Doctoral Thesis

Heat and mass transfer in a shrinking packed bed of zinc oxide and charcoal undergoing solar carbothermal reduction

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HEAT AND MASS TRANSFER IN A SHRINKING PACKED BED OF ZINC OXIDE AND CHARCOAL UNDERGOING SOLAR CARBO THERMAL REDUCTION

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

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presented by
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Preface

This work is focused on the modeling of a solar chemical reactor for the carbothermic reduction of zinc oxide. It is part of a larger project, the Solzinc project, aiming at reducing the greenhouse gas emissions during production of zinc. The major source of motivation for me during the three years of this work has been the possibility to take part in this scientific adventure which might have a significant and positive impact on our environment in the future.

I wish to express my sincere thanks to those who helped me in the completion of this thesis. First of all I would like to thank my advisor Prof. Aldo Steinfeld for his strong enthusiasm, and the confidence he put on my work. It is his indefatigable devotion to the field of renewable energies which made this project possible. I would like to thank Prof. Philipp Rudolf von Rohr for agreeing to be the co-examiner of this work.

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Abstract

The cyclic process from solar energy to electricity via solar-processed zinc-air fuel cells is being investigated within the project Solzinc. Its objective is to develop and operate a 300 kW solar chemical reactor for the carbothermic reduction of zinc oxide. The reactants, zinc oxide powder and beech charcoal dust, are placed in a reaction chamber in a batch mode, forming a reacting packed bed subject to thermal radiation. The products are zinc, CO and CO₂. Zinc production via the solar route offers CO₂ emission reduction by a factor of 5 vis-à-vis the conventional fossil-fuel-based electrolytic or Imperial Smelting processes. Zinc can serve as a fuel in Zn-air fuel cells or can be further reacted with H₂O to form high-purity H₂.

This work deals with modeling the shrinking packed bed of a solar chemical reactor for the carbothermic reduction of zinc oxide. The design of the Solzinc reactor is first tested on a 5 kW scale before scale-up, and supported by the numerical simulations presented in this work.

The thermodynamic analysis of the process shows that below about 1000 K, ZnO and C are thermodynamically stable components. Above 1410 K, the reduction reaches completion, and the chemical system consists of a single gas phase containing Zn(g), CO and CO₂. The ZnO reduction with charcoal is based on two intermediate solid-gas reactions: the reduction of ZnO with CO and the charcoal gasification. A kinetic model is developed by thermogravimetry for each reaction.

Using the kinetic model of the ZnO reduction with charcoal, the heat transfer in the shrinking packed bed of the solar reactor is modeled. It involves solving, by the finite-volume technique, a 1D unsteady-state energy equation that couples heat transfer to the chemical kinetics for a shrinking packed bed exposed to thermal radiation. Validation is accomplished by comparison with experimentally measured temperature profiles and Zn production rates as a function of time, obtained from the 5 kW solar reactor tested in a high-flux solar furnace.

The importance of knowing accurately the effective thermal conductivity coefficient of the powder mixture is revealed in this first model. A radial heat flow apparatus is built for the measurement of this coefficient in the range 470-872 K. The extrapolation of the effective thermal conductivity at higher temperatures is done by taking advantage of the Rosseland approximation for optically thick medium. The material property required for this method is the extinction coefficient, which is measured with two different experimental set-ups at ambient temperature.

The heat transfer model is then extended to mass transfer by accounting for gas diffusion and convection in the packed bed. The quasi-steady-state Navier-Stokes equation is coupled to chemical rate laws and the energy equation in the solid phase. The model allows the determination of the temperature, velocity, pressure drop, gas concentration, reaction extent and reaction rates profiles as a function of control parameters such as boundary temperatures and the C:ZnO molar ratio. The simulated data are compared to experimental data obtained from the 5 kW and 300 kW reactors.
Résumé

Le cycle de la transformation d'énergie solaire en électricité par l'intermédiaire de piles à combustible, alimentées par du zinc produit grâce à de l'énergie solaire, est étudié dans le projet Solzinc. Les réactants sont de la poudre d'oxyde de zinc et de la poussière de charbon de bouleau qui sont placés dans une chambre de réaction par lots, formant un lit poreux réactif sujet à des radiations thermiques. Les produits sont du zinc, du CO et du CO2. La production de zinc par la voie solaire permet une réduction des émissions de CO2 d'un facteur 5 par rapport aux procédés conventionnels utilisant des combustibles fossiles, comme l'électrolyse ou la pyrométalurgie. Le zinc peut être ensuite utilisé dans une pile à combustible zinc-air ou convertit en H2 par réaction chimique avec de l'H2O.

Ce travail traite de la modélisation d'un lit poreux se rétrécissant sous l'effet de la carboréduction de l'oxyde de zinc et appliqué à un réacteur chimique solaire. Le concept du réacteur est d'abord testé à une échelle de 5 kW avant de passer à une échelle de 300 kW, et est soutenu par les simulations numériques présentées dans ce travail.

L'analyse de la thermodynamique du processus chimique montre qu'en dessous de 1000 K, le ZnO et le C sont thermodynamiquement stables. Au-dessus de 1410 K, la réduction est achevée et le système est composé d'un mélange gazeux formé de Zn(g), CO et de CO2. La réduction du ZnO par du C est basée sur 2 réactions hétérogènes et parallèles : la réduction du ZnO par du CO et la gazéification du charbon. Un modèle cinétique est développé par thermogravimétrie pour chacune des réactions.

Le transfert de chaleur est modélisé pour le lit poreux en tenant compte du rétrécissement du lit et en utilisant le modèle cinétique de la réduction du ZnO avec le charbon. Cela implique la résolution par la technique des éléments finis de l'équation de transfert de chaleur unidimensionnelle et transitoire, couplée à la cinétique d'une réaction chimique. Le système est appliqué à un lit poreux se rétrécissant et exposé à des radiations thermiques. La validation du modèle est effectuée en comparant les profils de température ainsi que les taux de production de zinc mesurés sur le réacteur de 5 kW testé dans un four solaire.

L'importance du coefficient de conductivité thermique pour les lits poreux réactifs est soulignée dans ce premier modèle. Un appareil à flux radial est construit pour mesurer cette propriété entre 470 et 872 K. La conductivité thermique effective est ensuite extrapolée grâce à l'approximation de Rosseland pour les milieux optiquement épais. La propriété nécessaire pour cette méthode est le coefficient d'extinction, qui est mesuré à température ambiante avec deux montages expérimentaux différents.

Le modèle de transfert de chaleur est ensuite généralisé pour prendre en compte le transport des gazes par diffusion et convection dans le lit poreux. L'équation de Navier-Stokes quasi-stationnaire est couplée aux taux de réactions et à l'équation de transfert de chaleur dans la phase solide. Le modèle permet la détermination de la température, vitesse, chute de pression, concentration des gazes et de la conversion chimique en fonction de paramètres tels que la température aux extrémités et le rapport molaire C:ZnO. Les résultats du modèle sont ensuite comparés aux données expérimentales obtenues sur les réacteurs de 5 kW et 300 kW.
Symbols

\( A \quad \) surface, \( \text{m}^2 \)
\( c \quad \) concentration, \( \text{mol m}^{-3} \)
\( \text{Cp} \quad \) specific heat, \( \text{J kg}^{-1} \text{K}^{-1} \)
\( C \quad \) exponential constant
\( C_1, C_2 \quad \) constants
\( D \quad \) diffusion coefficient, \( \text{m}^2 \text{s}^{-1} \)
\( \text{D} \quad \) diameter, \( \text{m} \)
\( d \quad \) particle diameter, \( \text{m} \)
\( E_A \quad \) activation energy, \( \text{J mol}^{-1} \)
\( E \quad \) energy, \( \text{J} \)
\( f \quad \) dimensionless factor
\( f_r \quad \) particle volume fraction
\( g \quad \) gravitational acceleration, \( \text{m s}^{-2} \)
\( h \quad \) sample depth, \( \text{m} \)
\( h \quad \) enthalpy per unit mass, \( \text{J mol}^{-1}, \text{J kg}^{-1} \)
\( h_0 \quad \) enthalpy of formation, \( \text{J mol}^{-1} \)
\( H \quad \) enthalpy, \( \text{J} \)
\( I \quad \) radiative intensity, \( \text{W m}^{-2} \text{sr} \)
\( J \quad \) diffusion flux, \( \text{kg s}^{-1} \text{m}^{-2} \)
\( k \quad \) rate constant, chemical reaction limited, \( \text{mol s} \text{kg}^{-1} \text{m} \)
\( k_m \quad \) rate constant, mass transfer limited, \( \text{m s}^{-1} \)
\( k \quad \) thermal conductivity, \( \text{W m}^{-1} \text{K}^{-1} \)
\( k_D \quad \) permeability, \( \text{m}^2 \)
\( l \quad \) film thickness; path length, \( \text{m} \)
\( L \quad \) bed height, \( \text{m} \)
\( L_H \quad \) heater length, \( \text{m} \)
\( m \quad \) mass fraction
\( m \quad \) mass flow, \( \text{kg s}^{-1} \)
\( m^* \quad \) mass flux, \( \text{kg s}^{-1} \text{m}^{-2} \)
\( m'' \quad \) mass flow per unit volume, \( \text{kg s}^{-1} \text{m}^{-3} \)
\( M \quad \) molar mass, \( \text{kg mol}^{-1} \)
\( n \quad \) reaction order
\( n \quad \) number of moles, \( \text{mol} \)
\( n \quad \) number of rays
\( n \quad \) number of chemical component
\( n \quad \) unit vector normal to surface
\( N \quad \) number of measurements
\( N \quad \) number of element in grid
Symbols

\( N_p \) number of particles
\( p \) pressure, Pa
\( P \) electrical power, W
\( q^* \) heat flux, W m\(^{-2}\)
\( q'' \) heat source term, W m\(^{-3}\)
\( \dot{Q} \) rate of energy, W
\( r \) radius, m
\( r \) reaction rate, mol s\(^{-1}\) m\(^{-3}\), kg s\(^{-1}\) m\(^{-3}\)
\( r'' \) reaction rate per unit surface, mol s\(^{-1}\) m\(^{-2}\)
\( R \) universal gas constant, mol K\(^{-1}\)
\( R \) R-squared for linear regression
\( \mathcal{G} \) random number between 0 and 1
\( s \) standard deviation of the extinction coefficient, 1/m
\( \hat{s} \) unit vector into a given direction
\( S \) path, m
\( t \) time, s
\( t_{95\%} \) 95%-quantile from the t-distribution for \( N-1 \) degrees of freedom
\( T \) temperature, K
\( u \) velocity in x-direction, m s\(^{-1}\)
\( u \) velocity vector, m s\(^{-1}\)
\( V \) volume, m\(^3\)
\( W \) work, W
\( x, y \) Cartesian coordinates, m
\( X \) reaction extent or conversion
\( z_{1,2} \) dummy functions

Greek symbols
\( \alpha \) constant for the charcoal gasification, mol m\(^{-2}\)
\( \alpha \) acceptance angle of detector, rad
\( \beta \) extinction coefficient, 1 m\(^{-1}\)
\( \overline{\beta} \) mean extinction coefficient, 1/m
\( \delta \) distance between particles, m
\( \varepsilon \) emissivity
\( \varepsilon_{q/q_0} \) relative error in the radiative flux ratio obtained by MC
\( \Delta G \) Gibb’s free enthalpy, J mol\(^{-1}\)
\( \Delta t \) time step, s
\( \theta \) polar angle, rad
\( \kappa \) absorption coefficient, m\(^{-1}\)
\( \lambda \) wavelength, m
\( \mu \) viscosity coefficient, kg m\(^{-1}\) s\(^{-1}\)
\( v \) C:ZnO stoichiometric ratio
\( \zeta \) size parameter, \( \pi d/\lambda \)
Symbols

$\rho$ density, kg $m^{-3}$; mol $m^{-3}$

$\rho$ reflectivity

$\sigma$ Stefan-Boltzmann constant, W $m^{-2}K^{-4}$

$\sigma_i$ Lennard-Jones parameter for component $i$, Å

$\sigma_s$ scattering coefficient, m$^{-1}$

$\Phi$ phase function

$\tau$ viscous stress tensor

$\psi$ azimuthal angle, rad

$\omega$ single scattering albedo

$\Omega$ solid angle, sr

$\Omega$ collision integral for the Chapman-Enskog theory

Subscripts

c conduction

c critical layer

chem for the chemical reaction

$D$ for Darcy’s law

eff effective

exp experimental

g gas

$i$ dummy index; incoming

$l$ referring to the path length

$s$ solid

SiC at the SiC radiative plate

$p$ particle

$r$ radiation

ref reference

sim simulated

$\lambda$ spectral

$0$ initial value; at the top of the bed

Others

$\bar{f}$ average of $f$

$\tilde{f}$ characteristic value of $f$

Abreviations

GC Gas chromatograph

lhs left hand side

PSI Paul Scherer Institut

rhs right hand side

TG Thermogravimetry

WIS Weizmann Institute of Science
Chapter 1

Introduction

The prospect of crude oil shortage and atmospheric pollution is an incentive for our civilization to develop new technologies for the production of renewable energy carriers. Solar energy has the potential to satisfy the total energy demand of the Earth [57], but its unequal distribution restricts its possible exploitation to a limited number of countries. By efficient conversion into a chemical fuel like hydrogen or zinc, solar energy can be stored and transported to less sunny regions. Therefore, solar chemical storage could provide a solution not only to mobile applications like cars, but also relieve the world economy from its oil dependency.

High-temperature solar thermochemical processes have been investigated for a few decades in lab-scale receivers and chemical reactors. The basic idea behind solar process technology is to concentrate solar radiation with parabolic mirrors in order to achieve the temperature required to drive endothermic chemical reactions. Research efforts are mainly oriented toward hydrogen production by thermal dissociation of water, decomposition of hydrogen sulfide, or multi-step thermochemical processes involving metal oxides. Solar upgrade and decarbonisation of fossil fuels, thermal recycling of waste materials as well as solar production of commodities are some among the other possible solar thermochemical processes [57].

The thermal dissociation of water or metal oxides requires reaction temperatures exceeding 2300 K [33, 48, 59], which is difficult to achieve efficiently in a solar chemical reactor using today's state of the art solar concentrators. An alternative is the thermal carbo-reduction of zinc oxide (Figure 1.1), which operates at reasonable rates above 1400 K. This process has already been experimentally demonstrated using carbon as a reducing agent [1, 42, 46]. The zinc produced can be either directly used in zinc-air fuel cells or batteries, or reacted with water to form hydrogen. In either case, the chemical product from these power generation processes is zinc oxide, which in turn needs to be reduced to zinc to close the material cycle.
Figure 1.1: Concentrated solar radiation delivers the process heat for the carbothermic reduction of zinc oxide. The zinc produced is a solar chemical fuel that can be stored and transported to the desired site, where it is converted into electricity or hydrogen. The product of the reverse reaction, zinc oxide, is recycled into the solar reactor.

The cyclic process from solar energy to electricity via solar-processed zinc-air fuel cells is being investigated within the European Union's project Solzinc [71]. The key objective of this project is to develop and operate a 300 kW solar chemical reactor in order to demonstrate the technology at a pre-industrial scale. The reactants, zinc oxide powder (mean particle size 100 μm) and beech charcoal dust (mean particle size 180 μm), are placed in a reaction chamber in batch mode, forming a reacting packed bed subject to thermal radiation. The design of the reactor is first tested in a 5 kW reactor before scale-up, and supported by the numerical simulations presented in this work.

Reactor modeling is an essential tool to optimize the efficiency of the system, because it helps analyze and quantify the phenomena taking place in the reactor. It can also reduce the development costs by anticipating the consequences of design changes. Simulations of heat and mass transfer phenomena or thermal stresses are usually performed by numerically solving a set of differential equations in a discretized domain. Boundary and initial conditions can either be based on measured data, or they can be formulated such as to predict results for an unknown reactor configuration. However, a model may only be used for prediction purpose if it includes all necessary mechanisms to ensure a correct extrapolation. This is especially true for chemical reactors, where scaling-up effects do exist and often have their source in complex mass transport phenomena [55]. The legitimacy of a descriptive model is
given by the extent to which it can be validated, i.e. by reproducing input/output responses from available experimental data.

Solar irradiation is intermittent, since it depends on weather conditions and day time. For that reason, the design and the operation of solar chemical reactors are characterized by this transient nature. Batch reactors like the reactor investigated in the Solzinc project have also strong transient components, like the heat-up time, changing bed level and reaction extent. Therefore, a simulation intending to model such a solar chemical reactor from start-up until shut-down must include a time-dependence in the governing equations.

It is also essential to take into account the deformation of the domain geometry in problems involving the shrinkage of a reacting porous media. A few studies present models involving moving boundaries for the pyrolysis or gasification of char particles. In the work by Villermaux et al., the shrinking velocity is assumed linear over the domain [66], Bellais et al. compared different shrinking strategies [9] and Morell et al. used a transformation to map the moving boundary problem to a fixed domain [41]. The melting of a granular packed bed was analyzed by Hao and Tao in a non-thermal equilibrium [22], showing the influence of the local heat transfer coefficient on the accuracy of the model. Belghit et al. developed a steady-state numerical model of a moving chemical bed reactor for coal gasification using concentrated solar radiation [8]. The model couples a reaction rate with mass conservation and energy equations in a one-dimensional packed-bed. It allows the determination of the temperature profiles for both the gas and the solid phases, the velocity and the pressure drop profiles as a function of control parameters such as incident radiative flux, gas flow rate and particle size. The dynamic of fluids in porous media is detailed by Bear [7], and has been theoretically and experimentally examined by Olaide on a packed bed subjected to solar irradiation [44]. Comparison of different methods for the computation of multicomponent diffusion in high temperature flows has been studied by Désilets et al. [17].

Among the numerous works investigating reacting packed beds, we note the work by Zhou et al. who simulated the combustion of straw in a packed bed [77] and Ravi et al., who developed a heat transfer model for pyrolysis in an annular packed bed [52]. Recurrent in these studies is the significance of the effective thermal conductivity of the reacting packed bed. A reference work on heat transfer in porous media was written by Kaviany [30]. Many studies proposing models to estimate the effective thermal conductivity coefficient in packed beds have been published [6, 27, 64, 76]. An alternative is to measure this property, as described by Maglic et al. [36] in a work reviewing the most important measurement techniques. Solar chemical reactors usually operate at temperatures above 1000 K, where radiation heat transfer cannot be neglected. Different strategies combining conductive and radiative heat transfer are given by Siegel and Howell [56], or Matthews et al. [38]. These studies are based on the fundamentals of thermal radiation in packed beds, reviewed by Tien [61], and more recently by Baillis and Sacadura [3]. Theoretical models cannot establish themselves as satisfactory tools for the prediction of thermal material properties in porous media, because of their inability to characterize the effects of particle shape and size distribution. This reveals the crucial importance of using reliable data for material properties, which should be based on accurate measurements rather than on approximate correlations.
Chapter 1. Introduction

This thesis deals with simulations of the heat and mass transfer in the shrinking packed bed of the Solzinc reactor. It intends to contribute to the field of solar energy and chemical reactor modeling. A thermodynamic analysis as well as three kinetic models for the carbothermal reduction of zinc oxide are examined in Chapter 2.

The 5 kW and 300 kW reactors developed in the Solzinc project are described in Chapter 3. Experimental campaigns took place at the Laboratory for High Temperature Solar Technology at the Paul Scherrer Institute (PSI) for the 5 kW reactor and at the Solar Research Facilities at the Weizmann Institute of Science (WIS) for the 300 kW reactor.

