduction

The potential of integrating solar process heat into the production of iron was investigated by performing exploratory studies on the carbothermal reduction of \( \text{Fe}_2\text{O}_3 \) at temperatures between 1300 K and 2390 K [30]. The highest Fe content (~ 78 %) was obtained at temperatures between 1850 K and 2000 K, whereas lower amounts of Fe were detected at temperatures above 2100 K due to the formation of by-products (\( \text{Fe}_3\text{C} \)). The use of methane as an alternative carbonaceous reducing agent for the co-production of Fe and synthesis gas by the combined reduction of \( \text{Fe}_3\text{O}_4 \) and reforming of \( \text{CH}_4 \) has been proposed and tested at a solar furnace at the Paul Scherrer Institute using a directly irradiated fluidized bed reactor [31]. Iron oxide particles, fluidized by \( \text{CH}_4 \), reacted to Fe and FeO at temperatures between 1073 K and 1273 K, yielding Fe purities up to 68 wt.%. The production of magnesium and boron via the solar-driven carbothermal reduction of \( \text{MgO} \) and \( \text{B}_2\text{O}_3 \), respectively, has been also experimentally investigated in a directly irradiated solar reactor at reduced pressures and temperatures in the range of 1360 – 1539°C using pelletized mixtures of wood charcoal, the respective oxide, and 10 wt.% sugar as a binder [32]. Efficient quenching of the gaseous products prevented re-oxidation of the metal vapors in the off-gas stream and facilitated high Mg contents (~ 95 wt.%) in the gaseous products, whereas only solid products in the form of boron carbide were formed in the carbothermal reduction of boria.

1.3.3 Scrap metal and metallurgical waste recycling

As high-grade metallic mineral reserves are progressively being depleted, the average grade of unexploited ores is gradually dropping.
However, the use of lower-grade minerals induces a considerable increase in the energy consumption during the stages of mining and minerals processing due to the additional energy required for the separation and transport of the unwanted materials in the ore. Indeed, a 1.4% decline in the copper ore grade was shown to have a dramatic effect on the energy consumption in the pyrometallurgical production of copper and induced a 200% increase in the energy-related GHG emissions [6]. Therefore, the less-energy intensive scrap metal and metallurgical waste recycling processes are gaining increasing scientific and industrial interest lately. Unlike conventional recycling processes that make use of induction, arc, plasma, and fossil-fuel-powered blast furnaces, concentrated solar radiation has the additional advantage of supplying clean thermal energy to drive the production of valuable feedstock from waste materials.

Remelting of aluminium scrap was experimentally demonstrated at the German Aerospace Center’s solar furnace using a solar rotary kiln with a capacity of 1 – 2 kg Al and a maximum rotational speed of 6 rpm [33]. At temperatures close to 800°C, Al scrap was molten and discharged along with slag into molds positioned at the back side of the kiln. A pilot-scale solar thermal recycling plant capable of melting 20 kg Al scrap is currently under development [34].

The solar-driven recovery of metals via the carbothermal reduction of electric arc furnace (EAF) dust, one of the most common byproducts in the metallurgical industry derived from the treatment of galvanized steel scrap, has been investigated for its technical feasibility using an indirectly irradiated 10 kW_{th} solar reactor. In this reactor concept, solar radiation is absorbed by an intermediate graphite absorber and reradiated to the reaction
chamber. The reactor was operated in both batch and continuous mode and the solid feedstock, consisting of 87% EAF dust and 13% activated charcoal, was treated at temperatures between 850°C and 1130°C. At 1130°C, 99% of the Zn and Pb initially contained in the EAF dust was distilled [35].

1.4 Solar energy in the extractive metallurgy of zinc

In addition to the formerly discussed and other numerous applications of concentrated solar energy in the fields of minerals processing and extractive metallurgy, the solar-driven extraction of zinc via the carbothermal reduction of ZnO has attracted considerable attention. The attractiveness of this process is attributed to its thermodynamic favorability at moderate temperatures (> 1220 K), the conversion of ZnO to Zn without the formation of undesired byproducts, the limited degree of Zn(g) reoxidation in the off-gas stream, and the product versatility. Besides its extensive application as a metal commodity, zinc can be used as a solid fuel for electricity generation in Zn-air batteries and fuel cells [36], [37].

1.4.1 Primary Zn production

In the conventional primary zinc production sulphidic and oxidic concentrates are processed for the extraction of zinc via either the electrolytic or the pyrometallurgical processing routes [38]–[40]. In the dominating pyrometallurgical process, the Imperial Smelting Furnace (ISF) process [41], Zn is extracted in a blast furnace by carbothermally reducing ZnO to form Zn(g) and CO in a highly endothermic reaction according to:

\[
\text{ZnO}(s) + C(s) = \text{Zn}(g) + \text{CO} \quad \Delta H_{298 \text{K}}^0 = 239.9 \text{ kJ mol}^{-1} \quad (1.8)
\]
Equation (1.8) proceeds at above 1220 K via the solid-gas reaction [42]:

\[ \text{ZnO}(s) + \text{CO} = \text{Zn}(g) + \text{CO}_2 \quad \Delta H_{298}^o = 67.5 \text{ kJ mol}^{-1} \quad (1.9) \]

where CO is formed by the Boudouard reaction:

\[ \text{CO}_2 + \text{C}(s) = 2 \text{CO} \quad \Delta H_{298}^o = 172.4 \text{ kJ mol}^{-1} \quad (1.10) \]

The heat required to drive the reaction is provided by the exothermic combustion of coke in preheated air entering into the furnace bosh. Thus, coke is supplied in excess of the stoichiometric C:ZnO amount (α), and typically \( \alpha \approx 4 \text{–} 5 \). Although providing the process heat inside the furnace considerably increases the heat transfer rate to the reacting feedstock and permits the use of larger furnace units vis-à-vis preceding Zn production processes [40], the introduction of air into the furnace induces higher \( \text{CO}_2 \) concentrations and, hence, oxidation potential in the furnace off-gas. Therefore, zinc vapor has to be rapidly condensed (Eq. 1.11) to prevent the reoxidation reactions (Eq. 1.12 & 1.13) to proceed:

\[ \text{Zn}(g) = \text{Zn}(l) \quad (1.11) \]
\[ \text{Zn}(g) + \text{CO}_2 = \text{ZnO}(s) + \text{CO} \quad (1.12) \]
\[ \text{Zn}(g) + \text{CO} = \text{ZnO}(s) + \text{C}(s) \quad (1.13) \]

In the conventional ISF process, zinc vapor is scrubbed from the furnace off-gas with lead droplets in a lead splash condenser [40]. Zinc vapor is thereby rapidly quenched and absorbed into molten lead, and \( \text{Zn}(g) \) reoxidation is mostly avoided. Separation of zinc from the Zn-Pb alloy proceeds upon cooling from 550°C to 450°C by taking advantage of the decrease in the solubility of zinc in lead at lower temperatures. Liquid zinc separates as a layer over Pb(l), and is tapped out for further refining, whereas the liquid
lead is recirculated to the condenser inlet for recovery of fresh Zn(g). While several other concepts have been proposed in the literature [43]–[46], some of which have been tested at pilot scale or commercially operated, the lead splash condenser remains the only commercial zinc condensation process in operation today.

By replacing fossil fuels by concentrated solar energy, the amount of carbonaceous materials needed to reduce ZnO to Zn(g) could be decreased by $75 – 80\%$ ($\alpha = 1$) as carbon would then serve exclusively as a reducing agent and not as the primary source of process heat. A previous study [47] investigating the effect of the C:ZnO molar ratio on the minimum temperature required for thermodynamically complete conversion of ZnO to Zn(g) showed that moderate temperatures (1623 K) are required even for $\alpha = 0.6$, thus favoring the use of sub-stoichiometric amounts of carbon ($\alpha < 1$) in a solar-driven process. Besides the additional CO$_2$ savings generated by operating with sub-stoichiometric amounts of carbon, low C:ZnO molar ratios were also shown to have a positive effect on the thermal efficiency of the process [47]. However, sub-stoichiometry is expected to induce higher CO$_2$ concentrations in the reactor off-gas and thus favor Zn(g) reoxidation. Additionally, depending on the reactor type and the size and morphology of the reacting feedstock, kinetic limitations may arise for $\alpha < 0.7$. Therefore, selection of the optimal value of $\alpha$ for the solar-driven carbothermal ZnO reduction involves a trade-off between reactor thermal efficiency, the extent of Zn(g) vapor reoxidation in the off-gas, and reaction kinetics. Figure 1.1 depicts the thermodynamic equilibrium composition of the system at a ZnO:C molar ratio of 1:0.8 and total pressure of 1 bar [48]. At this molar ratio, formation of Zn(g) is thermodynamically favorable at temperatures
above 1150 K, whereas complete chemical conversion of ZnO to Zn(g) is obtained at about 1420 K. At temperatures below 1190 K, predominantly Zn(g) and CO are formed. However, the partial pressure of CO$_2$ ($p_{CO_2}$) increases with temperature, leading to $p_{CO}/p_{CO_2} = 3$ above 1420 K.

![Figure 1.1](image)

**Figure 1.1.** Variation of the equilibrium composition as a function of temperature for the system ZnO + 0.8 C at 1 bar.

### 1.4.2 Secondary Zn production

Following the general trends toward increasing waste material recycling, the percentage of recycled feedstock in zinc smelting is steadily growing. Primary processes may still account for the dominant share in zinc production, but secondary production exhibits high growth rates over the last 20 years due to shortage of zinc sulphide ore concentrates in the market and expanding global demand. In particular, zinc recovery from secondary
materials increased from \(~10\%\) to \(30\%\) of the global zinc production between 1994 and 2009 [49], [50]. Besides the formerly discussed ecological advantages and energy savings from materials recycling, secondary zinc recovery is becoming an appealing route for zinc production due to the lower cost of the feedstock compared to zinc-containing ores and due to the absence of sulphur in secondary Zn-bearing materials. The use of secondary ZnO sources also reduces the sensitivity to price fluctuations in the concentrate market by achieving feedstock diversification. In practice, primary smelters often use zinc scrap or metallurgical waste along with ZnS concentrates as feedstock material, thus making the borders between primary and secondary production not clearly defined [51].

Secondary zinc is produced most commonly either by remelting Zn-containing metal scrap at temperatures close to \(365\,^\circ\text{C}\) [51] or by recovering it from metallurgical zinc-bearing dusts and drosses. One of the most common metallurgical waste materials utilized for secondary production of zinc is dust derived from recycling of galvanized steel in electric arc furnaces (EAFs). During this process \(15–25\,\text{kg}\) of EAF dust are generated per ton of steel recovered. It consists mainly of Zn (\(18–35\,\text{wt.\%}\) as ZnO, ZnS, and ZnCl\(_2\)), Fe (\(30–40\,\text{wt.\%}\) as Fe and Fe oxides), as well as Ca and Si compounds and is categorized as a hazardous solid waste material [52], [53]. However, since the Zn content in EAF dusts is too low to economically treat them for Zn in zinc recovery facilities, they undergo a further treatment in pyrometallurgical [54]–[57] and hydrometallurgical [58]–[60] processes. More than \(95\%\) of the EAF dust treatment capacity is provided by pyrometallurgical processes, the dominating of which is the so-called Waelz process [55], [56]. In the Waelz process, EAF dust is fed continuously into a
rotary kiln along with a carbonaceous reducing agent and a slag-forming sand or lime. The kiln is slightly inclined for enabling residence times of 6 – 9 hours. The charge is transformed at about 1200°C into iron-rich Waelz slag (composed mainly of 35 – 45 wt.% Fe, 17 – 25 wt.% CaO, 7 – 10 wt.% SiO₂) and Waelz oxide (WOX) [52]. The latter is produced upon the volatilization of the non-ferrous components of the charge, mainly Zn and Pb, during the carbothermal reduction and their subsequent oxidation in an air flow entering through the discharge end of the kiln. Under normal operating conditions, the process is autothermal. The crude WOX generated contains about 60 – 65% Zn, mainly in the form of ZnO. In addition, chlorides (3 – 7 wt.% Cl as NaCl, KCl, CaCl₂, ZnCl₂, PbCl₂, Pb(OH)Cl) and fluorides (0.05 – 0.2 wt.% F as NaF, KF, CaF₂) are accumulated. These compounds restrict the direct feeding of WOX to the primary Zn electrolytic production plant as they are detrimental to the anodes used for zinc electrowinning. Thus, the last step of the Waelz process comprises usually washing of crude WOX and aims at the removal of halides from the crude WOX. The end product, which constitutes a Zn concentrate (65 – 68 wt.% Zn), with chlorine and fluorine contents below 0.1 wt.% and 0.15 wt.%, respectively, is then obtained upon leaching of WOX [61]. Washed WOX enters the Zn cycle as an input feedstock along with Zn-containing ores. The effluent, containing the dissolved components, can be either released as wastewater after its further treatment (e.g. precipitation of heavy metals and neutralization) to comply with the water pollution regulations or crystallized in an evaporation-crystallization unit.

Since the washing process of crude WOX is accompanied by difficult wastewater treatment or wastewater discharge into the sea, in the current
work an alternative cleaner process route for the purification of WOX is pursued using concentrated solar energy to provide the process heat, as depicted in Figure 1.2.

Figure 1.2. Process flow diagram for the conventional steel and zinc industry, and alternative routes using concentrated solar energy.

In a solar-driven thermal process – referred as “solar clinkering” –, the purification of crude WOX will proceed via volatilization of the halides at high temperatures. The solar-clinkered product might then be used as feedstock for the solar-driven carbothermal production of secondary zinc, whereas the clinker dust containing the evaporated halogens as well as a portion of Zn lost during the process due to chemical bonding to halides
might be sold to the chemical industry [62]. Zinc losses can be accepted to some extent because of the high purity of the clinker WOX.

### 1.4.3 Solar reactor technology

Previous research on the integration of concentrated solar energy into the extractive metallurgy of zinc has focused mainly on the carbothermal reduction of primary ZnO sources according to Eq. (1.8). In particular, this process has been experimentally demonstrated using various solar reactor concepts and reducing agents.

A directly irradiated, continuously gravity-fed 10 kW\(_{th}\) solar reactor has been tested for performing the carbothermal reduction of ZnO with beech charcoal at Paul Scherrer Institute’s high flux solar simulator [25]. At temperatures between 1113 K and 1446 K and a ZnO:C molar ratio of 1:1, peak Zn(g) production rates up to 0.135 mol/min and solar thermochemical efficiencies as high as 12.4% were obtained. However, ZnO-to-Zn(g) conversions only up to 14% were reached due to insufficient residence time of the feedstock in the solar reactor and to the entrainment of unreacted particles by the vortex flow toward the reactor outlet [63].

The feasibility of an annular-type, windowed 20 kW\(_{th}\) solar receiver-reactor for performing the carbothermal reduction of ZnO powder with graphite has been experimentally investigated at the Weizmann Institute of Science’s solar tower. After 1 h of steady-state operation at temperatures close to 1613 K, ZnO-to-Zn(g) conversions below 10% were obtained due to poor reactor insulation which resulted in considerable heat conduction losses and, thus, posed a limitation on the reaction kinetics [64]. To prevent
contamination of the quartz window by particle depositions and condensable gases evolving in the reaction chamber, researchers at the Weizmann Institute of Science designed, fabricated, and experimentally tested a non-windowed solar reactor in which a ceramic crucible made of SiC replaces the window. Mixtures of ZnO powder and charcoal at a ZnO:C molar ratio of 1:0.8 were loaded into the reaction chamber prior to the start of each experimental run and the mechanical stability and chemical inertness of the crucibles were investigated at temperatures up to 1473 K. Peak Zn(g) production rates up to 0.07 mol/min were obtained, but the reaction rates decreased exponentially as the reactants were progressively consumed and the reaction front moved away from the hot crucible surface [65].

Extensive research work has been conducted using an indirectly irradiated 10 kW_{th} packed-bed solar reactor. Early experiments with this reactor concept were performed at PSI’s solar furnace and ETH’s high-flux solar simulator to investigate the effect of process temperatures (1350 – 1600 K), ZnO:C molar ratio (1:0.7 – 1:0.9), and type of reducing agent (beech charcoal, activated charcoal, and petcoke) on the reactor performance and chemical conversion. Complete conversion of ZnO to Zn(g) and thermal efficiencies in the range of 14 – 21% were obtained [66]. After slight modifications to the reactor design aiming to improve its thermal efficiency according to the generic guidelines provided in [67], [68], the effect of the carbonaceous agent and carrier gas (N\textsubscript{2} and CO) on the overall reaction rate was studied at temperatures between 1373 K and 1573 K [69]. The improved 10 kW_{th} packed-bed solar reactor configuration presented in [69] will be discussed in detail in the next chapter. Based on the results obtained with the 10 kW_{th} prototype, this reactor concept was scaled-up and tested in a
300 kW\textsubscript{th} pilot plant at the Weizmann Institute of Science’s solar tower. Experimental runs were performed at temperatures between 1300 K and 1500 K and ZnO:C molar ratios in the range of 1:0.8 – 1:1 using beech charcoal as the reducing agent. Zinc production rates of up to \(\sim\) 50 kg/h were obtained, leading to reactor efficiencies up to 30\% [70]. After the successful experimental demonstration of the process at pilot plant scale, a conceptual design of a 5 MW\textsubscript{th} demonstration plant and a 30 MW\textsubscript{th} commercial plant was performed [71].

Further insight into the heat and mass transport phenomena occurring during the solar-driven carbothermal reduction of ZnO has been gained by numerical modeling studies. A simplified 1-D transient heat and mass transfer model was initially developed for a shrinking packed bed of beech charcoal and ZnO particles [72], [73]. The computational domain of this model was restricted exclusively to the packed bed of reactants and temperatures obtained experimentally with the indirectly-irradiated 10 kW\textsubscript{th} solar reactor were used as boundary conditions. However, a reactor model coupling the effects of heat transfer to the reaction kinetics of the carbothermal ZnO reduction, able to simulate the absorption and transfer of the incoming solar radiation, and to identify the major sources of heat losses in the reactor, has not yet been developed and would significantly contribute to process optimization.

1.5 Thesis outline

This thesis focuses on the solar-driven production of Zn via the carbothermal reduction of both primary and secondary ZnO sources. It proposes and experimentally demonstrates a sustainable and environmentally
cleaner path using concentrated solar energy for the recovery of Zn from Waelz oxide. It further encompasses experimental and numerical work aiming to improve the robustness and efficiency of the solar reactor technology employed for affecting the solar-driven carbothermal production of Zn.

Chapter 2 provides a description of the indirectly-irradiated 10 kW<sub>th</sub> solar reactor. The reader is guided through the principal advantages and disadvantages of the reactor technology. Particular emphasis is placed on the current technical limitations, including the solar reactor itself as well as the off-gas treatment system.

Chapter 3 investigates the technical feasibility of the reactor for performing the solar clinkering of crude WOX and the carbothermal reduction of solar-clinkered WOX. In the solar clinkering experiments, the focus is in elucidating the influence of temperature and irradiation time on the composition of clinkered WOX. In the carbothermal reduction experiments, the main focus lies on the Zn production rate and Zn content in the condensed product.

Chapter 4 presents a transient numerical model of the 10 kW<sub>th</sub> solar reactor that couples conductive, convective, and radiative heat transfer to the chemical kinetics of the ZnO carbothermal reduction. The incident solar radiation serves as the driving boundary condition, and the net radiative heat fluxes within the reactor are determined by applying the radiosity enclosure theory. The temperature distribution in the reactor components and the packed bed are then obtained by solving the unsteady energy conservation equations. Model validation is accomplished by comparison to experimental data in terms of temperatures, Zn, CO, and CO<sub>2</sub> production rates, product
yield, and solar-to-chemical energy conversion efficiency obtained with the 10 kW<sub>th</sub> packed-bed solar reactor. The model is then extended to identify the major sources of heat loss and process irreversibilities, and to predict the performance of a semi-continuously fed batch reactor.

Chapter 5 is devoted to the off-gas treatment system of the solar reactor for the carbothermal Zn production. After providing the reasons for the unsuitability of the conventional lead splash condenser technology for integration into a solar-driven thermochemical plant, the development of an alternative zinc condenser to produce liquid zinc from the gas products evolving from the solar carbothermal reduction of ZnO is investigated. After a comprehensive literature review of the kinetics of Zn(g) oxidation in CO<sub>2</sub>–CO atmospheres, and of metal vapor condensation concepts for the production of liquid metals, a potential alternative Zn condensation process is identified. The technical feasibility of the proposed condensation process is assessed by the development of a transient model of simultaneous heat and mass transfer that links the competing condensation rates and kinetics of zinc vapor oxidation for solar reactor conditions. The condenser model allows the establishment of design specifications and operating conditions of a zinc condenser prototype.

Chapter 6 presents the comprehensive numerical and experimental investigations carried out to overcome one of the most significant technical challenges in commercializing the specific solar reactor technology: the elimination of the transparent quartz window. The windowless reactor design is aided by a numerical model that couples Monte Carlo ray-tracing, thermal, and structural analyses. Experimental investigations involve thermal testing of different intermediate solar absorber materials in terms of their
structural stability, oxidation resistance, and heat transfer efficiency as well as potential limitations their use imposes on the maximum operating temperature of the windowless reactor. The experimental work is culminated by demonstrating the technical feasibility of the windowless solar reactor for performing the carbothermal ZnO reduction under various operating conditions.

Chapter 7 provides a summary of the key findings and conclusions of the work, and presents an outlook for further research activities with particular emphasis on the development of the specific solar reactor technology.
Chapter 2

The packed-bed two-cavity solar reactor

This chapter serves as a bridge between the introduction and the main part of this thesis and provides the key features of the indirectly-irradiated solar reactor technology previously introduced in Chapter 1. This solar reactor technology was employed in the current work for affecting the carbothermal production of zinc from primary and secondary ZnO sources due to its simplicity, ease of operation and high level of maturity.

2.1 10 kW\textsubscript{th} solar reactor prototype

The schematic configuration of the 10 kW\textsubscript{th} solar reactor prototype is shown in Figure 2.1. It is designed for beam-down operation as obtained through a Cassegrain optical configuration that makes use of a hyperbolic reflector at the top of a solar tower to redirect sunlight collected by a heliostat field to a receiver-reactor located at ground level [74], [75]. The solar reactor consists of two cavities in series, separated by a 170 mm-diameter 5 mm-thick SiC-coated graphite plate. The upper cavity (UC) is subjected to concentrated solar irradiation entering through a 65 mm-diameter circular aperture with a 120 mm-diameter 2 mm-thick quartz window. A water-cooled 3-D compound parabolic concentrator (CPC) [76] integrated to the aperture augments the solar flux concentration and reduces reradiation losses. The lower cavity (LC) is an octagonal, 135 mm-diameter, 170 mm-high enclosure that serves as the reaction chamber and contains a
packed bed of solid reactants. With this arrangement, concentrated solar radiation is efficiently absorbed by the upper cavity, re-radiated by the hot separation plate towards the lower cavity, and absorbed by the upper surface of the packed bed. The main function of the separation plate is to protect the quartz window against contamination by particle depositions and condensable gases evolving in the reaction chamber, and thus it alleviates a major problem encountered in windowed solar reactors.

![Diagram of the 10 kW packed-bed solar reactor](image)

**Figure 2.1.** Schematic of the 10 kW$_{th}$ packed-bed solar reactor.

The gaseous products are swept out through a 50 mm-diameter outlet port located on the lateral walls of the lower cavity, above the packed bed. The walls of the lower cavity are lined with 8 mm-thick SiC plates to prevent the diffusion of condensable gaseous products into the surrounding insulation material. Both cavities are well insulated to reduce heat conduction losses.
2.2 Principal advantages and disadvantages

This simple reactor design has been demonstrated for different high-temperature solar thermochemical processes, including the solar carbothermal reduction of ZnO [66], [69], [70] and the steam gasification of carbonaceous feedstock [77], [78] on both laboratory (5 – 10 kW\textsubscript{th}) and pilot plant (150 – 300 kW\textsubscript{th}) scales.

At the current state, the reactor is operated in batch mode (1 batch per day for pilot and industrial scale realization of the technology). It offers simplicity of design, ease of operation while the often challenging feeding of reactants into a hot reactor is omitted. The packed bed concept further permits high degree of feedstock diversification as the reactor is capable of processing even bulky materials basically without pre-treatment. This represents an immense advantage over other reactor concepts for certain types of feedstock.

However, an important shortcoming of this reactor technology is associated with the superficial rather than volumetric heating of the feedstock. Heat transfer through the packed bed was shown to be the rate-limiting factor for the deeper regions of the bed both for the solar-driven carbothermal reduction of ZnO [72] and the steam gasification of carbonaceous materials [77], [79], thus preventing volumetric reaction of the feedstock. Consequently, the current realization of the technology is suitable only for processes in which the solid feedstock is converted predominantly into gaseous products. Treatment of high-ash containing feedstocks or reactants that are mainly converted into solid products leads to the formation of an insulating layer on top of unreacted material located beneath the reacting surface, thus posing a limitation on the batch size. Hence, in order
to effectively treat these types of feedstock and increase the product yield incorporation of continuous or semi-continuous feeding of reactants and removal of products is required.

