FLUIDIZED BED ROASTING OF ZINC SULFIDE CONCENTRATE: FACTORS AFFECTING THE PARTICLE SIZE DISTRIBUTION

by

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Abstract

An experimental programme was established to study the effect of process parameters on the agglomeration behaviour of particles within a fluidized bed zinc concentrate roaster. A 102 mm internal diameter pilot scale roaster was designed, constructed and commissioned. Tests were then conducted with two industrial zinc concentrates at different temperatures (875-975°C), superficial gas velocities (0.25-0.5 m/s), oxygen enrichments (inlet oxygen concentration: 21-30 vol%), stoichiometric excess oxygen (0-80%), initial inert bed materials (silica and alumina) and average bed particle sizes (81-223 μm).

With the exception of one experiment, all experiments were carried out with a zinc concentrate containing 53-54 wt% Zn, 30.5-31 wt% S, 4.5 wt% Fe, 3.5 wt% Pb, 0.34 wt% Cd, 0.145 wt% Cu, and 1.5 wt% SO₄/S, with 80% of particles smaller than 24 μm. One experiment tested a different zinc concentrate, containing 51 wt% Zn, 30 wt% S, 8.1 wt% Fe, 4.7 wt% Pb, 0.14 wt% Cd, 0.05 wt% Cu, 1.5 wt% SO₄/S, with 80% of particles smaller than 33 μm.

The experimental results indicated that the temperature and excess oxygen had the greatest effect, followed by bed material, its size distribution and the superficial gas velocity. Agglomeration increased when excess oxygen approached 0%. Lead, present in small proportion in the concentrate (3.5 wt% Pb), was observed to segregate to the larger bed particles. Lead sulfide volatilized from the zinc concentrate and deposited as a lead oxide/sulfate melt onto inert bed particles which caused fine particles to stick to the surface of larger particles. The lead concentration in the agglomerated particles suggested that the agglomeration mechanism, similar to the coating mechanism, relies on the transport of lead species from reacting particles to inert particles.

The generalized slugging-bubbling fluidized bed reactor model (GSBM) handled seamlessly the transition from bubbling to slugging fluidization, using probabilistic averaging. The ratio of the bubble diameter to the column diameter was employed to correlate the probability of each of these fluidization flow regimes. The generalized fluidized bed reactor model was coupled to a solids reaction model and used to evaluate the effect of roasting parameters on the oxygen concentration in contact with the particles.

Modelling of the fluidized bed under industrial (bubbling) and laboratory (slugging) conditions indicated that the effect of various parameters on the particle-averaged oxygen concentration depended greatly on the reactor in question (industrial vs laboratory). For the laboratory roaster, the effect of particle size was negligible, while the effect of excess oxygen was significant. For the industrial roaster, the effect of excess oxygen depended on the average particle size. For a relatively large average bed particle size (150 μm), the effect of excess oxygen was limited. For a small average bed particle size (65 μm), the effect of excess oxygen was large, comparable to that in the laboratory roaster.
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Nomenclature