Chapter 4 presents a heat transfer model in a shrinking packed bed exposed to thermal radiation. This numerical simulation involves solving, by the finite-volume technique, the one-dimensional transient energy equation coupled to chemical kinetics. The bed is modeled as a continuum shrinking due to the chemical reaction. The numerical method applied for solving the set of partial differential equations in a shrinking grid is also presented in this chapter. Validation is accomplished by comparison with experimentally measured temperature profiles and Zn production rates as a function of time, obtained for the 5 kW Solzinc reactor tested in a high-flux solar furnace. However, the effective temperature-dependent thermal conductivity is fitted so as to match the experimentally measured and simulated temperature field. This accentuates the need for reliable data on thermal properties of the reactant mixture. Hence, the effective thermal conductivity is experimentally determined in the range 470 - 872 K by the radial heat flow method. The setup, method and results are presented in Chapter 5. For the extrapolation at higher temperatures, the relevant material property is the extinction coefficient. Chapter 6 describes the experimental set-up and numerical methodology for the determination of the extinction coefficient for the reactant mixture used in the Solzinc reactor.

Chapter 7 extends the heat transfer model described in Chapter 4 to mass diffusion and convection in a shrinking packed bed, allowing the implementation of a more elaborated chemical model, and opening the door to predictive possibilities. In this heat and mass transfer model, the quasi-steady-state Navier-Stokes equation is coupled to chemical rate laws and the energy equation in the solid phase. In the two models presented in Chapter 4 and 7, the porosity of the medium is assumed constant. The material properties of the ZnO and charcoal used in the experiments are described in the Appendix.
Chapter 2

Chemical thermodynamics and reaction kinetics

2.1 Introduction

Modelling a chemical reactor requires detailed knowledge of the chemical processes taking place in the reactor. This is particularly important for the two models presented in Chapter 4 and Chapter 7, in which the heat and mass transfer mechanisms of the bed are directly affected by the chemical reactions. It is therefore essential to gain enough insight into the thermodynamics and kinetics of the carbothermic reduction of ZnO in order to model the Solzinc reactor.

The carbothermic reduction of ZnO can be represented by the overall net reaction:

\[ ZnO + \nu C = Zn + (2\nu - 1)CO + (1 - \nu)CO_2 \]  (2.1)

where \( \nu \) denotes the stoichiometric molar ratio C:ZnO. Reaction (2.1) proceeds endothermically (\( \Delta H^{\circ}_{298K} = 350.4 \text{ kJ/mol} \)) above 1230 K, via the solid-gas intermediate reactions [10]:

\[ ZnO(s) + CO(g) = Zn(g) + CO_2(g) \]  (2.2)

\[ CO_2(g) + C(s) = 2CO(g) \]  (2.3)

The dissociation of ZnO into its elements is omitted from consideration because its reaction rate is negligible at temperatures below 1800 K [40] compared to the rate of reaction (2.2). The equilibrium mole fraction of ZnO(g) in the saturated vapor is, at most, \( 5 \times 10^{-5} \) at 1700 K, and is therefore neglected here [48,68].

First, the enthalpy change and the equilibrium composition of reaction (2.1) are presented and analysed. These analyses give the basic information about the energy and chemical equilibrium of the chemical process. However, the equilibrium composition does not provide information on how fast a thermodynamically possible reaction will occur. This rate is given by a kinetic analysis.

The rate of a chemical reaction depends on various parameters, amongst others the gas and solid temperatures, the gas concentrations, the reaction extent and the particle geometry. Three kinetic models are presented in this chapter, one for each of the reactions (2.1)-(2.3).
The first one describes the kinetics of the overall ZnO carboreduction (Equation 2.1), which is used in the heat transfer model in Chapter 4. The second kinetic model is the charcoal gasification by CO$_2$. This model, along with the third model, the kinetics of the ZnO reduction, allows a more detailed and rigorous analysis of the chemical and mass transport phenomena occurring in the packed bed of the Solzinc reactor (Chapter 7).

### 2.2 Enthalpy change

Figure 2.1 shows the enthalpy as a function of the temperature ($h$-$T$ diagram) for the ZnO+C process under stoichiometric (1 mol of C per mol of ZnO) and adiabatic conditions. The reactants are first heated up to 1473 K before conversion into Zn vapors and CO. In the cooling phase, Zn loses its latent heat of vaporisation and fusion, resulting in a Gibb’s free energy difference $\Delta G_{18}$ at room temperature nearly twice as small as the enthalpy of formation $\Delta h_{23}$ at 1473 K. Note that the energy required to perform the reaction at $T = 1473$ K is more than four times greater than the energy required to heat up the reactant to this temperature.

![Figure 2.1: $h$-$T$ diagram of the ZnO+C process for a stoichiometric molar mixture.](image-url)
2.3 Equilibrium composition

The thermodynamic equilibrium composition of the system ZnO + νC at 1 bar and over the range of temperatures of interest is shown in Figures 2.2a and 2.2b for ν = 1 and 0.8, computed using the HSC Outokumpu code [53]. Below about 900 K, ZnO and C are thermodynamically stable components. In the temperature range 900-1340 K, they are used by reactions (2.2) and (2.3). Above 1340 K, the reduction reaches completion and the chemical system consists of a single gas phase containing an equimolar mixture of Zn(g) and CO for ν = 1, and a 1:0.6:0.2 molar mixture of Zn(g):CO:CO₂ for ν = 0.8. The effect of understoichiometry on the equilibrium composition has been previously examined for ν ranging from 0 (thermal decomposition) to 1, and it was found that the minimum temperature requirement for which ZnO is completely converted into Zn(g) is 1623 K for ν as low as 0.6, but this minimum temperature increases sharply to above 2000 K when ν is further reduced [58]. Besides the savings in carbon and, consequently, avoidance of CO₂, operation with ν < 1 would be advantageous because of the higher fraction of solar energy stored in chemical form in Zn [72]. In contrast, understoichiometry may have adverse effects because high CO₂ partial pressures favored Zn re-oxidation [10], which to some extent can be avoided via rapid quench using lead-splash condensers, a technique which consists in condensing zinc vapor by molten lead dropets in a series of condensation chambers [21].

Figure 2.2a: Thermodynamic equilibrium composition of the system 1 mol ZnO + ν mol C for ν = 1.
Chapter 2. Chemical thermodynamics and reaction kinetics

2.4 Kinetics of the overall reaction (ZnO + C → Zn + CO)

When a reactive carbonaceous material is used as the reducing agent, such as the charcoal powder used in these experimental studies, the interfacial kinetics of reaction (2.2) become the rate controlling mechanism. Assuming a shrinking spherical particle model with an unreacted core [11], the reaction rate of ZnO particles with CO is defined based on the particle surface area.

\[ r^n = \frac{1}{4\pi \cdot r_p^2} \frac{dn_{ZnO}}{dt} \]  

(2.4)

where \( r_p \) is the time-dependant radius of a shrinking particle. For \( n_{ZnO} \) moles of ZnO containing \( N_p \) particles, \( n_{ZnO} = \frac{4}{3} N_p \rho_{ZnO,p} \pi r_p^3 \), and further assuming a first order rate constant for the surface reaction [11], \( r^n = k \cdot p_{CO} \), the reaction rate takes the form:

\[ \frac{dn_{ZnO}}{dt} n_{ZnO}^{\frac{2}{3}} = -4\pi \left( \frac{3}{4 N_p \rho_{ZnO,p} \pi} \right)^{\frac{2}{3}} p_{CO} \cdot k \]  

(2.5)
or, in terms of the reaction extent, \( X = 1 - n_{ZnO} / n_{o,ZnO} \),

\[
\frac{dX}{dt} = (1 - X)^{2/3} \cdot k \left[ 4\pi \left( \frac{3}{4N_F p_{ZnO,p} \pi} \right)^{2/3} \cdot P_{CO} \cdot n_{o,ZnO} \right] \tag{2.6}
\]

The temperature dependency of the rate constant \( k \) is determined by imposing the Arrhenius law:

\[
k = k_0 \cdot \exp\left( -\frac{E_A}{RT} \right) \tag{2.7}
\]

The kinetic parameters were determined by thermogravimetry (TG), a technique which involves monitoring the weight loss of a sample in a chosen atmosphere as a function of temperature (Figure 2.3).

The measurements were carried out using a modified Netzsch TASC-419 thermobalance, in which an electrically heated Al\(_2\)O\(_3\) tube contained a water-cooled quartz cold-finger condenser for trapping Zn vapor [54]. A mixture of ZnO powder (Fluka 96479; mean particle size of 1 \( \mu \)m; BET of 5.2 \( \text{m}^2/\text{g} \)) and carbon (beech charcoal powder from Chemivron, mean particle size of 180 \( \mu \)m; BET of 0.38 \( \text{m}^2/\text{g} \)), with a ZnO:C molar ratio of 1:0.8, was loaded on an alumina flat holder and placed in the thermobalance. The sample was heated at a rate of 10 K/min under 25 ml/min N\(_2\) carrier flow, while its mass was recorded (Figure 2.4).

No ZnO deposits were observed at the end of the TG experiments, performed under non-equilibrium conditions. Figure 2.5 shows the Arrhenius plot by applying Equation (2.6) to the TG experimental data.

---

**Figure 2.3:** Schematic of a thermobalance, in which a ZnO+C sample is heated up at a constant rate, while its weight is recorded.
Figure 2.4: The temperature ramp and the mass decrease in the thermobalance.

Figure 2.5: Arrhenius plot by applying Equation (2.6) to the TG experimental data.

The apparent activation energy obtained by linear regression ($R^2 = 0.978$) is $E_a = 201.5 \pm 1.7$ kJ/mol. Note that $E_a$ is not the inherent state activation energy because it depends on the gas diffusion resistances. Comparison with similar kinetic parameters from the literature is not possible because there is no data available for the same reaction, kinetic model and reactant material. This last point is important because the charcoal used in the reactant mixture is a heterogeneous material which can have very different reactivities, depending on the fabrication process and the particles shape.
Equations (2.6)-(2.7) are rewritten in an effort to deliver a more general reaction rate equation that will be used in the energy equation of Chapter 4.

\[ r_{ZnO+C} = k_i \left(1 - X\right)^{1/3} \exp \left( -\frac{201500}{RT} \right) \]  

\( r_{ZnO+C} \) is equal to the rate of moles of ZnO and C reacting per unit time and unit volume. \( k_i \) is a combination of intensive material properties, the CO partial pressure and the pre-exponential factor of Equation (2.7). This term cannot be evaluated at this stage because of the unknown CO partial pressure. It will thus be fitted to the experimental data obtained with the Solzinc reactor, as described in Chapter 4.

### 2.5 Kinetics of the charcoal gasification

The decomposition of beech charcoal is characterized by a two-step process. The first step happens during the pyrolysis, which is a thermal cracking and evaporation step producing char and occurring at temperatures above 800 K for beech charcoal. The second and more important step is the CO2 gasification of the residual char (Equation 2.3). In these processes, several single reactions are usually involved, which can occur simultaneously or one after the other.

#### 2.5.1 Pyrolysis

An overview of the possible reactions that can take place during the pyrolysis of beech charcoal is given below.

\[ C(s) + H_2O(g) = CO(g) + H_2(g) \]  

(2.9)

\[ C(s) + 2H_2(g) = CH_4(g) \]  

(2.10)

\[ CO(g) + 3H_2(g) = CH_4(g) + H_2O(g) \]  

(2.11)

\[ CO(g) + H_2O(g) = CO_2(g) + H_2(g) \]  

(2.12)

Thermogravimetry experiments have shown that the pyrolysis reaches high rates at temperatures above 900 K, well below the temperatures where ZnO carbothermic reduction takes place. Due to the relatively small amount of volatiles present in the charcoal, the pyrolysis step is then already completed when the gasification starts (i.e. at approx. 1150 K). The mass of charcoal lost during pyrolysis has been measured to be less than 12% of the total beech charcoal mass. For these reasons, pyrolysis is neglected in this work, and the gasification (Equation 2.3) is assumed to be the only reaction taking place along with the ZnO reduction (Equation 2.2) during the carbothermic reduction of ZnO. All TG samples were therefore preheated to 1573 K at 40 K/min in an inert atmosphere to remove the volatiles in the charcoal. This was done in order to avoid any pyrolysis during the proper CO2 gasification.
Chapter 2. Chemical thermodynamics and reaction kinetics

2.5.2 Gasification model

In this sub-chapter, the kinetic parameters of reaction (2.3) are computed using a combination of theoretical models and experimental data obtained by thermogravimetry (TG). The thermobalance was of type Netzsch STA 409 CD, where the samples were heated up to 1823 K at a rate of 40 K/min under an Ar/CO₂ flow of 150 ml/min. Several experiments were conducted with a CO₂ volume fraction ranging from 4% to 40%. No carbon deposits were observed at the end of the TG experiments, performed under non-equilibrium conditions.

The model chosen to evaluate the CO₂ gasification is based on the shrinking core model described in [34]. The model assumes that the reaction occurs first at the outer skin of the particle. The reaction zone then moves into the solid leaving behind completely converted material. Thus, at any time there exists an unreacted core of charcoal which shrinks in size during the reaction. This model can be controlled via three different mechanisms: gas film control, chemical reaction control and ash layer control. This last control mechanism cannot be used for the charcoal gasification because of the negligible amount of ash present in the charcoal.

In the shrinking core model, the mass flux \( r^* \) relative to a particle surface is proportional to the decrease in mass of this particle and inversely proportional to its surface.

\[
r^* = \frac{1}{4\pi \cdot r_p^2} \frac{dn_c}{dt}
\]

where \( r_p \) is the radius of one particle and \( n_c \) the number of moles of carbon in the particle.

\[
n_c = \frac{\rho_{C,p} \cdot 4}{M_C} \cdot \pi \cdot r_p^3
\]

The time-derivation of Equation (2.13) is:

\[
\frac{dn_c}{dt} = \frac{\rho_{C,p} \cdot 4}{M_C} \cdot \pi \cdot 3 \cdot r_p^2 \frac{dr_p}{dt}
\]

In Equations (2.14) and (2.15), \( \rho_{C,p} \) is the density of a C-particle and \( M_C \) is the carbon molar mass. The relation between the radius of one particle and the reaction extent \( X \) can be written as follows:

\[
1 - X = \left( \frac{r_p^3}{r_{p,0}^3} \right)^{\frac{1}{3}}
\]

or in terms of the particle radius:

\[
r_p = r_{p,0} \left( 1 - X \right)^{\frac{1}{3}}
\]
Combining Equations (2.13), (2.15) and (2.18):

\[
\frac{dr_p}{dt} = -\frac{1}{3} r_p(1 - X)^{\frac{1}{2}} \frac{dX}{dt} 
\]

(2.18)

Combining Equations (2.13), (2.15) and (2.18):

\[
r^* = \frac{Pc,\rho}{3MC} r_p(1 - X)^{\frac{1}{2}} \frac{dX}{dt} 
\]

(2.19)

\[
r^* = \alpha \cdot (1 - X)^{\frac{1}{2}} \frac{dX}{dt} \quad \text{with } \alpha = \frac{Pc,\rho}{3MC} r_p
\]

(2.20)

The constant \( \alpha = 11.2 \text{ mol/m}^2 \) is a function of only intensive material properties of beech charcoal.

Up to this point, no conclusion has been made on the rate controlling mechanism. In the case of a rate controlled by the chemical reaction, the reaction rate is related to the reaction temperature \( T \) by an Arrhenius function. For higher temperatures, where the rate is controlled by the diffusion of \( \text{CO}_2 \) molecules through the gas film around the particle, the relevant parameters are defined by mass transport correlations. The demarcation temperature between these two mechanisms is 1425 K. It was determined by a best-fit approach, where the experimental results were compared to the model using different demarcation temperatures.

### 2.5.3 Chemical reaction control

The flux relative to a particle surface \( r^* \) for a \( n \)-order heterogeneous reaction limited by the chemical rate can be formulated as follows [34]:

\[
r^* = k \cdot \rho_{\text{CO}_2}^n
\]

(2.21)

where \( k \) is the rate constant \( \rho_{\text{CO}_2} \) the \( \text{CO}_2 \) partial pressure at the surface of the particle and \( n \) is the reaction order.

The Arrhenius law states that:

\[
k = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right)
\]

(2.22)

where \( k_0 \) is a pre-exponential factor and \( E_a \) is the activation energy of the reaction. Combining Equations (2.20)-(2.22) and taking the logarithm yields:

\[
\ln\left((1 - X)^{\frac{1}{2}} \frac{dX}{dt}\right) = -\frac{E_a}{RT} + \ln\left(k_0\right) - \ln\left(\alpha\right) + n \cdot \ln\left(\rho_{\text{CO}_2}\right)
\]

(2.23)

There are three unknowns in this equation that must be determined experimentally: the reaction order \( n \), the pre-exponential factor \( k_0 \) and the activation energy \( E_a \). The reaction extent \( X \) is recorded in the experiments as a function of time or temperature. Figure 2.6 shows the left hand side (lhs) of Equation (2.23) as a function of the \( \text{CO}_2 \) partial pressure for
different temperatures. The slope of these curves is obtained by linear regression. This slope is equal to the reaction order $n$ at each of these temperatures. Averaging these values, the reaction order for the chemical rate controlled mechanism is $n = 0.61$.

![Figure 2.6: Reaction order regression for beach charcoal at different temperatures.](image)

The same principle of linear regression is used to obtain the activation energy $E_A$ and the pre-exponential factor $k_0$. Equation (2.23) is modified in such a way that the lhs in Equation (2.24) becomes a linear function of the inverse of the temperature $T$.

\[
\ln \left( (1 - X)^{3/2} \frac{dX}{dt} \right) + \ln(\alpha) - n \cdot \ln(p_{CO_2}) = -\frac{E_A}{R \cdot T} + \ln(k_0)
\]  

(2.24)

The lhs of Equation (2.24) is obtained from six distinct TG experiments and plotted over $1/RT$ (Figure 2.7). An averaged linear regression curve is also shown in this figure, whose slope is equal to the activation energy $E_A$. The pre-exponential factor $k_0$ is the exponential of the value of this curve at the point where it crosses the ordinate.
The reaction rate is rewritten in a form that will be suitable for its use in the mass transfer and energy conservation laws of Chapter 7. Combining Equations (2.20)-(2.22) yields:

\[
\frac{dX}{dt} = \frac{k_0}{\alpha} (1 - X)^{\frac{1}{2}} \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \cdot \rho_{CO_2}^n
\]  \hfill (2.25)

Let \( r_C \) be the reaction rate in moles per unit time and unit volume charcoal powder. Taking advantage of the definition of the reaction extent \( X = 1 - \frac{n_C}{n_{C,0}} \) yields

\[
r_C = \frac{\rho_c}{M_c} \frac{k_0}{\alpha} (1 - X)^{\frac{1}{2}} \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \cdot \rho_{CO_2}^n
\]  \hfill (2.26)

To summarize, the evaluation of the TG experimental results gives a reaction order \( n = 0.61 \), activation energy \( E_A = 1.60 \times 10^5 \) J/mol and a pre-exponential factor \( k_0 = 104.6 \) mol s/m kg.
2.5.4 Gas film control

The Film Theory [16], shown schematically in Fig 2.8, assumes that a stagnant film exists near every interface.