Additionally, despite the protective action of the separation plate against fouling of the quartz window, the latter remains a troublesome and fragile component that is not easy to keep completely uncontaminated. Elimination of the window would overcome one of the most significant technical hurdles toward industrial scale application.

Finally, the use of beam-down optics reflecting impinging solar radiation toward the ground [80] might be considered as another disadvantage of this reactor technology. Although permitting installation of the reactor and the off-gas treatment system close to the ground, beam-down central receiver systems are less developed than elevated tower receiver concepts and are characterized by increased optical losses due to the insertion of a hyperbolic or elliptical reflector between the heliostat field and the elevated focal point. Rigid support of the reflector at an elevation of about \(~2/3\) that of a tower receiver and the need for an array of CPCs to recover the lost magnification at the reactor aperture induce a considerable increase in the investment costs of a beam-down plant as well [81]. To reduce the magnification of the image produced at the receiver aperture, another beam-down optical system configuration proposes the use of flat instead of curves optics for the reflector and positioning of the reactor closer to the reflector. In this way, the beam down length is substantially reduced and relatively high concentration ratios can be achieved at the reactor aperture without the need of CPCs. However, as the flat tower reflector will be exposed to considerably higher
heat fluxes advanced thermal design of the reflector will be required to avoid exceeding its maximum working temperature limit [82].

The use of beam-down optics represents an inherent disadvantage of the solar reactor technology considered in the current work. On the contrary, current technical limitations related to the types of feedstock that can be effectively processed in the solar reactor or to presence of the quartz window can be overcome with more research and development. Part of this work will present the respective ongoing activities directed toward the advancement of the solar reactor technology.
Chapter 3

Solar-driven zinc recycling\(^1\)

As formerly presented, increasing costs in the primary zinc production serve as the main driver for the zinc industry to consider alternative Zn-containing sources under more sustainable conditions. Washed WOX is the most commonly used raw material for secondary Zn production. However, since the industrial washing treatment of crude WOX generates further waste streams, alternative resources for the upgrade of crude WOX are gaining attention [62]. In this chapter, process routes for the thermal purification (“solar clinkering”) of WOX and the carbothermal production of Zn from solar-purified WOX are experimentally investigated using concentrated solar energy as an alternative source of the process heat.

3.1 Experimental setup

3.1.1 PSI’s High-Flux Solar Simulator

Experimentation was carried out using PSI’s High-Flux Solar Simulator (HFSS) [25]. This research facility comprises an array of ten high-pressure Xe arc lamps, each mounted in the primary focal point of an ellipsoidal specular reflector. Thermal radiative power of up to 50 kW\(_{th}\) can be delivered at peak radiative fluxes exceeding 11,000 suns (1 sun = 1 kW/m\(^2\))

to a secondary common focal plane by utilizing the optics of the ellipsoidal reflectors. Thus, solar receivers and reactors can be tested under controlled conditions closely approximating the radiative heat transfer characteristics of highly concentrating solar systems. Power flux intensities and the power input delivered to the test target can be regulated by varying the number of Xe-arc lamps in operation, adjusting the electric power of each lamp or the relative position of the test target to the secondary focal plane, and/or by controlling the Venetian blind-type shutter located between the arcs and the test target. The solar radiative power input and flux intensities are measured optically with a calibrated charge-coupled device (CCD) camera focused on an Al₂O₃-plasma coated Lambertian target positioned at the secondary focal plane with an accuracy of ± 10% and verified using a water-cooled copper-coiled calorimeter.

3.1.2 Solar reactor configuration and peripheral equipment

The reactor configuration used to experimentally investigate the potential of solar-driven zinc recovery from Waelz oxide has already been detailed in Section 2.1. To redirect the horizontally incoming beams from the HFSS into vertical beams entering the reactor, a 50 x 50 cm² water-cooled, Al-polished 45°-deflection mirror is used. A flow diagram of the experimental setup is shown in Figure 3.1. Inert gas (N₂) mass flow rates are controlled by Bronkhorst flow meters (EL-flow series). Two L_N min⁻¹ (L_N means liters at normal conditions; mass flow rates are calculated at 273 K and 1 bar) enter the upper cavity, and flow through small gaps around the separation plate into the lower cavity to prevent reaction gas from reaching the quartz window. Additionally, nitrogen was injected at three L_N min⁻¹
directly below the separation plate. After exiting the reactor, the carrier gas and gaseous products flow through a water-cooled condenser where part of the condensable products deposit before passing through a filtering system. The composition of the non-condensable product gases behind the filter is analyzed online by gas chromatography (Micro GC M200, 0.01 Hz sampling rate; Agilent Technologies, Santa Clara, CA).

**Figure 3.1.** Flow diagram of the experimental setup comprising the solar concentrating system, the solar reactor, the off-gas system, and the diagnostic instrumentation.

All experiments were performed at slightly above ambient pressure, with relative pressures of ~5 – 10 mbar. The pressure is monitored online in the lower cavity of the reactor (P1) and upstream of the filter unit (P2). A pressure relief valve opening at a relative pressure of 150 mbar prevents
damage of the quartz window in the case of clogging of the off-gas system. Packed-bed, reaction chamber walls, and off-gas temperatures are measured at eight locations by type-K thermocouples. Temperatures at the top \( T_{B2} \) and bottom of the packed bed \( T_{B1} \) provide the temperature difference across the bed. For the carbothermal reduction, \( T_{B2} - T_{B1} \) indicates the remaining unreacted material and ash. The temperatures of the UC insulation cone \( T_{U1} \) and of the inner SiC lining approximately 8 mm below the separation plate \( T_{W1} \) are representative for the upper and lower cavity, respectively.

### 3.2 Materials and Methods

#### 3.2.1 Materials

The crude and washed WOX used for the experiments originated from the Waelz kiln at Befesa Freiberg, Germany. Washed WOX was derived in the washing plant upon a three-step leaching of crude WOX. The elemental composition in % (w/w) of a dried sample is listed in Table 3.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Crude WOX (wt.%)</th>
<th>Washed WOX (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>60.05</td>
<td>68.30</td>
</tr>
<tr>
<td>Pb</td>
<td>3.64</td>
<td>5.17</td>
</tr>
<tr>
<td>Cl</td>
<td>5.57</td>
<td>0.43</td>
</tr>
<tr>
<td>K</td>
<td>3.49</td>
<td>0.09</td>
</tr>
<tr>
<td>Na</td>
<td>1.62</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe</td>
<td>1.64</td>
<td>2.64</td>
</tr>
<tr>
<td>C</td>
<td>1.33</td>
<td>1.39</td>
</tr>
<tr>
<td>S</td>
<td>0.58</td>
<td>0.16</td>
</tr>
<tr>
<td>F</td>
<td>0.12</td>
<td>0.20</td>
</tr>
</tbody>
</table>

\( ^a \) Oxygen is complementary to 100 %. 
For crude WOX, Zn, Pb, and Fe are present primarily in their oxidized state with ZnO being the main constituent in the range 71 – 77 wt.% [83], whereas the remaining components are in the form of chlorides (ZnCl₂, PbCl₂, NaCl, and KCl) and sulfates. For washed WOX, the ZnO content varies in the range of 83 – 87 wt.%. The pronounced decrease in the K, Na, and Cl contents in washed WOX is attributed to the depletion of chlorine by washing, which generates Zn-, Pb-, and Fe-enriched mixtures. The water content of the crude and washed WOX determined by drying at 105°C for 24 h is 1.1 wt.% and 12.6 wt.%, respectively. To ensure well-characterized properties and precise ZnO:C molar ratios in the starting reacting mixture, commercial ZnO (Alfa Aesar, Ward Hill, MA: 011558, purity: 99.0% min, mean particle size 44 μm) was used as feedstock in several carbothermal reduction runs for comparison with runs using crude, washed, and clinker fed WOX as feedstock. Beech charcoal gravel (proFagus, Bodenfelde, Germany; carbon content 83 wt.%, particle size 1.0 – 2.0 mm) was used as reducing agent because it is a widely available biogenic material suitable for the CO₂-neutral solar carbothermal reduction of ZnO [69]. It contains 83 wt.% C, 9.74 wt.% O, 3.02 wt.% H, 0.38 wt.% N, 0.01 wt.% S, and 2.2 wt.% ash. The ash composition is listed in Table 3.2. Softening and fusion occur at 1210°C and 1415°C, respectively [69].

The composition of raw materials was analyzed by x-ray powder diffraction (XRD; Phillips, Almelo, the Netherlands; XPert MPD/DY636, CuKα, \( \lambda = 1.540598 \, \text{Å}, \, 2\theta = 20 – 90^\circ, \) step size 0.05°, scan speed 0.01°/s) and their morphology was examined by scanning electron microscopy (SEM, SmartSEM, Carl Zeiss Supra 55VP; Carl Zeiss, Oberkochen, Germany). As expected, ZnO, PbO, Fe₂O₃, NaCl and KCl were the
dominating phases in crude WOX. No NaCl and KCl were detected for the washed WOX. The SEM pictures of the crude and washed WOX, commercial ZnO, and beech charcoal are shown in Figure 3.2. The commercial ZnO and the majority of the crude and washed WOX particles exhibited a wurtzite crystal structure: a hexagonal lattice consisting of two interconnecting sublattices of Zn\textsuperscript{2+} and O\textsuperscript{2−}, which allow the tetrahedral coordination of Zn and O atoms. All ZnO sources comprised highly agglomerated grains with negligible intraparticle porosity, indicating that the porosity can be attributed mainly to the interparticle void spaces. Crude and washed WOX also contained fine needles and sponge-like structures. Beech charcoal was highly branched and contained tubular pores.

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>44.81</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>20.00</td>
</tr>
<tr>
<td>MgO</td>
<td>14.44</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>4.36</td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
<td>3.52</td>
</tr>
<tr>
<td>MnO</td>
<td>3.01</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>2.43</td>
</tr>
<tr>
<td>FeO</td>
<td>2.20</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>1.29</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>0.94</td>
</tr>
<tr>
<td>Zn</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02</td>
</tr>
</tbody>
</table>
3.2.2 Experimental procedure

Experiments can be classified into two main types: i) solar clinkering tests aiming at the effective thermal purification of WOX and ii) tests for the carbothermal production of Zn from solar-purified WOX.

For the solar clinkering experiments, batches of crude WOX were loaded on a crucible made of heat-resistant austenitic stainless steel (Böhler H525, 1.4841; Böhler, Kapfenberg, Germany) resulting in a ~ 40 mm-thick porous bed. The upper and lower cavities were initially flushed with N₂. After ensuring O₂ concentration below 300 ppm, the HFSS was ignited and the shutter opening was increased stepwise at a 10% increment every 3 min, allowing the gradual heating of the packed bed to the desired...
temperature $T_{B1}$. This temperature was maintained constant for different time intervals (0, 15, 30, and 75 min) depending on the goal of each experiment. At the end, the shutter was closed and the HFSS was switched off. The carrier gas flow was maintained until the cavity cooled down. The same procedure was followed for the carbothermal reduction experiments. ZnO:C molar ratios of reactants ranged between 1:0.8 and 1:1.25. The values listed in Table 3.1 were used for the calculation of the molar ratios when crude or washed WOX were used as feedstock. The initial packed bed height was $\sim$40 mm. $T_{B2}$ was kept constant until the CO and CO$_2$ concentrations approached zero, indicating that the reaction neared completion. The Zn production rate was calculated from the oxygen balance in CO and CO$_2$. This calculation slightly overestimated the amount of Zn produced because it did not account for the oxygen content in charcoal and impurity oxides (PbO, Fe$_2$O$_3$, etc.) present in crude, washed, or clinkered WOX, a fraction of which may end up in CO or CO$_2$ as well. Products were analyzed for their Zn, Pb, Cl, F, K, Na, and Fe content by elemental analysis, for their phase composition by XRD, and for their morphology by SEM.

3.3 Experimental runs

3.3.1 Solar clinkering

Fifteen experimental runs were carried out with the solar radiative power input in the range of 4.1 – 4.85 kW$_{th}$. Under approximately steady-state conditions, the packed-bed top ($T_{B2}$) and bottom ($T_{B1}$) temperatures reached 1050 – 1310°C and 1000 – 1285°C, respectively. A representative run with 470 g of crude WOX is shown in Figure 3.3.
Figure 3.3. Solar reactor temperatures and molar flow rates of CO, CO$_2$, and H$_2$ during a representative solar clinkering experiment with 470 g of crude WOX.

After the stepwise increase of the radiative power input to 3.2 kW$_{th}$ within the first 18 min, the upper cavity temperature ($T_{U1}$) increased to 840°C and the one at the top of the packed bed ($T_{B2}$) to 420°C. Small amounts of CO$_2$ were attributed to residual oxygen. The full opening of the shutter after 27 min was immediately followed by the formation of higher CO$_2$ amounts. After 40 min, the reaction proceeded at higher rates once $T_{B2}$ and $T_{B1}$ reached 965°C and 360°C, respectively. The temperature gradient across the packed bed decreased with time due to the shrinkage of the bed; a temperature difference of ~ 90°C ($T_{B2} = 1310°C$ and $T_{B1} = 1220°C$) was observed at steady-state conditions. The gas flow rate of CO$_2$ reached a maximum of 0.012 mol/min after 55 min, while CO and H$_2$ were also detected in the off-
gas flow. CO became the predominant component of the off-gas at higher temperatures, consistent with the Boudouard equilibrium (Eq. 1.10). \( T_{BI} \) stabilized after 100 min and the evolution of CO and CO\(_2\) ceased, indicating the consumption of the carbon contained in the crude WOX. The desired \( T_{BI} \) of 1220°C was reached after 130 min and maintained during 30 min before turning off the HFSS.

The clinkered WOX collected from the crucible contained 68.1 wt.% Zn, 0.92 wt.% Cl, and 0.79 wt.% Pb. Other elements present in lower percentage were Fe and Ca. The effectiveness of solar clinkering in terms of the Zn content was comparable to the one acquired by the industrial washing process (see washed WOX in Table 3.1). The decrease of Pb content was even better. ZnO, Fe\(_2\)O\(_3\), MnO, PbO, and KCl were detected by XRD analysis, while no NaCl peaks were found. A representative SEM picture of clinkered WOX that underwent partial melting is shown in Figure 3.4.

![SEM of solar-clinker WOX](image)

**Figure 3.4.** SEM of solar-clinker WOX.
Condensed by-products were deposited on the condenser walls, the outlet pipes, and the filter. XRD analysis revealed the presence of ZnO, Zn, NaCl, KCl, PbO, and Pb. Zn was presumably formed by the reduction of ZnO with the small amount of carbon contained in crude WOX (~ 1.3 wt.%). Films of ZnO were formed on the Zn surface upon exposure to air. NaCl, KCl, and PbO evaporated at the temperatures investigated, thus decreasing the Cl and Pb content of the processed crude WOX. The formation of Pb can be attributed to the reduction of PbO with CO, either at the surface of the off-gas system components or during condensation in the aerosol.

The normalized mass balance is shown in Figure 3.5 for all 15 solar clinkering experiments. Also indicated are the nominal temperatures at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed and the irradiation time period at this temperature level. The mass balance is satisfactorily closed for most experiments. Deviations from 100% are partially attributed to the discrete measurements of the gas composition (0.01 Hz sampling rate). CO, CO$_2$, and H$_2$ accounted for ~ 5 – 11% of the mass and were linked to the amount of carbon in crude WOX (~ 1.3 wt.%). Temperature had a profound effect on the amount of condensed by-products because of the non-linear dependence of the vapor pressure with temperature, which favors vaporization from crude WOX. Larger amounts of condensed by-products were detected with increasing irradiation times, indicating that evaporation was not completed for the short tests.
Figure 3.5. Normalized mass balance for the solar clinkering experiments. The nominal temperatures at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed and the irradiation time period at this temperature level are indicated in the x-axis.

A comparison of the compositions of crude, washed, and solar-clinkered WOX with respect to the Zn, Cl, and Pb content is provided in Figure 3.6. In this figure, the irradiation time period for solar clinkering was 30 min. A notable decrease of Cl and Pb with increasing temperature was observed, which was accompanied by an increase in the Zn content. As ZnCl$_2$ and PbCl$_2$ exerted higher vapor pressures compared to other Cl- and Pb-compounds (see Table 3.3), they were vaporized at lower temperatures.
The volatilization of KCl, NaCl, PbO, and Pb was favored with increasing temperature, leading to further purification of crude WOX. A Cl content of 0.42 wt.%, comparable to that of washed WOX, was reached after 30 min irradiation at $T_{B1} = 1250^\circ$C. At $T_{B1} > 1265^\circ$C, the Cl content further decreased below 0.1%. In contrast to the conventional WOX washing process, very low residual Pb contents of 0.09 wt.% and 0.04 wt.% were obtained by solar clinkering at $T_{B1} = 1265^\circ$C and 1285°C, respectively. This effective purification is of particular importance because it enables the direct neutralization of the product in the Jarosite step of the primary Zn production cycle [84] without the need to pass it through the roaster.

![Graph showing Zn, Cl, and Pb content of crude, washed, and solar-clinkered WOX.](image)

**Figure 3.6.** Zn, Cl and Pb content of crude, washed, and solar-clinkered WOX.
### Table 3.3. Boiling points of Cl and Pb compounds.

<table>
<thead>
<tr>
<th>Element/compound</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
<td>732</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>950</td>
</tr>
<tr>
<td>KCl</td>
<td>1413</td>
</tr>
<tr>
<td>NaCl</td>
<td>1465</td>
</tr>
<tr>
<td>PbO</td>
<td>1470</td>
</tr>
<tr>
<td>Pb</td>
<td>1749</td>
</tr>
</tbody>
</table>

**Figure 3.7.** Normalized mass and elemental (Zn, Pb, and Cl) balances for 5 selected solar clinkering runs. The nominal temperatures at the bottom \(T_{B1}\) and top \(T_{B2}\) of the packed bed and the irradiation time period at this temperature level are indicated in the x-axis.
The clinkered WOX and condensed by-products were analyzed for their Zn, Cl, and Pb content. The normalized mass and elemental balances are shown in Figure 3.7 for five selected solar clinkering experimental runs at $T_{B1} = 1120^\circ$C, $1180^\circ$C, $1250^\circ$C, $1265^\circ$C, and $1285^\circ$C. Also indicated are the nominal temperatures at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed and the irradiation time period at this temperature level. Satisfactory closing of the mass balance for Zn was accomplished. Diffusion of gaseous products into the insulation material presumably accounted for the missing Cl and Pb, as well as molten Pb accumulated at the bottom of the crucible. An error source of the analysis was the inhomogeneous character of the products, especially for Pb as its accurate content determination in the clinkered WOX is difficult due to the occurrence of molten PbO and Pb phases.

### 3.3.2 Solar carbothermal reduction of ZnO and WOX

A series of 14 experimental runs with ZnO:C molar ratios between 1:0.8 and 1:1.25 was carried out using crude, washed, and solar-clinker WOX and commercial ZnO. Temperatures in the range of 1110 – $1210^\circ$C and 1170 – $1320^\circ$C were reached at approximately steady state at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed, respectively. A representative run with clinker WOX and a ZnO:C molar ratio of 1:0.86 is shown in Figure 3.8. After the first 20 min, $T_{B2} = 340^\circ$C and $T_{B1} = 65^\circ$C, and the evaporation and decomposition of volatiles occurred along with the evolution of small amounts of CO$_2$ and H$_2$. H$_2$ reached its concentration peak about 20 min later. The formation of CO started at $T_{B2} = 480^\circ$C. The carbothermal reduction proceeded at high rates above $900^\circ$C as evidenced by the strong increase of the CO molar flow rate, which peaked at 0.033 mol/min after...
83 min. This is consistent with the change in the slope of $T_{B1}$ and the subsequent decrease of the temperature difference across the bed. CO$_2$ represented only a small fraction of the gaseous product, indicative of its consumption via the Boudouard equilibrium (Eq. 1.10). The Zn production rate reached a maximum of 0.036 mol/min. $T_{B2}$ stabilized at 1260°C and CO evolution decreased as the reaction neared completion. Toward the end of the experimental run, the small temperature difference between $T_{B1}$ and $T_{B2}$ (~50°C), along with the low gas evolution, indicated complete conversion of the reactants.

**Figure 3.8.** Solar reactor temperatures and molar flow rates of Zn, CO, CO$_2$, and H$_2$ during a representative experimental run for the solar-driven carbothermal reduction of clinkered WOX, using 240 g of reactants with a ZnO:C molar ratio of 1:0.86.
A visual inspection of the residue revealed the presence of unreacted charcoal. Solid products were collected from the condenser, outlet pipes, and filter. The SEM picture of Figure 3.9 shows round agglomerated particles formed upon condensation and coalescence of Zn vapor.

![SEM image of condensed products from the solar carbothermal reduction.](image)

**Figure 3.9.** SEM of condensed products from the solar carbothermal reduction.

The normalized mass balance is shown in Figure 3.10 for all 14 solar carbothermal experiments. Also indicated are the nominal temperatures at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed and the ZnO:C molar ratio. Off-gas accounts for $\sim 18 - 32\%$ of the initial mass, while the remainder was collected in the form of condensed products and reaction residue. Diffusion of condensable gas products into the insulation was partly responsible for the unclosed mass balance. This was corroborated by comparing of the total amount of Zn recovered in the off-gas to that calculated by integration of the production rate based on CO and CO$_2$ evolution over time. Typically, $60 - 80\%$ of the ZnO reduced (based on the integration of CO and CO$_2$ evolved) could be recovered in the off-gas system.
as pure metallic Zn. However, as previously indicated, the calculation does not account for oxygen content in the reducing agent and feedstock’s impurities.

Figure 3.10. Normalized mass balance of the solar carbothermal reduction experiments with different feedstock. The nominal temperatures at the bottom ($T_{B1}$) and top ($T_{B2}$) of the packed bed and the ZnO:C molar ratio are indicated in the x-axis.

Condensed products from the experimental runs with washed WOX contained Zn in the range 85.2 – 92.4 wt.%, Pb in the range 3.4 – 3.8 wt.%, and Cl in the range 0.26 – 1.35 wt.%. An XRD analysis, shown in Figure 3.11, revealed the presence of Zn, ZnO, and Pb for all ZnO sources, apart from commercial ZnO that showed no Pb as expected. With solar-clinkered WOX as the reactant, the intensity of the Pb diffraction peaks was significantly lower, indicating a higher purity of Zn. This was expected
because the Pb content was reduced to much lower levels by solar clinkering compared to industrial washing. Pb resulted either from PbO vaporization and reduction with CO or to some extent directly from the carbothermal reduction of PbO.

**Figure 3.11.** XRD pattern of the condensed products for a representative run with a) washed WOX (ZnO:C = 1:1.25, 1280°C); and b) solar-clinkered WOX (30 min at \(T_{BL} = 1250°C\), ZnO:C = 1:0.86, 1260°C).
The variation of the Zn production rate for the carbothermal reduction of the various ZnO feedstock—namely: crude, washed, and solar-clinkered WOX, and for commercial ZnO— is shown in Figure 3.12 for ZnO:C molar ratios in the range of 1:0.9 – 1:0.97.

![Figure 3.12](image_url)

**Figure 3.12.** Variation of the packed-bed top temperature and Zn production rate during the carbothermal reduction of crude, washed, and solar-clinkered WOX, and commercial ZnO.

Both crude and washed WOX yielded faster reduction rates compared to solar-clinkered WOX and commercial ZnO. This is attributed to the inherently different morphology and properties of the various ZnO sources, affecting heat/mass transfer and intrinsic kinetics. The solar-clinkered WOX exhibited a lower specific surface area available for the solid-gas reaction (Eq. 1.9) due to partial sintering and melting. Note that the content of oxides other than ZnO (mainly PbO) in the crude and washed WOX resulted in an
overestimation of the CO and CO\textsubscript{2} evolved from the carbothermal reduction of ZnO by up to 15% and 19%, respectively, as calculated from the asymptotic conversions. In terms of the maximum reduction rates, crude, washed, solar-clinkered WOX, and commercial ZnO yielded similar values to each other.

The effect of the heat treatment temperature during solar clinkering of crude WOX on the Zn production rate during the carbothermal reduction was explored with three solar-clinkered WOX samples that were purified at different temperatures, namely at $T_{B1} = 1075^\circ$C, 1120$^\circ$C, and 1180$^\circ$C during 30 min. The variation of temperature and chemical conversion as a function of time during the carbothermal reduction of these three samples is shown in Figure 3.13.