Letters

\( A \quad \text{Bed cross-sectional area [m}^2\text{]}\)
\( A_d \quad \text{Distributor area per orifice [m}^2\text{]}\)
\( \alpha_i \quad \text{Interphase mass transfer exchange area [m}^{-1}\text{]}\)
\( Ar \quad \text{Archimedes number (Ar} = d_f^3 = \frac{p_d(p_p-p_g)g d_f^3}{\mu_s^2} \text{)} [-]\)
\( A_{sp} \quad \text{Dimensionless group (A}_{sp} = \frac{C_A \nu_c C_p}{\nu_A C_T c_k} \text{(section 5.2.3)} [-]\)
\( CD_{ei} \quad \text{Product of the total gas concentration (sum of all gaseous species) times the gas diffusivity of i (section 5.2.3) [mol/(m s)]}\)
\( C_{Hi} \quad \text{Molar concentration of species i in H-phase [mol/m}^3\text{]}\)
\( \bar{C}_i \quad \text{Particle-averaged molar concentration for species i in entire bed [mol/m}^3\text{]}\)
\( C_{i,in} \quad \text{Inlet molar concentration of species i [mol/m}^3\text{]}\)
\( C_{ji} \quad \text{Concentration of gaseous species i, j=c: core, o: bulk gas phase, s: surface (section 5.2.3) [mol / m}^3\text{]}\)
\( \bar{C}_{ji} \quad \text{Particle-averaged molar concentration for species i in phase j [mol/m}^3\text{]}\)
\( C_{Li} \quad \text{Molar concentration of species i in L-phase [mol/m}^3\text{]}\)
\( C_{pc} \quad \text{Heat capacity of unreacted core (section 5.2.3) [J/(kg K)]}\)
\( C_{pe} \quad \text{Volumetric heat capacity of product layer (section 5.2.3) [J/(m}^3\text{ K)]}\)
\( C_S \quad \text{Concentration of solid reactant (section 5.2.3) [mol / m}^3\text{]}\)
\( C_T \quad \text{Total gaseous molar concentration (C}_{T} = \frac{C_T}{RT} \text{) [mol/m}^3\text{]}\)
\( D \quad \text{Reactor diameter [m]}\)
\( DD_0 \quad \text{Lower bound of bubbling-slugging transition interval [-]}\)
\( DD_1 \quad \text{Upper bound of bubbling-slugging transition interval [-]}\)
\( D_e \quad \text{Effective bubble diameter [m]}\)
\( D_{e,0} \quad \text{Initial effective bubble diameter [m]}\)
\( D_{e,AT_o} \quad \text{Effective gas diffusivity at temperature To for gaseous reactant A [m}^2\text{/s]}\)
\( D_{e,GT_o} \quad \text{Effective gas diffusivity at temperature To for gaseous product G [m}^2\text{/s]}\)
\( D_{e,\infty} \quad \text{Maximum bubble diameter due to coalescence and growth [m]}\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{e,\text{max}}$</td>
<td>Maximum effective bubble diameter [m]</td>
</tr>
<tr>
<td>$D_g$</td>
<td>Gas diffusivity [m$^2$/s]</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle surface to volume mean diameter [m]</td>
</tr>
<tr>
<td>$d_{pi}$</td>
<td>Average diameter of each size fractions (Chapter 3) [m]</td>
</tr>
<tr>
<td>$d_p^*$</td>
<td>Dimensionless particle diameter $(d_p\left(\frac{\rho_g(\rho_p-\rho_g)}{\mu_g}\right)^{1/3})$ [-]</td>
</tr>
<tr>
<td>$D_{\text{radial}}$</td>
<td>Radial diffusion coefficient of solids in a fluidized bed [m$^2$/s]</td>
</tr>
<tr>
<td>$d_v$</td>
<td>Particle volume mean diameter (Chapter 3) [m]</td>
</tr>
<tr>
<td>$E$</td>
<td>Bed expansion [m/m]</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy [J/mol]</td>
</tr>
<tr>
<td>$E_{\text{max}}$</td>
<td>Maximum slugging bed expansion [m/m]</td>
</tr>
<tr>
<td>$\text{ExcessO}_2$</td>
<td>Stoichiometric excess of oxygen [-]</td>
</tr>
<tr>
<td>$f$</td>
<td>Solids mean residence time factor [-]</td>
</tr>
<tr>
<td>$F_{\text{Carryover}}$</td>
<td>Solids flowrate in carryover [kg/s]</td>
</tr>
<tr>
<td>$F_{\text{Feed}}$</td>
<td>Solids flowrate in feed [kg/s]</td>
</tr>
<tr>
<td>$F_{Hi}$</td>
<td>Molar flowrate of species i in H-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{Hi,in}$</td>
<td>Inlet molar flowrate of species i in H-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{HT}$</td>
<td>Total molar flowrate in H-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{Li}$</td>
<td>Molar flowrate of species i in L-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{Li,in}$</td>
<td>Inlet molar flowrate of species i in L-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{LT}$</td>
<td>Total molar flowrate in L-phase [mol/s]</td>
</tr>
<tr>
<td>$F_{\text{Overflow}}$</td>
<td>Solids flowrate in overflow [kg/s]</td>
</tr>
<tr>
<td>$Fr$</td>
<td>Froude number $(Fr = \frac{U_{\text{max}}}{\sqrt{gD}})$ [-]</td>
</tr>
<tr>
<td>$f_s$</td>
<td>Slug shape factor [m$^3$/m$^3$]</td>
</tr>
<tr>
<td>$F_{T}$</td>
<td>Total molar flowrate in reactor [mol/s]</td>
</tr>
<tr>
<td>$G$</td>
<td>Dimensionless group $(G = -\frac{\rho_c C_{\text{pc}} T_0}{\nu_A G_4(-\Delta H)})$ (section 5.2.3) [-]</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration due to gravity (9.81) [m/s$^2$]</td>
</tr>
<tr>
<td>$H$</td>
<td>Expanded bed height [m]</td>
</tr>
</tbody>
</table>