![Figure 2.8: CO₂ concentration profile around a particle.](image)

The mass flux across this thin film can be written in terms of a mass transfer coefficient $k_m$:

$$r^* = k_m \cdot (c_{CO_2} - c(r_p)) \quad (2.27)$$

in which $c_{CO_2}$ and $c(r_p)$ are the bulk and interfacial CO₂ concentrations in the gas. Assuming that the chemical reaction is faster than the gas diffusion through the gas film, the CO₂ concentration at the particle surface is zero.

$$r^* = k_m \cdot c_{CO_2} \quad (2.28)$$

The flux across this film can also be calculated in terms of the diffusion coefficient $D$ and the film thickness $l$. This approximation reflects the assumption that the solution is dilute.

$$r^* = \frac{D}{l} \cdot c_{CO_2} \quad (2.29)$$

Comparing Equations (2.28) and (2.29) yields:

$$k_m = \frac{D}{l} \quad (2.30)$$

For simplicity, the film thickness $l$ is assumed constant, although in reality, it might be influenced by parameters like the gas velocity around the particle or the particle size and shape.
Chapter 2. Chemical thermodynamics and reaction kinetics

The temperature dependence of the diffusion coefficient is given by the Chapman-Enskog Gas Theory [14]:

\[ D = C \cdot T^{\frac{3}{2}} \]  \hspace{1cm} (2.31)

where \( C \) is a constant. Combining Equations (2.29), (2.31) and the ideal gas law yields:

\[ r^* = C \cdot T^{\frac{3}{2}} \frac{p_{CO_2}}{I} \frac{1}{RT} \]  \hspace{1cm} (2.32)

The time derivative of the reaction extent is obtained from Equations (2.20) and (2.32).

\[ \frac{dX}{dt} = C T^{\frac{3}{2}} \frac{p_{CO_2}}{I} (1-X)^{\frac{3}{2}} \frac{1}{\alpha R} \]  \hspace{1cm} (2.34)

As is the case of the limitation by the chemical step, the reaction rate is rewritten in a form that will be suitable for its use in the mass transfer and energy conservation laws of Chapter 7. Let \( r_{CO} \) be the reaction rate in moles per unit time and volume zinc oxide powder.

\[ r_c = \frac{\rho_c C T^{\frac{3}{2}} p_{CO_2} (1-X)^{\frac{3}{2}}}{M_c (1-X) I \frac{1}{\alpha R}} \]  \hspace{1cm} (2.35)

The ratio \( C/I = 1 \cdot 10^6 \), is found experimentally by fitting the TG experiments with the model.

2.5.5 Validation

Equations (2.26) and (2.35) give the reaction rate per unit mass for the two cases, where the kinetics of the charcoal gasification is either limited by the chemical reaction or by the gas diffusion through the gas film. These rates can be applied to a simulation of a thermogravimetry experiment, which can be easily compared to the measured data. In the first experiment, 31.6 mg of beech charcoal sample was heated up to 1823 K at a rate of 40 K/min under an Ar/CO\(_2\) flow of 150 ml/min. The CO\(_2\) concentration in the sample varied from 13.1% to 20.6%, depending on the CO production rate during the gasification. After 29 min, which corresponds to a temperature of 1546 K, the charcoal had been totally converted to CO. In a second experiment, the 28.1 mg sample was heated up under the same conditions, except that the CO\(_2\) concentration in the sample varied from 27.1% to 41.2%. In this case, all the charcoal was converted by the time the temperature reached 1495 K after 27 min. Figure 2.9 shows the experimental and simulated reaction extents as a function of the sample temperature for the two cases. Agreement is good, especially for the higher CO\(_2\) partial pressures.
Figure 2.9: Measured and simulated reaction extent during the gasification of two charcoal samples.
2.6 Kinetics of the ZnO reduction with CO

The reduction of ZnO with CO, Equation (2.2), was studied by thermogravimetry (TG) by R. Müller and R. Palumbo at PSI. There is no available reference for this work at the moment, but publication of the results will follow. A crucible containing 100 mg of ZnO was heated from 300K to 1500K at a rate of 0.331 K/s. Isothermal experiments were also conducted at temperatures of 1300K, 1400K, and 1600K. Measured variables were %-mass of the ZnO, temperature, and time. The partial pressure of CO was constant for each experiment and ranged from 9% to 26%. Argon was the purge gas and the combined flow rates of Ar and CO were 100ml/min. The CO partial pressure for each experiment was measured from the bulk gas exiting the TG using a gas chromatograph.

A Taylor expansion non-linear regression analysis was implemented in a numerical method program to calculate an apparent Arrhenius coefficient, the activation energy and the exponent of the reaction extent. The resulting reaction rate equation is:

\[
\frac{dX}{dt} = \frac{83.3 \cdot p_{CO}}{(1 + 5.42 \cdot p_{CO})} \cdot \exp\left(-\frac{93700}{RT}\right) \cdot (1 - X)^{0.40}
\]  

(2.36)

As for the charcoal gasification, the reaction rate is rewritten in order to obtain the number of moles reacted per unit volume ZnO powder and per unit time.

\[
r_{ZnO} = \frac{\rho_{ZnO} \cdot 83.3 \cdot p_{CO}}{M_{ZnO} \cdot (1 + 5.42 \cdot p_{CO})} \cdot \exp\left(-\frac{93700}{RT}\right) \cdot (1 - X)^{0.40}
\]

(2.37)

2.7 Chapter summary

The analysis of the thermodynamic and kinetics evaluation of the carbothermal reduction of ZnO is a key element for modelling the macroscopic mass transport of the Solzinc reactor. The reaction proceeds endothermically above 1230 K via two solid-gas intermediate reactions. For a C:ZnO stoichiometric ratio of 0.8, under thermodynamic equilibrium above 1420 K, the reduction reaches completion and the chemical system consists of a single gas phase containing a mixture of Zn(g), CO and CO2. The model for the kinetics of the overall ZnO carboreduction is based on the shrinking core model and uses an Arrhenius law for the temperature dependency. The activation energy \( E_A = 201.5 \) kJ/mol was obtained by comparing this model with experimental data obtained by thermogravimetry. The kinetics of the gasification of beech charcoal powder is the result of a similar analysis, but with a more detailed model in which the reaction rate is either limited by the chemical reaction or by mass transport. For the chemical reaction limiting step, the activation energy \( E_A = 1.61 \cdot 10^5 \) J/mol with a pre-exponential factor \( k_0 = 104.6 \) mol s/m kg and a reaction order \( n = 0.61 \). In the case where the reaction rate is limited by mass transport, the temperature dependence is given by the Chapman-Enskog Theory and the reaction order is 1.
Chapter 3

Reactor design and experimentation

The key objective of the Solzinc project [71] is to develop and operate a 300 kW solar chemical reactor in order to demonstrate the technology at a pre-industrial scale\(^1\). This chapter\(^2\) describes the facilities and the reactors tested in this project. Results from a typical experimental run are also presented.

3.1 Testing facilities

The two testing facilities used in this work are briefly described. The 5 kW reactor is used at PSI\(^3\)'s solar furnace, whereas the 300 kW reactor is built for the WIS\(^4\)'s solar tower unit.

3.1.1 PSI's solar furnace

The solar furnace at PSI [23] consists of a 120 m\(^2\) flat heliostat on-axis with a 8.5 m-diameter fixed parabolic concentrator, delivering up to 45 kW with a peak solar concentration exceeding 5000 suns (1 sun = 1 kW/m\(^2\)). Input solar power and power fluxes are measured optically on a Lambertian target with a calibrated CCD camera. A 45°-mirror redirects the incoming beam downwards, before it enters the reactor from the top, as depicted in Fig. 3.1.

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\(^1\) The reactor design, fabrication and testing has been performed jointly by the ETH-PSI project team. The author of this thesis was a member of this team.

\(^2\) Selected material in this chapter has been published in [46].

\(^3\) Paul Scherrer Institut, Switzerland

\(^4\) Weizmann Institute of Science, Israel
3.2.2 WIS’s solar tower

The solar facility at WIS features a field of 64 large, multi-faceted mirrors (heliostats), each measuring 7 x 8 m. Each heliostat tracks the movement of the sun independently and reflects its light onto a 75 m² reflector attached to a tower at about 45 m above ground level. Using this reflector, concentrated sunlight can be beamed down into the solar reactor [75].

![Heliostat field and solar tower diagram]

Figure 3.2: Optical scheme at WIS’s solar facility.

3.2 Reactor design

The design of the reactor is first tested in the 5 kW reactor illustrated in Figure 3.3 [12] before scale-up. Figure 3.4 shows the 300 kW version of this reactor, whose reaction chamber is 10 times larger and 5 times higher. The reactors feature two cavities in series, with the first (top) one functioning as the solar absorber and the second (bottom) one as the reaction chamber. A common SiC plate separates them. The first cavity is made of SiC and contains a windowed aperture to let in concentrated solar radiation. The second cavity is a well-insulated cylinder and contains a packed bed of a ZnO-C mixture that is subjected to irradiation emitted by the SiC plate. With this arrangement, the first cavity protects the quartz window against particles and condensable gases and further serves as a thermal shock absorber. A 3D compound parabolic concentrator (CPC [69]) is incorporated at the aperture to augment the solar concentration ratio by a factor of about 2, resulting in average incident radiative fluxes through the aperture exceeding 2600 suns. Reactants are placed in the reaction chamber before the run for batch operation; Carrier gas flows into the reaction chamber through an inlet port located on the lateral wall to sweeps out the product gases via a tangential outlet port located on the opposite side. This carrier gas is either pure N₂ for the 5 kW reactor or a mixture of N₂ and recycled CO and CO₂ for the 300 kW reactor. The reactor is specifically
designed for beam-down incident radiation. Generic design guidelines for such a two-cavity reactor concept have been described by Wieckert et al. [73].

Figure 3.3: 5 kW solar chemical reactor configuration for the carbothermic reduction of ZnO, featuring two cavities in series, with the first one functioning as the solar absorber and the second one as the reaction chamber. Not shown in this picture is the carrier gas inlet port (see Figure 3.4).

3.3 Experimental results

In a typical run with the 5 kW reactor, 500 g of a ZnO+C mixture are placed in the reaction chamber. The shutter controlling the power input is progressively opened to avoid thermal shocks and the reaction starts after 15 min (Figure 3.5). The temperature of the 1st cavity is measured by a solar-blind pyrometer\(^1\) and the temperature of the 2nd cavity is measured with a type-S thermocouple located in the SiC wall. The gas composition is monitored by gas chromatography (GC). CO is the main gaseous product and CO\(_2\) represents 5–15% of the sum CO+CO\(_2\). The H\(_2\) is mainly released during pyrolysis of the beech charcoal.

\(^1\) This blind-pyrometer is not affected by the reflected solar irradiation because it measures in a narrow wavelength interval around the 1.4 \(\mu\)m wavelength where solar irradiation is mostly absorbed by the H\(_2\)O in the atmosphere [63].
Figure 3.4: 300 kW solar chemical reactor for the carbothermic reduction of ZnO, allowing a maximal load of 464 kg ZnO+C.
Figure 3.5: Solar power input, reactor temperature, and product gas flow rates during a representative batch run with 500 g of ZnO-C mixture [46]. The solar-blind pyrometer used to record the inner cavity temperature operates above 780 K.
Chapter 4

Heat transfer model

4.1 Introduction

This chapter\(^1\) deals with a numerical model simulating the transient heat transfer processes occurring within the shrinking packed bed of the 5 kW Solzinc reactor. It involves solving the one-dimensional transient energy equation coupled to the reaction kinetics described in Chapter 2.4. A ZnO+C bed is modeled as a continuum undergoing shrinking due to the carbothermic reduction of the ZnO. The goal is to gain insight into the dynamics of heat transfer within a shrinking grid, and develop a reliable model for the packed bed of the Solzinc reactor. First, the governing equations are formulated and the numerical method explained. Secondly, numerical results are compared with those obtained experimentally.

4.2 Model description

A transient reactor model is formulated that couples radiation and conduction heat transfer with the chemical kinetics. The model domain is shown in Figure 4.1 and consists of the packed-bed of the ZnO and C mixture divided into \(N\) discrete disk-layers (control volumes). The top of the bed is exposed to radiation emitted by the SiC plate, which is assumed a gray emitter at uniform time-dependent temperature \(T_{\text{SiC}}(t)\), measured experimentally. Radiative heat absorbed at the top is transferred by conduction and radiation through the bed. The bottom boundary condition is given by the experimentally measured time-dependent temperature \(T_0(t)\). The bed is modeled as a 1-D continuum shrinking due to the chemical reaction. The shrinking of the bed is caused by the endothermic chemical transformation of solid phase reactants (ZnO and C) into gas phase products (Zn, CO, and CO\(_2\)). The 1-D approximation is supported by preliminary 2D axial-symmetric simulations of a non-shrinking packed bed that predicted uniform temperature in the radial direction and by experimental measurements that showed uniform bed shrinking in the vertical direction [46]. The chemical reaction rate is given by Equation (2.8), with the activation energy for the Arrhenius equation determined by thermogravimetry (see Chapter 2.4). For simplicity, convection heat transfer to the gas products is omitted from consideration in this model. Total pressure is constant and equal to 1 bar.

\(^1\) Selected material in this chapter has been published in [47].
Figure 4.1: The ZnO-C packed-bed is modeled as a 1D-continuum exposed to radiation at the top and undergoing shrinking due to the chemical reaction.

### 4.3 Governing equations

The general energy balance equation for an open system with \( n \) components is:

\[
\frac{dE}{dt} = \dot{Q} - W + \sum_{i=1}^{n} \dot{m}_{i,in} \left( h_{i,in} + \frac{u_{i,in}^2}{2} + g \cdot x_{i,in} \right) - \sum_{i=1}^{n} \dot{m}_{i,out} \left( h_{i,out} + \frac{u_{i,out}^2}{2} + g \cdot x_{i,out} \right) \tag{4.1}
\]

The following simplifications are made and Equation (4.1) is applied to the control volume with volume \( dV \) shown in Figure 4.2.

- Only the solid phase is considered
- No work is done in the control volume: \( W = 0 \)
- No mass enters the system: \( \dot{m}_{i,in} = 0 \)
- Kinetic energy and gravitational effects are neglected
- For a solid, \( E = H \)
- \( \dot{Q} = \dot{Q}_c \) is the rate of energy transferred by conduction and radiation to the control volume
The change in enthalpy of the mass in the domain becomes:

\[
\frac{dH}{dt} = \dot{Q}_c - \dot{m}_g \cdot h_g
\]  

(4.2)

The enthalpies are given as a function of the enthalpy of formation \( h^0_f \) at a reference temperature \( T_{ref} \):

\[
d \left[ m_s \left( \int_{T_{ref}}^{T} C_{ps} \cdot dT + h^0_f \right) \right] = \frac{d}{dt} \left( \dot{Q}_c - \dot{m}_g \cdot h_g \right)
\]  

(4.3)

\( m_s \) is the mass of the solid phase in the volume element. Its volumetric rate of change from the solid phase into the gas phase is given by Equation (2.8). Assuming constant \( C_p \) and applying the chain rule:

\[
m_s \cdot \frac{d}{dt} \left( C_{ps} \left( T - T_{ref} \right) + h^0_f \right) + \left( C_{ps} \left( T - T_{ref} \right) + h^0_f \right) \frac{dm_s}{dt} = \dot{Q}_c - \dot{m}_g \cdot h_g
\]  

(4.4)

The second term on the lhs represents the mass decrease, or shrinking, of the control volume. The enthalpy of the gas after the reaction \( h_g \) is the sum of the enthalpy of formation \( h^0_f \) of the solid at \( T_{ref} \), the enthalpy difference required to heat up the solid phase from \( T_{ref} \) to the reaction temperature \( T \), and the enthalpy of change \( \Delta h_{chem} \) used for the chemical reaction (see Figure 2.1):

\[
h_g = h^0_f + C_{ps} \left( T - T_{ref} \right) + \Delta h_{chem}
\]  

(4.5)

The number of gas molecules leaving the reactor is equal to the number of solid molecules being reacted \( \dot{m}_g = \dot{m}_s = r_{ZnO+C} = -\frac{d m_s}{dt} \). Thus:

\[
m_s \cdot C_{ps} \frac{dT}{dt} - \dot{m}_s C_{ps} \left( T - T_{ref} \right) - \dot{m}_s h^0_f = \dot{Q}_c - \dot{m}_g \cdot C_{ps} \left( T - T_{ref} \right) - \dot{m}_g h^0_f - \dot{m}_s \cdot \Delta h_{chem}
\]  

(4.6)
4 terms cancel, leaving:

\[ m \cdot C_p \frac{dT}{dt} = \dot{Q}_c - \dot{m} \cdot \Delta h_{chem} \]  \hspace{1cm} (4.7)

Replacing \( \dot{Q}_c \) by the Fourier law for heat conduction and dividing Equation (4.7) by an infinitely small volume yields:

\[ \rho \cdot C_p \frac{d}{dx} \frac{dT}{dt} = \frac{d}{dx} k_{eff} \frac{dT}{dx} - q_{chem} \]  
with \( q_{chem} = r_{ZnO+C} \cdot \Delta h_{chem} \) \hspace{1cm} (4.8)

The effective thermal conductivity \( k_{eff} \) of the packed bed is found in this model by matching numerically calculated and experimentally measured temperatures. The boundary conditions are:

initial: \[ T(x,t=0) = 300 \text{ K} \] \hspace{1cm} (4.9)

top: \[ q_{f}(x=L) = \frac{\sigma(T_{SC}^{4}-T_{ext}^{4})}{1 + \frac{1}{\varepsilon_{SC}} - 1} \] \hspace{1cm} (4.10)

bottom: \[ T(x=0,t) = T_0(t) \] \hspace{1cm} (4.11)

where \( T_{SC}(t) \) and \( T_0(t) \) are experimentally measured.

The particles of the bed undergo a transformation from the solid phase to the gaseous phase, which is caused by the heterogeneous chemical reactions between the different reactants. The gas products flow out of the bed, decreasing the total mass of solid reactants and the bed height. The bed is then said to be "shrinking". It is therefore necessary to have a consistent procedure in the simulation that makes the whole grid shrink.

This is done after every time step by shrinking the thickness of each control volume \( i \) at a rate

\[ \frac{dx_i}{dt} = \frac{\dot{m}_{i,s}}{A \rho_i} \] \hspace{1cm} (4.12)

The height of the bed is thus:

\[ L(t) = \sum_{i=1}^{N} \Delta x_i \] \hspace{1cm} (4.13)
4.4 Numerical method

The resolution of such a non-linear problem is best handled numerically. The system formed by the equation of heat transfer, Equations (4.8)-(4.11), and the reaction rate equation, Equation (2.8), must first be discretized and then solved iteratively at each time step. This sub-chapter explains the procedure applied to solve the system of equations and presents the different techniques used to improve the efficiency of the numerical scheme. The accuracy of the numerical simulation is estimated by calculating the relative difference in the reaction extent $X$ for $N = 600$ and $1200$. This relative difference is equal to $10^{-5}$.

4.4.1 Discretization

Equation (4.9) is discretized using the finite volume formulation as described in [49]. This approach is preferred to the finite difference method for its ability to deal easily with non-uniform grids. In the finite volume method, the discretization equations are derived by integrating the partial differential equations (PDEs) over a small region known as control volume. Each of these control volumes is associated with a discrete point at which the dependent variables are to be evaluated. The values of the discrete variables are determined at the center of each control volume, as shown in Figure 4.3. The values of the variables at the control volume faces are denoted with the subscript $i-1/2$ and $i+1/2$.