![Figure 3.13](image.png)

**Figure 3.13.** Variation of temperature and chemical conversion as a function of time during the solar carbothermal reduction of three solar-clinkered WOX samples that were purified at $T_{B1} = 1075^\circ$C, 1120$^\circ$C, and 1180$^\circ$C during 30 minutes.
Comparable asymptotic conversions were obtained for all samples. Slower rates were expected at higher clinkering temperatures because of the decrease of the specific surface area due to partial sintering/melting, but this effect was not observed for the temperatures considered.
Chapter 4

Dynamic modeling of the 10 kW_{th} solar reactor\(^2\)

While experimental investigations have proven the technical feasibility of the 10 kW_{th} packed-bed solar reactor for performing carbothermal Zn production processes, numerical modeling can substantially complement understanding of the heat transfer mechanisms occurring throughout the packed-bed during the process. Besides enhancing process understanding and providing useful predictions on the process performance under variable operating conditions, a solar reactor model capable of identifying the major sources of heat losses would serve as a guide for design modifications aiming to further improve reactor efficiency.

As discussed in Chapter 1, a simplified 1-D transient heat and mass transfer model coupled to the reaction kinetics was initially developed to investigate the carbothermal reduction of ZnO with beech charcoal in the 10 kW_{th} packed-bed solar reactor [72], [73], but the model domain was restricted exclusively to the packed bed of reactants and, instead of the solar radiative input, experimentally measured temperatures were employed as boundary conditions. Thus, the model was unable to simulate the absorption and transfer of concentrated solar radiation, as required for optimizing the solar reactor design and predicting its performance.

In this chapter, a comprehensive dynamic model that couples radiative, conductive and convective heat transfer to the apparent chemical kinetics of the ZnO carbothermal reduction is developed for simulating the operation of the solar reactor by solving the unsteady energy conservation equations over the complete domain using incident solar radiation as the driving boundary condition.

### 4.1 Reactor model

The computational domain is depicted in Figure 4.1 and encompasses the three main zones of the reactor: a) the upper cavity (solar absorber), b) the lower cavity (reaction chamber), and c) the reactor insulation and outer steel shell.

#### 4.1.1 Upper cavity

The radiative heat transfer, solved by applying the enclosure theory [85], follows the methodology developed for a similar geometry [86]. Segmentation into $N_{UC} = 23$ surface elements was applied as depicted in Figure 4.1 and specified by recursive grid refinement to ensure grid-independent solutions. The cold surface corresponds to a part of the water-cooled CPC assembly, extending between the quartz window and the top of the insulation cone. The semi-gray band approximation over three wavelength bands was implemented according to the spectral selectivity of the window, as listed in Table 4.1 [87].
Figure 4.1. Surface segmentation of the solar reactor components comprising the upper cavity (UC) and lower cavity (LC), adopted for the application of the radiosity method for enclosures. Also shown is a schematic representation of the 1D grid employed for solving the energy conservation equations in the packed bed and the SiC walls, as well as of the 2D grid in the reactor insulation.

Table 4.1. Band-approximated hemispherical radiative properties of the fused quartz window [87].

<table>
<thead>
<tr>
<th>Spectral Band</th>
<th>Absorptance A (%)</th>
<th>Transmittance U (%)</th>
<th>Reflectance R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band 1, 0 - 0.17 µm</td>
<td>90.6</td>
<td>0.0</td>
<td>9.4</td>
</tr>
<tr>
<td>Band 2, 0.17 – 3.5 µm</td>
<td>2.8</td>
<td>83.5</td>
<td>13.6</td>
</tr>
<tr>
<td>Band 3, 3.5 - ∞ µm</td>
<td>86.6</td>
<td>0.0</td>
<td>13.4</td>
</tr>
</tbody>
</table>
With the assumptions of (i) all other upper cavity surfaces being opaque-gray-diffuse, (ii) uniform temperature, radiative heat fluxes and radiative properties over each surface element, and (iii) non-participating medium within the enclosure, the net radiative heat flux $q''_k$ on surface element $k$ is obtained by solving a system of linear equations for each of the three spectral bands considered:

$$q''_k = q''_{o,k} - q''_{i,k} + q''_{l,k} - q''_{e,k}$$  \quad (4.1)$$

$$q''_{o,k} = FF_{b,\lambda T_k} E_k \sigma T_k^4 + R_k q''_{i,k} + FF_{b,\lambda T_{solar}} U_k q''_{e,k}$$  \quad (4.2)$$

$$q''_{i,k} = \sum_{j=1}^{N_{IC}} F_{k-j} \cdot q''_{o,j}$$  \quad (4.3)$$

where subscripts $o$, $i$, $l$, and $e$ refer to the outgoing, incoming, leaving domain, and externally supplied radiative fluxes, respectively, $\sigma$ is the Stefan-Boltzmann constant, $T$ is the temperature, $T_{solar} = 5780$ K, and $F_{k,j}$ is the configuration factor between elements $k$ and $j$ obtained by Monte Carlo (MC) ray tracing using $3 \cdot 10^4$ rays emitted per surface element. The hemispherical emittance $E_k$, transmittance $U_k$ and reflectance $R_k$ of the surfaces comprising the upper cavity are listed in Table 4.2 [88]–[90]. The $FF_{b,\lambda T_k}$ term represents the fraction of Planck’s hemispherical blackbody emissive power at temperature $T_k$ emitted within the wavelength band and is approximated using infinite series [85]:

$$FF_{0-\lambda T_k} = \frac{15}{\pi^4} \sum_{n=1}^{\infty} \frac{e^{-nz}}{n} \left( z^3 + \frac{3z^2}{n} + \frac{6z}{n^2} + \frac{6}{n^3} \right)$$  \quad (4.4)$$
Dynamic modeling of the 10 kW_th solar reactor

\[ FF_{b, \lambda T_k} = FF_{0-\lambda_2 T_k} - FF_{0-\lambda_1 T_k} \]  

(4.5)

where \( z = C_2/(\lambda T) \), and \( C_2 = 14387.69 \text{ } \mu\text{m K} \) is a constant in Planck’s spectral energy distribution.

**Table 4.2.** Chemical composition and total hemispherical radiative properties of the upper cavity components [88]–[90].

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Absorptance A (%)</th>
<th>Transmittance U (%)</th>
<th>Reflectance R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ins. cone</td>
<td>ALTRA® KVS - 184/400 (80 % Al_2O_3–20 % SiO_2)</td>
<td>60.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Sep. plate</td>
<td>SiC-coated graphite plate</td>
<td>88.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cold surface</td>
<td>Copper (oxidized)</td>
<td>87.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The outgoing heat flux \( q''_{o,k} \) from surface \( k \) is composed of the radiative flux emitted at temperature \( T_k \) within the corresponding wavelength band (Eq. 4.2, first term RHS), the reflected radiative flux arriving at the element \( k \) from the remaining surface elements (Eq. 4.2, second term RHS), and the radiative flux transmitted through the semi-transparent window, applicable only to \( n_{window} = 6 \) (Eq. 4.2, third term RHS). For the opaque gray-diffuse surfaces, \( q'_{l,k} = q''_{e,k} = 0 \). For the semi-transparent quartz window,
\( q_{e,k}^{''} = q_{\text{solar}}^{''} \), i.e. the concentrated solar radiative flux, and

\[
q_{i,k}^{''} = R_{k} q_{e,k}^{''} + FF_{b,\lambda_{k}} E_{k} \sigma T_{k}^{4} + U_{k} q_{i,k}^{''}
\]  

(4.6)

where the first term on the RHS of Eq. 4.6 denotes the window’s reflection losses of the incident solar irradiation \( q_{\text{solar}}^{''} \), while the last two terms stand for the reradiation losses from the solar reactor comprising the thermal radiation emitted and transmitted by the window to the surroundings. The concentrated solar radiative flux is considered diffuse due to the presence of the CPC at the reactor’s aperture. The solution to the system of linear equations was obtained by coupling Eq. (4.2) & (4.3) and solving iteratively until the relative change of \( q_{o,k}^{''} \) and \( q_{i,k}^{''} \) between successive iterations falls below 10\(^{-3}\) for each of the three spectral bands.

The net radiative flux \( q_{k}^{''} \) serves as boundary condition to the 1D-radial unsteady energy conservation equations for the quartz window (Eq. 4.7) and the separation plate (Eq. 4.8),

\[
\rho c_{p} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) +
\]

\[
+ \nabla \left( \nu_{\text{in}} \cdot \left( T - T_{\text{gas, UC}} \right) \nu_{\text{out}} \cdot \left( T - T_{\text{env}} \right) \right) + \nabla (q_{k}^{''})
\]

(4.7)

\[
\rho c_{p} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) +
\]

\[
+ \nabla \left( \nu_{\text{UC}} \cdot \left( T - T_{\text{gas, UC}} \right) + q_{k}^{''} \right) + \nabla \left( \nu_{\text{LC}} \cdot \left( T - T_{\text{gas, LC}} \right) + q_{j}^{''} \right)
\]

(4.8)

and the 2D-axisymmetric unsteady energy conservation equation for the
insulation cone,

\[ \rho c_p \frac{\partial T}{\partial t} = \nabla (k \nabla T) \quad (4.9) \]

where \( r \) is the radial coordinate in the reactor, \( \rho \) is the density, \( c_p \) is the specific heat capacity, \( k \) is the thermal conductivity, and \( h \) is the convective heat transfer coefficient. The second term on the RHS of Eq. (4.7) denotes the convective heat exchange of the quartz window with inert gas flow in the UC and the environment, while the last term denotes the net radiative heat flux \( q_k'' \). For the separation plate (Eq. 4.8), the second term on the RHS denotes the convective heat exchange of the SP with the inert gas flow in the UC and the net radiative heat flux, \( q_k'' \), whereas the last term stands for the convective heat transfer on the lower surface of the SP and the net radiative flux, \( q_j'' \), directed toward the LC. Equation (4.9) is subject to the boundary condition:

\[ k \nabla T \cdot \hat{n} = h_{UC} \cdot (T - T_{gas, UC}) + q_k'' \quad \text{at} \quad r = r_{ic}(z) \quad (4.10) \]

Equations (4.7) – (4.9) were discretized using the forward Euler scheme and solved by the finite volume method. Regarding the cold surface, its temperature was maintained constant at 298 K as all the radiant heat absorbed by this component was assumed to be dissipated by water-cooling.

### 4.1.2 Lower cavity

The enclosure theory is applied for the surface segmentation depicted in Figure 4.1 (\( N_{LC} = 10 \)), which, assuming all surfaces being opaque-gray-diffuse, yields a system of equations in terms of the net radiative fluxes \( q_j'' \):
\[
\sum_{j=1}^{N_{LC}} \left( \delta_{ij} - F_{i-j} \right) \frac{1 - \varepsilon_j}{\varepsilon_j} \right) q''_j = \sum_{j=1}^{N_{LC}} \left( \delta_{ij} - F_{i-j} \right) \sigma T_j^4
\] (4.11)

where \( \delta_{ij} \) is the Kronecker delta function, \( F_{i,j} \) are the analytically obtained [85] configuration factors between elements \( i \) and \( j \), and \( \varepsilon_j \) is the emissivity of element \( j \). The linear system was solved using the Gauss-Seidel iterative technique until the L2-norm of the changes in \( q''_j \) between two successive iterations falls below \( 10^{-3} \).

Analogous to the upper cavity, \( q''_j \) serves as boundary condition to the 1-D axial unsteady energy conservation equation for the packed-bed,

\[
m_f c_p,\text{eff} \frac{\partial T}{\partial t} = (Q_{\text{cond,bed,in}} - Q_{\text{cond,bed,out}}) + \frac{dm_{\text{ZnO}}}{dt} \Delta h_{\text{rxn}}(T) + Q_{\text{wall,bed}}
\] (4.12)

where \( m_f \) is the mass of the solid feedstock, \( c_p,\text{eff} \) is the effective specific heat capacity, \( Q_{\text{cond,bed}} \) is the conductive heat exchange between adjacent packed bed cells, \( \Delta h_{\text{rxn}} \) is the enthalpy of reaction, \( Q_{\text{wall,bed}} \) is the heat flow from the SiC walls to the packed bed. Equation (4.12) is subject to the boundary condition:

\[
Q_{\text{cond,bed,in}} = q'' \text{bed surface} \cdot A_{\text{bed surface}} \quad \text{at} \quad z = H_{\text{bed}}
\] (4.13)

It was discretized using the forward Euler scheme and solved by the finite volume method. The 1D simplification was justified by the radially uniform temperature profiles obtained by 2D axisymmetric simulations. The packed bed domain is treated as a shrinking continuum as the solid feedstock is converted into gaseous products during the carbothermal reduction of ZnO. A finer grid resolution is employed towards the top of the bed to adequately
resolve the steep gradients. The details of the numerical grid, comprising a finer grid portion of \( N_c \) cells close to the bed surface and a coarser grid portion of \( N_d = N_{\text{bed}} - N_c \) cells at the deeper regions of the bed, are shown in Figure 4.1.

Heat is transferred to the deeper bed regions largely by conduction across the SiC walls. The portion of the SiC walls adjacent to the packed bed shares the same 1D shrinking grid with the bed, as depicted in Figure 4.2. The temperature at each SiC wall cell is determined by solving the 1-D axial unsteady energy conservation equation,

\[
m c_p \frac{dT}{dt} = \left( Q_{\text{cond,wall, in}} - Q_{\text{cond,wall, out}} \right) - Q_{\text{wall,bed}} - Q_{\text{wall,ins}} + SC_{\text{wall}} \quad (4.14)
\]

where \( Q_{\text{cond,wall}} \) is the conductive heat flow between adjacent SiC wall cells, \( Q_{\text{wall,ins}} \) is the heat exchange with the surrounding reactor insulation, as shown in Figure 4.2, and \( SC_{\text{wall}} \) corresponds to the sensible enthalpy losses associated with the changes in size of the SiC wall cells:

\[
SC_{\text{wall}} = h_{\text{wall}} \cdot \rho_{\text{wall}} \cdot A_{\text{wall}} \cdot \frac{dz}{dt} \quad (4.15)
\]

where \( A_{\text{wall}} \) is the cross sectional area of the SiC walls, \( h_{\text{wall}} \) is the sensible enthalpy of the SiC wall cells, and \( \frac{dz}{dt} \) is the shrink rate of a SiC wall cell and is equal to that obtained for the adjacent packed bed cell:

\[
\frac{dz}{dt} = \left( \frac{dm_{\text{ZnO}}}{dt} \right) \cdot \rho_{\text{ZnO, b}} \cdot \phi_{\text{ZnO, b}} + \left( \frac{dm_{\text{charcoal}}}{dt} \right) \cdot \rho_{\text{charcoal, b}} \cdot \phi_{\text{charcoal, b}} \right) \cdot A^{-1}_{\text{bed}} \quad (4.16)
\]
where \( A_{bed} \) is the cross sectional area of the packed bed, and \( \rho \) and \( \varphi \) represent the bulk density and the volume fraction of ZnO and charcoal in the solid feedstock, respectively.

\[
\frac{dL_{bed}}{dt} = \sum_{i=1}^{N_{bed}} \left( \frac{dz}{dt} \right)^i 
\]

(4.17)

The corresponding energy conservation equation is given by:

\[
m c_p \frac{dT}{dt} = \left( Q_{\text{cond},\text{wall,in}} - Q_{\text{cond},\text{wall,out}} \right) - Q_{\text{wall,ins}} + SC_{\text{wall}} + S_{h,\text{wall}}
\]

(4.18)

where \( SC_{wall} \) is associated with the enthalpy gain due to the size change of the grid according to Eq. (4.17), and \( S_{h,\text{wall}} = q^{*}_{\text{upper SiC wall}} \cdot A_{\text{lateral, upper wall}} \) is the radiative heat absorbed by the SiC wall.

Figure 4.2. Heat flows associated with the \( i^{th} \) FV cell of the packed bed and adjacent SiC wall.

On the contrary, the SiC wall portion extending above the packed bed region is treated as a single FV cell, growing at a rate equivalent to the shrink rate of the entire packed bed:
4.1.3 Reactor insulation and outer steel shell

The 2D axisymmetric energy conservation equation was solved for the reactor insulation and the outer steel shell

\[
\frac{dH}{dt} = \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) + S \tag{4.19}
\]

where \( S \) is the volumetric heat source/sink term and encompasses the conductive heat exchange with the SiC walls and/or the convention losses to the surroundings. The governing equation was discretized in space using the finite-volume method and integrated in time using the forward Euler scheme.

4.2 Domain properties

4.2.1 Packed bed effective thermal conductivity

The effective axial thermal conductivity of the packed bed \( k_{\text{eff, bed}} \) is dependent on the thermal properties and chemical composition of the solid feedstock, the packing arrangement of the particles, and the thermal conductivity of the gas flowing through the voids of the packed bed. It is calculated as a mass-fraction weighted average of the effective thermal conductivity of its solid constituents ZnO, C, and ash:

\[
k_{\text{eff, bed}} = y_{\text{ZnO}} k_{\text{eff, ZnO}} + y_{\text{C}} k_{\text{eff, C}} + y_{\text{ash}} k_{\text{eff, ash}} \tag{4.20}
\]

where \( y_j \) is the mass fraction, and \( k_{\text{eff, j}} \) is the axial effective thermal conductivity of the feedstock component \( j \), respectively. The effective thermal conductivity \( k_{\text{eff, j}} \) is given by [91]–[93]:

---

Dynamic modeling of the 10 kW\textsubscript{th} solar reactor 65
\[ k_{\text{eff}, j} = k_g \epsilon_v \left( 1 + \beta \frac{h_{\text{rv}, j} d_{p,j}}{k_g} \right) + \frac{\beta (1 - \epsilon_v)}{\epsilon_v + \frac{1}{\varphi} + \frac{d_{p,j} h_{\text{rs}, j}}{k_g}} + \gamma \left( \frac{k_g}{k_{s,j}} \right) + \frac{1}{2} \rho_g c_{p,g} d_{p,j} u_{sf} \]  

(4.21)

where \( k_g, \rho_g, \) and \( c_{p,g} \) are the thermal conductivity, density and heat capacity of the gas mixture flowing in the interparticle void spaces, \( \epsilon_v \) is the bed void fraction, \( \beta \) is the ratio of the average length between two adjacent particles to the mean particle diameter \( d_{p,j} \), \( \varphi \) is the ratio of the effective thickness of the fluid film adjacent to the contact surface of two solid particles to the particle diameter, \( \gamma = 2/3 \) is the ratio of the length of solid affected by thermal conduction to the mean particle diameter, and \( u_{sf} \) is the superficial velocity. The first term on the RHS of Eq. (4.21) refers to the effective thermal conductivity with motionless fluid in the interparticle void spaces and the second term accounts for axial heat dispersion. The bed void fraction was considered constant at temperatures where chemical reactions occur only to a very limited extent (< 872 K). At these temperatures, it was set equal to \( \epsilon_v = 0.6 \) in order to yield good agreement with the experimentally determined values for the effective thermal conductivity as obtained by the radial heat flow method [72]. At higher temperatures, the carbothermal reduction proceeds at different rates across the packed bed, leading to a wider grain size distribution and thus lower interparticle porosity. Therefore, in the absence of experimental data, a moderate decrease in the bed void fraction from 0.6 to 0.4 was assumed over the temperature range of 872 – 1600 K.
The factor $\beta$ ranges typically between 0.82 for close and 1 for loose packings. In the current work, a moderate value of 0.9 was used due to the random packing of the feedstock. The ratio $\varphi$ is defined as [92]:

$$\varphi = \varphi_1 + \left(\varphi_1 - \varphi_2\right) \cdot \frac{\varepsilon_v - 0.260}{0.216}$$

(4.22)

where $\varphi_1$ and $\varphi_2$ are calculated by:

$$\varphi_1 = \frac{\left(\frac{\kappa-1}{\kappa}\right)^2 \cdot \sin^2 \theta_i}{\ln \left(\kappa - (\kappa-1) \cdot \cos \theta_i\right) - \frac{\kappa-1}{\kappa} \left(1 - \cos \theta_i\right)} - \frac{2}{3} \frac{1}{\kappa}$$

(4.23)

with $\kappa = \frac{k_s}{k_g}$, and $\sin^2 \theta_i = \frac{1}{n_i}$, where $n$ is the number of contact points on a semispherical surface of one particle, $n_1 = 1.5$ and $n_2 = 4\sqrt{3}$. The void-to-void radiative heat transfer coefficient, $h_{rv,j}$, is:

$$h_{rv,j} = \frac{0.1952 \cdot \varepsilon_v \cdot (T/100)}{1 + \frac{\varepsilon_v}{2(1-\varepsilon_v)} \cdot \frac{1-\varepsilon_j}{\varepsilon_j}}$$

(4.24)

where $\varepsilon_j$ is the emissivity of component $j$, and $T$ is the temperature in K. The solid surface-to-surface radiative heat transfer coefficient is given by:

$$h_{rs,j} = 0.1952 \left(\frac{\varepsilon_j}{2-\varepsilon_j}\right) \cdot \left(\frac{T}{100}\right)^3$$

(4.25)

The thermal conductivity of the individual particles of the carbonaceous material is calculated according to [94]:

$$k_{s,c} = \left(\frac{\rho_{C,s}}{4511}\right)^{3.5} \cdot T^{0.5}$$

(4.26)
where $\rho_{C,s}$ is the charcoal particle density. For ZnO particles, the thermal conductivity is [95]:

$$k_{s,ZnO} = 4.506 \cdot 10^{-12} \cdot T^4 - 2.984 \cdot 10^{-8} \cdot T^3 + 7.998 \cdot 10^{-5} \cdot T^2 - 1.034 \cdot 10^{-1} \cdot T + 57.02$$  \hspace{1cm} (4.27)

and for ash, $k_{s,ash} = 3.0 \frac{W}{m \cdot K}$ [96]. The thermal conductivity of the gas mixture is calculated according to [97]:

$$k_g = \sum_{i=1}^{N_{ga}} \frac{k_i}{1 + \sum_{j=1}^{N_{ga}} \phi_{ij} \frac{x_j}{x_i}}$$  \hspace{1cm} (4.28)

where $x_i$ and $x_j$ are the molar fractions of species $i$ and $j$ in the gas phase, and $\phi_{ij}$ is a non-dimensional parameter expressed by:

$$\phi_{ij} = \frac{1}{2\sqrt{2}} \cdot \left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}} \cdot \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2$$  \hspace{1cm} (4.29)

where $\mu_i$ and $M_i$ are the dynamic viscosity and the molar mass of species $i$ in the gas phase.

### 4.2.2 Radiative properties

The emissivities of the separation plate and the SiC wall were set to 0.88 [89] and 0.85 [88], respectively. The packed bed surface emissivity was calculated as the mass-fraction weighted average emissivity of ZnO, C, and ash:
Dynamic modeling of the 10 kW$_{th}$ solar reactor

\[ \varepsilon_{\text{bed surface}} = y_{ZnO} \varepsilon_{ZnO} + y_C \varepsilon_C + y_{\text{ash}} \varepsilon_{\text{ash}} \]  \hspace{1cm} (4.30)

where \( \varepsilon_{ZnO} = 0.85 \) [98] and \( \varepsilon_C = 0.93 \) [99], and \( \varepsilon_{\text{ash}} \) decreases monotonically from 0.75 to 0.43 with temperature [100].

### 4.2.3 Interphase heat transfer

Forced convection at the surface of the quartz window towards the cavity \((z = H_{\text{window}})\) and at both surfaces of the separation plate \((z = H_{\text{plate}} \text{ and } z = H_{\text{plate}} + t_{\text{plate}}, \text{ where } t_{\text{plate}} \text{ is the SP thickness})\) is calculated using the Nusselt correlation for a fluid flow over a horizontal flat plate [101]:

\[ \overline{\text{Nu}} = 0.664 \text{Re}^{0.5} \text{Pr}^{1/3} \]  \hspace{1cm} (4.31)

where \( L_C \) is the characteristic length equal to the window and separation plate diameters, respectively. Forced convection at the surface of the UC insulation cone \((r = r_{ic}(z) \text{ as shown in Figure 4.1})\) is calculated using [101]:

\[ \overline{\text{Nu}} = 3.66 + \frac{0.065 \left( \frac{D}{H_{\text{UC}}} \right) \text{Re}_D \text{Pr}}{1 + 0.04 \left[ \left( \frac{D}{H_{\text{UC}}} \right) \text{Re}_D \text{Pr} \right]^{2/3}} \]  \hspace{1cm} (4.32)

where \( \overline{D} = (D_{\text{win}} + D_{\text{SP}}) / 2 \), and \( H_{\text{UC}} \) is the height of the upper cavity.