xv
**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_c$</td>
<td>Convective heat transfer coefficient (section 5.2.3) [J/(m$^2$ K s)]</td>
</tr>
<tr>
<td>$H_{mf}$</td>
<td>Bed height at minimum fluidization [m]</td>
</tr>
<tr>
<td>$h_r$</td>
<td>Radiational heat transfer coefficient (section 5.2.3) [J/(m$^2$ K$^4$ s)]</td>
</tr>
<tr>
<td>$I$</td>
<td>Slug surface integral (section 5.1.8) [-]</td>
</tr>
<tr>
<td>$J$</td>
<td>Axial solids flux due to bubbles [kg m$^{-2}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Effective thermal conductivity of product layer (section 5.2.3) [J/(m s K)]</td>
</tr>
<tr>
<td>$k_{LH}$</td>
<td>Interphase mass transfer coefficient [m/s]</td>
</tr>
<tr>
<td>$k_m$</td>
<td>Gas-particle mass transfer coefficient [m/s]</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Gas reaction rate constant [s$^{-1}$]</td>
</tr>
<tr>
<td>$k_0^r$</td>
<td>Pre-exponential constant for reaction rate constant (section 5.2.3) [m/s (depends on reaction orders)]</td>
</tr>
<tr>
<td>$k_s(T_c)$</td>
<td>Reaction rate constant at temperature $T_c$ (section 5.2.3) [m/s (depends on reaction orders)]</td>
</tr>
<tr>
<td>$L$</td>
<td>Slug length (section 5.1.8) [m]</td>
</tr>
<tr>
<td>$m$</td>
<td>Reaction order with respect to solid reactant $S$ (section 5.2.3) [-]</td>
</tr>
<tr>
<td>$M_{bed}$</td>
<td>Bed mass [kg]</td>
</tr>
<tr>
<td>$M_{Concentrate}$</td>
<td>Mass of concentrate equivalent to one mole of zinc sulfide [g concentrate / mol ZnS]</td>
</tr>
<tr>
<td>$M_{ZnS}$</td>
<td>Molar weight of zinc sulfide [g ZnS / mol ZnS]</td>
</tr>
<tr>
<td>$n$</td>
<td>Reaction order with respect to gaseous reactant $A$ (section 5.2.3) [-]</td>
</tr>
<tr>
<td>$n_{O_2}$</td>
<td>Number of moles of oxygen [moles]</td>
</tr>
<tr>
<td>$Nu_c$</td>
<td>Modified Nusselt number for convection ($Nu_c = Rh_c/k_e$)(section 5.2.3) [-]</td>
</tr>
<tr>
<td>$Nu_r$</td>
<td>Modified Nusselt number for radiation ($Nu_r = Rh_rT_o^3/k_e$)(section 5.2.3) [-]</td>
</tr>
<tr>
<td>$n_{ZnS}$</td>
<td>Number of moles of zinc sulfide [moles]</td>
</tr>
<tr>
<td>$P_{bubbling}$</td>
<td>Probability of bubbling [-]</td>
</tr>
<tr>
<td>$P_{slugging}$</td>
<td>Probability of slugging [-]</td>
</tr>
<tr>
<td>$p_{stream}$</td>
<td>Particle size distribution function of stream [-]</td>
</tr>
<tr>
<td>$P_T$</td>
<td>Total reactor pressure [Pa]</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant, 8.314 [J/ (mol K)]</td>
</tr>
</tbody>
</table>
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_A )</td>
<td>Reaction rate of gas A (section 5.2.3) ([\text{mol}/(\text{m}^2 \text{s})])</td>
</tr>
<tr>
<td>( r_C )</td>
<td>Radius of core (section 5.2.3) ([\text{m}])</td>