![Figure 4.3: Grid-point cluster for the one-dimensional finite volume formulation.](image)

Once discretized in space, the equation is discretized in time. The numerical solution of a transient problem is formulated by stepwise integration of the PDE. In the implicit, or Euler backward scheme, the spatial terms are evaluated at the unknown time level $t+\Delta t$. In practice this leads to a coupling of the equations for each control volume at the time $t+\Delta t$, and the need to solve a system of algebraic equations to advance the solution. The central difference implicit finite volume representation of Equation (4.8) is:

$$\rho_s C_p \frac{T_i^{t+\Delta t} - T_i^t}{\Delta t} \Delta x_i = \frac{k_{i-1/2}}{\Delta x_{i-1/2}} \left( T_{i-1}^{t+\Delta t} - T_i^{t+\Delta t} \right) - \frac{k_{i+1/2}}{\Delta x_{i+1/2}} \left( T_i^{t+\Delta t} - T_{i+1}^{t+\Delta t} \right) + q_i^{\prime\prime} \Delta x_i$$

where

$$\Delta x_{i+1/2} = \frac{1}{2} (\Delta x_i + \Delta x_{i+1})$$
\[ \Delta x_{i-1/2} = \frac{1}{2} (\Delta x_i + \Delta x_{i-1}) \]  

(4.16)

\( T_{i+1} \) is solved for \( i = 1 \ldots N \) at each time step. To calculate the interface conductivity \( k_{i-1/2} \), the correct procedure is to compute the harmonic mean of the heat conductivity coefficient between the control volumes \( i \) and \( i+1 \). This approach is based on the computation of the heat flux at the interface, and not on the assumption of a linear variation of the heat conductivity coefficient between the control volumes \( i \) and \( i+1 \). This method ensures accurate results in case of important spatial variations in the thermal conductivity [49].

\[
k_{i+1/2} = \frac{(\Delta x_i + \Delta x_{i+1})k_{i+1}k_i}{\Delta x_i k_{i+1} + \Delta x_{i+1} k_i} \tag{4.17}
\]

Similarly for the interface conductivity \( k_{i-1/2} \):

\[
k_{i-1/2} = \frac{(\Delta x_i + \Delta x_{i-1})k_{i-1}k_i}{\Delta x_i k_{i-1} + \Delta x_{i-1} k_i} \tag{4.18}
\]

The system of Equations (4.14)-(4.16) is solved using the TDMA algorithm [49]. Figure 4.4 shows a simplified flow-diagram of the simulation program. The iterative solution at the upper boundary is under-relaxed to ensure convergence.

---

![Flow Diagram](image_url)

Figure 4.4: Simplified flow diagram of the shrinking bed simulation
4.4.2 Remeshing algorithm

As a result of the higher temperature and the subsequent higher reaction rate, the decrease in size of the control volumes on the top of the bed is faster than in the rest of the bed. In the numerical simulation, the longest possible time step $\Delta t$ depends on the size of the smallest control volume of the grid. Eventually the top control volumes of the grid could become excessively small, which would considerably increase the computational time. To address this issue, the two top control volumes of the grid are merged as soon as one of them decreases below a threshold value $\Delta x_{lim}$, as shown in Figure 4.5.

![Figure 4.5: before (a) and after (b) merging of the two top control volumes of the grid](image)

The size of the first element after merging is thus:

$$\Delta x_{1,\text{new}} = \Delta x_1 + 2 \cdot \Delta x_2$$

(4.19)

The calculation of the temperature of this element is based on the law of conservation of energy. The enthalpy in the new element must be equal to the sum of the enthalpy in the two old merged elements:

$$\rho_s A \left( \frac{\Delta x_1}{2} + \Delta x_2 \right) \cdot \left( C_p \left( T_{1,\text{new}} - T_{\text{ref}} \right) + h_f^0 \right) = \rho_s A \frac{\Delta x_1}{2} \left( C_p \left( T_1 - T_{\text{ref}} \right) + h_f^0 \right)$$

$$+ \rho_s A \Delta x_2 \left( C_p \left( T_2 - T_{\text{ref}} \right) + h_f^0 \right)$$

(4.20)
It follows that:

\[ T_{i, \text{new}} = \frac{(\Delta x_1 T_i + 2\Delta x_2 T_2)}{(\Delta x_1 + 2\Delta x_2)} \]  

Thus, this mechanism of merging elements ensures the conservation of mass and energy. However, there is no guarantee of a constant rate of reaction before and after the merging occurs. This problem can be avoided by increasing the number of elements in the grid, but at the expense of a longer computational time.

The remeshing mechanism is activated as soon as the size of an element in the grid becomes smaller than a threshold value \( \Delta x_{\text{lim}} \) given by

\[ \Delta x_{\text{lim}} = f_R \cdot \Delta x_{\text{lim}} \mid_{r=0} \]  

where \( f_R \) is an empirically determined factor, usually on the order of a few percent.

### 4.4.3 Mesh generator

The simulation program employs a mesh generator that produces a finer grid in the upper part of the bed where the heat flux and the chemical reaction have their maximum amplitude. However, as the shrinking of the grid progresses, the fine mesh initially generated at the top of the bed is removed by the merging mechanism. This scheme thus increases the general accuracy of the simulation during the heat-up phase but its benefits are lost when the shrinking of the grid is advanced. A remedy to this problem is given in Chapter 7 in which an improved shrinking algorithm is presented.

### 4.4.4 Adaptive time step control

The computational time of a transient numerical simulation can reach impracticable values if no adaptive control is exerted over its time step. The purpose of adaptive time step control is to achieve some predetermined accuracy in the solution with minimal computational effort. The resulting gain in efficiency can sometimes be of several orders of magnitude [50].

The heat transfer model features two mechanisms which adapt the time step during the simulation in order to minimize the computational time. The first is an acceleration mechanism which increases the time step \( \Delta t \) by a few percent whenever fast convergence is achieved. Fast convergence is defined here as when the simulation converges during a given number of consecutive time steps with less than a given number of iterations. If the simulation does not converge, \( \Delta t \) is decreased. This results in a constantly maximised \( \Delta t \), which reduces the total computational time.

If convergence can not be achieved, a re-looping mechanism is activated. The temperature and the reaction extent of the previous time step are always recorded, which allows the simulation to go one step back in time. Figure 4.6 shows a flow diagram of the accelerating and re-looping procedures.
Figure 4.6: Flow diagram of the accelerating and re-looping mechanisms.

Usually, implementation of adaptive time step control requires that the stepping algorithm gives an estimation of its truncation error [50]. The time step is then a direct function of the truncation error and the desired degree of accuracy. In the model presented in this chapter, the time step is always kept at such a low value that the truncation error is negligible. The time step is thus here only optimized so as to minimize the computational time.

4.5 Experimental validation

Solar tests over the temperature range 1350-1600 K were performed at PSI's solar furnace with the 5 kW reactor prototype described in Chapter 3. The results produced by the model are compared to two solar experimental runs, (a) and (b), carried out under the experimental conditions set out in Table 4.1. A thermocouple is submerged in the bed at a height of 30 mm to provide validation for the model. Note that the boundary conditions at the top and bottom are given by Equations (4.10) and (4.11), respectively, where \( T_{SiC}(t) \) and \( T_0(t) \) are experimentally measured and shown in Figure 4.7. For run (a), the temperature of the SiC plate increases from 300 K to a maximum of 1572 K after 87 min. For run (b), it reaches a maximum of 1723 K after 80 min. Afterwards, the shutter controlling the incoming solar radiation is closed and the SiC plate undergoes cooling.
Table 4.1: Experimental conditions of the two solar experimental runs (a) and (b)

<table>
<thead>
<tr>
<th>Solar run</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:ZnO molar ratio</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Initial ZnO+C batch [kg]</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>ZnO+C residual [kg]</td>
<td>0.315</td>
<td>0.005</td>
</tr>
<tr>
<td>Initial bed temperature [K]</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Input power [kW]</td>
<td>6.2</td>
<td>8.7</td>
</tr>
<tr>
<td>CPC's entrance diameter [m]</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>CPC's acceptance angle [deg.]</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Reactor's aperture diameter [m]</td>
<td>0.065</td>
<td>0.065</td>
</tr>
<tr>
<td>Mean solar flux at aperture [W/m²]</td>
<td>1868</td>
<td>2622</td>
</tr>
<tr>
<td>$L(t=0)$ [m]</td>
<td>0.063</td>
<td>0.069</td>
</tr>
<tr>
<td>Measured $T_0(t)$</td>
<td>Fig.4.7a</td>
<td>Fig.4.7b</td>
</tr>
<tr>
<td>Measured $T_{SC}(t)$</td>
<td>Fig.4.7a</td>
<td>Fig.4.7b</td>
</tr>
</tbody>
</table>
Figure 4.7: Measured temperature profiles $T_{\text{sc}}(t)$ and $T_0(t)$ at the boundaries for the two solar experimental runs (a) and (b), described in Table 4.1.

There are two unknowns in this model: the pre-exponential factor $A_0$ for the reaction kinetic parameter and the temperature-dependent effective thermal conductivity $k_{\text{eff}}$. $A_0$ is fitted so that the total amount of ZnO+C reacted is the same in the experiment and the simulation. $k_{\text{eff}}$ is fitted to the experimental data so that the temperature measured by the thermocouple submerged in the bed is equal to the simulated temperature at the corresponding location in the model. The resulting effective thermal conductivity is shown in Figure 4.8. This method predicts values for $k_{\text{eff}}$ below 0.1 W/mK at temperatures below 800 K, and an increase at higher temperatures where radiation heat transfer becomes more important.
Figures 4.9 (a) and (b) show the calculated temperature profiles along the bed as a function of time (every 10 minutes), for the two runs (a) and (b), respectively. Three stages are observed. During the first 40 minutes, the upper portion of the bed is heated from ambient temperature to above 1000 K, but temperatures are not high enough for the reaction to occur. Afterwards, the temperature at the top exceeds 1200 K and the reaction proceeds at reasonable rates. The right end of the temperature curves is shifted to the left with time because of the shrinking of the bed. Finally, after 87 minutes for run (a) and 90 minutes for run (b), the shutter is closed, the bed undergoes cooling, and the reaction stops. $L$ ($t=110$ min) equals 3.9 and 0.1 cm for runs (a) and (b) respectively. The remaining height of the bed is larger for run (a) because temperatures are about 200 K lower than those for run (b). Also shown in Figure 4.9 (dots) is the temperature measured by a thermocouple submerged in the bed at a height of 30 mm.
Figure 4.9: Calculated temperature profiles along the packed-bed every 10 minutes for the two solar experimental runs (a) and (b). The dots correspond to the measured values and the numbers correspond the time, in minutes, at which the data has been calculated or recorded.
Figure 4.10 shows the variation of the temperature with time at a height of 30 mm for the two runs (a) and (b) of Table 4.1. Solid curves represent the numerical prediction; the dotted curves represent the measurements. The agreement between calculated and measured values is within 1.6 \% ± 1 \% for run (a), and 3.5 \% ± 3.9 \% for run (b) (mean difference ± standard deviation). Note in Figure 4.10 that, for run (b), the thermocouple was destroyed after 70 minutes, when the bed shrunk below it and exposed it to direct irradiation and corrosive Zn(g).

![Figure 4.10: Calculated and measured temperature variation with time at a height of 30 mm for the two solar experimental runs (a) and (b).](image)
The calculated (solid curve) and measured (dotted curve) rate of ZnO decomposition is shown in Figure 4.11 for both experimental runs (a) and (b). The calculated values are the result of the integration over the bed of the reaction rate (Equation 2.8) for each control volume at each time step. The experimental values are determined by the sum of CO+2CO₂ moles, recorded by on-line gas chromatography. The agreement between model and experiment is remarkably good.

Figure 4.11: Calculated and measured reaction rate vs. time for the two solar experimental runs (a) and (b), described in Table 4.1.
4.5 Scaled-up reactor

The validated model is now used to predict the performance of a scaled-up reactor with a reaction chamber half a meter high, designed for a load of 464 kg ZnO+C mixture. $T_D$ is set to a constant 300 K. $T_{SiC}$ is heated from 300 K to 1600 K at a rate of 50 K/min and then held at a constant 1500, 1600, or 1700 K during the rest of the simulation. $k_{eff}$ is taken as being equal to the values determined by the radial heat flow method for the temperature range 500-900 K, and to the values determined by Zehner et al. method for 900-1700 K [64]. The total simulation time was 5 hours.

![Temperature profiles along the bed as a function of reaction time (given in minutes) for an scaled-up reactor and for $T_{SiC}=1600$ K. The numbers correspond to the simulated time in minutes.](image)

Figure 4.12: Temperature profiles along the bed as a function of reaction time (given in minutes) for an scaled-up reactor and for $T_{SiC}=1600$ K. The numbers correspond to the simulated time in minutes.

Figure 4.12 shows the temperature profiles along the bed as a function of time, for $T_{SiC}=1600$ K. Analogous to the small-scale reactor, the temperature at the top exceeds 1200 K after 30 minutes and the bed shrinks at the approximately constant speed of $2.8 \times 10^{-5}$ m/s as the reaction progresses. A large temperature gradient is obtained in the top layer, which is typical of ablation processes where heat transfer through the bed becomes the rate controlling mechanism. After 5 hours of operation, the bed shrunk by 87%. Figure 4.13 shows the predicted rate of Zn production for the 3 different SiC-plates temperatures. The rate is approximately constant, except for the 30-minute start-up heating phase. For $T_{SiC} = 1700$ K, the reactor is emptied after 194 min.
Gravity pressure differences might influence the predicted bed shrinkage because a higher bed density increases the thermal conductivity. Thermoconductivity measurements made with the set-up described in Chapter 5 show that a 50% increase in $\rho_s$ produces a 20% increase in $k_{\text{eff}}$, which in turn results in the model predicting a 5% increase in the Zn output rate.

4.6 Chapter summary

In this chapter, the 1D-transient energy conservation equation was solved numerically using the finite volume technique for a shrinking packed bed of a ZnO+C mixture. Validation was accomplished with experimentally measured temperature profiles and ZnO decomposition rates as a function of time, obtained for a 5 kW solar reactor subjected to high-flux radiation. The model was further used to estimate the performance of a scaled-up reactor. After a start-up heating phase, whose duration depends on the boundary and initial conditions, the temperature at the top exceeds 1200 K and the bed shrinks at an approximately constant speed as the reaction progresses at reasonable rates. Conditions are typical of ablation processes, where the heat transfer through the bed becomes the rate controlling mechanism.
Chapter 5

Thermal conductivity measurement

5.1 Motivation

One of the most sensitive parameters in simulations coupling heat transfer and chemistry is the effective thermal conductivity \( k_{\text{eff}} \). Kinetic parameters for chemical reactions usually have a strong temperature dependency and heat transfer can even become the limiting step for the efficiency of a chemical reactor. This is in particular the case for the carbothermic reduction of ZnO in a packed bed reactor, as shown in [47]. It is therefore essential to have at our disposal a reliable effective thermal conductivity when computing the temperature field in a reacting material.

Heat transfer in a packed bed is usually dominated by heat conduction and radiation heat transfer between the particles. There are other mechanisms present as well, but they can be neglected in the packed bed considered in this work. If the fluid in the packed bed is stagnant, convection between the gas phase and the particles can be neglected. Leaving out the convection term, the total heat flux \( q^* \) is defined as the sum of the heat flux by conduction \( q^c \) plus the total radiative flux \( q^r \) given by the Rosseland approximation in a gray medium [56]:

\[
q^* = q^c + q^r = -k_e \frac{dT}{dx} - \frac{16}{3\beta} \sigma T^3 \frac{dT}{dx}
\]  

(5.1)

The effective thermal conductivity is then defined as the sum of the conductive term \( k_e \) and a temperature dependent radiative term which is a function of the extinction coefficient \( \beta \).

\[
k_{\text{eff}} = k_e + k_r = k_e + \frac{16}{3\beta} \sigma T^3
\]  

(5.2)

The primary quantifiable parameters influencing the thermal conductivity of a packed bed are the thermal conductivity of the solid phase, the thermal conductivity of the fluid phase and the porosity [64] of the bed. Other parameters, such as the structure of the solid matrix or the contact resistance between the non-consolidated particles, also play an important role [30]. Numerous studies trying to model heat conduction in packed beds have been published [20,26,27,32,64,76]. However, these studies do not characterize the effects of particle shape and size distribution, which make them difficult to interpret in our case. Furthermore, many models cannot predict the correct degree of temperature dependence observed [5].
Chapter 5. Thermal conductivity measurement

For engineering applications, the effective thermal conductivity must be known with an accuracy that often cannot be guaranteed by theoretical models. The alternative is thus to measure $k_{\text{eff}}$ directly. Except for Olorunyolemi et al. who studied the influence of sintering on the thermal conductivity of various ZnO powders [45], no previous work has been done on measuring the effective thermal conductivity of a ZnO+C powder mixture. The following chapter describes a method for measuring the effective thermal conductivity of ZnO+C and presents the results obtained with this method.

5.2 Measurement technique

In general, the measurement of transport properties presents some intrinsic difficulties compared to the measurement of other important fundamental properties such as thermodynamic quantities, because the determination of a flux is involved. Defining and controlling the heat flow path and then measuring the heat flux are the most difficult tasks for the calculation of the proportionality constant relating a heat flux and a temperature gradient. This proportionality constant is defined as the effective thermal conductivity $k_{\text{eff}}$.

A great variety of methods have been used in order to measure the thermal conductivity of packed beds. An overview of the most common thermal conductivity measurement techniques as well as technical details can be found in [36] and [64]. These methods are usually classified as transient or steady state methods.

In transient methods the thermal response to a sudden change in the boundary conditions is recorded at some position in the probe. This change is commonly a temperature jump or a heat pulse. The thermal conductivity is then obtained by fitting the solution of the Fourier equation to the measured time-dependent temperature response. If the heat pulse is generated by a laser, the measurement time is relatively short and the probe is small, which makes it a well-suited technique for reactive materials. On the other hand, the cost is often prohibitive because it requires a powerful laser.

In steady-state methods, the operator tries to establish a steady temperature gradient in the probe, while controlling the heat flux. The achieved temperature difference is then compared to the solution of the Fourier equation in order to obtain the effective thermal conductivity coefficient. Of all the possible techniques, the radial heat flow method is particularly suited for powders, although its measurement time can be relatively long at higher temperatures. The choice of the method depends on the following factors:

- The nature of the material (solid or powder)
- The expected magnitude of the effective thermal conductivity
- The required accuracy
- The maximum allowed test time
- The desired temperature range
- The allocated capital

1 A complete analysis of the heat transfer, as well as an important part of the experimental work done with the experimental apparatus, was performed for the diploma thesis of A. Hofmann [25].
5.3 Experimental set-up

Measurements performed using the steady-state radial heat flow method are presented in this chapter. Guidelines for the construction of such an apparatus are given in [37]. The apparatus is depicted in Figure 5.1. It features two concentric cylinders of radius $r_1 = 30$ mm and $r_2 = 80$ mm, the inner one containing the central electric heater of length $L_H = 500$ mm, and the powder placed between the two cylinders. The power $P$ produced by this heater induces a temperature gradient in the powder. An additional shell heater coiled around the outer cylinder is used to adjust the temperature gradient. Two temperature sensors are placed in the inner and outer cylinders.

![Figure 5.1: Radial heat flow apparatus.](image-url)
Chapter 5. Thermal conductivity measurement

Thus, the effective thermal conductivity is calculated as:

\[ k_{\text{eff}} = \frac{P \cdot \ln\left(\frac{r_2}{r_1}\right)}{2\pi L_H (T_1 - T_2)} \]  

(5.3)

The greatest advantage of the radial heat flow method is its ability to measure the effective thermal conductivity of any loose-fill material with good accuracy at higher temperatures. Furthermore, the required large specimen size is advantageous for a heterogeneous probe like the ZnO+C mixture, because it averages the effect of local inhomogeneities.