Natural convection at the surface of the quartz window towards the surroundings \((z = H_{\text{window}} + t_{\text{window}}, \text{ where } t_{\text{window}} \text{ is the window thickness})\) and at the outer shell is calculated according to [101]:

\[ \overline{\text{Nu}} = 0.54 \text{Ra}^{1/4} \text{L}_c \]  \hspace{1cm} (4.33)
\[
\overline{\text{Nu}} = 0.27 \text{Ra}_{L_c}^{1/4} \quad (4.34)
\]
\[
\overline{\text{Nu}} = 0.825 + \frac{0.387 \text{Ra}_{L_c}^{1/6}}{1 + \left(\frac{0.492}{\text{Pr}}\right)^{9/16}}^{8/27} \quad (4.35)
\]

where \( \text{Ra}_{L_c} = g \beta \cdot (T_{\text{surface}} - T_{\text{env}}) \cdot L_c^3 \rho_{\text{air}} / (\mu_{\text{air}} \alpha_{\text{air}}) \), \( g = 9.81 \text{m/s}^2 \) is the gravitational acceleration constant, \( L_c \) is the characteristic length evaluated individually at each FV cell based on the surface-area-to-perimeter ratio, and \( \beta = 2/(T_{\text{surface}} + T_{\text{env}}) \) and \( \alpha \) are the thermal expansion coefficient and thermal diffusivity of the fluid, respectively. The two correlations, (Eq. 4.33 & 4.34), proposed for natural convection occurring on the upper and lower surfaces of hot plates are applied to the upward-facing \((z = H_{\text{reactor}})\) and downward-facing \((z = 0)\) sides of the outer shell, respectively. For the calculation of the natural convection heat transfer coefficients on the vertical part of the reactor shell \((r = r_{\text{shell}})\) the Nusselt correlation proposed for vertical cylinders, (Eq. 4.35), is implemented.

Heat losses relating to the actively cooled reactor parts are modeled using a Nusselt correlation proposed for forced turbulent heat convection in ducts of hydraulic diameter \( D_h \) [101]:

\[
\overline{\text{Nu}} = \frac{\left(\frac{f}{8}\right) \left(\text{Re}_{D_h} - 1000\right) \text{Pr}}{1 + 12.7 \left(\frac{f}{8}\right)^{0.5} \left(\text{Pr}^{2/3} - 1\right)} \quad (4.36)
\]

where the Darcy friction factor \( f \) is determined from the Haaland formulation using roughness values of stainless steel:
\[
\frac{1}{\sqrt{f}} = -1.8 \log \left[ \left( \frac{\varepsilon / D_h}{3.7} \right)^{1.11} + \frac{6.9}{Re_{D_h}} \right] \tag{4.37}
\]

where \(\varepsilon / D_h\) is the relative roughness of the duct internal surface.

### 4.3 Reaction kinetics and enthalpy of reaction

The reaction rate was experimentally obtained by dynamic thermogravimetric measurements [72], [73]. Based on the highly reactive nature of the beech charcoal gravel used, the interfacial kinetics of reaction (1.9) are considered to be the rate determining step. Assuming (i) spherical ZnO particles consumed according to the shrinking particle model with an unreacted core, and (ii) a first-order reaction rate constant \(k_1\) for reaction (1.9), the reduction rate of ZnO can be expressed as:

\[
r^* = -\frac{1}{4\pi r_p^2} \frac{dn_{ZnO}}{dt} = k_1 p_{CO}
\]

where \(r_p\) is the radius of a ZnO particle, \(n_{ZnO}\) is the molar amount of ZnO, and \(p_{CO}\) is the partial pressure of CO. Further assuming constant ZnO:C molar ratio throughout the thermogravimetric measurements and defining the reaction extent \(X\) as:

\[
X = 1 - \frac{n_{ZnO}}{n_{ZnO,o}}
\]

where \(n_{ZnO,o}\) is the initial molar amount of ZnO in the sample, the reaction rate can be expressed by a first-order Arrhenius-type rate law:

\[
\frac{dX}{dt} = 4\pi \cdot k_0 \cdot e^{\left( \frac{E_a}{RT} \right)} \cdot p_{CO} \cdot \left( \frac{3}{4\pi \cdot N_p \cdot \rho_{ZnO,b}} \right)^{2/3} \cdot (1 - X)^{2/3} \cdot n_{ZnO,o}^{-1/3}
\]

\(\tag{4.40}\)
where \( k_0 \) and \( E_a \) are the apparent pre-exponential factor and activation energy, \( N_p \) is the number of particles contained in \( n_{ZnO} \) moles of ZnO, and \( \rho_{ZnO,b} \) is the bulk density of ZnO. Assuming equilibrium gas composition, the apparent activation energy \( E_a = 291.2 \text{ kJ mol}^{-1} \) was obtained by linear regression of the dynamic thermogravimetric measurements. The apparent pre-exponential factor \( k_0 = 4.32 \times 10^{10} \text{ mol} \cdot \text{s} \cdot \text{m}^{-1} \cdot \text{kg}^{-1} \) was specified by fitting the numerically predicted Zn(g) production rates to the experimentally measured values in the packed-bed solar reactor. Determination of this apparent Arrhenius parameter from existing experimental studies was not feasible due to differences in the fluid flow arrangement, and particle packing conditions between the thermogravimeter and the packed-bed solar reactor. The production rates of CO and CO\(_2\) are obtained assuming equilibrium composition of the product gases and are related to the ZnO reduction rate through:

\[
\frac{\text{dm}_j}{\text{dt}} = \gamma_j \frac{M_j}{M_{ZnO}} \frac{\text{dm}_{ZnO}}{\text{dt}} \tag{4.41}
\]

where the subscript \( j \) refers to the Zn(g), CO, and CO\(_2\) and \( \gamma_j \) is the equilibrium molar amount of species \( j \) per molar amount of ZnO reacted as determined by thermodynamic equilibrium calculations of the ZnO/C system. The thermodynamic equilibrium composition of the system at a ZnO:C molar ratio of 1:0.8 was already shown in Figure 1.1 (see Section 1.4.1). The specific enthalpy change of the pertinent reaction as a function of temperature is shown in Figure 4.3, with reactants and products both at temperature \( T \).
Experimental runs and model validation

4.4.1 Experimental runs

Model validation was accomplished by comparing numerically computed and experimentally measured temperatures, Zn, CO, and CO$_2$ production rates, product yield, and solar-to-chemical energy conversion efficiency obtained with the 10 kW$_{th}$ lab-scale solar reactor during two experimental runs conducted under the conditions summarized in Table 4.3. The experiments were carried out in batch mode. Mixtures of ZnO powder (Alfa Aesar, Ward Hill, MA: 011558, purity: 99.0% min, mean particle size
44 µm) and beech charcoal (proFagus, Bodenfelde, Germany; carbon content 83 wt.%, mean particle size 1.47 mm) at a ZnO:C molar ratio of 1:0.8 were loaded into the reaction chamber prior to the start of each experiment.

Table 4.3. Experimental conditions of the two solar experimental runs used for model validation.

<table>
<thead>
<tr>
<th>Run #</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:C molar ratio ( - )</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>m_{feedstock} (g)</td>
<td>323.7</td>
<td>491.1</td>
</tr>
<tr>
<td>L_{bed} (mm)</td>
<td>35.0</td>
<td>53.0</td>
</tr>
<tr>
<td>Q_{solar, max} (kW)</td>
<td>6.1</td>
<td>5.0</td>
</tr>
<tr>
<td>m_{N_2, upper cavity} (L N \cdot min^{-1})</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>m_{N_2, lower cavity} (L N \cdot min^{-1})</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Approximately 323.7 and 491.1 g of reactants were used in the two experiments, leading to an initial packed bed height of 35 mm and 53 mm, respectively. The same experimental procedure as that described for the carbothermal reduction tests in Section 3.2.2 was followed. The solar radiative power input Q_{solar} was regulated as described in Section 3.1.1 and measured with a water-cooled copper-coiled calorimeter with its aperture positioned at the exit of the CPC. The location of the type-K thermocouples used for validation of the numerical model is illustrated in Figure 4.4. Thermocouples U1 and B2 are representative for the temperature of the upper cavity and the top surface of the packed bed, respectively, whereas thermocouple B3 measured the temperature of 20 mm below the initial top
surface, and B1 of the bottom of the packed bed.

**Figure 4.4.** Schematic cross-sectional view of the 10 kW<sub>th</sub> packed-bed solar reactor showing the locations of the type-K thermocouples.

### 4.4.2 Simulation results and model validation

A total of $N_{\text{bed}} = 150$ and 240 FV cells for the 35 mm- and 53 mm-high packed beds, respectively. The steep-gradient region at the upper portion of the packed bed covered about 57% of the total packed bed height and was discretized using $N_c = 100$ and 160 cells, respectively. The number of grid cells was specified by recursive grid refinement to ensure grid-independent results. The variation of the measured solar radiative power input, and the
measured and numerically simulated temperatures as a function of time for the two experimental runs is shown in Figure 4.5.

**Figure 4.5.** Numerically calculated (solid and dashed lines) and experimentally measured (open markers) temperatures, and the measured solar radiative power input $Q_{\text{solar}}$ during the experimental runs with a) 35 mm- and b) 53 mm-high packed bed.

The gradual increase of $Q_{\text{solar}}$ during the first 30 – 40 min corresponded to the reactor heat-up and was accompanied by a strong rise in $T_{U1}$ and $T_{B2}$ owing to efficient radiative transfer. On the contrary, temperatures $T_{B3}$ and $T_{B1}$ showed a slower response to variations of the solar power input due to
the low thermal conductivity (0.1 – 0.2 W m\(^{-1}\) K\(^{-1}\)) of the packed bed at temperatures below 1200 K. At temperatures above \(T_{B2} = 1200 – 1300\) K, the carbothermal reduction of ZnO proceeded at reasonable rates as the top layer of the packed bed was converted to gaseous products. Bed shrinkage enhanced the heat transfer to the deeper layers of the bed, as evidenced in experimental run 1 by the change in the slopes of \(T_{B3}\) and \(T_{B1}\) after the first 32 min and 67 min, respectively. Upon consumption of the feedstock, \(T_{B3}\) and \(T_{B1}\) increased and asymptotically approached a value close to \(T_{B2}\). After turning off the HFSS, a gradual decrease of the reactor temperatures was observed because of heat leaving the reactor via conduction, convection and reradiation. For both solar runs, good agreement was achieved between the experimentally measured and numerically simulated temperatures, in spite of the uncertainties in the Nu correlations and radiative properties. Overestimation of the experimentally measured \(T_{B1}\) towards the end of the experimental run 1 is attributed to adhesion of sintered, unreacted ZnO particles on the thermocouple tip as well as to the lower final bed height predicted by the simulation (\(L_{bed,\,final} = 0.11\) mm) vis-à-vis the experimentally obtained value (\(L_{bed,\,final} = 0.5\) mm).

A comparison of the numerically calculated and experimentally measured production rates of Zn(g), CO, and CO\(_2\) for experimental runs 1 and 2 is shown in Figure 4.6. The numerically calculated global production rate of the gaseous products was specified by summing the production rates of the species over all the FV cells of the packed bed:

\[
\left( \frac{dm_i}{dt} \right)_{global} = \sum_{i=1}^{N_{cell}} \left( \frac{dm_i}{dt} \right)^i
\]  

(4.42)
The model replicates the onset of the carbothermal ZnO reduction and the temporal variation of the gas production rates reasonably well, considering the uncertainties involved in the physical properties and the apparent reaction kinetics. A parity plot comparing the numerically calculated to the experimentally determined amounts of Zn(g), CO, and CO$_2$ produced throughout the experimental runs 1 and 2 is shown in Figure 4.7.

**Figure 4.6.** Numerically calculated (solid and dashed lines) and experimentally measured (open markers) production rates of Zn(g), CO, and CO$_2$ during the experimental runs with a) 35 mm- and b) 53 mm-high packed bed.
Figure 4.7. Comparison of the numerically calculated and experimentally determined amounts of Zn(g), CO, and CO\textsubscript{2} produced throughout the experimental runs 1 (filled markers) and 2 (open markers).

The variation of the numerically calculated instantaneous packed bed height and bed shrink rates as a function of time for both experimental runs is shown in Figure 4.8. The packed bed height $L_{\text{bed}}$ dropped monotonically at average bed shrink rates of 0.63 and 0.65 mm min$^{-1}$ upon commencement of the carbothermal ZnO reduction and reached a final value of 0.11 mm and 0.13 mm for experimental runs 1 and 2, respectively.
Figure 4.8. Numerically calculated instantaneous packed bed height and bed shrink rates during the experimental runs with a) 35 mm- and b) 53 mm-high packed bed.

Figure 4.9 shows the numerically calculated temperature profiles throughout the packed bed at 5 min intervals for experimental run 1. The temperature gradient in the axial direction increased during the reactor heat-up period and a temperature difference of \(\sim 850\) K between the top surface and the bottom of the packed bed was reached after the first 30 min, indicating poor heat transfer to the deeper bed layers. As the packed bed shrinks, the bottom temperature increases and, consequently, the temperature gradient decreases, yielding a total bed height reduction of 30 mm and a temperature difference of \(\sim 120\) K after 75 min.
Figure 4.9. Temperature profiles throughout the packed bed of ZnO and beech charcoal shown at 5 min intervals for the experimental run with the 35 mm-high packed bed.

Energy partitioning of the solar radiative input for experimental run 1 is shown in Figure 4.10. During reactor heat-up, corresponding to the first 30 min, a considerable portion of the solar power input was stored as sensible heat within the reactor materials. As the UC and LC temperatures increased, the energy used for sensible heating decreased whereas the conduction and convection heat losses became dominant. Refrigerated parts in the UC represented the main heat sink, dissipating about 2 kW of heat. Upon commencement of the carbothermal reduction, the heat sink associated
with the enthalpy change of the chemical reaction reached 11% of $Q_{solar}$ at approximately steady-state conditions. Reradiation losses due to the thermal emission of the UC components to the surroundings and window’s reflection losses increased throughout the experimental run from 14% to 27% of $Q_{solar}$, owing to the increasing temperatures. The numerically calculated instantaneous solar-to-chemical energy conversion efficiency is defined as:

$$
\eta_{\text{solar-to-chem}} = \frac{\dot{n}_{\text{Zn(g)}} \frac{LHV_{\text{Zn(g)}}}{\text{Zn(g)}} + \dot{n}_{\text{CO}} \frac{LHV_{\text{CO}}}{\text{CO}}}{Q_{\text{solar}} + \dot{n}_{\text{C}} \frac{LHV_{\text{C}}}{\text{C}}}
$$

(4.43)

where LHV is the lower heating value of the species, is also shown in Figure 4.10. The numerator of Eq. (4.43) denotes the chemical energy stored in the gaseous products of the reaction and the denominator is the sum of the solar power input and the chemical energy stored in the solid feedstock. The peak and time-averaged solar-to-chemical energy conversion efficiencies are defined as the maximum and average values obtained over the duration of the carbothermal reduction. Numerically calculated peak and time-averaged $\eta_{\text{solar-to-chem}}$ of 15.5% and 12.3% for experimental run 1 were in good agreement with the experimentally determined values of 18.4% and 12.96%, respectively. The small discrepancy in the peak efficiency is attributed to the lower maximum Zn(g) and CO production rates predicted by the numerical model, as indicated in Figure 4.6. Peak and average solar-to-chemical energy conversion efficiencies for experimental run 2 were similar, 17.4% and 13.4%, respectively, and showed good agreement with the simulated values of 16.9% and 13.3%, respectively.
Figure 4.10. Energy partitioning of the solar radiative input power for the experimental run with the 35 mm-high packed bed. Also indicated is the instantaneous solar-to-chemical energy conversion efficiency.

Since heat dissipation through the water-cooled parts was identified as a major source of heat losses in the reactor, $\eta_{\text{solar-to-chem}}$ could be further increased by eliminating refrigerated surfaces in the upper cavity. However, keeping the quartz window well below its maximum operational temperature (1050°C) [102] can be achieved only by active cooling of the quartz glass. Thus, omission of the water-cooling system can be envisioned only in a windowless reactor design, which will additionally reduce the window’s reflection losses but at the expense of introducing additional convective heat losses from the UC to the surroundings. A windowless solar reactor design would also overcome an important technical hurdle toward
scaling up. This is because the quartz window remains a troublesome and fragile component that, as its size increases, is difficult to keep clean from dust depositions and/or condensable gases evolving in the reaction chamber. Identifying a suitable construction material for the separation plate that exhibits structural stability and thermal shock resistance under non-uniform high-flux irradiation and chemical stability in air, represents the main challenge toward the realization of a windowless solar reactor.

4.5 Semi-continuously-fed 10 kW<sub>th</sub> solar reactor

As previously discussed in Chapter 2, the current one-batch-per-day operation of the solar reactor is suitable for thermochemical processes in which the solid feedstock is converted predominantly into gaseous products such as the carbothermal reduction of ZnO or the thermal gasification of low-ash containing carbonaceous feedstock. However, in processes involving solid products such as the thermal purification of low-purity secondary ZnO sources (see Chapter 3) or high-ash containing feedstock, poor heat transfer to the deeper bed layers poses a limitation on the batch size. Incorporation of semi-continuous feeding of reactants could, thus, effectively improve the product yield and the solar-to-chemical energy conversion efficiency. Additionally, that would overcome the difficulty faced in scale-up two-cavity reactor installations also for thermochemical processes in which the solid feedstock is converted into gaseous products, where the large thermal inertia of the reactor leads to undesirable prolonged cooling periods and poses a significant challenge to feeding new feedstock into the hot solar reactor on the next day. A practical realization might make use of a pusher-type furnace design [103], which enables the semi-
continuous removal of solid products and/or residual mass at the end of each operation cycle with feeding fresh feedstock into the hot solar reactor in push steps.

In order to investigate the effect of introducing cold feedstock ($T = 292$ K) into the hot solar reactor, the operation of a 10 kW$_{th}$ semi-continuously fed reactor was simulated for seven consecutive cycles. Figure 4.11 shows the variation of the solar radiative power input, lower cavity temperature $T_{B2}$, the Zn(g) production rate, and the solar-to-chemical energy conversion efficiency as a function of time for semi-continuous feeding of seven 35 mm-high packed beds of ZnO and beech charcoal at a ZnO:C molar ratio of 1:0.8.

![Figure 4.11](image)

**Figure 4.11.** Temporal variation of the radiative solar power input, LC temperature, Zn(g) production rate, and solar-to-chemical energy conversion efficiency for semi-continuously feeding of seven 35 mm-high packed beds of ZnO and beech charcoal into a 10 kW$_{th}$ packed-bed solar reactor.
The first operation cycle corresponds to the experimental conditions explained in Section 4.4.1. The solar power input for the consecutive cycles was assumed equal to the value at the end of the 1st cycle (4 kW). A small rise in the LC temperature at the end of each cycle is attributed to the absence of any heat sink associated with the reaction enthalpy after the complete conversion of the solid feedstock. The feeding of new feedstock into the hot solar reactor at the beginning of each cycle was accompanied by a steep decrease in the LC temperature since the cold reactants acted as a large heat sink in the reaction chamber. This temperature drop reached approximately 115 K in the beginning of the 2nd cycle. The quasi-steady LC temperature value in the second cycle was about 60 K lower than in the first cycle as an effect of the lower $Q_{solar}$, and led to a slight decrease in the Zn(g) production rate. After the 3rd cycle, the evolution of the LC temperature, Zn(g) production rate and solar-to-chemical energy conversion efficiency follows a cyclic pattern. The peak efficiency increased by 2.4% to 17.9% from the 1st to the 2nd cycle due to the reduced energy share required for the sensible heating of the reactor components after the first cycle, and stabilized at about 16.9% after the 3rd operation cycle. In parallel, the time required for the completion of each cycle decreased from 90 min to 70 min between the 1st and 2nd cycle due to the absence of the initial reactor heating up period. Finally, unlike in processes such as the carbothermal ZnO reduction, operation of the reactor in semi-continuous mode is expected to induce a considerable increase in the product yield for thermochemical processes in which the batch size is limited by poor heat transfer through the packed bed.
Chapter 5

An alternative off-gas treatment system for
the solar carbothermal production of liquid Zn$^3$

Effective quenching of the gaseous products evolving during the
carbothermal reduction of primary and secondary ZnO-containing sources is
crucial for preventing Zn(g) reoxidation in the off-gas system. As the gas
temperature in the off-gas system decreases, the equilibrium of Eq. (1.12) is
shifted to the product side favoring reoxidation of zinc vapor by CO$_2$. At low
temperatures, reoxidation can also proceed via reaction with CO (Eq. 1.13)
to form ZnO and elemental carbon, but the reaction rates are apparently low
as minimal carbon formation has been detected in operating industrial
condensers. As formerly presented, quenching of the off-gas in the 10 kW$_{th}$
packed-bed solar reactor proceeds in a water-cooled condenser. A more
sophisticated off-gas treatment system specially designed for the production
of fine zinc dust by quenching the flue gases with cold off-gas recycled back
after zinc-dust separation in a cyclone was used at a pilot-plant scale
(300 kW$_{th}$) [37], [70]. The solar-produced Zn dust allows for flexible
chemical storage of solar energy and can be used for electricity generation
using Zn-air batteries [36], while the reoxidized Zn can be recycled back to

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$^3$ Material in this chapter has been published in: N. Tzouganatos, M. Dell’Amico,
1109, 2015.
the solar reactor in the form of ZnO, thus closing the thermochemical cycle. While Zn(g) reoxidation is successfully suppressed with these quenching concepts, both quenching processes produce solar Zn in the solid state. For the industrial application of zinc as a metal commodity, however, it is advantageous to condense zinc vapor to liquid rather than solid to avoid remelting the metal for subsequent refining and casting. Adapting the conventional lead splash condenser in a solar thermochemical plant has several disadvantages however due to its mechanical complexity, its high operating and maintenance costs, and the health, safety, and environmental issues relating to the use of lead. Furthermore, because concentrated solar energy is used instead of coke combustion as the source of high-temperature process heat for driving the carbothermal reduction, the resulting off-gas has significantly lower CO$_2$ content ($p_{CO_2} < 0.05$ atm; $\frac{p_{CO_2}}{p_{CO}} < 0.14$ [70]) and consequently is less thermodynamically favorable toward zinc reoxidation, as it will be shown in the analysis that follows. This can facilitate the application of simpler zinc condenser concepts. In this chapter, the development of an alternative off-gas quenching unit aiming to produce liquid zinc from the gas products of the solar carbothermal reduction of ZnO is proposed and numerically investigated.