</tr>
<tr>
<td>( \text{Re}_{mf} )</td>
<td>Reynolds number at minimum fluidization ( \left( \text{Re} = \frac{\rho U_{mf} D}{\mu} \right) ) ([-])</td>
</tr>
<tr>
<td>( J )</td>
<td>Rate of reaction of oxygen ([\text{mol} \text{ m}^{-2} \text{ s}^{-1}])</td>
</tr>
<tr>
<td>( R_p )</td>
<td>Particle radius ([\text{m}])</td>
</tr>
<tr>
<td>( r_S )</td>
<td>Reaction rate of solid S (section 5.2.3) ([\text{mol}/(\text{m}^2 \text{s})])</td>
</tr>
<tr>
<td>( Sh )</td>
<td>Modified Sherwood number ( \left( \text{Sh} = \frac{R_p k_m}{D_e A_T o} \right) ) ([-])</td>
</tr>
<tr>
<td>( T )</td>
<td>Reactor temperature ([\text{K}])</td>
</tr>
<tr>
<td>( T )</td>
<td>Slug to slug distance (tail-to-nose) (section 5.1.8) ([\text{m}])</td>
</tr>
<tr>
<td>( T_C )</td>
<td>Core temperature (section 5.2.3) ([\text{K}])</td>
</tr>
<tr>
<td>( t_{cr} )</td>
<td>Time for complete reaction of solid particle ([\text{s}])</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>Initial temperature (section 5.2.3) ([\text{K}])</td>
</tr>
<tr>
<td>( t_{radial} )</td>
<td>Radial mixing time (lateral mixing time) ([\text{s}])</td>
</tr>
<tr>
<td>( T_S )</td>
<td>Surface temperature (section 5.2.3) ([\text{K}])</td>
</tr>
<tr>
<td>( t_{turnover} )</td>
<td>Turnover time (axial mixing time) ([\text{s}])</td>
</tr>
<tr>
<td>( T_W )</td>
<td>Wall temperature (section 5.2.3) ([\text{K}])</td>
</tr>
<tr>
<td>( U )</td>
<td>Reactor superficial gas velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_b )</td>
<td>Bubble rise velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_{b\infty} )</td>
<td>Isolated bubble rise velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_c )</td>
<td>Dimensionless core temperature ( \left( \frac{T_c}{T_0} \right) ) (section 5.2.3) ([-])</td>
</tr>
<tr>
<td>( U_H )</td>
<td>H-phase superficial gas velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_L )</td>
<td>L-phase superficial gas velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_{mf} )</td>
<td>Superficial gas velocity at minimum fluidization ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_{ms} )</td>
<td>Minimum slugging velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_s )</td>
<td>Dimensionless surface temperature ( \left( \frac{T_s}{T_0} \right) ) (section 5.2.3) ([-])</td>
</tr>
<tr>
<td>( U_s )</td>
<td>Slug velocity ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_{s\infty} )</td>
<td>Slug velocity of a single slug in a bed at minimum fluidization ([\text{m}/\text{s}])</td>
</tr>
<tr>
<td>( U_{\text{t}\ast} )</td>
<td>Terminal velocity calculated for spherical particles of ( 2.7d_p ) ([\text{m}/\text{s}])</td>
</tr>
</tbody>
</table>
Nomenclature