However, this large size is also the main drawback of the method: it leads to a relatively long test time to achieve steady-state conditions. Other difficulties which can arise with this setup are:

- The temperature sensors may be rather large and may be much more conductive than their surroundings, so that they act as thermal bridges affecting the temperature readings.
- The temperature sensors may be contaminated by the specimen material.
- The exact positioning of the inner cylinder in the middle of the outer cylinder is difficult.

The configuration of the system is mainly influenced by the magnitude of the effective thermal conductivity of the sample relative to its surrounding. For a powder containing ceramic material like ZnO, the thermal conductivity is expected to be low. Special attention will thus be given to the relative conductivity of the insulation material around the sample and to the direction of the heat flow.

Heat flows spontaneously from a hot to a cold region. Theoretically, because of the mid-plane and axial symmetries of the device, the heat produced by the central heater flows in the radial direction only at the mid-plane. The situation is different at the side boundaries, where the heat will tend to flow in the axial direction and influences the flow pattern over the whole sample. Although the cylindrical structure of the apparatus inherently reduces the need for thermal guarding or additional thermal insulation, four guard heaters are still needed at the extremity of the cylinders in order to reduce the axial heat flow. The thermocouples measuring the temperatures \( T_1 \) and \( T_2 \) are located at \( L_H / 2 \) in order to benefit from the mid-plane symmetry.

5.4 Measurement procedure

ZnO and beech charcoal contain a small amount of water, which could cause a short circuit if it evaporates during the measurement and recondenses on the electrical wires. The sample material is thus dried in an oven at a temperature of 120 °C for 3 hours before the experiment. It is then placed into the cavity between the inner and outer cylinders. After this, the apparatus is sealed and flushed for one hour with a 10 l/min \( N_2 \) flow in order to prevent any unwanted reaction of the charcoal with oxygen.
The temperature of each heater is adjusted by a PID controller, with a maximum heating rate of 4K/min to prevent any overheating of the heating wires. Steady-state conditions are usually reached within one hour, with a temperature difference of about 100 K between $T_1$ and $T_2$, depending on the chosen average sample temperature.

### 5.5 Results

Three series of measurements were performed on the ZnO+C mixture at average sample temperatures of 470 K, 672 K and 872 K. The powder bulk density $\rho_s$ was set to 680 kg/m$^3$ for two of the measurements ("Exp 1" and "Exp 2"), and 1005 kg/m$^3$ for the third one ("Exp 3"). C:ZnO molar ratio was 0.9 for all samples. The results are shown in Figure 5.2.

![Figure 5.2: Measured effective thermal conductivity vs. temperature. Details about the calculation of the error are presented in chapter 5.6.](image)

All curves show a variation of the effective thermal conductivity $k_{\text{eff}}$ with the temperature, which is a combination of at least 3 possible effects:

- The proportion of radiative heat transfer increases with increasing temperature. This fraction does not exceed 22% of the total heat transfer at 872 K as computed with the Rosseland approximation (Equation 5.2).
- There is an inverse relationship between temperature and thermal conductivity in dense ZnO and carbon [62]. This effect cannot be quantitatively related to the thermal conductivity of powders due to the complex structures of a particulate medium.
- ZnO powder starts to sinter at temperatures above 773 K, at a rate which depends on the particle size distribution, the powder bulk density, the purity of the mixture and the...
temperature. Sintering is responsible for the growth of the neck region surrounding the interparticle contact points, which in turn increases the thermal conductivity [45]. The two measurements with $\rho_s = 680 \text{ kg/m}^3$ show results that can be considered equal within the error margin, except at $T = 872 \text{ K}$, where the difference is slightly larger. The effective thermal conductivity is approx. 15% higher for $\rho_s = 1005 \text{ kg/m}^3$, which is explained by the higher contact surface between particles for a higher powder bulk density.

5.6 Error analysis

All major sources of errors were quantified analytically and by using the commercial finite element software ANSYS. Figure 5.3 shows a comparison of the different error sources for the first measurement with $\rho_s = 680 \text{ kg/m}^3$ at $T = 672 \text{ K}$.

![Pie chart showing different error sources](image)

Figure 5.3: Proportion of the different error sources for the first measurement with $\rho_s = 680 \text{ kg/m}^3$ at $T = 672 \text{ K}$.

The largest error source comes from the computation of the electrical power $P$. This relatively high value is not due to the intrinsic error of the measurement device (0.2%), but due to the impossibility of achieving perfect steady-state conditions. 20% of the error comes from the measurement of the temperature, i.e. the error of the thermocouples as well as eccentricity effects. The imperfections of the mid-plane symmetry leads to an axial heat flow generating 14% of the error. The rest can be attributed to the geometrical measurement of the different parts in the apparatus.
Chapter 6

Measurement of the extinction coefficient

6.1 Introduction

For the extrapolation of the effective thermal conductivity coefficient at higher temperatures in an optically thick medium, the material’s property of relevance is the extinction coefficient. In such a medium, radiation travels only a short distance before being absorbed, meaning that energy transfer depends only on the conditions in the immediate vicinity of the location considered. For this situation, it is possible to formulate the equation of radiative heat transfer into a diffusion relation like that for heat conduction [56]. This equation is called the Rosseland diffusion equation:

\[ q_e'' = \frac{16}{3\beta} \sigma T^3 \frac{dT}{dx} \]  \hspace{1cm} (6.1)

The effective thermal conductivity can be extracted from this equation and Fourier’s law for heat conduction:

\[ k_{eff} = k_c + \frac{16}{3\beta} \sigma T^3 \]  \hspace{1cm} (6.2)

6.2 Radiative transfer analysis

The variation of the radiation intensity \( I_{\lambda} \) traveling along a path \( S \) through an absorbing, emitting, and scattering medium is given by the equation of radiative transfer and illustrated in Figure 6.1 [6]:

\[ \frac{dI_{\lambda}}{dS} = -\beta_{\lambda}(S)I_{\lambda}(S) + \kappa_{\lambda}(S)I_{\lambda b}(S) + \frac{\sigma_{\lambda}(S)}{4\pi} \int_{0}^{2\pi} I_{\lambda}(S, \Omega_i) \Phi(\Omega, \Omega_i) d\Omega_i \]  \hspace{1cm} (6.3)
$\beta_x$ is the spectral extinction coefficient of the material and is defined as the sum of the scattering and absorption coefficients:

$$\beta_x = a_x + \sigma_s$$  \hspace{1cm} (6.4)$$

The albedo for scattering at a single wavelength, $\omega_s$, is defined as the ratio of the scattering coefficient to the extinction coefficient.

$$\omega_s = \frac{\sigma_s}{\beta_x} = \frac{\sigma_s}{\sigma_s + a_x}$$  \hspace{1cm} (6.5)$$

The extinction coefficient has units of reciprocal length, and is a function of pressure, temperature, wavelength, and composition of the material. A review on experimental work up to 1991 for the determination of the radiative properties of particulate media was conducted by Agarwal and Mengüç [2]. Previous pertinent studies include the experimental characterization of the radiative properties of dispersed media [3], the experimental determination of the extinction coefficient of packed beds [28,29,31,35] and liquid suspensions [13], and the development of an experimental system for measuring the scattering albedo, extinction and scattering coefficients, phase function, and asymmetry factor of particulates in the infrared [39].
Chapter 6. Measurement of the extinction coefficient

The basic approach for the experimental determination of $\beta_\lambda$ consists of measuring the attenuation of a light beam and solving Equation (6.3) after quantifying the source terms, i.e. the 2nd and 3rd terms in the right hand side of the equation. The gain by spontaneous emission can be neglected by simply performing the measurements at ambient temperature. However, quantification of the gain by incoming scattering requires knowledge of phase function $\Phi$ and scattering albedo $\omega$. Neglecting spontaneous emission and assuming constant $\beta_\lambda$ and $\sigma_\lambda$ along the radiation path, Equation (6.3) simplifies to

$$\frac{dI_\lambda}{dS} = -\beta_\lambda I_\lambda(S) + \frac{\omega_\lambda \beta_\lambda}{4\pi} \int I_\lambda(S, \Omega_i) \Phi(\Omega, \Omega_i) d\Omega_i$$

(6.6)

This chapter describes the experimental set-up and numerical methodology for determination of the extinction coefficient of the reactant mixture used in the Solzinc reactor.

6.3 Experimental set-up

Two different setups were used for the measurements. One uses a Si and PbSe light detector coupled with a spectrometer and a fiber optic. The other uses a photodiode directly connected to a precision voltmeter to measure the light intensity. For both setups, experimentation consists of measuring the light intensity with and without the ZnO+C mix, as well as the height of the powder layer. The radiation source is a commercial tungsten bulb heated to 3273 K and positioned 10 cm above the sample.

(a) radiation source

ZnO+C

acceptance angle $\alpha$

h

fiber optic

Si or PbSe detector

spectrometer

Figure 6.2: Experimental set-up (a): a fiber optic coupled to a spectrometer.

For the set-up (a), pictured in Figure 6.2, radiation is captured by a 200 $\mu$m-diameter fiber optic and sent to a Triax spectrometer, equipped with a Si detector for the range 300-1000 nm and a PbSe detector for the range 1000-5000 nm. Calibration is accomplished by using a LaCr$_2$O$_3$ radiation source at 1123 K. Figure 6.3 shows the radiative flux measured by the two
Chapter 6. Measurement of the extinction coefficient

types of fiber optics, SiO₂ and fluoride glass, normalized by the Planck's spectral distribution of a blackbody at 1123 K.

![Normalized intensity spectral distribution as measured by set-up (a) using a blackbody radiation source at 1123 K and two types of fiber optics: SiO₂ and fluoride glass.](image)

Figure 6.3: Normalized intensity spectral distribution as measured by set-up (a) using a blackbody radiation source at 1123 K and two types of fiber optics: SiO₂ and fluoride glass.

The discontinuities at 1000, 1800, 2500, 3200 and 4000 nm are the result of different gratings and filters employed for enhancing the spectrometer's sensitivity. Also shown in Figure 6.3 is the Planck's spectral distribution of a blackbody at 3273 K, which peaks at 885 nm and closely approaches the spectral distribution of the W-bulb. In the visible to near IR spectrum, the SiO₂ fiber optic features a higher relative transmissivity as compared to the fluoride glass fiber optic. The product of the normalized intensity and the Planck's distribution of a 3273 K blackbody is maximum at 1000 nm. Therefore, this wavelength is selected for the subsequent measurements.

For set-up (b), radiation in the range 350-1100 nm is captured by a 5 mm-diameter Si-photodiode (Figure 6.4). It generates an electrical current that is transformed into a voltage difference measured by a high precision voltmeter. Its drawback lies in the difficulty of measuring the height of the bed with high accuracy.
The measured signal intensity corresponds to the radiative intensity $I_\lambda$ integrated over a partial solid angle, and is equal to the radiative flux given by:

$$q_\lambda = 2\pi \int_0^\alpha I_\lambda \hat{n} \hat{s} \, d\theta$$  \hspace{1cm} (6.7)

The radiative flux is assumed to be uniformly distributed over the detector's aperture, as supported by the Monte Carlo analysis presented in the next section. Therefore, the ratio of signal intensities measured with and without the sample is equal to the ratio of fluxes expressed by Equation (6.7).

### 6.4 Experimental results and Monte-Carlo modeling

ZnO+C samples with a C:ZnO molar ratio of 0.9 were employed in the experimental set-ups described above. Figure 6.5 shows the ratio of radiative flux measured at depth $h$ to that measured at the top of the sample, using both experimental set-ups (a) and (b).
Figure 6.5: Variation of the radiative flux ratio $q''/q_0''$ with depth obtained with the experimental set-ups (a) and (b); measured values (data points) and exponential fitting (solid curves).

The average variation of $q''/q_0''$ with depth can be well approximated by an exponential law,

$$q''/q_0'' = e^{-Ch}$$

with $C = -9830 \text{ m}^{-1}$ and $-7081 \text{ m}^{-1}$ for set-ups (a) and (b), respectively. The larger dispersion of the data points for set-up (a) is attributed to the sensitivity of the measurement to the particle size distribution. The higher values of the measured radiative flux ratio for set-up (b) are in part due to the wider acceptance angle of the photodiode and to the different angular distribution of radiative intensity over the detector's aperture. Table 6.1 gives the average depth and corresponding radiative flux ratio $q''/q_0''$ for representative data points measured with set-ups (a) and (b). $\beta$ is determined by solving Equation (6.6) using the average measured data listed in Table 6.1.
Table 6.1: Average depth and radiative flux ratio $q''/q_0''$ for representative data points measured with set-ups (a) and (b).

<table>
<thead>
<tr>
<th>Set-up</th>
<th>Wavelength range [nm]</th>
<th>Exponential factor $h$ [m$^{-1}$]</th>
<th>$q''/q_0''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1000</td>
<td>9830</td>
<td>$7.28 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>(b)</td>
<td>350–1100</td>
<td>7081</td>
<td>$7.9 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

The collision-based Monte-Carlo (MC) ray-tracing technique is applied [19]. Its implementation for the simulation of the set-ups (a) and (b) is depicted in Figure 6.6.

Figure 6.6: Schematic of the application of MC to model the experimental set-ups (a) and (b).
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The acceptance angles are 22° and 180° for set-ups (a) and (b), respectively. The ratios of the aperture diameter $D$ to the bed depth $h$ are in the range 0.2-0.4 and 5-10 for set-ups (a) and (b), respectively. In both cases, the sample diameter is much larger than the aperture's diameter. Thus, the detector is not directly irradiated. Stochastic paths of a large number of rays emitted by the radiation source penetrate the ZnO-C particulate medium, so that the path length $l$ to the probable point of attenuation is determined by

$$l = -\frac{\ln R_l}{\beta}$$

(6.9)

where $R_l$ is a random number from a uniformly distributed set between 0 and 1. Here, another random choice, depending on the albedo, determines whether the ray is either absorbed or scattered. The probability of absorption is $1 - \omega$. If the ray is scattered, its direction forms an angle $\theta$ with the direction of incidence, which is obtained by solving numerically

$$R_\theta = \frac{1}{2\pi} \int_0^\pi \Phi(\theta, \psi) \sin \theta d\theta$$

(6.10)

$\Phi(\theta, \psi)$ is the scattering phase function. For a mean particle size of 100 μm and for wavelengths in the IR region around 1000 nm, the particle size parameter and the particle volume fraction are $\xi \approx 10^2$ and $f_r \approx 0.4$, respectively. Thus, independent scattering can be assumed, as referred to by the map of independent/dependent scattering for particulate media [60]. Since particles are randomly oriented and shaped, the scattering phase function is evaluated for diffusely reflecting spheres:

$$\Phi(\theta) = \frac{8}{3\pi} (\sin \theta - \theta \cos \theta)$$

(6.11)

This function is plotted in Figure 6.7 and shows a strong tendency for backward scattering.

![Figure 6.7: Scattering phase function for diffuse reflecting sphere.](image)
The history of a generic ray is then a complete random sequence, which terminates when the ray is either absorbed within the medium, escapes through the top and lateral boundaries, or reaches the detector's aperture. This procedure is repeated for a large number of rays for obtaining statistically meaningful results. A sample of $5 \cdot 10^8$ rays is used for each Monte Carlo run. The Monte-Carlo statistical error was estimated by varying the number of rays ($n_1=5 \cdot 10^8$ and $n_2=3 \cdot 10^9$) and calculating the relative difference in the radiative flux ratio:

$$
\varepsilon_{q/q_0} = 1 - \left( \frac{q^*}{q_0} \right)_{n_1} \left( \frac{q^*}{q_0} \right)_{n_2}
$$

(6.12)

This error has been found to be smaller than 0.1% for both set-ups. Since $\beta$ is not known a priori, the problem is solved iteratively until the radiative flux ratio $q^*/q_0^*$ from Table 6.1 is matched.

The scattering albedo is varied between 0 and 1 to show its influence on the extinction coefficient. Results are shown in Figure 6.8.

For $\omega = 0$, there is no scattering. Solving Equation (6.6) and integrating it over the aperture acceptance angle, yields

$$
q^*(h)/q_0^* = e^{-\beta h}
$$

(6.13)

In this case, Equations (6.8) and (6.13) have the same form, which implies that $\beta$ is equal to the exponential factor listed in Table 6.1. Increasing $\omega$ results in an increase of the number of rays detected after scattering, and in a decrease of the number of rays detected directly (no-scattering). Thus, $\beta$ increases with increasing $\omega$ in order to match the measured $q^*/q_0^*$. The
fact that the curve for set-up (a) is less sensitive to the variation of $\omega$ than that for set-up (b) is attributed to the different acceptance angles of both set-ups. For example, for $\omega = 0.64$, scattered rays contribute 22% to the detected intensity in set-up (a), and 54% in set-up (b). Obviously, this percentage reaches 100% for $\omega = 1$. Further aspects contributing to the different values of $\beta$ for the two set-ups are derived from the wavelength dependence. While the signal measured by set-up (a) is at 1000 nm, the one measured by set-up (b) is integrated over the range 350-1100 nm.

For large diffusely reflecting spheres ($\xi > 5$), the scattering albedo $\omega = \rho$ [56]. The reflectivity of a powder mixture consisting of two components can be approximated as

$$\rho = f_{v, ZnO} \cdot \rho_{ZnO} + f_{v, C} \cdot \rho_{C}$$ (6.14)

where $\rho_{ZnO}$ and $\rho_{C}$ are respectively the hemispherical total reflectivity of the ZnO and C particles [62], and $f_{v, ZnO}$ and $f_{v, C}$ are their corresponding measured volume fractions. Therefore, for ZnO+C samples with a C:ZnO molar ratio of 0.9, the albedo is $\omega = 0.64$.

### 6.5 Spectral analysis

Using set-up (a), radiation attenuation was measured in the range 500-1000 nm and $\beta$ computed for $\omega = 0.64$. Results are shown in Figure 6.9. For $600 \text{ nm} \leq \lambda \leq 1000 \text{ nm}$, $\beta$ is approximately constant at 10775 m$^{-1}$. Its value increases by 11% at 500 nm as a result of the higher absorptivity of ZnO at shorter wavelengths [62].

![Figure 6.9: Spectral variation of the extinction coefficient.](image-url)
6.6 Statistical analysis

The simplified equation of radiative transfer, Equation (6.6), was solved for the measured data points of Figure 6.5 obtained with both set-ups. Assuming $\omega = 0.64$, the computed values of $\beta$ are presented in Figure 6.10 in the form of a whiskers plot.

![Whiskers plot for values of $\beta$](image)

The ends of the whiskers show the minimum and maximum, whereas the edges and centerlines show the upper and lower quartiles and the median. The 95% confidence interval is given by [43]:

$$
\bar{\beta} - \frac{t_{0.025} \cdot s}{\sqrt{N}} \leq \beta \leq \bar{\beta} + \frac{t_{0.025} \cdot s}{\sqrt{N}}
$$

(6.15)

The assumption of normally distributed data was verified by applying the Kolmogorov-Smirnov test for goodness of fit to both data populations [11]. A two-sided rank sum Wilcoxon test was performed to verify that the two independent samples do not have equal medians. The final statistical results for $\beta$ are given in Table 6.2.