5.1 Zinc vapor oxidation and condensation

5.1.1 Zinc vapor oxidation studies and kinetic models

Zinc vapor oxidation reactions have been shown to proceed heterogeneously on a solid substrate or ZnO deposited on the reaction
surface [104]–[114]. Previous studies of Zn(g) oxidation by CO$_2$ carried out at temperatures between 973 K and 1273 K and partial pressures of Zn(g) in the range of 0.01 – 0.45 atm report reaction rates in the range of $10^{-9}$ to $10^{-7}$ mol cm$^{-2}$ s$^{-1}$. The kinetics of Zn(g) oxidation in CO$_2$-CO-N$_2$ mixtures were first studied for typical ISF gas compositions by Scott and Fray [106] at temperatures between 1073 K and 1203 K and $p_{Zn(g)}$ up to 0.17 atm. Zinc vapor was generated by passing a CO$_2$-CO-N$_2$ gas mixture through a packed bed of ZnO pellets and was then flown through a SiO$_2$ tube at a lower temperature, thereby allowing reoxidation to occur. The selected Zn(g) generation method, however, imposed a significant composition constraint ($p_{Zn(g)} \leq p_{CO_2}$). The experimental data were fitted to a reversible, second-order rate expression:

$$r'' = k_1 \cdot \left( p_{Zn(g)} p_{CO_2} - \frac{p_{CO}}{K_{eq}} \right)$$

where $k_1$ is the forward reaction rate constant and $K_{eq}$ is the equilibrium constant for reaction (1.12). Clarke and Fray [108] studied the heterogeneous oxidation of Zn(g) in CO$_2$-CO-Ar atmosphere at temperatures between 973 K and 1123 K and $p_{Zn(g)}$ in the range of 0.01 – 0.1 atm using the same experimental setup. Two distinct reaction rate regimes were identified: (i) below 1073 K, coarse ZnO deposits were detected in the silica reactor tube and the reaction rate was proposed to be controlled by the excess $p_{Zn(g)}$:

$$r'' = k_1 \cdot \left( p_{Zn(g)} - p_{Zn(g)}^{eq} \right)$$

and (ii) for temperatures above 1073 K and $p_{CO} > 0.2$ atm, fine-grained ZnO prevailed and the surface desorption of CO was claimed to be the rate-limiting step of the reaction:
\[ r'' = k_1 \cdot \left( p_{Zn(g)} p_{CO_2} \frac{p_{CO}}{K_{eq}} \right) \cdot \left( p_{CO} - p_{CO}^{eq} \right) \]  

(5.3)

where \( p_{CO}^{eq} \) is the partial pressure of carbon monoxide at chemical equilibrium. Investigations of the Zn(g) oxidation reaction over a wider range of compositions \( (p_{Zn(g)} \geq p_{CO_2}) \), and at higher \( p_{Zn(g)} \), were facilitated by the modified reactor-flow apparatus used by Leonard [110] and Stansbury [111]. In their study, zinc vapor was generated by saturation of a CO stream passing over a silica boat of Zn(l) and then mixed with CO\(_2\) in a high-temperature zone to form a homogeneous reacting mixture. It was then passed through a low-temperature reactor tube where reoxidation occurred. For temperatures in the ranges of 1013 – 1273 K and 1243 – 1263 K, and Zn(g) partial pressures of up to 0.28 atm and 0.22 atm, respectively, the reaction was proposed to be independent of the partial pressure of the reacting gases and zero-order rate expressions were formulated for two temperature regimes:

\[ \ln r'' = 2.934 \cdot 10^3 \left( \frac{1}{T+273} \right) - 1.585 \quad 765 \, ^\circ\text{C} \leq T < 883 \, ^\circ\text{C} \]  

(5.4)

\[ \ln r'' = 1.807 \cdot 10^3 \left( \frac{1}{T+273} \right) - 2.761 \quad 883 \, ^\circ\text{C} \leq T \leq 1000 \, ^\circ\text{C} \]  

(5.5)

A major shortcoming of the experimental methodology is, however, the exclusion from the reaction rate analysis of the material deposited at the entrance region of the silica reactor tube. Furthermore the possibility of ZnO forming via the reaction of Zn(g) with CO (Eq. 1.13) either in the vapor generation or the reaction zone is ignored by the use of CO as an inert carrier
Dell’Amico and See [104], [105] used an alternative Zn(g) generation technique to investigate the oxidation reaction in CO$_2$-CO-N$_2$ atmosphere at compositions typical of those observed in the ISF off-gas system ($p_{Zn(g)}$, $p_{CO_2}$, and $p_{CO}$ in the range of 0.04 – 0.12 atm, 0.10 – 0.17 atm, and 0.11 – 0.27 atm, respectively). A zinc-saturated N$_2$ gas stream was produced by bubbling the gas through a Zn(l) bath and passed into the zinc vapor reactor held at the selected oxidation temperature (1023 – 1273 K). Coarse-grained ZnO deposits of similar morphology and reaction rates of the same order of magnitude ($10^{-7}$ mol cm$^{-2}$ s$^{-1}$) as those obtained by Clarke and Fray [108] were reported. A semi-empirical kinetic rate expression similar in form to Eq. 5.2 was proposed:

$$r'' = 9.31 \cdot 10^{-4} \cdot e^{5610/T} \left( p_{Zn(g)} - p_{Zn(g)}^{eq} \right)$$

(5.6)

The work of Lewis and Cameron [112], [113] was motivated by the absence of a kinetic rate expression at higher Zn(g) partial pressures, as most of the existing studies were carried out at typical ISF gas compositions. In their study, zinc vapor was generated by saturation of an Ar stream flowing over a sealed crucible of Zn(l), and the oxidation was investigated at temperatures in the range of 1073 – 1273 K and partial pressures of Zn(g) between 0.18 atm and 0.45 atm. The higher zinc content reflected gas compositions obtained during operation of plasma furnaces for the recovery of zinc from steel plant waste dusts. The reaction system was proposed to follow a three-step mechanism involving the competing reactions (1.12), (1.13) and (1.10), and a plug flow model was used for the formulation of an overall kinetic rate expression:

$$r'' = k_1 \cdot p_{Zn(g)} \cdot p_{CO_2} + k_2 \cdot p_{Zn(g)} \cdot p_{CO}$$

(5.7)
where $k_1$ and $k_2$ are the forward rate constants of reactions (1.12) and (1.13), respectively. At high $p_{\text{CO}}/p_{\text{CO}_2}$ ratios, Zn(g) oxidation by CO prevailed in the system and the oxidation rate equation (5.7) was reduced to the $k_2' p_{\text{Zn(g)}} p_{\text{CO}}$ term, while at low $p_{\text{CO}}/p_{\text{CO}_2}$ ratios, the last term on the right-hand side (RHS) of equation (5.7) becomes negligible and the ZnO formation rate is proportional only to $p_{\text{Zn(g)}}$ and $p_{\text{CO}_2}$. Osborne et al. [114] investigated the kinetics in a Zn-CO-CO$_2$-N$_2$ system at gas compositions reflecting the ISF conditions ($p_{\text{Zn(g)}}$, $p_{\text{CO}_2}$, and $p_{\text{CO}}$ in the range of 0.01–0.09 atm, 0–0.58 atm, and 0–0.55 atm, respectively) and at temperatures between 1003 K and 1023 K. The method previously used by Leonard [110] and Stansbury [111] was implemented for the generation of Zn(g). The reaction rate was found to increase with increasing partial pressure of CO, despite it being a reaction product, leading to the conclusion that the rate-limiting step of the reaction is the autocatalytic oxidation of Zn(g) by CO. A kinetic rate model was developed on a mechanistic basis. The proposed mechanism supported the adsorption of Zn(g) on the silica surface before it reacted, either directly or after forming a “Zn-CO” species, with CO$_2$. The mechanism was claimed to support the autocatalytic character of the reaction and a corresponding reaction rate expression was formulated:

$$r'' = \frac{(k' + k'' \cdot p_{\text{CO}}) \cdot \left( p_{\text{Zn(g)}} p_{\text{CO}_2} - \frac{p_{\text{CO}}}{K_{eq}} \right)}{(1 + k''' \cdot p_{\text{Zn(g)}})}$$

(5.8)

where $k'$, $k''$, and $k'''$ are reaction rate constants of individual reaction steps and $K_{eq}$ is the equilibrium constant of reaction (1.12).

**Figure 5.1** represents an equilibrium phase stability diagram for the
For the solar carbothermal production of liquid Zn, carbothermal reduction of ZnO, including the equilibrium $p_{CO_2}/p_{CO}$ ratio curves for the reactions: $\text{Zn}(g) + \text{CO}_2 = \text{ZnO}(s) + \text{CO}$, $\text{Zn}(l) + \text{CO}_2 = \text{ZnO}(s) + \text{CO}$ and $2\ \text{CO} = \text{C}(s) + \text{CO}_2$ at selected values of $p_{\text{Zn}(g)}$ and $p_{CO}$.

Figure 5.1. Equilibrium phase stability diagram for the carbothermal reduction of ZnO at $p_{\text{Zn}(g)}$, $p_{CO} = 0.1$ atm and 0.5 atm. Indicated are the experimental conditions reported in zinc vapor oxidation studies and the gas atmosphere for the packed-bed solar reactor outlet for representative experimental runs at ZnO:C molar ratios of 1:0.8 and 1:0.9: Clarke and Fray [108] (▽), Dell’Amico and See [104] (□), Lewis and Cameron [112], [113] (◊), Osborne et al. [114] (○), Solar reactor (Δ).

This diagram shows regions of stability for gas and pure solid phases of ZnO and carbon. The carbothermal reduction of ZnO proceeds in the region...
enclosed between the equilibrium $p_{CO_2}/p_{CO}$ curves for Zn(g) oxidation by CO$_2$ and the reverse Boudouard reaction. Above the equilibrium curves of Zn(g) + CO$_2$ = ZnO(s) + CO, zinc vapor becomes unstable and oxidation is favored. A considerable increase in the reversion temperature of reaction (1.9) can be observed with increasing $p_{CO_2}/p_{CO}$ ratios at fixed $p_{Zn(g)}$. Also indicated in Figure 5.1 is a summary of the experimental conditions reported in Zn(g) oxidation studies and the solar reactor conditions for representative experimental runs at ZnO:C molar ratios of 1:0.8 and 1:0.9 [69], [70]. A typical range of $p_{CO_2}/p_{CO}$ ratios for the solar-driven process is 0.11 – 0.26 because of the elimination of coke combustion. Most prior studies investigated Zn(g) oxidation at considerably higher ratios. Only Lewis and Cameron [112], [113] and Osborne et al. [114] conducted significant numbers of experiments at $p_{CO_2}/p_{CO}$ ratios coinciding with typical solar reactor atmospheres. Lewis and Cameron’s work also considered $p_{Zn(g)}$ in the range 0.18 – 0.45 atm, thus reflecting typical $p_{Zn(g)}$ values of 0.2 atm for a representative solar carbothermal reduction of ZnO at a ZnO:C molar ratio of 1:0.8 (see Chapters 3 and 4). Therefore the reaction rate expression proposed by Lewis and Cameron (Eq. 5.7) is used in the current study.

### 5.1.2 Zinc vapor condensation and industrial condensers

Suppression of the thermodynamically favorable reoxidation reactions of Zn(g) by CO$_2$ and CO can be attained by rapid cooling of the gaseous products. Historically, advancements in the ZnO reduction processes and increasing zinc production rates have been the main drivers for the
development of novel Zn(g) condensation techniques. For example, the reaction products of a horizontal retort furnace process [38], comprising about 45% Zn(g) and 55% CO, would condense on the wall of surface-type fireclay condensers. This early design was suitable for the low Zn production rates (40 kg Zn/day) of a horizontal retort, but major shortcomings arose from the large number of condensers required and subsequently the high operational and maintenance costs. High-efficiency direct-contact condensation techniques became the center of interest for advanced Zn production technologies due to higher specific transfer areas, rapid transfer rates, relative simplicity of design and lower maintenance costs. In the New Jersey Zinc Company’s continuous vertical retort process [115] with a capacity of 8 tpd Zn, zinc was recovered from gas products of similar composition to a horizontal retort furnace by passing them countercurrently to a zinc splash condenser. In this arrangement, graphite rotors dipped into a Zn(l) pool created an intense shower of Zn(l) droplets to rapidly chill the furnace gases and absorb zinc vapor. The zinc pool was maintained at temperatures below 550°C through a water-cooled circulation system to keep equilibrium vapor losses to a minimum. Besides the New Jersey Zinc Process, zinc splash condenser technology has been adapted also in electrothermal [116] and plasma-arc [117] processes for zinc recovery from electric-arc furnace (EAF) dusts. Fuming of species other than zinc from the EAF feedstock however enhances the formation of heterogeneous condensation sites and, subsequently, contributes to fog and dross formation with a deleterious effect on zinc recovery. Another zinc condenser concept is the so-called “Wheaton-Najarian vacuum condenser” developed for the 2.44 m-bore electrothermic zinc furnace at Josephtown Zinc Smelter with a
capacity of 20 – 80 tpd Zn [118], [119]. This condenser recovered zinc by bubbling a mixture of Zn(g) with non-condensable gases upwardly through a Zn(l) bath enclosed in a U-tube chamber by suction. Brick baffles projecting normally to the inside of the roof of the condensing chamber were used to increase residence time and gas-liquid interfacial area through bubble breakup, as depicted in Figure 5.2. Zinc that condensed and accumulated in the condenser was periodically tapped out. Condensation efficiency of the order of 97 – 98% of theoretical was obtained when keeping the Zn(l) bath temperature in the range of 480 – 525°C [44]–[46].

![Figure 5.2. Schematic of the Wheaton-Najarian vacuum condenser (based on drawings by Najarian [46]).](image)

The dominating pyrometallurgical Zn blast furnace process (ISF), however, required a condenser capable of handling high gas flows with low
zinc concentration and of absorbing approximately 2.5 times the amount of heat absorbed by the Wheaton-Najarian (W-N) condenser per mole of Zn produced [120]. This is attributed to the heat liberated during cooling of an increased amount of non-condensable gases [41], [120]. A splash condenser was developed by the Imperial Smelting Company [41] to recover zinc vapor flowing countercurrent to a liquid lead droplet shower produced by the rotation of steel impellers immersed in a bath of liquid lead. A zinc-rich phase is separated from the Zn-Pb alloy leaving the condenser at 550°C with a Zn content of 2.26 wt.% by exploiting an immiscibility gap of the Zn-Pb binary system. The liquid stream is cooled down to 440°C, where the solubility limit of 2.02 wt.% is reached, and liquid zinc separates as a layer over Pb(l). The liquid zinc is tapped out and the liquid lead is recirculated to the condenser inlet for recovery of fresh Zn(g). The lead splash condenser technology thus requires a continuous supply of large amounts of liquid lead ranging between 300 and 400 tonnes per tonne of Zn produced to operate. Although this condenser has high operational and maintenance costs, and it uses lead that suffers from critical health, safety, and environmental issues, it remains the only commercially used zinc condensation process. Besides primary zinc production processes, the ISP lead splash condenser technology has been used in processes for zinc recovery from steel plant dusts and zinc-containing slag. Recovery of 98.4 wt.% pure zinc from lead-blast furnace slags using the Enviroplas process [121] has been successfully demonstrated at a 5.6 MVA scale [122]. Several other condensation technologies have been proposed for the recovery of Zn(l) from a body of molten lead [123]–[127]. A multi-compartment combined Zn(l)- and Pb(l)-splash condenser concept has been trialed to reduce the amount of Pb(l) recirculated [128].
lead-spray zinc condenser has been developed by SKF Plasma Technologies AB for zinc recovery from high-zinc-containing carbon steel dusts, but operation was terminated due to economic reasons after switching from processing carbon steel dusts to low-zinc-containing (<6 wt.%) alloy-steel dusts. Other zinc condensers such as of Solnordal et al. [43] experimentally investigated the feasibility of using a fluidized bed of zircon sand to condense zinc from smelter off-gases as a solid. They reported the rapid cooling of the gas-vapor mixtures from about 1200°C to 500°C within 8 ms and Zn recovery exceeding 90%. The solid zinc condenser product, however, has disadvantages because it needs to be remelted for subsequent refining and casting of ingots.

In the solar reactor process [69], [70], reaction gases also need to be rapidly quenched from the thermodynamically stable gas outlet temperature of 1473 K to temperatures where the kinetic rate of Zn reoxidation is slow. Major shortcomings for the application of the conventional lead splash condenser in a solar thermochemical plant arise from its size, mechanical complexity, and other issues described previously. Bubbling gas condensation through a bath of Zn(l) like the W-N vacuum condenser has advantages of simplicity (no moving mechanical parts), intensity (smaller size), and no need of a secondary liquid metal phase. Solar reactor off-gas products are characterized by high $p_{CO}/p_{CO_2}$ ratios compared with those in an ISF, and the oxidation potential can be further decreased by operation with increased amount of carbon in the feedstock (ZnO:C molar ratios lower than 1:0.8) to produce gas compositions similar to the electrothermic furnace. A decrease in the flow rate of the inert carrier gas ($N_2$) allows for a significant reduction of the heat liberated during Zn(g) absorption and
for the solar carbothermal production of liquid Zn

reduces the problem of heat dissipation that was reported to be the most significant shortcoming of the W-N condenser [45], [46]. The W-N condenser design was not adopted for wide commercial application as it was initially developed for handling low gas volumes and gas atmospheres with low oxidation potential, and it was thus less suited to ISF conditions. However, with trends toward new technologies such as arc furnaces for zinc production and their formation of high concentration, lower volume Zn(g)-CO streams, molten zinc bath condensers should be reconsidered. This does also apply to future new zinc processes such as the solar-driven thermochemical plants considered in this study. Therefore, the molten zinc bath condenser concept is chosen in the current study aiming at producing liquid Zn from the product gas evolving from the solar carbothermal reduction of ZnO.

The operating conditions for the solar zinc reactor-condenser process can be characterized by a plot of the variation of Zn vapor pressure and equilibrium Zn(g) partial pressure for reaction (1.12) at $p_{CO} / p_{CO2}$ ratios in the range $2 \rightarrow 10000$ [129], along with points relevant to the operation of the 10 kW$_{th}$ packed-bed solar reactor, as shown in Figure 5.3. Typical solar reactor gas products containing 19.9% Zn(g) leave the reactor at 1473 K and a $p_{CO} / p_{CO2}$ ratio of 3.8 (point A). This gas composition corresponds to the highest oxidation potential measured during typical experimental runs at ZnO:C molar ratios of 1:0.8 and 1:0.9 and is used as the base case scenario in the current study. Reoxidation of Zn(g) by CO$_2$ is thermodynamically unfavorable until the reversion temperature of 1314 K (point B) is reached, while condensation will commence only below the apparent saturation temperature of 1037 K (point C). Equilibrium condensation upon further
cooling of the gases to the temperature of the Zn(l) bath at 773 K (point D) follows the line CD. Thus, rapid quenching of the gas-vapor mixture should minimize the residence time and prevent ZnO formation in the temperature range between 1314 K and the kinetically unfavorable temperature of 773 K for the reversion reactions to occur.

Figure 5.3. Variation of the Zn vapor pressure and equilibrium Zn(g) partial pressure for reaction (1.12) at $p_{\text{CO}}/p_{\text{CO}_2}$ ratios in the range of 2 – 10000 along with points (A, B, C, D) relevant to the operation of the 10 kW$_{\text{th}}$ packed-bed solar reactor.

5.2 Condensation mechanism of vapor bubbles

The key process in a molten zinc bath condenser is the condensation of Zn(g) from gas-vapor bubbles, the initial composition being that of the solar reactor process gas. The condensation and collapse of vapor bubbles in
liquid baths has been extensively investigated at different degrees of subcooling, i.e., where the bath is maintained at temperatures below the apparent saturation temperature of the vapor. At high degrees of subcooling, bubble collapse is controlled by the inertia forces of the surrounding liquid and proceeds rapidly while no laminar boundary layer can be observed [130]–[133]. Heat transfer through the vapor-liquid interface governs the process at moderate temperature differences. Heat-transfer-controlled condensation of bubbles has been previously experimentally studied in miscible [134]–[140] and immiscible [141] liquids. Bubble condensation Nusselt numbers have been derived capable of describing the dynamic nature of the liquid-vapor interface, as opposed to the case of convective heat transfer from a solid object. A critical evaluation of Nusselt correlations for vapor bubble condensation in subcooled flows is provided by Rabello and Buongiorno [142]. The effect of non-condensable gases on the bubble collapse rate was investigated by Jacobs and Major [143] and Ullmann and Letan [144]. The dimensionless Jacob number, defined as the ratio of sensible to latent heat absorbed during the vapor-liquid phase change, is used to define the limits of the inertia-controlled and heat-transfer-controlled regimes of condensation:

\[ J_a = \frac{\rho_l \cdot c_{p,l} \cdot \left( T_{s}^* - T_\infty \right)}{\rho_v \cdot \Delta h_{fg}} \]  

(5.9)

where \( T_{s}^* \) is the apparent saturation temperature, \( T_\infty \) is the temperature in the bulk liquid, \( c_{p,l} \) is the specific heat capacity of the liquid, \( \Delta h_{fg} \) is the enthalpy of evaporation, and \( \rho_l \) and \( \rho_v \) are the density of the liquid and the vapor, respectively. Chen and Mayinger [136] specified interfacial heat transfer as rate-limiting up to \( J_a = 80 \), while a transition region of mixed effects was
identified before entering the liquid inertia-controlled regime ($Ja > 100$). Besides the temperature of the liquid bath, $Ja$ varies with the partial pressure of the condensing vapor in the gas mixture when non-condensable gases are present. As the condensation proceeds, the fraction of non-condensable gases increases, thereby inducing a decrease in the apparent saturation temperature. **Figure 5.4** shows the effect of the fraction of non-condensable gases on the apparent saturation temperature of Zn(g) and on the Jacob number during condensation of the gas-vapor mixture at selected temperatures of the Zn(l) bath.

![Figure 5.4](image.jpg)

**Figure 5.4.** Effect of the fraction of non-condensable gases on the apparent saturation temperature of Zn(g) and the Jacob number ($Ja$) for selected temperatures of the Zn(l) bath.
Inertia forces in the liquid phase govern condensation of a solar reactor gas-vapor mixture initially containing 19.9% Zn(g) in a highly subcooled Zn(l) bath maintained at 500°C, as indicated by the initial $Ja = 600$. Transition to the heat-transfer controlled regime is reached at $\Delta T_{sub} = T_s^* - T_\infty = 55$ K, corresponding to 99.3% content of non-condensable gases in the gas-vapor mixture.

### 5.3 Formulation of heat- and mass-transfer model

#### 5.3.1 Governing equations

A simplified, zero-dimensional transient heat and mass transfer model of a single bubble rising through a Zn(l) bath was developed to investigate the competing condensation rates and kinetics of oxidation of zinc vapor for a wide range of gas compositions. Neglect of the heat and mass transfer resistance within the bubble is justified by vigorous toroidal circulation of gas inside the bubble by virtue of the viscous drag of the outer fluid as described by Garner and Hammerton [145]. In the case of condensing bubbles, circulation is further enhanced by the shrinking effect of the vapor-liquid interface. With the assumptions of (i) no interaction between individual bubbles, (ii) constant liquid bulk temperature due to high thermal conductivity of the liquid phase, (iii) constant relative velocity between bubbles and liquid, (iv) constant total pressure of 1 bar throughout, (v) reaction rate expressions as proposed by Lewis and Cameron for the reoxidation of Zn(g), and (vi) reactions occurring in the thermodynamically favorable regions according to Figure 5.3, the mass conservation equation is:
\[
\frac{dm_b}{dt} = M_{\text{Zn}} \cdot r_{Zn(g),\text{cond}} \tag{5.10}
\]

where \(m_b\) is the mass of the bubble containing zinc vapor, non-condensable gases and the solid species involved in the reactions (1.10), (1.12), and (1.13). The RHS term accounts for the mass of the condensate exchanged with the liquid bath defined by the condensation molar source multiplied by the molar weight of Zn. The conservation equation of species \(k\) in the bubble is [146]:

\[
\frac{dm_k}{dt} = M_k \cdot r_k \tag{5.11}
\]

where \(r_k = \sum_{j=1}^{3} r_{k,j}\) is the formation/consumption rate for CO, CO\(_2\), N\(_2\), ZnO, and C, and \(r_{Zn(g)} = \sum_{j=1}^{3} r_{Zn(g),j} + r_{Zn(g),\text{cond}}\) is the consumption rate for Zn(g). The summation accounts for the mass change of species \(k\) at the three individual steps involved in the Zn(g) oxidation reaction mechanism (Equations (1.12), (1.13), and (1.10)). The energy conservation equation expressed in terms of the sensible enthalpy \(h_s\) is [147]:

\[
\begin{align*}
&m_b c_{p,\text{eff}} \frac{dT_b}{dt} + \sum_{k=1}^{6} r_k h_{s,k} = -h_{A_b} \left( T_b - T_{Zn(l)} \right) \\
&- r_{Zn(l),\text{cond}} h_{s,Zn(l)} + r_{Zn(l),\text{cond}} \Delta h_{gf}^{\circ} + \sum_{j=1}^{3} r_j \Delta h_{rxn,j}^{\circ} \tag{5.12}
\end{align*}
\]

where \(c_{p,\text{eff}}\) is the effective specific heat capacity, \(T_b\) is the temperature of the gas-vapor mixture, \(h_{s,k}\) is the sensible enthalpy of species \(k\), \(h\) is the
convective heat transfer coefficient, $r_{\text{Zn(l)}, \text{cond}}$ is the molar production rate of liquid zinc, and $A_b$ is the interfacial area calculated assuming a spherical bubble. The second term on the RHS of equation (5.12) represents the energy of mass exchanged with the liquid phase, while the two last terms denote the heat of condensation and the heat of reactions (1.12), (1.13), and (1.10) at standard conditions. Different correlations are applied for the interfacial heat transfer coefficient depending on the physical phenomena taking place and the controlling mechanism of condensation. The Hughmark correlation [148], initially developed for flows around rigid spheres, is employed during cooling of the gas-vapor mixture to the apparent saturation temperature (line segment AC in Figure 5.3):

$$h = \begin{cases} \frac{k_l}{D_b} \left( 2 + 0.6 \frac{\text{Re}_b^{1/2}}{\text{Pr}_l^{1/3}} \right) & 0 \leq \text{Re}_b \leq 776 \\ \frac{k_l}{D_b} \left( 2 + 0.27 \text{Re}_b^{0.62} \text{Pr}_l^{1/3} \right) & \text{Re}_b \geq 776 \end{cases}$$

(5.13)

where $\text{Re}_b = \frac{u_{rel} D_b}{v_l}$ is the bubble Reynolds number, $u_{rel}$ is the relative velocity between gas and liquid, $D_b$ is the bubble diameter, and $v_l$, $k_l$, and $\text{Pr}_l$ represent the kinematic viscosity, thermal conductivity, and Prandtl number of the liquid, respectively. In the inertia-controlled regime the kinetic theory of gases can be used for the vapor-liquid interface. The heat transfer coefficient is then obtained using the Hertz-Knudsen-Shrage equation [149] corrected for a curved interface [150], [151]:

$$h = \frac{4}{4 - 3 K_c} \left( \frac{1}{2 \pi M_{\text{Zn}}} \right)^{1/2} \left\{ K_c \frac{p_{\text{Zn(g)}}}{T_b^{1/2}} - K_e \frac{p_{\text{Zn(l)}}}{T_{\text{Zn(l)}}^{1/2}} \right\} \frac{\Delta h_{gf}}{T_b - T_{\text{Zn(l)}}}$$

(5.14)
where $p_{Zn(l)}$ is the saturation partial pressure of zinc vapor at $T_{Zn(l)}$, and $K_C$ and $K_E$ are the condensation and evaporation coefficients. $K_C$ is defined as the ratio of incident vapor molecules absorbed by the liquid phase to the molecules impinging onto the liquid-vapor interface, and $K_E$ is the ratio of molecules entering the vapor phase to the molecules leaving the liquid phase. The simplification $K_C = K_E = 0.96$ is used as was measured for the condensation coefficient at a solid-liquid Zn interface by Rapp et al. [152]. In the heat-transfer controlled condensation regime the following correlation proposed by Chen and Mayinger [136] for $Re_b \leq 10000$ and $2 \leq Pr_l \leq 15$ is implemented:

$$h = \frac{k}{D_b} \left( 0.185 \ Re_b^{0.7} \ Pr_l^{1/2} \right) \quad (5.15)$$

### 5.3.2 Numerical method and code verification

An adaptive time-stepping technique is employed for the entire calculation procedure to enhance the robustness of the code and to achieve the desired solution accuracy with minimum computational effort [153]. The automatic control of the time step is based on the estimation of the local truncation error associated with the time integration scheme. Considering an ordinary differential equation of the form:

$$\frac{dy}{dt} = F(t, y(t)) \quad (5.16)$$

an estimate of the local error $\tau$ at $t+\Delta t$ is obtained by applying the explicit Euler integration scheme using two time steps of different size, $\Delta t$ and $\Delta t/2$:

$$y_{t+\Delta t} = y_t + \Delta t \cdot F(t, y_t) \quad (5.17)$$
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\[ y_{t+\frac{\Delta t}{2}} = y_t + \frac{\Delta t}{2} \cdot F(t, y_t) \]  

(5.18)

\[ y'_{t+\frac{\Delta t}{2}} = y_{t+\frac{\Delta t}{2}} + \frac{\Delta t}{2} \cdot F(t + \frac{\Delta t}{2}, y_{t+\frac{\Delta t}{2}}) \]  

(5.19)

\[ \tau_{t+\Delta t} = y'_{t+\Delta t} - y_{t+\Delta t} \]  

(5.20)

The local error estimate is compared with a prescribed local error tolerance value \( \tau_{TOL} \) to either accept the current time step size or calculate the optimal time step \( \Delta t^* \):

\[ \Delta t^* = 0.9 \Delta t \frac{\tau_{TOL}}{\tau_{t+\Delta t}} \]  

(5.21)

where 0.9 is a damping factor used to decrease the risk of rejection of the next time step. The local error tolerance value \( \tau_{TOL} \) is set equal to \( 5 \cdot 10^{-3} \) to ensure an acceptable accuracy of the solution with minimum computational effort. A study has been conducted to facilitate the selection of an appropriate value for the local error tolerance. Values below \( 10^{-2} \) have been shown to have a negligible effect on the solution accuracy.