$U_t^*$ Dimensionless terminal velocity $(U_t \left( \frac{\rho_p^2}{\mu (\rho_p - \rho_g) g} \right)^{1/3})[-]

U_v$ Void (bubble or slug) rise velocity [m/s]

$U_{voo}$ Free void (bubble or slug) velocity [m/s]

$U_w$ Dimensionless wall temperature $(U_w = \frac{T_w}{T})$(section 5.2.3) [-]

$X$ Conversion of particle $(1 - (\frac{X_i}{X})^3 = 1 - \xi_3^3)$(section 5.2.3) [-]

$X_{Ao}$ Molar fraction in bulk gas phase for gaseous reactant A [-]

$\overline{X}$ Average conversion of mono-sized particles [-]

$\overline{X}$ Average conversion of a wide size distribution of particles [-]

$X_{Go}$ Molar fraction in bulk gas phase for gaseous product G [-]

$X_i$ Conversion of component i [-]

$x_i$ Gas mole fraction (section 5.2.3) [-]

$x_i$ Mass fraction of each size fractions (Chapter 3) [-]

$Y$ Ratio of volumetric flowrate of bubbles to the excess gas flowrate [-]

$z$ Vertical position in bed [m]

Greek Letters

$\beta$ Constant to account for change in mass due to reaction [-]

$\beta$ Dimensionless group $(\beta = \frac{C_{Ao} D_k T_{AO} (-\Delta H_R)}{k_{s} E_a})$(section 5.2.3) [-]

$\beta_d$ Fraction of solids carried up by a bubble within its drift [-]

$\beta_w$ Fraction of solids carried up by a bubble within its wake [-]

$\Delta F_{O2}$ Number of moles of oxygen reacted per unit time [moles/sec]

$\Delta \nu$ Difference in gas stoichiometric coefficient due to reaction [-]

$\Delta z$ Finite height in bed (control volume) [m]

$\epsilon_{mf}$ Bed voidage at incipient fluidization [m$^3$/m$^3$]

$\epsilon_H$ H-phase gas volume fraction [m$^3$/m$^3$]

$\epsilon_L$ L-phase gas volume fraction [m$^3$/m$^3$]

$\eta_s$ Effectiveness factor (section 5.2.3) [-]

$\kappa$ Elutriation velocity constant [s$^{-1}$]
Nomenclature

\( \mu \) Gas viscosity [Pa s]

\( \nu_A \) Stoichiometric coefficient of gas A (section 5.2.3) [-]

\( \nu_S \) Stoichiometric coefficient of solid S (section 5.2.3) [-]

\( \nu_G \) Stoichiometric coefficient of gas G (section 5.2.3) [-]

\( \nu_i \) Stoichiometric coefficient for compound i [moles i / moles reaction]

\( \omega_c \) Dimensionless core molar fraction of component i \((\omega_c = \frac{x_i}{x_{i0}})\) (section 5.2.3) [-]

\( \omega_s \) Dimensionless surface molar fraction of component i \((\omega_s = \frac{x_i}{x_{i0}})\) (section 5.2.3) [-]

\( \phi_H \) H-phase solids volume fraction [m³/m³]

\( \phi_L \) L-phase solids volume fraction [m³/m³]

\( \phi_s \) Thiele modulus of solid particle \((\phi_s = \frac{\nu_A R_p k_{f0} C_A^{n-1} C_s}{D_{eA} T_0})\) [-]

\( \psi_H \) H-phase volume fraction [m³/m³]

\( \psi_L \) L-phase volume fraction [m³/m³]

\( \Delta H \) Heat of reaction (section 5.2.3) [J/mol]

\( \rho_C \) Core density (section 5.2.3) [kg/m³]

\( \rho_g \) Gas density [kg/m³]

\( \rho_p \) Particle density [kg/m³]

\( \tau \) Average residence time of solid particles in fluidized bed [s]

\( \theta \) Dimensionless time \((\theta = k_s(T_0)C_A^nC_s^{m-1}t/R_p)\) (section 5.2.3) [-]

\( \theta_{cr} \) Dimensionless time for complete reaction of solid particle [-]

\( \xi_c \) Dimensionless position of core \((\xi_c = \frac{\tau}{\tau_c})\) (section 5.2.3) [-]
Acknowledgements

This thesis would not have been possible without the initial enquiries of Murray Brown of Teck Cominco. The project spawned from talks with Bob Kerby and Greg Richards, first at the 1998 Conference of Metallurgists in Calgary, followed by a visit in Trail, B.C., in September of the same year. The project materialized before I graduated from my Master’s in Metals and Materials Engineering in April 1999.