<table>
<thead>
<tr>
<th>Set-up</th>
<th>Mean value $[m^{-1}]$</th>
<th>Standard deviation $[m^{-1}]$</th>
<th>95% confidence interval $[m^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>10103</td>
<td>1950</td>
<td>±615</td>
</tr>
<tr>
<td>(b)</td>
<td>7850</td>
<td>800</td>
<td>±337</td>
</tr>
</tbody>
</table>

Table 6.2: Statistical results for $\beta$
Chapter 6. Measurement of the extinction coefficient

The theoretical value of $\beta$, calculated for large opaque diffusely reflecting spheres is given by

$$\beta = \frac{3}{2} \frac{f_r}{d} = 6000$$  (6.16)

and is independent of the wavelength and the particle's reflectivity. This value is within the order of magnitude of those obtained experimentally. However, it depends strongly on the particle diameter and therefore, it serves only as a comparison value. Since particles have a diameter in the range 20-300 $\mu$m, their position relative to detector's aperture can significantly affect the amount of radiation detected. This is especially the case for the 200 $\mu$m-diameter aperture of the fiber optic, as corroborated by the large dispersion of the measured data points in Figure 6.5. Thus, the value of $\beta$ reported for set-up (b) is believed to be more accurate.

6.7 Effect on the effective thermal conductivity

Taking advantage of the Rosseland approximation for optically thick medium, Equation (6.2), the extinction coefficient can be used to extrapolate the effective thermal conductivity at higher temperatures. Figure 6.11 shows the effective thermal conductivity as measured with the radial heat flow device presented in the previous chapter and the extrapolated values at higher temperatures. The reference thermal conductivity $k_c$ at $T = 0$ K is fitted so as to minimize the difference between measured and extrapolated values. At $T = 1600$ K, radiation heat transfer through the porous medium makes up to 60% of the overall heat transfer.

![Effective Thermal Conductivity Graph](image)

Figure 6.11: Measured and extrapolated effective thermal conductivity $k_{eff}$. 
Also plotted in Figure 6.11 is a theoretical prediction for the effective thermal conductivity from the model of Zehner et al. [67]. The significant parameters of this model are the temperature $T$, the volume fraction $f_v$, the emissivity $\varepsilon$ of the mixture, the particle diameter $d$ and a form factor. This model clearly overestimates the heat transfer by conduction and underestimates the effect of temperature on the effective thermal conductivity. Thus, measurements of the thermal properties of heterogeneous material such as a ZnO+C mixture are necessary.

6.8 Chapter Summary

A set of measurements of the radiation attenuation through a ZnO-C particulate medium using two experimental set-ups was conducted: (a) a fiber optic coupled to a spectrometer, and (b) a photodiode detector. For both set-ups, the equation of radiative transfer was numerically solved iteratively by the Monte-Carlo method assuming large diffusely-reflecting spherical particles, until the computed radiation intensity matched the experimentally measured values. The difference in the determined values of the extinction coefficient is attributed to the different wavelength range and to the high sensitivity of the 200 $\mu$m-diameter aperture of the fiber optic to the location of particles of comparable size.
Chapter 7

Heat and Mass transfer model

7.1 Motivation

The step from a descriptive to a predictive model is necessary for gaining vital information on the design and the performances of a chemical reactor. Changing the geometry or the boundary conditions is only allowed when the model includes all necessary mechanisms to ensure a correct extrapolation. This is especially the case for chemical reactors, where scaling-up effects do exist and often have their source in complex mass transport phenomena [55].

The heat transfer model presented in chapter 4 is able to simulate the thermochemical processes occurring within the packed bed of the 5 kW Solzinc reactor. However, it uses a simple kinetic model based on the direct reaction between ZnO and charcoal (Equation 2.1) that does not consider the dependence of the CO partial pressure in the bed. In reality, the carbothermal reduction of ZnO proceeds via two intermediate solid-gas reactions: the reduction of ZnO with CO (Equation 2.2) and the charcoal gasification (Equation 2.3) [10]. The kinetic parameters of both reactions are given in Chapter 2 and depend on the CO2 or CO partial pressure, the temperature and the reaction extents.

This chapter presents a heat and mass transfer analysis for a reacting and shrinking packed bed applied to the solar carbothermic reduction of zinc oxide. It is an upgrade of the heat transfer model of Chapter 4 because it uses an improved kinetic model based on the two parallel reactions (2.2) and (2.3). Since the kinetic parameters depend on the CO2 and CO partial pressure, the gas concentrations in the packed bed must be computed by performing a complete mass transfer analysis.

This chapter further describes the numerical method applied and compares the results obtained from the simulation with data measured on the 5 kW and 300 kW reactors of the Solzinc project (described in Chapter 3).
7.2 Model description

The model is based on the same domain as shown in Figure 4.1, in which the packed-bed of the ZnO and C mixture are discretized into a one-dimensional grid of \( N \) disk-layers. Temperature boundary conditions are the same as in the heat transfer model of Chapter 4 and are given by two time-dependent functions: \( T_{Slc}(t) \) for the temperature of the radiative plate at the top and \( T_0(t) \) for the temperature at the bottom of the bed. The gases produced in the bed exit the top of the bed after flowing through the ZnO and charcoal particles. Total pressure is equal to 1 bar at the top of the bed. The local gas temperature is assumed to take the local solid temperature. The shrinking of the bed is caused from the endothermic chemical transformation of solid phase reactants (ZnO and C) into gas phase products (Zn, CO, and CO\(_2\)). The thickness of each control volume \( i \) decreases at a rate:

\[
\frac{dx_i}{dt} = \Delta x_i \left( \frac{r_{ZnO,i} + r_{C,i}}{\rho_{ZnO} + \rho_C} \right)
\]

(7.1)

The chemical reaction rate are given by Equations (2.26) and (2.35) for the charcoal gasification \( r_C \) and by Equation (2.37) for the reduction \( r_{ZnO} \) of ZnO by CO.

7.3 Governing equations

The model is described by a system of 9 non-linear partial differential equations (PDEs) solved iteratively at each time step. These are:

- The energy equation to compute the temperature field in the solid phase. Gas and solid phase are assumed to have the same temperature. The energy required to heat up the gas up to the solid temperature is taken into account in the energy equation for the solid phase.

- 3 mass transfer equations to compute the concentration profile in the bed for each of the gas species (Zn(g), CO, CO\(_2\)). These equations account for the convection and diffusion fluxes of each species in the bed. H\(_2\) produced during the pyrolysis is neglected because it does not interfere with the two main reactions, the ZnO reduction and the charcoal gasification.

- Reaction rates \( r_C \) and \( r_{ZnO} \) are obtained using the kinetic parameters described in Chapter (2.5) and (2.6). They are multiplied by an empirically determined correction factor to take into account the difference between conditions in the thermobalance and the packed bed of the reactor. Multiplied by the reaction enthalpy \( \Delta h_{chem} \) for each reaction, they serve as heat sinks in the energy equation to account for the endothermic reactions (2.2) and (2.3).
The mass source terms for the production of CO, CO₂ and Zn(g) can be derived from the chemical equilibrium of reaction (2.2) and (2.3):

\[ r_{CO} = M_{CO} (2r_c - r_{ZnO}) \]  \hspace{1cm} (7.2)

\[ r_{CO_2} = M_{CO_2} (r_{ZnO} - r_c) \]  \hspace{1cm} (7.3)

\[ r_{Zn} = M_{Zn} r_{ZnO} \]  \hspace{1cm} (7.4)

- The general equations for the computation of the fluid flow are based on the principle of conservation of mass, energy of momentum [74]. There are three unknowns: the gas velocity \( u \), the pressure \( p \) and the gas density \( \rho_g \).

The interdependency of the equations upon one another is shown in the following table. This illustrates the high degree of complexity of the system.

<table>
<thead>
<tr>
<th>Equation</th>
<th>solves...</th>
<th>( T )</th>
<th>( X_{ZnO} )</th>
<th>( X_C )</th>
<th>( V )</th>
<th>( p )</th>
<th>( \rho )</th>
<th>( c_{CO} )</th>
<th>( c_{CO_2} )</th>
<th>( c_{Zn} )</th>
<th>( r_{ZnO} )</th>
<th>( r_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>( T )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mass transfer for CO</td>
<td>( c_{CO} )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mass transfer for CO₂</td>
<td>( c_{CO_2} )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mass transfer for Zn</td>
<td>( c_{Zn} )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Reaction rate ZnO reduction</td>
<td>( r_{ZnO} ), ( X_{ZnO} )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Reaction rate C gasification</td>
<td>( r_C ), ( X_C )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Momentum</td>
<td>( p )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mass conservation</td>
<td>( V )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ideal gas law</td>
<td>( \rho )</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

### 7.3.1 Energy equation

The general energy balance equation for an open system with \( n \) components is:

\[
\frac{dE}{dt} = \dot{Q} - W + \sum_{i=1}^{n} \dot{m}_{i,in} \left( h_{i,in} + \frac{u_{i,in}^2}{2} + g \cdot x_{i,in} \right) - \sum_{i=1}^{n} \dot{m}_{i,out} \left( h_{i,out} + \frac{u_{i,out}^2}{2} + g \cdot x_{i,out} \right)
\] \hspace{1cm} (7.5)

The following simplifications are made and Equation (7.5) is applied to the control volume with volume \( dV \) shown in Figure 7.1. The control volume is schematically partitioned between the solid and the gas phase.
Both the solid and the gas phase are considered

- No work done in the control volume: \( W = 0 \)
- For the solid phase, no mass entering the system: \( m_{\text{in}} = 0 \)
- \( m_s \) is proportional to the sum of the reaction rates for the ZnO reduction by CO and the charcoal gasification specified in Chapter (2.5) and (2.6):
  \[
  m_s = dV \left( r_c + r_{\text{ZnO}} \right) = dV \left( r_{\text{CO}} + r_{\text{CO}_2} + r_{\text{Zn}} \right)
  \]

- Kinetic energy and gravitational effects are neglected
- \( E = H \) for the solid phase
- \( \dot{Q}_c \) is the rate of energy transferred to the solid phase by conduction and radiation.
- \( \dot{Q}_{s-g} \) is the rate of energy transferred from the solid to the gas phase by convection and radiation. The bed is assumed pseudo-homogeneous, which means that the temperature of the solid and the gas are identical [70].

As shown in Figure 7.1: Energy balance on control volume for the heat transfer model.

Applied on both the solid and the gas phases, Equation (7.5) reduces to:

\[
\frac{dH}{dt} = \dot{Q}_c - \dot{Q}_{s-g} - m_s h_s
\]

for the solid phase

(7.6)

\[
\frac{dE_g}{dt} = \dot{Q}_{s-g} + m_{g,\text{in}} h_{g,\text{in}} - m_{g,\text{out}} h_{g,\text{out}} + m_s h_s
\]

for the gas phase

(7.7)

Further neglecting the energy accumulation in the gas phase \( \left( \frac{dE_g}{dt} = 0 \right) \), the convective term can be directly obtained from Equation (7.7):

\[
\dot{Q}_{s-g} = m_{g,\text{out}} h_{g,\text{out}} - m_{g,\text{in}} h_{g,\text{in}} - m_s h_s
\]

(7.8)
Combining Equations (7.6) and (7.8) yields:

\[
\frac{dH}{dt} = \dot{Q}_c - \dot{m}_{g,\text{out}} \cdot h_{g,\text{out}} + \dot{m}_{g,\text{in}} \cdot h_{g,\text{in}} + \dot{m}_s \cdot h_s - \dot{m}_s \cdot h_g
\]  

(7.9)

The enthalpies of the solid phase are given in function of the enthalpy of formation \(h^0_{f,s}\) at a reference temperature \(T_{\text{ref}}\):

\[
d\left[ m_s \left( \int_{T_{\text{ref}}}^T C_p, dT + h^0_{f,s} \right) \right] = \dot{Q}_c - \dot{m}_{g,\text{out}} \cdot h_{g,\text{out}} + \dot{m}_{g,\text{in}} \cdot h_{g,\text{in}}
\]  

(7.10)

Neglecting mass storage in the gas phase, a mass balance on the control volume yields:

\[
\dot{m}_{g,\text{in}} + \dot{m}_s = \dot{m}_{g,\text{out}}
\]  

(7.11)

Assuming a constant \(C_p\) and applying chain rule yields:

\[
m_s C_p_s \frac{dT}{dt} + \left( C_p_s \left( T - T_{\text{ref}} \right) + h^0_{f,s} \right) \frac{dm_s}{dt} = \dot{Q}_c - \dot{m}_{g,\text{in}} \cdot h_{g,\text{in}} - \dot{m}_s \cdot h_{g,\text{out}} + \dot{m}_{g,\text{in}} \cdot h_{g,\text{in}}
\]  

(7.12)

with \(\frac{dm_s}{dt} = -\dot{m}_s\), several terms cancel:

\[
m_s C_p_s \frac{dT}{dt} = \dot{Q}_c + \dot{m}_s \left( C_p_s \left( T - T_{\text{ref}} \right) + h^0_{f,s} - h_{g,\text{out}} \right) + \dot{m}_{g,\text{in}} C_{p_g} \left( T_{\text{in}} - T_{\text{out}} \right)
\]  

(7.13)

The enthalpy of the gas leaving the volume element is defined as follows:

\[
h_{g,\text{out}} = h_s + \Delta h_{\text{chem}} + C_{p_g} \left( T_{\text{out}} - T \right) = h^0_{f,s} + C_p_s \left( T - T_{\text{ref}} \right) + \Delta h_{\text{chem}} + C_{p_g} \left( T_{\text{out}} - T \right)
\]  

(7.14)

Combining Equations (7.13) and (7.14) yields:

\[
m_s C_p_s \frac{dT}{dt} = \dot{Q}_c + \dot{m}_s C_{p_g} \left( T - T_{\text{out}} \right) + \dot{m}_{g,\text{in}} C_{p_g} \left( T_{\text{in}} - T_{\text{out}} \right) - \dot{m}_s \Delta h_{\text{chem}}
\]  

(7.15)

The volumetric heat sink term induced by the endothermic reactions is defined as the sum of the reaction rate times the reaction enthalpy for both the ZnO reduction by CO and the charcoal gasification:

\[
m_s \Delta h_{\text{chem}} = r_{ZnO} \cdot \Delta h_{2\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2} + r_{C} \cdot \Delta h_{\text{C} + \text{CO}_2 \rightarrow \text{CO}}
\]  

(7.16)
Replacing $\dot{Q}_e$ by the Fourier's law for heat conduction and dividing Equation (7.15) by an infinitely small volume yields the energy equation for the heat and mass transfer model.

$$\rho \cdot C_p \frac{dT}{dt} = \frac{d}{dx} k_{eff} \frac{dT}{dx} + \dot{m}_s \cdot C_p \left( T - T_{out} \right) + \dot{m}_{in} \cdot C_p \left( T_{in} - T_{out} \right) - r_{ZnO} \cdot \Delta h_{ZnO \rightarrow CO_2 + Zn + CO} - r_c \cdot \Delta h_{C + CO_2 \rightarrow 2CO}$$

(7.17)

### 7.3.2 Mass conservation equation

Consider the general control volume $V$ bounded by a surface $A$ illustrated in Figure 7.2.

The integral form of the mass conservation principle for a control volume is [74]:

$$\iiint \frac{\partial \rho_s}{\partial t} dV + \iiint_A \rho_s \mathbf{u} \cdot \mathbf{n} dA = \iiint_V r_{chem} dV$$

(7.18)

The first term on the lhs represents the instantaneous rate of change of mass in the control volume. The second term represents the net convective flux of mass out of the control volume. The term on the rhs represents the mass generated by the chemical reaction. After using the divergence theorem to close the surface integral into a volume integral, one can derive a differential equation valid for every point within the control volume. Applied to the heat and mass transfer model of this chapter, the one-dimensional form of Equation (7.18) is:

$$\frac{\partial}{\partial t} \rho_s + \frac{\partial}{\partial x} \rho_s \cdot u = r_{CO} + r_{CO_2} + r_{Zn}$$

(7.19)

The three terms on the rhs represent the total amount of CO, CO$_2$ and Zn produced per unit time and unit volume and given by Equations (7.2)-(7.4).
7.3.3 Conservation of momentum

The integral form of the conservation of momentum for the same control volume is:

\[
\int_V \frac{\partial}{\partial t} (\rho_s u) \, dV + \int_{A^i} \rho_s u (u \cdot n) \, dS = -\int_{A^f} \rho n \, dS + \int_{A^f} n \cdot \tau \, dS \tag{7.20}
\]

The first term on the lhs of Equation (7.20) represents the instantaneous rate of change of momentum in the control volume. The second term represents the net flux of momentum out of the control volume and is called the inertia term. The two terms on the rhs are the net pressure force and net surface force exerted by the surrounding on the control volume. Taking advantage of Stokes's postulate for the net surface force term, or viscous term, the one dimensional form of Equation (7.20) is [74]:

\[
\frac{\partial}{\partial t} \rho_s u + \frac{\partial}{\partial x} \rho_s u \cdot u = -\frac{\partial p}{\partial x} + \mu \frac{\partial^2 u}{\partial y^2} \tag{7.21}
\]

Because the analysis presented in this work is one dimensional, the gas velocity \( u \) is known only as a function of the \( x \) coordinate, i.e. parallel to the fluid flow direction. Therefore, the space derivative of the velocity \( u \) in the \( y \)-direction cannot be directly calculated. However, one can reasonably assume that the flow profile between the particles in the bed is parabolic, as illustrated in Figure 7.3.

![Figure 7.3: The flow pattern between two particles in the bed is assumed parabolic.](image)

The velocity profile in the direction perpendicular to the flow direction has the form:

\[
u(y) = \bar{u} \left( C_1 y^2 + C_2 \right) \tag{7.22}
\]

where \( \bar{u} \) is the average gas velocity. Assuming \( u = 0 \) at the surface of the particles, the pressure drop due to viscous effects can be expressed as a function of the constant viscosity coefficient \( \mu \), the local average fluid velocity \( \bar{u} \) and the average distance \( \delta \) between the particles.

\[
\nabla p_{\text{friction}} = \mu \frac{\partial^2 u}{\partial y^2} = -\mu \frac{3 \bar{u}}{\delta^2} \tag{7.23}
\]
An interesting confirmation of this approach is given by Darcy's law, which states that the pressure drop of a fluid flowing through a porous media is proportional to the fluid velocity and inversely proportional to a constant $k_D$ called the permeability.

$$\nabla P_{\text{Darcy}} = -\frac{u \mu}{k_D} \quad (7.24)$$

The permeability is an intensive material property of a porous media, which must be either directly measured or obtained from correlations. A purely empirical formula is given by Bear [7] in which $k_D$ is related to the mean particle diameter $d$.

$$k_D = 6.17 \cdot 10^{-4} d^2 \quad (7.25)$$

Both the parabolic profile and Darcy's law approaches yield approximately the same pressure drop for an average particle diameter of 100 $\mu$m and an average particle spacing of 5 $\mu$m. The parabolic profile approach is used in the heat and mass transfer model presented in this chapter.

The flow regime in a packed bed depends on the Reynolds number, defined as the ratio between inertia and viscous forces:

$$Re = \frac{\rho_s u d}{\mu} \quad (7.26)$$

In the bed of the Solzinc reactor, $Re$ is of the order $10^2$. For such low value, the flow is called a creeping flow, or stokes flow and the inertia term of the momentum equation (7.21) can be neglected [15].