The correct implementation of the numerical method has been assessed by performing a code verification study using the method of manufactured solutions [154]. The assessment of the implementation is based on conducting a time-step refinement study in which the global error between the numerical solution and an “exact” manufactured solution is evaluated as the time step size is reduced. Thus, the code verification study has been conducted using a fixed time step size for the entire calculation procedure rather than an adaptive time step. The order of accuracy of the numerical method is determined from the rate at which the numerical solution tends to
the “exact” manufactured solution. A correct implementation of the numerical method can be ensured when the actual order of accuracy for the individual terms in the governing equations approaches the nominal order of accuracy in the asymptotic range of convergence. For equations (5.10) – (5.12) the actual order of accuracy approaches unity with decreasing time step size when applying the explicit Euler integration scheme as depicted in Figure 5.5, which indicates the correct implementation of the numerical method.

Figure 5.5. Actual order of accuracy $p$ as a function of the time step $\Delta t$ for the a) mass and b) energy conservation equations.
5.4 Numerical results and discussion

In the following, the modeling results are described and discussed based on process conditions typical for the solar carbothermal ZnO reduction process.

5.4.1 Numerical results

The temperature of the Zn(l) bath, the initial bubble diameter, the relative velocity between bubbles and liquid, as well as the fraction of non-condensable gases in the vapor-gas mixture are the main parameters affecting the total process time and condensation efficiency. Bath temperatures in the range of 500 – 650°C were investigated to allow efficient operation of the condenser while maintaining an adequate margin above the melting point to avoid solidification. Although the majority of studies on gas bubbles rising in liquid baths involve sparging or submerged lance injection, these techniques entail a high risk of clogging by solid products formed during Zn(g) reoxidation and are not considered practical for the zinc vapor reactor application. Pumping or suction of the vapor-gas mixture through a Zn(l) bath in a similar manner to the W-N vacuum condenser favors the formation of large gas bubbles. In line with the findings of Haberman and Morton [155], bubble diameters in the range of 10 – 80 mm are considered in the current study.

Haberman and Morton [155] further identified increasing terminal rise velocities with increasing bubble size. For bubbles in the 10 – 80 mm range, the terminal velocity is independent of the properties of the surrounding liquid and can be obtained according to [155]:

\[
\text{velocity} = \text{constant} \times \text{bubble diameter}^{1/3}
\]
Relative velocities between bubbles and liquid in the range between 0.02 m/s and 0.2 m/s, the terminal rise velocity for a 10 mm-diameter bubble, were therefore studied in the current work. To investigate the effect of the presence of non-condensable gases in the mixture, the initial fractions of non-condensable gases were varied between 0.535 and 0.801. These conditions are typical for the 10 kWth packed-bed solar reactor (see Chapters 3 and 4) and correspond in this experimental setup to inert carrier gas (N₂) mass flow rates between 0.5 and 5 LN_min⁻¹, respectively. These conditions were used as the basis for modeling.

The variation of the gas temperature, the bubble diameter, the Zn(g) partial pressure, and the chemical conversions of Zn(g) to Zn(l) and ZnO as a function of time is shown in Figures 5.6a-d, respectively, for a bubble with an initial diameter of 45 mm and 80.1% non-condensable gases rising at 0.11 m/s in a Zn(l) bath at temperatures in the range of 500 – 650°C. The gas temperature drops monotonically to reach the corresponding Zn(l) bath temperature within less than 1 ms. Higher heat transfer rates are observed with decreasing bath temperatures owing to the higher thermodynamic driving forces. The obvious change in curvature in the temperature curves, which for $T_{Zn(l)} = 600^\circ C$ is clearly identifiable at 0.2 ms, is attributed to the transition from inertia-controlled to heat-transfer-controlled condensation regimes. A notable increase in the final bubble diameter from $D_b = 33.7$ mm at $T_{Zn(l)} = 500^\circ C$ to $D_b = 36.2$ mm at $T_{Zn(l)} = 650^\circ C$ is obtained due to the
non-linear increase of the equilibrium Zn(g) losses with temperature, as indicated in Figures 5.6b and c.

Figure 5.6. Variation of the: (a) gas temperature, (b) bubble diameter, (c) Zn(g) partial pressure, and (d) chemical conversion of Zn(g)-to-Zn(l) and Zn(g)-to-ZnO for a bubble with an initial diameter of 45 mm and 80.1% non-condensable gases rising at 0.11 m/s in a Zn(l) bath maintained in the temperature range of 500 – 650°C.

Figure 5.6d reveals that rapid quenching of the gas-vapor mixture to temperatures, where the formation of ZnO is kinetically hindered, enables the suppression of the reversion reactions of Zn(g) by CO₂ and CO and facilitates high Zn(l) yields. Conversion of Zn(g) to Zn(l) increases from
0.845 at \( T_{\text{Zn(l)}} = 650^\circ \text{C} \) to 0.992 at 500\(^\circ\)C, whereas only a small fraction of Zn(g) entering the condenser is predicted to form ZnO. The fraction of reversion \( X_{\text{Zn(g)-to-ZnO}} \) is in the range of \( 2.4 \cdot 10^{-7} \) to \( 3.6 \cdot 10^{-7} \). The heat flux from a bubble with an initial diameter of 45 mm, and 80.1% non-condensable gases, rising at 0.11 m/s in a Zn(l) bath maintained at 500\(^\circ\)C is shown in Figure 5.7.

![Figure 5.7. Heat flux from a bubble with an initial diameter of 45 mm and 80.1% non-condensable gases rising at 0.11 m/s in a Zn(l) bath maintained at 500\(^\circ\)C.](image)

The initial drop in the heat flux curve corresponding to cooling without condensation (line segment AC in Figure 5.3) is followed by a heat flux peak of 6500 W/cm\(^2\) as the gas-vapor mixture reaches the apparent saturation temperature of 1037 K and condensation commences. The notable
decrease in the heat flux at temperatures below 1037 K is attributed to the decreasing partial pressure of Zn(g) and, hence, mass transfer driving force. Large amounts of heat are released from the condensing bubble surface as a result of both the rapid Zn(g) condensation and the high enthalpy of condensation. Heat flux values shown in Figure 5.7 are comparable to fluxes of 1896 – 3564 W/cm² reported in Gunther’s cinematographic study [156] of the mechanism of highly subcooled ($\Delta T_{sub} = 245 – 256°C$) nucleate boiling of water.

The effect of the initial bubble diameter on the heat and mass transfer rates for a bubble with an initial content of 80.1% non-condensable gases rising at 0.11 m/s in a bath maintained at 500°C is shown in Figure 5.8 by plotting the variation of the gas temperature and chemical conversions as a function of time. An increase of the initial diameter from 10 mm to 80 mm induces a two orders of magnitude increase in the time required to reach the apparent saturation temperature and thermal equilibrium due to the decrease of the surface-area-to-volume ratio. For a 10 mm-diameter bubble, condensation commences after 7 µs to reach a $X_{Zn(g)-to-Zn(l)}$ of 0.992 after 60 µs, whereas a 80 mm-diameter bubble requires 1.12 ms to reach the same conversion. Lower heat transfer rates with increasing bubble diameter result in an increase of the asymptotic $X_{Zn(g)-to-ZnO}$ conversion from $1.3 \cdot 10^{-7}$ to $2.9 \cdot 10^{-7}$ due to the longer residence time of the gas-vapor mixture at temperatures favoring ZnO formation.

An increase in the gas-liquid relative velocity results in similar trends as a decrease in the initial bubble diameter, as shown in Figure 5.9 for a bubble with an initial diameter of 45 mm. An order of magnitude increase in the relative velocity reduces the time required to reach a $X_{Zn(g)-to-Zn(l)}$ of 0.992
from 1.32 ms to 0.39 ms due to the enhanced heat and mass transfer, whereas the asymptotic $X_{\text{Zn(g)-to-ZnO}}$ conversion decreases from $5.7 \cdot 10^{-7}$ to $1.7 \cdot 10^{-7}$.

**Figure 5.8.** Effect of the initial bubble diameter on the heat and mass transfer rates as illustrated by the variation of temperature and chemical conversions for a bubble with an initial content of 80.1% non-condensable gases rising at 0.11 m/s in a Zn(l) bath maintained at 500°C.
Figure 5.9. Effect of the relative velocity between gas bubbles and liquid on the heat and mass transfer rates as illustrated by the variation of temperature and chemical conversions for a bubble with an initial diameter of 45 mm and initial content of 80.1% non-condensable gases rising in a Zn(l) bath maintained at 500°C.

Figure 5.10 shows the effect of the molar fraction of non-condensable gases on the time variation of the bubble diameter and the chemical conversions of Zn(g) to Zn(l) and ZnO for a bubble with an initial diameter of 45 mm, rising at 0.11 m/s in a Zn(l) maintained at 500°C. The fraction of non-condensable gases in the bubble controls the thermodynamic driving force in the condensation process by affecting the Zn(g) partial pressure and,
consequently, the apparent saturation temperature. Thus, higher fractions of non-condensable gases induce a decrease in the shrinking rate of the bubble, as depicted in Figure 5.10a.

![Figure 5.10](image)

**Figure 5.10.** Effect of the molar fraction of non-condensable gases on the shrinking rate of the bubble and the time variation of the Zn(g)-to-Zn(l) and Zn(g)-to-ZnO chemical conversions for a bubble with an initial diameter of 45 mm rising at 0.11 m/s in a Zn(l) bath maintained at 500°C.

The increase of the final bubble diameter from 29.5 mm to 33.7 mm with increasing initial content of non-condensable gases is attributed to the volume occupied by the additional amount of N₂ in the gas-vapor mixture.
The fraction of non-condensable gases exhibits a negligible effect on the $X_{Zn(g)\rightarrow Zn(l)}$ conversion (Figure 5.10b), which varies between 0.992 and 0.998 at initial contents of 80.1% and 53.5% non-condensable gases, respectively. In contrast, $X_{Zn(g)\rightarrow ZnO}$ conversion increases by an order of magnitude from $2.37 \times 10^{-7}$ to $1.03 \times 10^{-6}$ at a lower content of non-condensable gases due to the first-order dependence of the reversion reaction rates on the partial pressures of $Zn(g)$, CO, and CO$_2$.

The effect of liquid bath temperature and fraction of non-condensable gases on the $X_{Zn(g)\rightarrow Zn(l)}$ conversion is shown in Figure 5.11.

![Figure 5.11](image)

**Figure 5.11.** Effect of the Zn(l) bath temperature and the fraction of non-condensable gases on conversion of Zn(g) to Zn(l).
The notable decrease in the $X_{\text{Zn(g)-to-Zn(l)}}$ conversion with increasing liquid zinc bath temperature is attributed to the non-linear increase of the equilibrium vapor losses with temperature. The variation of the $X_{\text{Zn(g)-to-Zn(l)}}$ conversion between 0.992 and 0.998 at initial molar contents of 80.1% and 53.5% non-condensable gases illustrates a negligible effect of the fraction of non-condensable gases on the condensation efficiency for a highly subcooled liquid bath maintained at 500°C. On the contrary, an increase in the content of non-condensable gases in the gas-vapor mixture from 53.5% to 80.1% induces a strong non-linear decrease in the Zn(g)-to-Zn(l) conversion from 0.956 to 0.845 for condensation in a liquid bath maintained at 650°C, which is attributed to the effect of their presence on the Zn(g) partial pressure and the apparent saturation temperature.

### 5.4.2 Discussion

Numerical heat and mass transfer modeling demonstrates that zinc vapor reoxidation reactions proceed considerably slower than condensation, thus preventing a considerable decrease of the Zn(g) partial pressure in the undersaturated vapor region due to oxidation by CO$_2$ and CO. The results suggest the technical feasibility of the molten zinc bath condenser concept for zinc gas condensation from high concentration Zn(g)-CO streams such as from a reactor for the solar carbothermal reduction of ZnO. The higher condensation rates obtained with decreasing initial bubble diameter and increasing gas-liquid relative velocity confirm the use of baffles in the Zn(l) bath such as that used in the W-N condenser to prevent coalescence of individual bubbles, enhance bubble breakup, and improve heat transfer. Furthermore, the negligible effect of fraction of non-condensable gases on
the condensation efficiency predicted for a highly subcooled liquid bath at 500°C is supported by observations on the operation of the pilot-scale W-N condenser mounted at the outlet of the electrothermic zinc furnace at the Josephtown Zinc Smelter. Rapid and almost complete condensation of zinc vapor was reported for operation at liquid bath temperatures in the range of 500 – 525°C, irrespective of the amount of accompanying non-condensable gases [45].
Chapter 6

Design, fabrication and experimental testing of a windowless two-cavity reactor

As discussed in detail in Chapter 2, the reactor technology employed in the current study for the solar-driven primary and secondary production of Zn has been successfully demonstrated for several thermochemical applications and reached a high level of maturity. However, despite the protective action provided by the separation plate against fouling of the quartz window, the latter still represents a troublesome and fragile component that is not easy to keep completely uncontaminated. Additionally, due to the poor scalability of quartz windows elimination of this component would facilitate commercialization of this solar reactor technology. In this chapter, numerical and experimental efforts taken to realize a windowless two-cavity solar reactor concept are presented. Investigations focus on identifying a structurally and chemically stable material that could serve as the intermediate solar absorber between the UC and the LC in place of the SiC-coated graphite plate under the highly demanding conditions of a solar thermochemical process. The resulting windowless reactor design is then successfully demonstrated by performing

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4 Material in this chapter has been prepared for publication as: N. Tzouganatos, C. Wieckert, A. Steinfeld, “Design, Fabrication and Experimental Testing of a 5 kWth Packed-Bed Reactor for Solar Thermochemical Processes”.


solar carbothermal ZnO reduction experiments under various operating conditions.

6.1 Experimental Setup

6.1.1 Solar reactor configuration and materials

The windowless reactor design was realized based on the 10 kW\textsubscript{th} packed-bed solar reactor described in Chapter 2. In the windowed configuration, the reactor is sealed against atmosphere at the window/CPC interface. In absence of the quartz window and since the roughness of the SiC walls in the existing reactor does not allow for creating a gas-tight seal at the separation plate/ SiC walls interface, design modifications had to be undertaken to prevent oxygen from entering the reaction chamber. A schematic representation of the new reactor configuration is shown in Figure 6.1. In that, the water-cooled CPC assembly positioned on top of the stainless steel vessel in the windowed reactor design (see Figure 2.1) was removed, and the LC walls were extended upwards by about 60 mm to reach a total LC height of 230 mm. In place of the CPC assembly, a holding ring (160 mm inner diameter, 290 mm outer diameter) made of Inconel alloy 617 is mounted on the upper face of the stainless steel vessel in order to allow for gas-tight mounting of the separation wall. The latter is mounted on top of the holding ring, while an Inconel 617 flange ring (160 mm inner diameter, 173.5 mm outer diameter) atop the separation wall is used to apply the gasket stress required for an effective initial seal, as depicted in Figure 6.2. In contrast to the preceding windowed reactor design, omission of the temperature-sensitive transparent window and use of highly oxidation-
resistant Inconel 617 parts permit operation of the windowless reactor without water cooling, which represents another major advantage of the new reactor design. The upper cavity is now an open solar-cavity receiver, and comprises the separation wall and high-temperature Al$_2$O$_3$/SiO$_2$ thermal insulation monoliths with a 60 mm-diameter circular aperture for the access of concentrated solar irradiation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Schematic of the 5 kW$_{th}$ windowless packed-bed solar reactor configuration using a circular plate as separation wall between the UC and the LC.}
\end{figure}

The SiC-coated graphite material that has hitherto been used in the windowed reactor design for the manufacture of the separation wall between the UC and the LC for experimentation under controlled atmospheres is not an attractive candidate for reactor operation in air. During experimentation with the windowed reactor, the different thermal expansion coefficients of
the SiC lining and the underlying graphite induced formation of cracks and lining failure. Although this does not represent a significant problem under the reducing atmosphere prevailing inside the windowed reactor, lining failure during operation in air would result in rapid oxidation of the underlying graphite.

Figure 6.2. Top and cross-sectional views of the holding ring-intermediate solar absorber-flange ring assembly. The solar absorber is mounted on the Inconel 617 holding ring, and the lower cavity (not shown) is gas sealed by applying the required gasket stress via the Inconel 617 flange ring. Two type-K thermocouples are embedded in the orifices of the holding ring part to allow for online monitoring of the temperature (i) 2 cm away from the outer edge (blind hole) and (ii) at the inner edge of the holding ring (through hole). During operation, the assembly is integrated to the upper face of the reactor stainless-steel shell (not shown).

Various geometrical configurations and structural materials were investigated in the current study for their suitability as solar absorber bodies in place of the SiC-graphite plate. In particular, the four solar absorber configurations depicted in Figure 6.3 were exposed to concentrated solar
Design, fabrication and testing of a windowless two-cavity reactor

radiation and investigated for their thermal and structural behavior, as well as their chemical resistance to air and the gaseous products evolving during the carbothermal reduction of ZnO, as will be discussed in detail in Section 6.4.

**Figure 6.3.** Photographs of the four solar absorber configurations investigated for their suitability for windowless solar reactor application: a) top-view of a 170 mm-diameter, 3 mm-thick circular Si-lined carbon-fiber-reinforced SiC ceramic matrix composite (C/SiC CMC) plate, b) top-view of a 170 mm-diameter, 3 mm-thick, 40 mm-high Si-lined C/SiC CMC quasi-hemispherical cavity, c) top- and front-views of a 170 mm-diameter, 3 mm-thick, 40 mm-high pressureless sintered alpha-SiC (SSiC) quasi-hemispherical cavity, and d) top- and front-views of a 170 mm-outer-diameter, 50 mm-inner-diameter, 3 mm-thick, 90 mm-high SSiC quasi-cylindrical enclosure.
Figure 6.3a and Figure 6.3b show top-view photographs of a 170 mm-diameter, 3 mm-thick circular plate and a 170 mm-diameter, 3 mm-thick, 40 mm-high quasi-hemispherical cavity, respectively, both made of Si-lined carbon-fiber-reinforced SiC ceramic matrix composite (C/SiC CMC). This novel class of structural materials aims at combining the outstanding intrinsic properties of SiC with enhanced fracture toughness in order to avoid the brittle fracture behavior exhibited by monolithic ceramic materials, and represents a very promising candidate for application in severe operating conditions such as those faced in a solar thermochemical reactor. Besides ceramic matrix composites, pure monolithic pressureless sintered alpha-SiC (SSiC) is considered in the current study as it exhibits a superior oxidation resistance in air at temperatures up to 1600°C. Key physical, thermal and mechanical properties [157], [158] of the two material types investigated are listed in Table 6.1. In presence of largely non-uniform distributions of the solar radiative flux, the use of a circular plate made of SSiC is not favored as high thermal stresses are expected to develop throughout the specimen during reactor operation. Indeed, SSiC circular plates tested under similar experimental conditions in a previous study [69] experienced brittle fracture during reactor heat-up. On the contrary, cavity geometries with higher surface area and concave shape, able to exchange thermal radiation with themselves, facilitate a reduction in the temperature gradient and, hence, the thermal stresses throughout the more structurally demanding SSiC specimens. Therefore, a quasi-hemispherical SSiC cavity of similar dimensions to the Si-lined carbon-fiber-reinforced SiC specimen and a 170 mm-outer-diameter, 100 mm-inner-diameter, 3 mm-thick, 90 mm-high quasi-cylindrical SSiC cavity were selected for further
Design, fabrication and testing of a windowless two-cavity reactor

investigation and are depicted in top and front views in Figures 6.3c and 6.3d, respectively.

Table 6.1. Key material properties of the solar absorber specimens [157], [158].

<table>
<thead>
<tr>
<th></th>
<th>Si-lined C-fiber-reinforced SiC CMC</th>
<th>Pressureless sintered alpha-SiC (SSiC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum operating temperature in air (°C)</td>
<td>1350</td>
<td>1600</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.4</td>
<td>3.15</td>
</tr>
<tr>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>20 – 40</td>
<td>125 (@ 20°C)</td>
</tr>
<tr>
<td>Expansion coefficient (10⁻⁶/K)</td>
<td>1.8 – 3.0</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>20 – 30</td>
<td>400</td>
</tr>
<tr>
<td>Flexural strength (3-point) (MPa)</td>
<td>50 – 95</td>
<td>400</td>
</tr>
<tr>
<td>Thermal shock parameter (W mm⁻¹)</td>
<td>46</td>
<td>26</td>
</tr>
<tr>
<td>Fracture toughness Kᵥ (MPa m¹/²)</td>
<td>23 – 30</td>
<td>4</td>
</tr>
</tbody>
</table>

The size and shape of the UC insulation monoliths varied for each solar absorber configuration as they are directly related to the radial distribution of the solar flux incident on the solar absorber. In specific, the height of the insulation monoliths is representative of the distance between the focal plane of the HFSS and the solar absorber and, hence, has a direct effect on the uniformity of the radiative flux incident on the solar absorbers since the light cone is diverging past the focal plane. Thus, in order to achieve a flux distribution that would induce relatively low radial temperature gradients
and thermal stresses throughout the solar absorbers, the design of the UC insulation was based on comprehensive numerical modeling and will be discussed in more detail in Section 6.2.