I wish to thank Teck Cominco for providing the opportunity to work as a co-op student at the Roaster/Acid plant during the period of September to December 1999. This work term allowed me to familiarize myself with the practical aspects of industrial fluidized bed roasting. My stay at the plant has been beneficial to this project due to the help of Karla Dick, Gordon Masuch, Mike McDowell and the plant personnel.

I also wish to thank Teck Cominco Metals Ltd. for their financial contribution, for providing samples and for the chemical analysis of laboratory roaster samples.

I am grateful to the Science Council of British Columbia for their direct support through a GREAT Scholarship.

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I am grateful to my co-supervisors, John Grace, Jim Lim and Greg Richards, for numerous discussions, reading preliminary drafts of this thesis and presenting much useful feedback.

I would also like to thank my many colleagues from the Fluidization Group. The group seminars and the many informal discussions on various aspects of fluidization have enriched my knowledge and understanding of this diversified and complex field.

Finally, I express my gratitude to Sylvie Bouffard, for her love, understanding, and support during the long months of this project.
In the electrolytic process, often named the roast-leach-electrowin process, roasting of zinc sulfide concentrates is the most common first step in the manufacture of zinc. In the last two decades, direct leaching of zinc concentrates in autoclaves (pressure leaching) has been used successfully as an alternative to roasting. Prior to the development of the electrolytic process, most, if not all zinc was produced by retort distillation. Today, the electrolytic process accounts for 80% of zinc production with the rest from pyrometallurgical processes, such as the blast furnace, electrothermic and retort processes.

Prior to the electrolytic zinc process, zinc was produced for centuries by the distillation of a mixture of zinc oxide ore and coal in retorts of various designs [1]. A mixture of zinc oxide and coal was heated above 1000°C in a coal-fired oven to produce zinc vapour, which was then condensed and collected. In 1738, William Champion patented the process in England, and by 1743, established a smelter in Bristol, U.K. [1]. By combining oriental knowledge and western large-scale technology, he brought commercial zinc production to Europe.

To overcome the shortage of calamine (zinc carbonate), the original source of zinc oxide, blende (zinc sulfide) was roasted to produce zinc oxide. In 1758, John Champion, William’s brother, patented the conversion of blende to zinc oxide by roasting in a coal-fired furnace. The Champion distillation process was used until about 1851. Because the Champion process involved cooling and withdrawing the crucible and the retort after each cycle, the process was labour-intensive and fuel-inefficient (24 tonnes of coal for each ton of zinc produced). The reader is referred elsewhere [2] for a more complete description of the early industrial production of zinc.
Chapter 1. Introduction

Around 1818, the development of the horizontal retort process in Belgium significantly improved the distillation process. Placed horizontally in a furnace, retorts could be charged and discharged without cooling. The popularity of the process grew rapidly, and by 1880, annual world production was estimated to be more than 200,000 metric tonnes of zinc, mostly from Germany and Belgium [3]. In 1950, this process still produced as much as 50% of the zinc. Nowadays, however, the horizontal retort process has disappeared from North America [4], in favour of the electrolytic zinc process. The use of retorts for the production of zinc has been the subject of several publications, and will not be discussed further herein.

During the development of the electrolytic zinc process, roasting was already commonly used to produce the feed material required for retort distillation. However, the electrolytic process imposes different requirements on roasting. To better understand the current requirements of the roasting process, the electrolytic zinc production process is presented in a somewhat chronological matter. The evolution of industrial roasters and the current fluidized bed roasting technology are then discussed. A brief introduction to fluidized beds and a review of the current operating knowledge follows. The chemistry, thermodynamics, and kinetics of roasting are reviewed in the following chapters.