### 7.3.4 Equation of State

The ideal gas law relates the pressure of a gas, its density and its temperature.

$$p = \frac{R \cdot T}{\sum m_i \cdot M_i} \quad \rho_s \quad \text{for } i = \text{CO, CO}_2 \text{ and Zn} \quad (7.27)$$

### 7.3.5 Mass transfer equation

The mass transfer equation computes the convective and diffusive flows for each gas species in a domain [16].

$$\frac{\partial}{\partial t} \rho_s m_i + \frac{\partial}{\partial x} \rho_s m_i u = -\frac{\partial J_i}{\partial x} + r \quad \text{for } i = \text{CO, CO}_2 \text{ and Zn} \quad (7.28)$$

The two terms on the lhs of Equation (7.28) represent the instantaneous rate of change of concentration for species $i$ and the net convective flux. The two terms on the rhs are the
diffusive flux and the mass source term. The usual formulation for the diffusion flux for of a specific species depends only on the composition gradient of that species:

\[ \dot{J}_i = -\rho_s D_{i,\text{eff}} \frac{\partial m_i}{\partial x} \]  

(7.29)

As a major drawback, this method lacks the essential condition of flux consistency for multicomponent gases mixtures containing more than 2 species, i.e. \( \sum J_i \neq 0 \). Ramshaw [51] improved this approach by proposing a correction to be added to the binary flux. The resulting diffusion flux is then forced to be consistent through the addition of a simple term:

\[ \dot{J}_i = -\rho_s D_{i,\text{eff}} \frac{\partial m_i}{\partial x} + m_i \rho_s \sum_j D_{i,j,\text{eff}} \frac{\partial m_j}{\partial x} \]  

(7.30)

In Equations (7.29) and (7.30), \( D_{i,\text{eff}} \) is the effective binary diffusion coefficient used when a gas diffuses in a mixture of \( n-1 \) gases [17]:

\[ D_{i,\text{eff}} = \frac{1 - m_i}{\sum_{j \neq i} x_j D_{i,j}} \]  

(7.31)

\( D_{i,j} \) is the binary diffusion coefficient between species \( i \) and \( j \) that can be calculated from the Chapman-Enskog theory for gaseous diffusion coefficients [14].

\[ D_{i,j} = 1.86 \cdot 10^{-2} T^{3/2} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{3/2} \]  

\[ \frac{p \Omega (\sigma_i + \sigma_j)^2}{4} \]  

(7.32)

The Lennard-Jones parameters \( \sigma_i, \sigma_j \) and the collision integral \( \Omega \) are molecular properties characteristic of the two species. Their value can be found in [24].

7.3.6 Dimensional analysis

A dimensional analysis gives order of magnitude estimates for quantities of interest and can help identifying the relevant terms in an equation. It is performed here on the preceding conservation laws to estimate their characteristic time \( \tilde{t} \), which is a measure of their reaction time to any change in the boundary conditions. The goal of this analysis is to show that the gas flow responds much faster to changes than the conductive and radiative heat flow, and that the transient terms of the mass transfer, momentum and mass conservation equations can therefore be neglected. This greatly simplifies the computation of the fluid flow, as will be shown later.
Chapter 7. Heat and Mass transfer model

The conservations laws are rewritten in terms of characteristic variable.

**Energy equation**

\[
\frac{\dot{\rho} \tilde{C}_p \tilde{T}}{t} \sim \frac{k \tilde{T}}{L^2} + \tilde{\dot{r}} \tilde{C}_p \tilde{T} + \tilde{\dot{r}} \Delta \tilde{h} \tag{7.33}
\]

**Mass conservation**

\[
\frac{\dot{\rho}_s \tilde{u}}{t} \sim \frac{\dot{\rho}_s \tilde{u}}{L} + \tilde{\dot{r}} \hat{\tilde{u}} \tag{7.34}
\]

**Momentum equation**

\[
\frac{\dot{\rho}_s \tilde{u} \tilde{u}}{t} \sim \frac{\Delta \tilde{p}}{L} + \frac{\tilde{\mu} \tilde{u}}{L^2} \tag{7.35}
\]

**Mass transfer equation**

\[
\frac{\dot{\rho}_s \tilde{m}}{t} \sim \frac{\dot{\rho}_s \tilde{m} \tilde{u}}{L} + \frac{\dot{\rho}_s \tilde{D} \tilde{m}}{L^2} + \tilde{\dot{r}} \tag{7.36}
\]

In a dimensional analysis, signs (+/-) do not play a role because the terms are compared with each other separately. The following values are used for the characteristic variables:

<table>
<thead>
<tr>
<th>Table 7.2: characteristic variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>(\dot{\rho}_i)</td>
</tr>
<tr>
<td>(\tilde{\rho}_s)</td>
</tr>
<tr>
<td>(\tilde{T})</td>
</tr>
<tr>
<td>(\tilde{k})</td>
</tr>
<tr>
<td>(\tilde{C}_p)</td>
</tr>
<tr>
<td>(\Delta \tilde{p})</td>
</tr>
<tr>
<td>(\tilde{\delta})</td>
</tr>
</tbody>
</table>
Chapter 7. Heat and Mass transfer model

The diffusion, convection, source and pressure terms on the rhs of Equations (7.33)-(7.36) are then compared to their respective transient terms on the lhs in order to calculate the corresponding characteristic time \( \tilde{t} \). For example, the characteristic time for the diffusion term in the energy equation is calculated as follows:

\[
\tilde{t} = \frac{\tilde{\rho} \tilde{C}_p \tilde{T}}{k \tilde{T}/\tilde{L}^2} \approx 400 \text{ s} \tag{7.37}
\]

The results summarized in Table (7.3) indicate that \( \tilde{t} \) for the energy equation is more than two orders of magnitude higher than for the mass conservation, momentum and mass transfer equations. Therefore, the mathematical description of the gas flow evolves in a pseudo steady state environment. In other words, there is no local accumulation of momentum, mass and concentration for the gas phase in the bed and the transient terms can be neglected.

Table 7.3: characteristic time for each of the terms of the conservation laws.

<table>
<thead>
<tr>
<th>Equation</th>
<th>( \tilde{t} ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>3000 400 400 -</td>
</tr>
<tr>
<td>Mass conservation</td>
<td>1 - 2 -</td>
</tr>
<tr>
<td>Momentum</td>
<td>0 2.10^{-7} 3.10^{-7}</td>
</tr>
<tr>
<td>Mass transfer</td>
<td>1 0.5 1 -</td>
</tr>
</tbody>
</table>

Another similar way of justifying this assumption is done by calculating the Lewis number.

\[
Le = \frac{k}{\rho_s C_p D} \approx 10^{-3} \tag{7.38}
\]

It shows that the ratio between heat diffusion and mass diffusion is small, and that mass transfer mechanisms are faster than heat transfer mechanisms.

In summary, the mass conservation, momentum and mass transfer equations are formulated as follows:

\[
\frac{\partial}{\partial x} \rho_s u = r_{CO} + r_{CO_2} + r_{Zn} \quad \text{(Mass conservation)} \tag{7.39}
\]

\[
0 = -\frac{\partial p}{\partial x} - \frac{3u}{\rho_s} \frac{\partial^2 u}{\partial x^2} \quad \text{(Momentum)} \tag{7.40}
\]

\[
\frac{\partial}{\partial x} \rho_s m_i u = \frac{\partial}{\partial x} \left( \rho_s D_i,\text{eff} \frac{\partial m_i}{\partial x} + m_i \rho_s \sum_i D_i,\text{eff} \frac{\partial m_i}{\partial x} \right) + r_i \quad \text{for } i = \text{CO, CO}_2 \text{ and Zn} \tag{7.41}
\]

\( \text{(Mass transfer)} \)
7.3.7 Computation of the fluid flow

The mass transfer equations contain a convective term which depends on the flow field. However, it is normally not possible to simply specify the flow field; rather, the local velocity component and density field must be calculated from the appropriate governing equations. The difficulty in the calculation of the velocity field lies in the unknown pressure field. The pressure gradient forms a part of the source term for the momentum equation, but there is no obvious equation for obtaining the pressure. Patankar developed the popular SIMPLE and SIMPLER algorithms to solve the compressible and incompressible flow fields iteratively [49]. In our case, the two simplifications made in the previous chapter (creeping flow and pseudo steady state) allow a more analytical approach for solving the pressure, density and velocity fields.

First, two auxiliary functions are defined:

\[ z_1(x) = \frac{\sum m_i \cdot M_i}{R \cdot T} \quad \text{for } i = \text{CO, CO}_2 \text{ and Zn} \quad (7.42) \]

\[ z_2(x) = \int_0^x (r_{\text{CO}}(\xi) + r_{\text{CO}_2}(\xi) + r_{\text{Zn}}(\xi)) d\xi \quad (7.43) \]

Since \( T \) is given, \( z_1 \) is known. The function \( z_2 \) is easily obtained from the reaction rate equations for all spatial discretization nodes. For further simplification, derivation with respect to \( x \) is denoted by a prime. After taking advantage of all possible simplifications, the stationary mass conservation, momentum equations and the equation of state yields:

\[ (\rho_g \cdot u)' = r_{\text{CO}} + r_{\text{CO}_2} + r_{\text{Zn}} \quad (7.44) \]

\[ 0 = -p' - \frac{3}{\delta^2} u \quad (7.45) \]

\[ \rho_g = z_1 p \quad (7.46) \]

with the boundary conditions:

\[ u(x = 0) = 0 \quad (7.47) \]

for the velocity and

\[ p(x = L) = p_0 \quad (7.48) \]

for the pressure. Integrating the mass conservation equation (7.44) yields

\[ \rho_g(x)u(x) - \rho_g(x = 0)u(x = 0) = z_2(x) \quad (7.49) \]
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after dropping x and taking into account Equation (7.47):

\[ \rho_\delta u = z_2 \]  

(7.50)

Combining the momentum equation (7.45) with Equations (7.46) and (7.50):

\[ 0 = -p' - \frac{3\mu z_2}{\delta^2 z_i p} \]  

(7.51)

\[ p' p = \frac{1}{2} (p^2)' = -\frac{3\mu z_2}{\delta^2 z_i} \]  

(7.52)

Using the pressure boundary condition (7.48) and integrating Equation (7.52) yields:

\[ p(x) = \left( p_0^2 + \frac{6\mu}{\delta^2} \int z_i (\xi) d\xi \right)^{1/2} \]  

(7.53)

The velocity field is then computed directly by deriving the discretized pressure field and inserting the values in Equation (7.45).

7.4 Numerical method

7.4.1 Solving the system of equation

The energy and mass transfer equations are discretized following the finite volume formulation described in [49]. This leads to one tridiagonal and three pentadiagonal equation systems that are solved by the TDMA algorithm and the pentadiagonal equation solver described in [18]. The system of Equations (2.26), (2.35), (7.17), (7.27), (7.40), (7.41), and (7.53) is then solved iteratively at every time step, with the reaction rates and the mass transfer equations being under-relaxed to ensure fast convergence. The accuracy of the simulation is estimated by calculating the relative difference in the ZnO+C residual for \( N = 800 \) and \( N = 1600 \). This difference is equal to \( 10^{-5} \).

7.4.2 Grid generator

As shown in the heat transfer model presented in Chapter 4, the highest temperature gradients and reactions rates are found in the top layer of the bed. The numerical scheme can be optimized and the computational time reduced by refining the grid in a critical layer \( L_c \) containing \( N_c \) elements at the top of the bed. The thickness of the layer is defined empirically. The size of the elements in the critical layer is defined as

\[ Ax_i = \frac{L - L_c}{((N - N_c) - 1/2)(N_c - i + 2)^c} \]  

for \( i = 1 \ldots N_c \)  

(7.54)
Where the exponential constant $C$ is fitted such as:

$$\sum_{i=1}^{N_c} \Delta x_i = L_c$$  \hspace{1cm} (7.55)

The elements in the rest of the domain have a constant size defined as

$$\Delta x_i = \frac{L - L_c}{((N - N_c)^{-1/2})} \quad \text{for } i = N_c + 1 \ldots N$$  \hspace{1cm} (7.56)

Figure 7.4 shows the element size and distribution over the grid for the case $N = 100$, $N_c = 50$, $L = 4.72$ cm and $L_c = 1$ cm. The scheme allows a strong reduction of the element size on the top of the bed without producing any excessive size difference between neighboring elements.

![Figure 7.4: Element size and distribution in the grid. Each point on the plot represents a grid element.](image)

**7.4.3 Remeshing algorithm**

As the shrinking of the elements progresses, the size of the top elements decreases, which slows down the simulation. To address this issue, the grid is remeshed as soon as the size of one of the top elements decreases below a threshold value $\Delta x_{lim}$. The new grid uses then the same element size distribution for the critical layer as computed at the time $t_0$. One of the elements in the rest of the domain is removed if necessary. In this way, the number of elements progressively decreases as the simulation progresses. Figure 7.5 shows the size and the distribution of the elements at three different times $t_0 < t_1 < t_2 = t_2'$ for the same initial grid as in Figure 7.4. From $t_0$ to $t_2$, the elements shrink according to Equation (7.1) and the front of the bed recedes. At the time $t_2$, $\Delta x_i < \Delta x_{lim}$ and the grid is remeshed, using the same element size distribution for the critical layer than at $t = t_0$. The values of the temperature $T$ and reaction extents $X_c$ and $X_{2nO}$ are linearly interpolated for the grid at $t = t_2'$ using the values...
at \( t = t_2 \). Compared with the remeshing algorithm proposed in Chapter 4, this strategy ensures a sufficiently fine mesh at the top of the bed during the whole simulation.

![Figure 7.5: The grid is remeshed as soon as the size of one of the top elements decreases below a threshold value \( \Delta x_{lim} \). Each point on the plot represents a grid element.](image)

### 7.5 Results and validation

#### 7.5.1 Application to a standard case

The dynamic behavior of the packed bed is investigated under the conditions set out in Table 7.4. \( T_0 \) is set to a constant 300 K. \( T_{SiC} \) is heated from 300 K to 1500 K at a rate of 60 K/min and then held at a constant 1500 K during the rest of the simulation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:ZnO molar ratio</td>
<td>0.9</td>
</tr>
<tr>
<td>Initial ZnO+C batch [kg]</td>
<td>116</td>
</tr>
<tr>
<td>Initial bed temperature [K]</td>
<td>300</td>
</tr>
<tr>
<td>Constant temperature ramp for ( T_{SiC} ) [K/min]</td>
<td>60</td>
</tr>
<tr>
<td>Final temperature for ( T_{SiC} ) [K]</td>
<td>1500</td>
</tr>
<tr>
<td>Constant temperature ( T_0 ) [K]</td>
<td>300</td>
</tr>
<tr>
<td>Simulation time [min]</td>
<td>180</td>
</tr>
</tbody>
</table>
In the following Figures (7.6)-(7.15), the right end of the curves always represents the top of the bed. Figure 7.6 shows the temperature profile along the bed as a function of time. First, the temperature at the top is increased during the 20 min heat-up phase. From this point, the rates of the chemical reactions are sufficiently high to start the shrinking process and the front of the bed starts receding. The temperature keeps a more or less constant profile at the top of the bed for the rest of the simulation, indicating that the shrinking of the bed occurs faster than the heat transfer through the bed. Therefore, heat transfer is the rate controlling mechanism for this process.

Figure 7.6: Temperature profile along the bed as a function of reaction time (given in minutes on the plot).
Figure 7.7 shows the reaction rate profiles per unit volume for the charcoal gasification and the ZnO reduction by CO$_2$ at four different times. As a result of the temperature increase, the reaction rates start to rise after 15 minutes. After 30 minutes, the charcoal in the very top layer (less than 1mm) has been completely reacted, which means that the rate of gasification is zero there. After 30 min, the reaction rates keep the same profile in the top layer until the end of the simulation.

\[
\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2
\]

\[
\text{C} + \text{CO}_2 = 2\text{CO}
\]

Figure 7.7: Volumetric reaction rate for charcoal gasification and the ZnO reduction by CO$_2$ at four different times (given in minutes on the plot).
The proportion of charcoal and ZnO along the bed changes during the process, as depicted in Figure 7.8. Starting with a uniform C:ZnO molar ratio of 0.9, the charcoal totally vanishes at the top of the bed after approx. 30 min. This directly influences the reaction rate, as shown in Figure 7.7.

The CO, CO₂ and Zn volumetric gas production rates \( r_{CO} \), \( r_{CO2} \) and \( r_{Zn} \) are given by Equations (7.2)-(7.4) and shown in Figures (7.9)-(7.11) after 15, 20 and 30 min in the top layer of the bed. Because reaction (2.2) needs one mole CO per mole ZnO and reaction (2.3) needs one mole CO₂ per mole C, both the CO and the CO₂ volumetric production rates can have negative values along the bed. There is a transition after approx. 20 minutes in the first millimeter of the bed, in which \( r_{CO} \) starts a decrease and \( r_{CO2} \) an increase due to the vanishing charcoal in this layer. After 30 min, the bed has shrunk by more than 8 mm and the volumetric gas production rates keep a constant profile along the bed until the end of the simulation.
Figure 7.9: CO, CO₂ and Zn volumetric gas production rates \( r_{CO}, r_{CO_2} \) and \( r_{Zn} \) after 15 minutes.

Figure 7.10: CO, CO₂ and Zn volumetric gas production rates \( r_{CO}, r_{CO_2} \) and \( r_{Zn} \) after 20 minutes.
Figure 7.11: CO, CO₂ and Zn volumetric gas production rates $r_{CO}$, $r_{CO₂}$ and $r_{Zn}$ after 30 minutes.

Figure 7.12 shows the gas velocity profiles at different times. It becomes significant after approx. 15 min, which is also the time at which the chemical reactions actually start.

Figure 7.12: Gas velocity profiles as a function of times (given in minutes on the plot).
Figure 7.13 shows the pressure drop along the bed for different times. Velocity and pressure drop are closely related together by Equation (7.40), which explains their similar (but inverted) profile shapes.

Figure: 7.13: Pressure drop along the bed for different times (given in minutes on the plot).
The mass transfer equation (7.41) solves the concentration profile for each gas species in the domain. The results are presented in Figure (7.14), in which the CO, CO₂ and Zn mole fraction profiles are given at four different times. The concentrations reach a more or less constant and uniform value after 30 min, except for the CO and CO₂ mole fraction in the top layer, which are affected by the locally stronger reaction rates.

Figure 7.14: CO, CO₂ and Zn mole fraction profiles are given at four different times (given in minutes on the plot).
Finally, the volumetric gas production rates $r_{CO}$, $r_{CO2}$ and $r_{Zn}$ are integrated over the whole bed height at every time step (Figure 7.15). The rates are approximately constant, except for a 20 minutes start-up heating phase.

![Graph showing gas output over time](image)

**Figure 7.15:** CO, CO$_2$ and Zn gas output as a function of time.

### 7.5.2 Influence of the C:ZnO molar ratio

The ratio of charcoal to ZnO in the bed can be varied as an input parameter in the model. This directly affects the chemical reaction rates and the gas flow profiles within the bed. According to Equation (2.1), the C:ZnO molar ratio $v$ can only be varied between 0.5 and 1, where $v = 0.5$ results in pure CO$_2$ and $v = 1$ results in pure CO. But the mass transport phenomena taking place within the bed are more complex, allowing the range $0.45 > v > 0.99$. Therefore, for $v < 0.5$, some ZnO is left unreacted if the reactor is operated until the whole charcoal is consumed. For $v > 0.99$, the CO$_2$ partial pressure becomes so small that the gasification of charcoal, Equation (2.3), cannot take place anymore.