6.1.2 Peripheral equipment

The windowless solar reactor was tested using PSI’s High-Flux Solar Simulator as the source of concentrated thermal radiation (see Section 3.1.1). The schematic layout of the peripheral equipment is provided in Figure 6.4. Minimal differences vis-à-vis the flow diagram of the windowed reactor shown in Figure 3.1 can be identified. No inert gas flows are injected into the upper cavity, whereas nitrogen is supplied at 5 L\textsubscript{N·min}^{-1} to the lower cavity in order to sweep out the gaseous products of the reaction. Also indicated in Figure 6.4 is the location of 10 type-K thermocouples embedded inside the reactor to measure temperature variations online. A representative value of the UC temperature is obtained by thermocouple U1 mounted close to the surface of the insulation monoliths. Thermocouples embedded in the two orifices of the holding ring, as depicted in Figure 6.2 and denoted I1 and A\textsubscript{e} in Figure 6.4, allow for continuous monitoring of the temperature gradient across the holding ring. The temperature at the region of maximum incoming solar radiative flux is measured by a thermocouple (A\textsubscript{c}) mounted at the center point of the non-directly irradiated lower surface of the solar absorber body. The temperature difference \( T\textsubscript{A_c} – T\textsubscript{A_e} \) indicates the level of thermal stresses developed throughout the solar absorber specimens during operation.
Design, fabrication and testing of a windowless two-cavity reactor

Figure 6.4. Schematic representation of the experimental setup showing the detailed type-K thermocouple and pressure measurement positions (example with the circular plate mounted on the Inconel 617 holding ring).

Thermocouples S1, W1, and W3 monitor the temperature of the SiC walls at different heights. $T_{B2}$ and $T_{B1}$ are representative for the lower cavity. For carbothermal reduction experiments, $T_{B2} - T_{B1}$ provides the temperature gradient across the packed bed and indicates the amount of remaining unreacted material and ash. The pressure is measured online in the lower cavity of the reactor (P1) and at the upstream side of the filter unit (P2). Pressure relief valves set to open at an overpressure of ~150 mbar prevent pressure build-up and protect pressure-sensitive components from being...
exposed to pressures exceeding their design points. All experiments were performed at slight overpressure of ~ 10 mbar in the reactor.

6.2 Numerical model and operation strategy

The design of the UC insulation monoliths as well as decisions on the operation strategy of the HFSS for each reactor configuration were aided by three coupled numerical models: (i) a 3D Monte Carlo (MC) ray-tracing simulation to acquire the solar radiative flux absorbed by the surfaces composing the upper cavity ($q_{abs}$), (ii) a 2D-axisymmetric FE thermal simulation using $q_{abs}$ as a driving boundary condition to compute the temperature distribution throughout the solar reactor, and (iii) a 2D-axisymmetric FE structural simulation using the temperature profiles throughout the solar absorber specimens as input to compute the corresponding stress distributions and predict potential material failure based on the Mohr-Coulomb failure theory [159], which is applicable for materials with compressive strengths that far exceed their tensile strength such as ceramics. Recursive simulations were conducted until determining the final reactor design and a suitable operation strategy for each solar absorber. The UC insulation shape and size, the position of the focal plane relative to the reactor aperture, the solar power input, and the reactor heat-up rate were varied until reaching an acceptable result in terms of structural stability of the solar absorber. Specifying the UC insulation size involved a trade-off between decreasing the non-uniformity of the radiative flux incident on the solar absorbers and increasing the thermal mass as well as self-shading of the reactor. A schematic of the simulation procedure depicting key variables obtained at every simulation step is shown in Figure 6.5.
Figure 6.5. Schematic depiction of the simulation procedure. The solar flux absorbed by the upper cavity components \( q_{abs}'' \) is used as an input to the thermal simulations providing the temperature distribution and maximum temperature difference \( \Delta T_{max} \) throughout the solar absorber configurations. The maximum (\( \sigma_1 \)), medium (\( \sigma_2 \)), and minimum (\( \sigma_3 \)) principal stresses, and safety factors (\( SF_{stress} \)) according to the Mohr-Coulomb stress criterion obtained from the structural simulations are used to assess potential fracture of the specimen during reactor operation.
6.2.1 Monte Carlo ray-tracing model

An in-house MC ray-tracing code [160] was used to compute the radiative flux absorbed by the UC components of the reactor. The 45°-angle, Al-polished mirror was modeled as a specularly reflecting surface with no optical losses. The upper cavity surfaces were handled as diffusely reflecting, and were radially and circumferentially segmented in order to obtain a high-resolution radiative flux map. Appropriate surface segmentation was achieved by recursive mesh refinement until reaching a well-resolved solution. A total of $10^7$ rays were used to simulate the radiation emitted by the eight Xe arc lamps of the HFSS used during the experiments.

6.2.2 Thermal FE model

A transient 2D-axisymmetric FE thermal model was developed for solving the energy conservation equation in the solid portion of the reactor using circumferentially averaged (2D) flux maps as driving boundary condition. The radiative heat exchange within the UC and LC was solved assuming diffusely emitting and reflecting surfaces, and non-participating media within the enclosures. Thermal radiation emitted from the exterior walls of the UC insulation and the reactor shell toward the surroundings ($T_{env} = 291.15$ K) is accounted for by including it as source term in the energy conservation equation of the respective grid elements. The radiative properties of the UC surfaces are listed in Table 6.2 [88], [161]. Since the governing energy conservation equation is solved only in the solid portion of the reactor, convective heat transfer affecting the UC and LC surfaces, as well as the exterior walls of the UC insulation and the
reactor shell, is modeled using empirical Nusselt correlations proposed for forced and natural convection. All simulations were performed without solid reactants in the lower cavity. The governing equations were solved using ANSYS Mechanical [162] with \( \sim 44000, \sim 45000, \) and \( \sim 55000 \) grid elements for the circular plate, quasi-hemispherical and quasi-cylindrical cavity configurations, respectively. Grid-independent results were yielded for an element size of \( 3 \cdot 10^{-3} \text{ m} \) and a time step of 10 s after recursive refinement of the spatial and temporal grids. To adequately resolve the steep temperature gradients, a locally refined grid was applied at regions close to the surface of the UC insulation \( (1 \cdot 10^{-3} \text{ m}) \) and throughout the solar absorber specimens \( (1 \cdot 10^{-4} \text{ m}) \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Absorptivity / Emissivity</th>
<th>Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insulation monoliths</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Solar absorber specimens</td>
<td>0.88</td>
<td>0.12</td>
</tr>
<tr>
<td>LC ReSiC walls</td>
<td>0.85</td>
<td>0.15</td>
</tr>
<tr>
<td>Steel shell</td>
<td>0.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

### 6.2.3 Structural FE model

To compute the stress distribution throughout the solar absorber specimens and predict a possible material failure, the numerically computed temperature distributions throughout the specimens were used as input into a
2D-axissymmetric FE structural simulation performed with ANSYS Mechanical [162]. A pressure load of 10 MPa was imposed on the upper outer edge of the solar absorber specimens to represent the gasket stress applied by the flange ring, whereas the vertical displacement of the lower outer edge of the specimen was set equal to zero. The stress-free temperature was set equal to 295.15 K. Similar spatial and temporal grid sizes as in the thermal FE model were applied and the governing equations were solved using ~26000, ~30000, and ~43000 grid elements for the circular plate, quasi-hemispherical and quasi-cylindrical configurations, respectively.

6.2.4 Numerical results

The final UC insulation shape and relative focal plane-reactor aperture position for each configuration are depicted in Figure 6.6. The reactor aperture is aligned to the secondary focal plane for all the solar absorber configurations except the quasi-cylindrical SSiC cavity, in which it is positioned 20 mm below the focal plane in order to achieve a more uniform flux distribution and further reduce the thermal stresses. In regard to the reactor heat-up rate, stepwise increase of the solar power input at about 300 W_{th} increments every 6 min until reaching the steady-state solar power input \( Q_{\text{solar}} \) was identified as a reasonable operation strategy for the HFSS. Similar reactor heat-up conditions were applied to all the solar absorber specimens to enable comparison of their structural behavior under comparable thermal stress loading. Table 6.3 lists \( Q_{\text{solar}} \) entering the reactor at the end of the reactor heat-up period for the three geometries investigated.
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Figure 6.6. Cross-sectional view of the upper cavity for the a) circular plate, b) quasi-hemispherical, and c) quasi-cylindrical configurations, comprising the solar absorber specimens and the insulation monoliths. The position of the type-K thermocouples measuring the UC temperature (U1) and the temperature at the lower surface center point of the solar absorber specimens (A_c), as well as the position of the secondary focal point of the HFSS relative to the reactor aperture for each configuration are also indicated.
Table 6.3. Partitioning of the incoming solar radiative power for the three cavity geometries investigated.

<table>
<thead>
<tr>
<th></th>
<th>Circular plate</th>
<th>Quasi-hemispherical cavity</th>
<th>Quasi-cylindrical cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{solar}}$ (kW)</td>
<td>4.75</td>
<td>4.75</td>
<td>4.35</td>
</tr>
<tr>
<td>$Q_{\text{abs, specimen}}$ (% of $Q_{\text{solar}}$)</td>
<td>83.8</td>
<td>91.6</td>
<td>93.3</td>
</tr>
<tr>
<td>$Q_{\text{abs, insulation}}$ (% of $Q_{\text{solar}}$)</td>
<td>15.2</td>
<td>7.0</td>
<td>0.9</td>
</tr>
<tr>
<td>$Q_{\text{abs, curve-protecting insulation}}$ (% of $Q_{\text{solar}}$)</td>
<td>-</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>$Q_{\text{reflected}}$ (% of $Q_{\text{solar}}$)</td>
<td>1.0</td>
<td>1.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The results are identical for the two quasi-hemispherical cavities (C/SiC CMC, SSiC) due to their similar optical properties. The value of $Q_{\text{solar}}$ was obtained for each configuration by recursive MC-thermal simulations aiming to achieve LC temperatures of $\sim 1200^\circ$C at steady-state conditions. Lower power input is required for the quasi-cylindrical SSiC cavity due to the smaller size and, hence, thermal mass of the UC insulation for this configuration. Also indicated in Table 6.3 is the partitioning of the solar power input among the UC surfaces. A major fraction (84 – 93 %) of $Q_{\text{solar}}$ is absorbed by the solar absorber specimens, while radiation absorbed by the UC insulation or reflected back outside the reactor composes 7 – 16 % of the solar power input. The circumferentially averaged (2D) distribution of incident solar flux absorbed on the surface of the solar absorber specimens is depicted in Figure 6.7.
For the circular plate, a peak radiative flux of 435 suns (1 sun = 1 kW/m²) is obtained at the center of the Si-lined C/SiC CMC. Decreasing flux values are encountered toward the edge of the plate owing to the divergence of the light cone past the aperture, while the outermost 1.25 cm-long annulus is not exposed to solar radiation (see also Figure 6.6). The flux distribution map acquired for the quasi-hemispherical configuration is applicable to both materials (C/SiC CMC, SSiC) due their similarity in terms of optical properties ($\alpha = 0.88$, $\rho = 0.12$). Higher peak fluxes, reaching ~ 500 suns at the center of the specimens for the chosen focal point position, are obtained compared to the circular plate since somewhat steeper radiative flux gradients were preferred over the exposure of the critical concave-to-convex transition region to high levels of solar radiation. For operation with the
quasi-cylindrical SSiC cavity, a 150 mm-outer-diameter, 84 mm-inner-diameter, 8 mm-thick insulation part ($\alpha = 0.6$, $\rho = 0.4$ [88]) extending over the upper 2.5 cm of the SSiC specimen, as depicted in Figure 6.6c, is incorporated for protection of the curved portion of the specimen from exposure to incident solar radiation. Lower fluxes compared to the previous solar absorber configurations are attributed to the larger surface area over which the incoming radiation is distributed.

Figure 6.8 illustrates the maximum principal stress distribution throughout the solar absorber specimens made of C/SiC CMCs at the highest thermal stress level. Also indicated in grey are the safety factors according to the Mohr-Coulomb stress criterion at structurally critical regions. Large radial temperature gradients throughout the specimen, along with the external stress applied by the gasket, induce high tensile stresses at the outer edge of the circular plate. The maximum principal stress, $\sigma_1$, acquires its maximum value (17.5 MPa) at this location whereas a safety factor of 1.4 is obtained. The quasi-hemispherical cavity is subjected to lower stress levels owing to the inherently different thermal expansion of this geometrical configuration. Peak maximum principal stress values of 11.4 MPa and 8.8 MPa are obtained at the gasket and the inflection point regions, respectively, leading to safety factors of 2.7 and 2.9. Figure 6.9 illustrates the maximum principal stress distribution and the safety factors according to the Mohr-Coulomb stress criterion for the cavities made of SSiC. Safety factors of 0.8 and 0.9 are obtained at the gasket and inflection point regions of the quasi-hemispherical cavity, respectively, as shown in Figure 6.9a. The considerable decrease in the safety factor values vis-à-vis the same geometrical configuration made of C-fiber-reinforced SiC CMC suggests
structural superiority of the latter under the solar flux distributions investigated, whereas safety factors below unity indicate potential material failure upon exposing the specimen to the maximum thermal loading conditions during reactor operation.

**Figure 6.8.** Maximum principal stress distributions throughout the a) circular plate and b) quasi-hemispherical cavity made of Si-lined carbon-fiber-reinforced SiC ceramic matrix composite (C/SiC CMC) at the highest thermal stress level. Indicated in grey are the safety factors according to the Mohr-Coulomb stress criterion at structurally critical regions.

**Figure 6.9b** illustrates that the outer edge and the curved portion connecting the horizontal to the vertical part of the specimen are the most structurally critical regions of the quasi-cylindrical SSiC cavity. Safety factors of 1.2 and 2.2 were obtained at the outer edge and the curved portion, respectively, thus
indicating structurally stable behavior of the specimen. The superior structural behavior of this specimen compared to the quasi-hemispherical SSiC cavity is attributed to its larger heat transfer area and the higher uniformity of the incident solar flux distribution, both leading to lower temperature gradients and, hence, thermal stresses throughout it.

Figure 6.9. Maximum principal stress distributions throughout the a) quasi-hemispherical and b) quasi-cylindrical cavity made of SSiC at the highest thermal stress level. Indicated in grey are the safety factors according to the Mohr-Coulomb stress criterion at structurally critical regions.
6.3 Experimental procedure

Experiments can be classified into two main types. In the first type, corresponding to initial experimental runs without solid reactants in the lower cavity, a conservative heat-up rate of the solar reactor as proposed by the numerical simulations was used to investigate the structural behavior of the solar absorber specimens and the Inconel parts. In the second type, batches of beech charcoal gravel (proFagus GmbH, Bodenfelde, Germany, particle size: 1.0 – 2.0 mm) and ZnO powder (Alfa Aesar 011558, purity: 99.0% min, mean particle size 44 µm) at a ZnO:C molar ratio of 1:0.8 were loaded into the reaction chamber prior to each experimental run and the duration of the heat-up period was halved. Typically, ~325 g of reactants were used, forming a 35 mm-high packed bed.

In both types of experiments, the solar reactor was initially purged with N\textsubscript{2} to ensure low O\textsubscript{2} concentrations. After acquiring O\textsubscript{2} concentrations below 200 ppm, the HFSS was ignited and the solar power input was increased to ~4.4 – 4.75 kW\textsubscript{th} in steps of about 300 W\textsubscript{th} over a time period of 96 min and 48 min for the first and second type of experiments, respectively. After reaching the desired $Q$\textsubscript{solar}, fine-tuning within the range of $+0 - 0.25$ kW\textsubscript{th} was performed in select experiments via adjustment of the electric power of individual Xe-arc lamps in order to achieve the desired steady-state temperature $T_{B_2}$. Before switching off the HFSS, the quasi-steady temperature $T_{B_2}$ was maintained for ~30 – 45 min for the first type of experiments, and until reaction completion for the carbothermal reduction tests. Stabilization of the temperature at the predetermined value was achieved by reducing the solar power stepwise to 75 – 80% of the nominal power input via adjusting the orientation of the Venetian blind shutter.
During cooling-down, the solar power input was ramped down from \( \sim 3.3 - 3.75 \text{ kW}_{th} \) to 0 kW\(_{th}\) over a period of 30 min in order to avoid imposing a thermal shock on the sensitive reactor components. \( Q_{solar} \) was measured with a water-cooled calorimeter with its aperture aligned to the reactor’s aperture.

### 6.4 Experimental results

#### 6.4.1 Material testing without solid feedstock

Experimental runs without solid reactants were carried out to investigate the performance of the solar absorber specimens with respect to their structural stability, chemical inertness, and thermal behavior. Under approximately steady-state conditions, the LC temperatures \( T_{B2} \) reached \( \sim 1200^\circ\text{C} \). The leak tightness of the solar reactor was monitored over the whole experimental duration by measuring the reactor overpressure online. A representative experimental run using the circular Si-lined carbon-fiber-reinforced SiC CMC plate as solar absorber body is shown in Figure 6.10. Also indicated on the right y-axis is the temporal variation of the solar power input. After the first 96 min of reactor heat-up, the UC and LC temperatures increased to \( T_{U1} = 1080^\circ\text{C} \) and \( T_{B2} = 925^\circ\text{C} \), respectively. The solar reactor was operated at the nominal radiative power input over the next 30 min until reaching the steady-state LC temperature of 1150°C. At this point, a distinct 5% drop in \( Q_{solar} \) corresponds to an adjustment of the shutter orientation aiming at the stabilization of the reactor temperatures at the desired level. The solar power input was decreased by a total of 25% over the next 45 min before turning off the HFSS.
Figure 6.10. Temporal variation of the reactor temperatures and solar radiative power input for a typical experimental run using the circular Si-lined carbon-fiber-reinforced SiC CMC plate as solar absorber body.

The temperature difference between the center point of the non-directly irradiated lower surface and the outer edge of the CMC plate, $T_{Ac} - T_{Ae}$, exhibited an increasing trend during reactor heat-up, as shown in Figure 6.11. Distinct rises in the experimentally measured temperature difference, reaching up to 90°C during the first two step increases of $Q_{solar}$, were obtained upon every stepwise increase of the solar power input as an effect of the largely non-uniform distribution of the solar flux incident on the CMC plate surface. Radial heat conduction across the CMC plate induced a decrease in the radial temperature difference, $T_{Ac} - T_{Ae}$, upon maintaining $Q_{solar}$ constant between two consecutive steps. Peak temperature differences of ~390°C were obtained upon opening the shutter to 100% and allowing
the nominal solar power input to enter the reactor. Considering an axial temperature difference of $\sim 50\,^\circ\mathrm{C}$ across the plate, as predicted by the thermal simulations, a maximum temperature difference of $\sim 440\,^\circ\mathrm{C}$ can be estimated between the center point of the upper surface and the outer edge of the CMC plate. This temperature difference is indicative of the maximum thermal stresses developed throughout the plate during reactor operation. Temperature difference $T_{Ac} - T_{Ae}$ drops upon the stepwise decrease of the solar power input after the first 126 min as an effect of the decreasing solar radiative power flux incident on the center of the plate, and reaches $\sim 350\,^\circ\mathrm{C}$ at 75% of the nominal solar power input after 160 min. A comparison of the experimentally measured and simulated temperature difference $T_{Ac} - T_{Ae}$ is provided in Figure 6.11. Discrepancies between the experimentally measured and numerically simulated values are attributed to i) uncertainties involved in the thermal and radiative properties adopted in the numerical model and ii) the exact location of thermocouple $A_c$. In specific, a $\sim 3\,\text{mm}$-thick layer of SiC ceramic paste was applied on the thermocouple tip prior to each experimental run in order to prevent its damage or adhesion on the lower side of the plate during reactor operation. This led to temperature measurements at a location slightly lower than the center point of the non-directly irradiated surface of the plate and, thus, to slight underestimation of the actual $T_{Ac} - T_{Ae}$.

The circular Si-lined carbon- fiber-reinforced SiC CMC plate was proven structurally stable and the reactor overpressure was maintained constant over the whole course of the experimental run and reactor cool-down, indicating leak tightness. Additionally, a successful overpressure build-up test was performed after the experimental run by closing the system behind the filter
unit and letting the pressure relief valve to open at ~ 150 mbar overpressure. Visual inspection of the CMC plate revealed the presence of spherical Si(s) particles on the upper plate surface, which were presumably formed at hot spots with temperatures exceeding the melting point of Si and their subsequent freezing upon switching off the HFSS. No distinct change in the morphology was observable on the lower side of the plate. A total mass loss of 0.88% over the course of the experimental run can be attributed to oxidation of free carbon and/or evaporation of Si, which is present either in the form of residual free silicon in the C/SiC matrix or in the Si lining, before a passivation SiO$_2$ layer is formed on the plate surface.

Figure 6.11. Experimentally measured (open markers) and numerically simulated (solid line) temperature difference between the lower surface center point ($T_{Ac}$) and the outer edge ($T_{Ae}$) of the circular Si-lined carbon- fiber-reinforced SiC CMC plate. Also indicated in the right y-axis is the solar radiative power input entering the solar reactor through the 60 mm-diameter circular aperture.
Similar reactor temperature variations were obtained during experimental runs with the quasi-hemispherical Si-lined carbon-fiber-reinforced SiC CMC cavity. Visual examination of the specimen revealed the formation of Si particles while a mass loss of 0.41% was obtained over the duration of the experimental run. The specimen withstood the thermal stresses developed at high temperatures, as predicted by the structural model, and the leak-tightness was maintained over the whole experimental run.

On the contrary, the same geometrical configuration made of SSiC did not withstand the load imposed on the material during reactor heat-up. A representative run with the quasi-hemispherical SSiC cavity is shown in Figure 6.12.

![Graph showing temporal variation of the reactor temperatures and solar radiative power input for a typical material testing experimental run using the quasi-hemispherical SSiC cavity as solar absorber body. Brittle fracture of the cavity during reactor heat-up and exposure of thermocouple B2 to direct radiation induces an abrupt increase in the measured lower cavity temperature ($T_{B2}$).]
Approximately 38 min after switching on the HFSS and after the increase of $Q_{\text{solar}}$ to $\sim 2 \text{ kW}_{\text{th}}$ the uneven thermal expansion throughout the specimen, caused by the largely non-uniform solar flux distribution, along with the externally applied mechanical stress at the gasket region, led to a brittle fracture of the SSiC cavity. The fracture is accompanied by a distinct rise in the measured lower cavity temperature $T_{B2}$ from $340^\circ \text{C}$ to $540^\circ \text{C}$ induced by the direct exposure of thermocouple B2 to solar radiation. Visual inspection of the fractured SSiC cavity revealed the formation of radial cracks extending between the outer edge of the SSiC cavity and the inflection point region, as illustrated in Figure 6.13.

**Figure 6.13.** Image of the fractured quasi-hemispherical SSiC cavity. Radial cracks extending between the outer edge and the inflection point region of the specimen can be observed. Upon fracture, the lower portion of the specimen dropped into the lower cavity and the reactor was exposed to the surrounding atmosphere.
Indeed, these regions were identified as the most critical by the numerical model which, however, predicted material failure upon opening the shutter to 100% and allowing the nominal solar power input to enter the reactor. The discrepancy between the experimentally observed and numerically predicted time of failure is attributed to the simplifying assumptions adopted in the numerical model and the uncertainties involved in the thermal and mechanical properties of the materials. In specific, the numerical model assumes isotropic, homogeneous, and crack-free materials and implements phenomenological macroscopic failure theories comparing a single-number stress value to the material strength (Mohr-Coulomb stress criterion) in order to predict potential material failure, without accounting for the specific material microstructure. However, in reality, microcracks formed during the manufacturing process are present inside the specimens. Since structural failure initiates from microflaws, their spatial distribution and density throughout the specimens is of great importance for describing the strength of the material [163]–[167]. Thus, the use of a single material strength value, instead of a spatial distribution of this measure, due to the lack of detailed information about the material microstructure limits the predictive accuracy of the model. More accurate prediction of a catastrophic failure could be attained via a detailed characterization of the microstructure of the specific specimen and implementation of the fracture toughness criterion investigating the conditions for the dynamic growth of an existing crack in the structure [168], [169]. The superior structural behavior of the quasi-hemispherical cavity made of low-strength CMC material compared to that made of high-strength SSiC can be attributed to the considerably higher fracture toughness of the CMC material (see Table 6.1). This implies that
monolithic SSiC are prone to catastrophic failure as they exhibit very limited ability to absorb strain energy and prevent crack propagation. On the contrary, the weak interfaces located between the C-fibers and the SiC matrix are the key factor for the higher material toughness of the CMC material as they allow for strain energy dissipation before fracture through mechanisms of crack deflection and bridging [170]–[172].

A representative experimental run using the quasi-cylindrical SSiC cavity as solar absorber body is shown in Figure 6.14.

![Temporal variation of reactor temperatures and solar radiative power input for a typical material testing experimental run using the quasi-cylindrical SSiC cavity as solar absorber body.](image)

Figure 6.14. Temporal variation of reactor temperatures and solar radiative power input for a typical material testing experimental run using the quasi-cylindrical SSiC cavity as solar absorber body.