1.1 Electrolytic zinc production

The electrolytic production of zinc first described more than 100 years ago in a 1883 patent by Léon Létrange [5] is the basis of the modern electrolytic process (Figure 1.1). After roasting the zinc concentrate, the calcine is generally leached in two stages: neutral leach and acid leach. In the neutral leach stage, calcine is added to neutralize the solution, while ferric iron is precipitated as ferric hydroxide, a gelatinous substance that renders filtration very difficult. Precipitation of iron in the neutral stage is the first step in purifying the zinc sulfate solution. Impurities such as arsenic, antimony, and germanium are co-precipitated with iron. The solution from the neutral leach stage is sent to the purification circuit. Solid residue from the neutral stage passes to the acid leach stage to dissolve the remaining zinc oxide. The residue from the acid leach stage contains precipitated iron and any undissolved solids, including incompletely
roasted zinc sulfide, zinc ferrite (ZnOFe₂O₃, a zinc-iron spinel produced during roasting), lead sulfate, and silica. Losses of zinc to zinc ferrite are discussed later. The impure zinc sulfate solution leaving the neutral leach stage is then purified. During purification, zinc dust is added in various stages to the solution to remove copper, cadmium, nickel, and cobalt. Depending on the impurities to be removed and the removal efficiency, as much as 5 to 10 % of the cathode zinc produced may be diverted from sales to the purification process. The purified solution is then sent to the electrolytic cells where zinc is deposited onto aluminum cathodes, and sulfuric acid is regenerated at the lead anodes. The depleted electrolyte, rich in sulfuric acid, is returned to the leaching step to process additional calcine. Cathodes are periodically removed from the cells to recover zinc by stripping (or peeling) the deposit from the aluminum cathodes.

Because the sulfate concentration within the electrolyte solution is usually controlled to remain within bounds, a sulfate balance must be performed on the entire electrolytic process. Any sulfate entering the system as zinc sulfate must be balanced by sulfate exiting the system into the residues and as a bleed from the spent electrolyte. Depending on their configuration and operation, some plants require soluble sulfates to offset losses. Close control of the zinc sulfate in the zinc calcine is an important roaster operating parameter.

The leach zinc recovery depends greatly on the ore and on the roasting conditions. Zinc recovery is higher for concentrates with lower iron content because zinc ferrite (ZnOFe₂O₃), a zinc-iron spinel, does not dissolve under mild acid conditions. However, hot acid solutions ensure zinc ferrite dissolution while, unfortunately, dissolving iron as well. Precipitation of the dissolved iron as ferric hydroxide was not technically attractive because of the gelatinous nature of ferric hydroxide precipitates.

During the 1960s, breakthroughs in the research of hydrometallurgical options to process zinc ferrite led to several patents of three types: jarosite process, goethite process, and hematite process. Depending on the process chosen, zinc ferrite is leached in hot acid while iron is precipitated as jarosite, MFe₃(SO₄)₂(OH)₆ (where M is typically Na⁺, NH₄⁺ and K⁺), goethite (FeO·OH) or hematite (Fe₂O₃). These crystalline precipitates are easily filterable. These
Chapter 1. Introduction

Zinc Concentrate

Air + O$_2$

Roasting

Acid Plant

Zinc Calcine

Neutral Leaching

Residue

Iron Precipitation

Iron Residue

Residue

Cd, Cu, Ni, Co Residue

ZnSO$_4$ Solution

Electrolysis

Zinc Cathodes

H$_2$SO$_4$ Solution

Melting and Casting

Zinc Ingots

Sulfuric Acid

Figure 1.1: Improved electrolytic zinc process

processes either treat the residue to recover the ferritic zinc as a separate stream from the electrolytic process, or precipitate iron in an intermediate step between the hot acid and neutral leach stages, as shown in Figure 1.1. These processes are described in more detail in references [6, 7, 8].