The influence of the C:ZnO molar ratio is investigated under the conditions set out in Table 7.4, except that $v$ is varied from 0.45 to 0.99. The overall reaction extent and the CO$_2$ fraction are plotted in function of $v$ in Figure 7.16. The overall reaction extent is defined as the total mass reacted divided by the initial mass in the bed. It peaks at $v = 0.97$ where the Zn yield is the highest and where the system reaches its maximal efficiency.

The CO$_2$ fraction is defined as the total CO$_2$ produced divided by the total of the CO$_2$ + CO produced. It is an important parameter for the quenching process because a too high CO$_2$ fraction favors the recombination of Zn with CO$_2$. For low $v$, most of the CO is produced
during a first 30 min phase where the charcoal is still not depleted in the top layer. After this, a layer of pure ZnO forms at the top of the bed, acting as thermal resistance and reducing the overall efficiency.

The optimal \( v \) is not necessarily the C:ZnO molar ratio, for which the Zn yield is the highest. The idea behind the solar carbothermal reduction of ZnO investigated in the Solzinc project is to convert as much solar energy as possible into Zn by using as little C as possible in order to minimize the CO\(_2\) emissions. Therefore, operation with \( v = 0.75-0.8 \) would result in approximately the same Zn yield as for \( v = 0.97 \), but with less charcoal. This problem can be bypassed by using biomass as the source of carbon.

![Figure 7.16: Overall reaction extent and CO\(_2\) fraction in function of \( v \)](image)

7.5.3 Validation

The results obtained with the model are compared to three experimental runs, (a), (b) and (c) carried out under the experimental conditions set out in Table 7.5. Experiments (a) and (b) have been performed at PSI with the small-scale reactor, whereas experiment (c) has been performed at the Weizmann Institute of Science (WIS) with the scale-up version of the reactor (see Chapter 3). For run (a) and (b), the bed temperature is measured by a thermocouple submerged at a height of 30 mm.
Table 7.5: Experimental conditions of the three solar experimental runs (a), (b) and (c).

<table>
<thead>
<tr>
<th>Solar run</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:ZnO molar ratio</td>
<td>0.8</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Initial ZnO+C batch [kg]</td>
<td>0.5</td>
<td>0.5</td>
<td>116</td>
</tr>
<tr>
<td>Initial bed temperature [K]</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Reactor's aperture diameter [m]</td>
<td>0.065</td>
<td>0.065</td>
<td>0.48</td>
</tr>
<tr>
<td>$L(=0)$ [m]</td>
<td>0.063</td>
<td>0.069</td>
<td>0.173</td>
</tr>
<tr>
<td>Measured $T_0(t)$</td>
<td>Fig.4.7a</td>
<td>Fig.4.7b</td>
<td>Fig. 7.17</td>
</tr>
<tr>
<td>Measured $T_{SC}(t)$</td>
<td>Fig.4.7a</td>
<td>Fig.4.7b</td>
<td>Fig. 7.17</td>
</tr>
</tbody>
</table>

Figure 7.17: Measured temperature profiles $T_{SC}(t)$ and $T_0(t)$ at the boundaries for the solar experimental run (c), described in Table 7.5. 25 min after the experiment started and during 15 min, the amount of concentrated sunlight entering the reactor was kept constant for safety reasons, which explains the slow increase in temperature of the radiative plate during this time.
Figures 7.18 and 7.19 show the variation of the temperature with time at a height of 30 mm for the two runs (a) and (b) of Table 7.5. Solid curves represent the numerical prediction; the dotted curves represent the measurements. For run (b), the agreement is relatively good, but for run (a), the simulated temperatures are too low after about 50 min (i.e. once the reaction started).

The temperature within the bed is mainly influenced by the effective thermal conductivity of the powder. In both cases, the temperatures are overestimated below 700 K and underestimated between 700 K and 1400 K. The Rosseland approximation used in this model to extrapolate the thermal conductivity at higher temperatures depends only on the temperature and the extinction coefficient. In reality, the effective thermal conductivity is also affected by sintering effects or variations in the porosity or the composition of the powder material. Furthermore, the Rosseland approximation loses accuracy near the boundaries if the temperature gradient is too high [56].

The speed at which the front of the bed recedes has also an important influence on the temperature within the bed. If the simulated reaction rate is too slow, e.g. due to a too low thermal conductivity, the distance between the irradiated front and the point situated at a height of 30 mm is larger than in the experiment. In such a case, the simulated temperature at a height of 30 mm would be too low, as it the case for run (a).

Figure 7.18: Calculated and measured temperature variation with time at a height of 30 mm for the solar experimental run (a).
The calculated (solid curve) and measured (dotted curve) rate of CO and CO$_2$ gas output is shown in Figures 7.20-7.22 for experimental runs (a), (b) and (c). The calculated values are the result of the integration over the bed of the reaction rate for each control volume at each time step. The experimental values are recorded by on-line gas chromatography. Overall, the agreement is good, but the model seems to underestimate the CO gas output for run (b) and (c).

The kinetic parameters for the reduction of ZnO with CO and the charcoal gasification have been determined separately by thermogravimetry. However, in the packed bed of the reactor, the ZnO and the charcoal powder are mixed together, which affects the gas diffusion at the particle level. This has a direct influence on the reaction rates, which can be become apparent if the quality of the mixing is not exactly the same between the different runs. Furthermore, it is difficult to obtain robust kinetic parameters for such a complex thermochemical system: pyrolysis, sintering of ZnO and porosity changes affect the gas composition, which are also explanations for the discrepancy between the measured and simulated data in Figures 7.21 and 7.22.

The important CO$_2$ production rate observed in run (c) is explained by an addition of air coming from a not perfectly gas-tight pump in the gas recycling system of the 300 kW reactor. This air reacts with the charcoal to form some additional CO$_2$. 

![Figure 7.19: Calculated and measured temperature variation with time at a height of 30 mm for the solar experimental run (b).](image)
Figure 7.20: Calculated and measured reaction rate vs. time for solar experimental runs (a) described in Table 7.5.

Figure 7.21: Calculated and measured reaction rate vs. time for solar experimental runs (b) described in Table 7.5.
7.6 Chapter Summary

In this chapter, the heat transfer model of chapter 4 is extended to a mass transfer analysis by accounting for gas diffusion and convection in the packed bed. It uses an improved kinetic model based on the two parallel reactions: the ZnO reduction by CO\(_2\) and the charcoal gasification. The quasi-steady-state Navier-Stokes equation is coupled to the chemical rate laws and the energy equation in the solid phase. The model allows the determination of the temperature, velocity, pressure drop, gas concentrations, reaction extents and reaction rates profiles. The influence of the C:ZnO molar ratio is investigated on the overall reaction extent and the CO\(_2\) output fraction. Finally, the simulated data are compared to experimental data obtained from a 5 kW and a 300 kW reactor.
Chapter 8

Summary and outlook

This thesis has investigated the fundamentals of heat and mass transfer phenomena in a shrinking packed-bed undergoing a high-temperature thermochemical transformation. The governing conservation equations have been formulated and corresponding numerical models have been developed and applied to a packed-bed solar chemical reactor designed for the carbothermic reduction of zinc oxide, in which the shrinking of the bed is caused by the transformation of solid phase reactants ZnO and C into gas phase products Zn(g), CO, and CO2.

The thermodynamics and kinetics of the carbothermic reduction of ZnO have been thoroughly examined. The reaction proceeds endothermically above 1230 K via two solid-gas intermediate reactions: the reduction of ZnO with CO and the charcoal gasification. Below about 1000 K, ZnO and C are thermodynamically stable components. Above 1410 K, the reduction reaches completion, and the chemical system consists of a single gas phase containing a mixture of Zn(g), CO, and CO2. The chemical kinetics of the overall ZnO carbo-reduction is based on the shrinking core mechanism, whose temperature dependency can be described by the Arrhenius law with activation energy $E_A = 201.5$ kJ/mol, determined experimentally by thermogravimetry. The kinetics of the gasification of beech charcoal powder involves two regimes where the reaction rate is either limited by the chemical reaction or by diffusion of gases. For the chemical reaction limiting regime, the activation energy is found to be $E_A = 1.61 \times 10^5$ J/mol with a pre-exponential factor $k_0 = 104.6$ mol s/m kg and a reaction order $n = 0.61$. For the mass transport limited regime, the temperature dependence is given by the Chapman-Enskog theory with reaction order 1. The gasification kinetic model was validated with thermogravimetry experiments.

The solar chemical reactor concept for the carbothermic reduction of ZnO features two cavities in series, with the first one functioning as the solar absorber and the second one as the reaction chamber. A 5 kW reactor prototype was fabricated and tested in a high-flux solar furnace. The transient heat transfer process occurring in the solar chemical reactor is numerically modeled. The 1D-transient energy conservation equation was solved numerically by the finite volume technique for a shrinking packed bed of a ZnO+C mixture. The model allows the determination of the temperature and reaction rate profiles in a shrinking domain as a function of the temperature at the boundaries. Validation was accomplished with experimentally measured temperatures and ZnO decomposition rates as a function of time obtained for the 5 kW solar reactor. Conditions observed were typical of ablation processes, where the heat transfer through the bed becomes the rate controlling mechanism.
This heat transfer analysis revealed the importance of knowing accurately the effective thermal conductivity coefficient of the powder mixture. Consequently, a radial heat flow apparatus was built for the measurement of this property in the range 470-872 K. Extrapolation to higher temperatures was accomplished by applying the Rosseland approximation for an optically thick medium. The material optical property required for this method is the extinction coefficient, determined by measuring the attenuation of radiation through a thin layer of ZnO+C powder. Its determination involved solving the equation of radiative transfer by the Monte-Carlo technique, until the computed radiation intensities matched the experimentally measured values.

The transient heat transfer model was then extended to a mass transfer analysis by accounting for gas diffusion and convection in the packed bed. The quasi-steady-state Navier-Stokes equation was coupled to chemical kinetics and the energy equation in the solid phase. The model allows the determination of the temperature, velocity, pressure drop, gas concentrations, reaction extents and reaction rates profiles as a function of the control parameters, such as boundary temperatures and the C:ZnO molar ratio. The computed results were compared to experimental data obtained from a 5 kW and a 300 kW reactor.

The heat and mass transfer analysis can be further developed to include additional aspects of chemical reactor engineering, such as powder sintering, charcoal pyrolysis and other intermediate chemical reactions, condensation of zinc vapor diffusing to colder regions of the bed, and the porosity variation. The limitations posed at the boundaries by the Rosseland approximation can be eliminated by using the two-flux method for radiative heat transfer in translucent media.

The reactor model developed in this investigation can in general be applied for high-temperature gas-solid thermochemical processes in shrinking packed-beds, such as carbothermic reduction of metal oxides, gasification of carbonaceous materials, and decomposition processes.
Material properties

The source of carbon for the carbothermic reduction of ZnO in the Solzinc project is a beech charcoal dust provided by the German company Chemviron Carbon GmbH. The ZnO comes from the German-based Grillo Werke AG. Both materials are powders which are mixed together in a C:ZnO molar ratio equal to 0.8:1 or 0.9:1. The density $\rho_s$ of the mixture is $450 \pm 50$ kg/m$^3$. But $\rho_s$ can also exceed 1000 kg/m$^3$, depending on the way it is mixed and the pressure exerted on the sample.

A.1 ZnO

The ZnO 2011 from Grillo is produced using the so-called American process, where a coal/zinc sulfide mix is smelted, followed by an oxidation of the zinc vapours. Zinc Oxide is an amorphous white or yellowish powder, insoluble in water and alcohol but soluble in acid and alkali. It is usually used as a pigment in compounding rubber, as a white pigment in the ceramics industry, as an opaque base in cosmetics, and it has other applications in the paper, the paints and the optical glass industries.

- Molar weight: 81.39 g/mol
- Density (crystal): 5660 kg/m$^3$
- Density (powder, measured): $1000 \pm 100$ kg/m$^3$
- BET (manufacturer specifications): 1.7 m$^2$/g
Appendix A. Material properties

- Composition (manufacturer specifications):

  Table A.1: ZnO composition

<table>
<thead>
<tr>
<th>Material</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>99.1%</td>
</tr>
<tr>
<td>Pb</td>
<td>0.19%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.011%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0014%</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0058%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.011%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0002%</td>
</tr>
<tr>
<td>Humidity 105°C</td>
<td>0.19%</td>
</tr>
</tbody>
</table>

- Emissivity (smooth surface) [62]:

  Table A.2: Emissivity at higher temperatures

<table>
<thead>
<tr>
<th>Integral normal emissivity</th>
<th>Temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>1140</td>
</tr>
<tr>
<td>0.81</td>
<td>1240</td>
</tr>
<tr>
<td>0.82</td>
<td>1330</td>
</tr>
</tbody>
</table>
• Scanning Electron Microscope (SEM) micrographs

In the pictures, the size of the ZnO particles ranges from 30-200 μm. They are made out of solid conglomerates (Figure A.1c) or μm-sized particles (Figure A.1d). The particles in Figure 1a seem to have been flattened, suggesting that they are made out of a porous matrix.

Figure A.1: SEM pictures of Grillo ZnO 2011.
Particle size distribution

The laser diffraction technique is applied to a ZnO sample. In this method, the powder from which the size distribution must be determined is suspended in an appropriate liquid, in this case H₂O. The suspension is pumped through a measuring cell and illuminated by a laser beam while affected by an ultrasonic pulse. The scattered light is collected by a detector and the size distribution of the particles can be calculated from the diffraction pattern.

Figure A.2: The cumulative distribution and probability density function as measured by the laser diffraction technique.

The results plotted in Figure A.2 show an average particle diameter of approximately 2 μm. This is in contradiction to the size of the particles observed on the SEM micrographs (Figure A.1), in which the average particle size is of the order of 100 μm. A possible reason for this discrepancy is the ultrasonic processing during the measurement, which might destroy the structure of the powder particles. The average particle size considered in this thesis is therefore based on the SEM pictures.
A.2 Beech charcoal dust

Charcoal is the solid residue remaining when wood is carbonised or pyrolysed under controlled conditions in a closed space such as a charcoal kiln. Control is exercised over the entry of air during the pyrolysis or carbonisation process so that the wood does not merely burn away to ashes, as in a conventional fire, but decomposes chemically to form charcoal. The pyrolysis process produces charcoal which consists mainly of carbon, together with a small amount of tarry residues, the ash contained in the original wood, combustible gases, tars, a number of chemicals (mainly acetic acid and methanol) and a large amount of water which is given off as vapor from the drying and pyrolytic decomposition of the wood.

- Molar weight: 12 g/mol
- Density (pure, measured\(^1\)): 1507 kg/m\(^3\)
- Density (bulk density, measured): 315 ± 30 kg/m\(^3\)
- BET: 0.13 m\(^2\)/g

The usual components of industrial charcoal are:

- \textit{C-fix}: The fixed carbon content is the most important constituent in metallurgy processes, e.g. like the Solzinc process, since it is the fixed carbon which is responsible for reducing the metal oxides to produce metal.

- \textit{Moisture}: It lowers the calorific or heating value of the charcoal. Its content is determined by oven drying a weighed sample of the charcoal and is expressed as a percentage of the initial wet weight.

- \textit{Volatiles}: The volatile matter other than water in charcoal comprises all those liquid and tarry residues not fully driven off in the process of carbonization. Increasing carbonization temperature and total time in the kiln decreases the volatile content, but also decreases the yield of charcoal produced from a given weight of wood. Thus for sustainable applications like the solar carbothermic reduction of ZnO, one must be aware that a low volatile content for better chemical reaction rates is associated with a low yield during the charcoal production.

- \textit{Ash}: The ash content is determined by heating a weighed sample to red heat with access of air to burn away all combustible matter. The residue is the ash. It is mineral matter, such as clay, silica and calcium and magnesium oxides, etc., present in the original wood and picked up as contamination from the earth during processing.

\(^1\) Measured by ARP / ECV GesmbH
8700 Leoben, Austria
Table A.3: beech charcoal dust composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-fix</td>
<td>83%</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt;8%</td>
</tr>
<tr>
<td>Volatiles</td>
<td>&lt;13%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;4%</td>
</tr>
</tbody>
</table>

- Optical properties
  The emissivity of charcoal found in the literature ranges from 0.74 to 0.95 [62]. It is basically temperature independent and reaches values as high as 0.98 at wavelengths below 600 nm. In this work, the emissivity of beach charcoal is assumed to be 0.82.

- SEM-micrographs
  Charcoal dust is actually a byproduct of the wood carbonisation. The extreme variations in shapes and sizes observable in Fig A.3a come from its organic nature. Figure A.3b shows the typical arrayed-shaped structures that can be found in tree fibres. The observable range of particle sizes is 10-300 μm.

Figure A.3: SEM pictures of beech charcoal dust.
Appendix A. Material properties

- Particle size distribution (vibrosieve analysis\(^1\)).

![Particle size distribution and residuum](image)

**Figure 4:** Particle size distribution and residuum measured by vibrosieve analysis.

A.3 Sintering analysis

A.3.1 Motivation

Sintering of powders is a thermal process that combines distinct powdered grains into one cohesive material \([4]\). It concerns mainly metallic and ceramic powders like ZnO. This mechanism can be seen as the welding together of separate powder particles into a single solid material, which takes place below the melting point of the material, but at a temperature sufficiently high to allow an acceptable rate of diffusion to occur. Sintering is responsible for grain growth, pore shrinkage or growth, particle modification and increase in bulk density \([65]\).

Understanding sintering effects is essential for performing good measurements of the effective thermal conductivity coefficient. When powder compacts are sintered, the initial stage is the growth of necks between contacting particles, which increases the thermal conductivity of the powder \([45]\). Furthermore, an increase in the bulk density and/or a hardening of the powder at higher temperatures have a direct influence on the design of a setup to measure this coefficient. For instance it is impossible to remove a hardened powder

\(^1\) Measured by Bühler AG
9240 Uzwil, Switzerland
from the radial heat flow device described in Chapter 5, used to measure effective thermal coefficients.

A.3.2 Experimental and results

Several tests were done with a tubular oven to test the sintering properties of ZnO and the mixture ZnO+C (C:ZnO molar ratio = 0.9). The purpose of this qualitative study is to observe at which temperature the material solidifies in order to estimate the temperature at which the sintering process starts. All tests lasted 5 hours, including heating up at a rate 25 K/min. The material was put in a ceramic crucible of about 7cm³ and inserted into the oven in a nitrogen atmosphere.

The following table summarises the observations made on the samples after testing.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature [K]</th>
<th>Observations after testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>673</td>
<td>No sintering</td>
</tr>
<tr>
<td>ZnO</td>
<td>873</td>
<td>Powder slightly more compact, partial sintering</td>
</tr>
<tr>
<td>ZnO</td>
<td>973</td>
<td>Powder relatively hard, advanced sintering</td>
</tr>
<tr>
<td>ZnO</td>
<td>1173</td>
<td>Powder hardened, totally sintered</td>
</tr>
<tr>
<td>ZnO+C</td>
<td>873</td>
<td>No sintering</td>
</tr>
<tr>
<td>ZnO+C</td>
<td>973</td>
<td>Powder more compact, partial sintering, chemical reaction started</td>
</tr>
</tbody>
</table>

The minimal sintering temperature for pure ZnO is approximately 873 K, whereas sintering starts only between 873 K and 973 K for ZnO+C. The addition of charcoal particles to pure ZnO seems to increase this minimal temperature by interfering with the sintering process.
Bibliography


[74] D. C. Wilcox, Basic Fluid Mechanics, DCW industries, La Cañada (CA), United-States, 1997.


Curriculum Vitae

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Refereed journals


Conference proceedings


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