Upon opening the shutter to 100% and delivering the nominal solar power input of 4.35 kW_th into the reactor, $T_{UI}$ and $T_{B2}$ reached 1400°C and 1125°C,
respectively. Considerably higher UC temperatures were reached during reactor heat-up vis-à-vis the experimental run using the circular plate as solar absorber body, owing to the lower thermal mass of the UC insulation for this geometrical configuration. Thus, the solar reactor was operated over a limited time span of 4 min and 6 min at 100% and 95% of the nominal solar power input, respectively, before reaching the quasi steady-state LC temperature \((T_{B2})\) of 1225°C. The temperature difference between the center point of the non-directly irradiated lower surface \((T_{Ac})\) and the outer edge \((T_{Ae})\) of the SSiC cavity peaked at \(\sim 593°C\) after 99 min and during operation of the reactor at the nominal \(Q_{solar}\). The temperature measured at the outer edge of the cavity under steady-state conditions \((T_{Ae} = 700°C)\) is considerably lower in comparison to that obtained with the circular plate configuration as an effect of the bigger SSiC cavity size and different solar flux distribution. This implies a significant reduction of the thermal load imposed on the Inconel holding ring. The quasi-cylindrical SSiC cavity remained intact over the whole experimental run, while no morphological change or mass loss could be detected after visual inspection and weighting of the specimen, respectively.

6.4.2 Carbothermal reduction experiments

After successful testing of the reactor leak-tightness, experiments were carried out to investigate the degree of chemical resistance of the solar absorber specimens to the product gases evolving during the carbothermal reduction of ZnO. The structural stability of the solar absorber specimens was tested under more severe loading conditions as imposed by reducing the reactor heat-up time by 50% compared to the tests described in Section
6.4.1. Temperatures in the range of $1202 - 1219^\circ C$ and $1041 - 1053^\circ C$ were obtained under approximately steady-state conditions at the top of the ZnO:C packed bed ($T_{B2}$) and behind the LC walls at a level corresponding to the bottom of the packed bed ($T_{W3}$), respectively. The temperature difference $T_{B2} - T_{W3}$ is used to indicate the temperature gradient across the packed bed and, hence, the remaining unreacted material and ash. Temperatures measured directly at the bottom of the packed bed ($T_{B1}$) cannot be used as failure of thermocouple B1 occurred over the course of the experiments.

The variation of solar reactor temperatures, gas product molar flow rates and solar power input as a function of time for a representative experimental run using the circular C/SiC CMC plate as solar absorber body is shown in Figure 6.15. Small amounts of CO can be detected after the first 40 min at LC temperatures of $T_{B2} = 590^\circ C$. After an initial moderate increase during the next 30 min, CO release exhibited a notable increase upon the commencement of the carbothermal reduction at temperatures above $T_{B2} = 1000^\circ C$. At approximately steady-state conditions, $T_{B2}$ stabilized at $\approx 1202^\circ C$. Peak CO and Zn(g) production rates of 0.042 mol/min and 0.053 mol/min, respectively, were reached after 105 min and 111 min, leading to a peak solar-to-chemical energy conversion efficiency of 12.8%.

Temperature differences between the center point of the non-directly irradiated lower surface and the outer edge of the CMC plate, $T_{Ac} - T_{Ae}$, followed a similar trend as those obtained in the first type of experiments, but a considerably higher peak of $516^\circ C$ was reached upon increasing $Q_{solar}$ to the nominal value after the first $\approx 48$ min as a result of the shorter heat-up period. The temperature difference decreased gradually by a total of $100^\circ C$ over the next 70 min due to the decrease in the solar power input and the
radial heat conduction across the circular plate, and reached $\sim 410^\circ C$ at steady-state conditions. The steady increase of $T_{W3}$ over the course of the experimental run until reaching a steady-state value of $1041^\circ C$ is indicative of the consumption of the solid feedstock in the LC. Stabilization of $T_{W3}$ as well as detection of only trace amounts of Zn(g), CO, and CO$_2$ by the GC after 160 min suggested completion of the chemical reaction, and the HFSS was turned off.

![Diagram](image)

**Figure 6.15.** Temporal variation of reactor temperatures, molar flow rates of Zn(g), CO, CO$_2$, and H$_2$, and solar radiative power input over the course of a typical experimental run for the solar-driven carbothermal reduction of commercial ZnO powder, using $\sim 325$ g of reactants with a ZnO:C molar ratio of 1:0.8 and the circular Si-lined carbon-fiber-reinforced SiC CMC plate as the intermediate solar absorber specimen.
After the end of the experimental run, small amounts of ash, unreacted ZnO powder, and charcoal gravel, corresponding to 3.6% of the initial feedstock mass, were detected in the reaction chamber, indicating almost complete conversion of the reactants. Condenser zinc vapor was recovered predominantly from the water-cooled condenser, while a lesser fraction was detected in the outlet pipes and the filter unit. The solar absorber body was proven structurally stable despite the higher loading conditions and the solar reactor remained leak tight over the whole experimental run. Visual examination of the directly irradiated side of the plate revealed local formation of spherical Si(s) particles at locations that reached temperatures exceeding the Si melting point. The absence of any morphological change on the lower side of the plate indicated no chemical interaction between the solar absorber material and the gaseous products evolving during the ZnO reduction.

Carbothermal reduction tests using the quasi-hemispherical Si-lined carbon-fiber-reinforced SiC CMC cavity and the quasi-cylindrical SSiC cavity as solar absorbers were carried out at quasi steady-state LC temperatures of $T_{B2} = 1212^\circ C$ and $T_{B2} = 1219^\circ C$, respectively. Both configurations remained undamaged while no evidence of chemical reaction between the solar absorbers and the product gases could be detected after visual inspection of the samples. Peak Zn(g) production rates of 0.05 mol/min and 0.048 mol/min were reached, leading to peak solar-to-chemical conversion efficiency of 12.85% and 15%, respectively. The $\sim 2\%$ increase in the conversion efficiency for the SSiC cavity is attributed to the lower solar radiative power input required for reaching and maintaining a constant temperature in the reaction chamber due to the lower thermal mass
of the UC insulation for this geometrical configuration.

In regard to the thermal performance, an analysis of the heat flow within the reactor during a typical experimental run with the circular C/SiC CMC plate was performed. Using temperature data collected during the experiment, power distribution and losses were assessed as a function of time and are provided in Figure 6.16.

An increased fraction of $Q_{solar}$ is stored as sensible heat within the reactor materials vis-à-vis the windowed reactor (see Figure 4.10) due to the larger size and, hence, thermal mass of the windowless reactor. Furthermore, the elimination of the quartz window introduces additional convective losses.
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from the UC to the surroundings. Operation of the reactor without active cooling eliminates a major source of heat losses, but has an adverse effect on the conduction and convection heat losses as the temperature difference between the reactor shell and the surroundings are larger. Solar-to-chemical energy conversion efficiencies of similar order of magnitude as those obtained with the windowed reactor were reached with all the solar absorber configurations. Since the reactor design aimed at the experimental demonstration of the windowless concept rather than achieving high efficiency, $\eta_{\text{solar-to-chem}}$ is expected to further increase after optimizing the reactor design. Considerably higher solar-to-chemical conversion efficiencies are to be expected at a pilot scale plant as the impact of increasing the reactor diameter-to-height ratio and, thus, the portion of heat delivered to the surface of the packed bed rather than the lateral walls of the LC will be larger than that of increasing the heat losses to the surroundings by virtue of the larger external surface area [86].
Chapter 7
Summary and outlook

This thesis concerned the investigation of solar-driven high-temperature pyrometallurgical processes for the production of Zn as well as further developments of the solar reactor technology for performing these processes. The work involved experimentation on the carbothermal reduction of primary and secondary ZnO sources carried out using a 10 kW$_{th}$ packed-bed solar reactor, as well as numerical modeling of the reactor prototype. It further proposed an alternative condenser concept for the recovery of zinc vapor from the reactor off-gas in the liquid rather than the solid state, and presented the actions taken toward the technical realization and experimental demonstration of a novel windowless two-cavity solar reactor concept.

7.1 Summary

7.1.1 Solar-zinc recycling

The solar-driven thermal purification of crude Waelz oxide via volatilization of the halides at high temperatures using concentrated solar energy as the source of the high-temperature process heat was proposed as an alternative cleaner route to the conventional washing treatment of crude WOX and experimentally demonstrated using a 10 kW$_{th}$ packed-bed solar reactor. Cl and Pb contents lower than those of washed WOX (< 0.1 wt.%) were attained by solar clinkering of crude WOX at elevated temperatures.
(\(T_{BI} > 1265^\circ\text{C}\)). Depletion of Pb and its compounds represented a major advantage of the proposed solar-driven process vis-à-vis the industrial washing process and led to higher ZnO contents (\(\sim 88\) wt.%) in the product. However, higher heat treatment temperatures during solar clinkering of crude WOX led also to higher amounts of Zn evaporated due to the chemical bonding to halides. Incorporation of continuous or semi-continuous feeding of reactants and removal of products in this process can improve product yield and thermal efficiency.

The solar-clinkered product was then used as feedstock for the production of secondary zinc. In particular, the solar-driven production of Zn via the carbothermal reduction of clinkered, washed, and crude WOX, and commercial ZnO was experimentally demonstrated using the same solar reactor. Beech charcoal was used as reducing agent for a CO\(_2\)-neutral carbothermal process. Zn contents of about 90 wt.% were obtained in the condensed products. Higher purities of Zn were acquired when using solar-clinkered WOX as the reactant due to the more effective purification of the crude WOX in the solar purification process compared to industrial washing. In terms of the peak Zn(g) production rates, all the ZnO sources investigated yielded values similar values to each other. Peak production rates are of particular importance since it is reasonable to assume that with prolonged reactor operation and continuous feeding of reactants, molar production rates of Zn(g) would stay at the measured peak as the system reaches a quasi-steady state.

7.1.2 Numerical model of the 10 kW\(_{th}\) packed-bed solar reactor

A transient reactor model coupling conductive, convective, and
Radiative heat transfer with the apparent reaction kinetics of the carbothermal ZnO reduction at a ZnO:C molar ratio of 1:0.8 was developed. The Monte-Carlo ray-tracing method was employed to determine the configuration factors in the upper cavity. The radiative heat exchange in the upper and lower cavities was solved by applying the enclosure theory. The packed bed was treated as a 1-D shrinking continuum as the solid feedstock is converted into gaseous products during the carbothermal reduction. Model predictions were in good agreement with experimental data in terms of reactor temperatures, gas production rates, product yield, and solar-to-chemical energy conversion efficiency obtained with the 10 kW th packed-bed solar reactor. A peak efficiency of 18.6% was achieved for a 35 mm-high packed bed at a reaction chamber temperature of $T_{B2} = 1580$ K. Conduction through the water-cooled components was identified as a major source of heat losses in the upper cavity, dissipating about 32 – 44% of the solar power input. The validated reactor model was adapted to predict the thermal performance of a solar reactor operating in a semi-continuous mode. In particular, the effect of incorporating semi-continuous feeding of reactants and removal of products was studied by simulating the reactor operation for seven consecutive ZnO:C batches, corresponding to ~ 8 h of daytime. Introduction of low-temperature reactants ($T = 292$ K) into the hot solar reactor upon complete conversion of the previous batch induced a temperature drop in the lower cavity by 115 K. The solar-to-chemical energy conversion efficiency increased by virtue of the reduced energy share required for sensible heating of the reactor components after the first cycle.
7.1.3 Zinc condenser

A zinc condenser concept involving bubbling of gas-vapor products of the solar carbothermal reduction of ZnO through a subcooled Zn(l) bath has been proposed to rapidly condense Zn(g) to Zn(l) and suppress reoxidation of Zn(g) by CO₂ and CO. A simplified mass- and heat-transfer model was developed to investigate the competing condensation rates and kinetics of oxidation of zinc vapor at solar reactor conditions. A $X_{\text{Zn(g)-to-Zn(l)}}$ conversion of 0.992 was predicted for a 45 mm-diameter bubble containing 80.1% non-condensable gases in a liquid bath maintained at 500°C, whereas successful suppression of the reversion reactions was demonstrated ($X_{\text{Zn(g)-to-ZnO}}=2.4 \cdot 10^{-7}$). A notable decrease in the $X_{\text{Zn(g)-to-Zn(l)}}$ conversion with increasing temperature due to equilibrium vapor losses supports the operation of a vacuum condenser at low temperatures by efficiently dissipating the large amounts of heat released during the rapid condensation process. The condensation rates were significantly enhanced by a decrease of the initial bubble diameter and increase of the relative velocity between the bubbles and liquid bath. A pronounced decrease of the Zn(l) yield with increasing fractions of non-condensable gases in the mixture suggests operation with a minimal amount of inert gases to maintain a predicted $X_{\text{Zn(g)-to-Zn(l)}}$ above 0.95 in a wide liquid bath temperature range and to minimize the heat liberated in the process.

7.1.4 Windowless reactor design and testing

A windowless packed-bed solar reactor concept was designed, fabricated and tested at PSI’s High-Flux Solar Simulator by performing (i) thermal tests without solid reactants in the LC and (ii) carbothermal ZnO
reduction experiments using various solar absorber configurations and materials. A circular plate and a quasi-hemispherical cavity made of Si-lined carbon-fiber-reinforced SiC ceramic matrix composite as well as quasi-hemispherical and quasi-cylindrical cavities made of pressureless sintered alpha-SiC were investigated for their suitability as solar absorber bodies. The reactor design and decisions regarding the operation strategy of the HFSS were aided by a coupled 3D MC - 2D axisymmetric thermal FE - 2D axisymmetric structural FE model.

Thermal tests were carried out at LC temperatures of about 1200°C using a conservative reactor heat-up rate in order to reduce the thermal stresses throughout the solar absorbers. The circular Si-lined C/SiC CMC plate and the quasi-cylindrical SSiC cavity remained intact and leak tightness of the reactor was demonstrated over the course of the experimental runs. Under similar solar flux distributions, the quasi-hemispherical Si-lined C/SiC CMC cavity exhibited superior structural behavior vis-à-vis the quasi-hemispherical SSiC cavity, which experienced brittle failure during reactor heat-up owing to its lower fracture toughness. Despite its structural superiority, the CMC material demonstrated lower chemical stability mainly due to evaporation of free Si located in the matrix and/or the lining at hot spots exceeding the maximum operating temperature of the material as well as due to oxidation of free carbon in air, leading to a mass loss of 0.41% over the experimental duration.

Carbothermal reduction experiments revealed structural stability of the solar absorber bodies under more severe loading conditions, as imposed by higher reactor heat-up rates, and chemical resistance to the gaseous products of the reaction. Peak Zn(g) production rates of ~ 0.05 mol/min were obtained
at LC temperatures in the range of 1202–1219°C, leading to solar-to-chemical energy conversion efficiencies of 12.8–15%. Overall, the technical feasibility of the packed-bed windowless solar reactor concept for performing thermochemical processes such as the carbothermal reduction of ZnO was successfully demonstrated and valuable experience on the thermal and structural behavior of potential solar absorber materials under these operating conditions was gained.

7.2 Outlook

As concentrating solar thermal technologies become progressively more widely deployed and the associated investment costs decrease, integration of these technologies into high-temperature metallurgical processing in a cost-effective way becomes more favorable. At the current stage, the carbothermal reduction of ZnO is the most developed solar-driven Zn production process. Nevertheless, there still exist areas for continued development until reaching the commercialization stage.

Based on experimental and numerical results presented in this work, further developments of the packed-bed solar reactor technology should focus mainly on ensuring reliable plant operation and on improving the efficiency and product yield. In pursuit of these goals, research and development activities should be directed both to the solar reactor as well as to the off-gas treatment system. In specific, main issues that should be addressed to improve the reactor robustness and plant efficiency include: (1) further material development of the intermediate solar absorber materials, (2) optimization of the reactor design in terms of solar-to-chemical conversion energy efficiency and product yield, (3) detailed experimental
and numerical investigation of the technical feasibility of a zinc condenser concept involving bubbling of gas-vapor products of the solar carbothermal reduction of ZnO through a subcooled Zn(l) bath.

### 7.2.1 Intermediate solar absorber materials

Experimental investigations revealed structural superiority of the C/SiC ceramic matrix composite (CMC) material compared to the monolithic SSiC under similar solar flux distributions. Ceramic matrix composites have been developed to exhibit considerably higher fracture toughness and achieve a damage tolerant quasi-ductile fracture behavior by introducing strain energy dissipation mechanisms into the material (e.g. crack deflection and bridging), while maintaining all the advantages of monolithic ceramics. As prevention of a catastrophic failure of the solar absorber material during reactor operation should, for safety reasons, be an unconditional requirement for solar thermochemical reactors, CMCs are considered as the most promising candidate toward achieving reliable plant operation. However, use of Si-lined C-fiber-reinforced SiC ceramic matrix composites revealed small mass losses upon their exposure to temperatures above ~1200 – 1300°C due to oxidation of free carbon present in the matrix or to evaporation of Si, which is present either in the form of residual free silicon in the C/SiC matrix or in the Si lining.

Thus, further research should be directed toward adjusting the chemical composition and manufacturing process parameters of the CMC materials in order to achieve product characteristics optimized for the particular solar thermochemical application. One of the most critical material parameters that can be optimized is the C-fiber content in the CMC. Specifying the
optimal C-fiber content involves a trade-off between structural stability and oxidation resistance in air as increasing the amount of C-fibers in the matrix would enhance the material’s structural stability but have an adverse effect on achieving high chemical resistance. However, the chemical stability of Si-lined C/SiC CMCs could be improved by enhancing the formation of a SiO$_2$ passivation layer on their surface, which will prevent oxidation of the free carbon in the matrix and minimize the slow degradation of the material in high-temperature oxidizing conditions. This can be achieved by uniformly heating the material prior to its use in the solar reactor to temperatures above $\sim 1200 – 1400^\circ$C using high heat-up rates in order to minimize exposure time at temperatures between 600°C and 900°C, where the formation of SiO$_2$ is limited by the reaction kinetics. Alternatively, removal of the residual free Si from the matrix and subsequent pore filling with an inert material like glass could minimize mass losses related to Si evaporation. However, any compositional changes in the CMCs should always be undertaken after considering the potential adverse effects they might have on the structural performance of the material.

Further research activities are to involve experimental testing of the optimized solar absorber materials in terms of chemical resistance and structural behavior under even more severe thermal loading conditions (e.g. even higher heat-up rates, sudden variations of the solar power input) than those applied in the current work in order to minimize the duration of the reactor heat-up period and identify the limits of the system. Additionally, materials with improved fracture characteristics such as SiC/SiC composites or SiC multilayer ceramics represent very promising candidates for high temperature applications in oxidizing environments and their suitability for
serving as the absorber materials under the largely non-uniform temperature distributions developed in the solar reactor needs to be experimentally investigated.

### 7.2.2 Optimization of thermal efficiency and product yield

The novel windowless reactor design concept exhibits solar-to-chemical efficiencies of similar order of magnitude as those obtained with the preceding windowed reactor design. Improvements in $\eta_{\text{solar-to-chem}}$ can be attained by optimizing the reactor design accordingly. In regard to the height of the lower cavity, lower height-to-diameter ratios are expected to have a positive effect on the reactor efficiency because a higher share of the solar power input would be delivered to the surface of the packed bed rather than the lateral walls of the lower cavity. Moreover, the shape and size of the UC should be modified to minimize the convective heat losses from the UC to the surroundings. For this constraint to be met, it is envisaged that future reactor development will have to incorporate a CFD analysis in tandem with the structural model presented in this work, such that the geometry of the UC may be optimized for its thermal performance while ensuring the mechanical stability of the system.

Enhancement of the solar-to-chemical energy conversion efficiency and product yield for processes involving solid rather than gaseous products (e.g. solar thermal purification of WOX) can be attained by incorporating semi-continuous feeding of reactants and removal of products. Although this is essentially a technical engineering task, realization of this concept would considerably widen the application range of this solar reactor technology. A semi-continuously operating reactor design can be envisaged to make use of
the operating principles of a pusher-type furnace [103], and a main challenge
toward its technical realization is expected to be the maintenance of the inert
atmosphere inside the solar reactor upon exchanging the converted feedstock
with a fresh batch of reactants.

A further potential reactor advancement that would certainly encourage
confidence in the integration of solar thermal technologies into the well-
established metallurgical industry of zinc is the hybridization of the solar
reactor by providing high-temperature process heat from another thermal
source (e.g. radiant electric elements, plasma torch, combustion) during the
night hours or under cloudy conditions in order to ensure round-the-clock
plant operation. Hybridization would: (1) diminish thermal stresses by
eliminating temperature swings of cyclic operation; (2) provide a steady
production rate desired for integration to downstream Zn processing, (3)
increase the throughput capacity of the thermochemical plant; and (4)
increase the overall energy efficiency by eliminating the daily heat-up of the
solar reactor. During hours of non-solar operation, it is envisioned that the
UC will be replaced by insulating material to avoid reradiation losses to the
surroundings.

7.2.3 Zinc condenser

Investigation of the competing Zn(g) condensation and oxidation rates
in a zinc condenser involving gas bubbling through a Zn(l) bath revealed
successful suppression of the reversion reactions and almost complete
conversion of Zn(g) at operating temperatures of about 500 – 525°C,
irrespective of the amount of non-condensable gases in the reactor off-gas.
Therefore, maintaining the operating temperature of the Zn condenser within
a relatively narrow range is crucial for the effective recovery of Zn. However, release of high amounts of heat during Zn(g) condensation is expected to induce a temperature increase in the liquid bath and to pose a major challenge on the engineering realization of this condenser concept. Further experimental and research work is thus required for the identification of the optimal design and operating conditions of such a condenser in order to enable effective heat dissipation and reliable operation in general.

Experimental work could encompass gas bubbling of air through a liquid of similar properties to Zn(l) in a transparent tube reflecting the design of the condensation chamber. In such an experimental setup, the effects of the geometrical shape and arrangement of the brick baffles inside the condensation chamber as well as the slope of the chamber to the horizontal on the uniformity of the flow, the degree of agitation, and bubble break-up could be investigated in order to identify the flow conditions that would ensure an effective Zn recovery. In addition to experimental work, the development of a reliable CFD model could assist in acquiring a more comprehensive understanding of the underlying fluid flow mechanisms. Numerical modeling could further incorporate a heat transfer analysis between the outer surface of the condensing chamber and the surroundings, in order to enable selection of the appropriate construction materials and of the optimal heat dissipation method.

### 7.2.4 Concluding remarks

Overall, the present work reveals the strong potential for producing Zn from primary and secondary ZnO sources using concentrated solar energy to provide the high-temperature process heat. Solar thermochemical processes
may still be a developing technology, but important technological advancements toward commercialization have been made in previous years. However, confidence in the well-established extractive metallurgical industry of zinc regarding integration of solar thermal technologies is still low due to the comparative advantage of the conventional zinc production technology in terms of viability. Therefore, besides future activities aiming to eliminate further technical limitations of solar thermochemical processes, it is envisaged that mid-term planning will involve the development of transitional strategies based on hybrid technologies using a mixture of concentrated solar technologies and conventional fuels. In the long term and as the cost associated with concentrated solar technologies will decrease, the profitability of solar-driven processing of minerals and extraction of metals will facilitate the effective use of high-temperature solar process heat in these industries.
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**Curriculum vitae**

**Name** Nikolaos Tzouganatos  
**Nationality** Greek  
**Date of birth** 08.03.1988

**2013 - 2016** Doctoral studies (Ph.D.) at the Professorship of Renewable Energy Carriers, Department of Mechanical and Process Engineering, ETH Zurich, Switzerland, and at the Solar Technology Laboratory, Paul Scherrer Institute, Switzerland; supervision: Prof. Dr. Aldo Steinfeld, Dr. Christian Wieckert

**2010 - 2012** Master studies (M.Sc.) in Energy Science and Technology at ETH Zurich, Switzerland

**2011 - 2012** Industrial internship (6-months) at Wärtsilä Switzerland Ltd., 2-stroke Marine Diesel Engines Development, Winterthur, Switzerland

**2005 - 2010** Diploma studies (M. Eng.) in Mechanical Engineering at the National Technical University of Athens, Greece; specialization in energy engineering

**1999 - 2005** High School Diploma and Abitur at the German School of Athens (Deutsche Schule Athen), Athens, Greece
**Scholarships and awards**

2016  

2015  
Best Presentation Award by the American Institute of Chemical Engineers for the oral presentation entitled “Carbothermal Zinc recycling in a Packed-Bed Solar Reactor – Experimental Demonstration and Dynamic Modeling”, presented at the Conference Session “Solid Wastes to Energy and/or Product” of the 2015 AIChE Annual Meeting, Salt Lake City, USA, 2015

2013  

2010  
Honorary Scholarship for academic excellence, Hellenic Ministry of Education

2010  
A. Samaras & S. Sinouri Award, highest GPA in the Mechanical Engineering Department of the National Technical University of Athens
List of publications

**Journal articles**


**Conference presentations (oral)**


Book contributions