1.1.1 Objectives of roasting

Based on the requirements of the unit processes of the electrolytic zinc process, roasting must:

- Maximize the conversion of zinc sulfide. In the traditional process, zinc sulfide is not
leached and ends up in the leach residue. Its presence in zinc calcine is unwanted.

- Maximize the amount of soluble zinc.
- Minimize the amount of zinc ferrite in the calcine.
- Optimize the amount of zinc sulfate in the product. Some sulfate is desirable in the calcine to compensate for sulfate losses during leaching, purification, and electrowinning.
- At least match the calcine consumption rate of the leaching process. In order for the roasting process to compensate for unscheduled shutdowns, the roasting process should be able to process zinc concentrate at a faster rate than calcine is consumed in the leaching process.

The second and third objectives are complementary. Their importance depends on the amount and type of iron in the concentrate as well as the method used to extract zinc from zinc ferrite. For plants not recovering zinc contained in zinc ferrite, fulfilling these two objectives is critical to maximize zinc recovery.

1.2 Roasting and its history

Because this thesis focuses on the roasting of zinc concentrates, other types of roasting, such as chloridizing or segregating roasting, are not described here. For more details on these, the reader may consult reviews [9, 10]. The roasting of sulfide ores has been practised for centuries. In 1546, in his book “De Re Metallica” Georgius Agricola presented different furnaces for roasting copper ores. Ores were roasted in stalls of about 2 by 3 meters. The productivity of stall roasting was limited (20 tons in 10 days) and the process was very labour intensive. Heap roasting replaced stall roasting in large scale production plants. Layers of ore were alternately stacked with layers of wood to form a heap. The heap was then ignited. A heap, 15 m wide and 30 m long, could produce 1700 tonnes of sinter in about 100 days. Roasting methods next progressed from the primitive heap roasting to the hand-rabbled reverberatory furnaces such as the Delplace, and later to the mechanically-rabbled reverberatories such as the Hegeler kiln and the Ropp furnace. A significant advance began with the development of the circular
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multiple-hearth roaster. The evolution of mechanical roasters was reviewed recently [11]. The present discussion focuses on the zinc industry.

1.2.1 Roasting prior to the electrolytic zinc process

Prior to the electrolytic zinc process, roasting of zinc sulfide produced the raw material required for the retort process. The 1906 book of Ingalls [12] and the 1922 book of Hofman [13], both on the metallurgy of zinc and cadmium, describe several furnaces used for the roasting of blende.

The first roasters were hand-raked and typically consisted of a flat hearth heated by a firebox at one end. The ore was charged at the flue end and moved slowly down toward the firebox, where it was discharged through a drop hole in the hearth. The raking action exposed new surfaces to the atmosphere and accelerated the reactions.

A number of mechanical roasters were developed before the success of the circular multiple-hearth roaster, the prototype being the McDougall roaster. The McDougall roaster evolved into numerous types, such as the Wedge, Skinner and Herreshoff roasters, which mainly differed in their mode of maintenance and the mechanical action of the rabble arms.

Figure 1.2 presents a Wedge roasting furnace where ore is fed onto the upper hearth, which, warmed by the heat generated in the roasting operation, serves to dry the concentrate. The rabbles are adjusted to gradually move the ore from the outer edge of the upper hearth toward the centre, and then through a drop hole into hearth 1. The rakes move the ore across the hearth to a slot near the periphery, through which it drops into hearth 2. Thus, in a zig-zag fashion, the ore progresses through the furnace until it drops into a car or conveyor beneath the lowest hearth.

1.2.2 Roasting for the zinc electrolytic process

Mechanical roasters were developed in parallel to the electrolytic zinc process. The Anaconda Copper Company and the Consolidated Mining and Smelting Company adopted the Wedge mechanical roaster in their new electrolytic zinc plants.
It was noted at an early stage during the development of the electrolytic zinc process that the formation of zinc ferrite during roasting detrimentally affects the recovery of zinc during leaching. It was recognized that higher temperatures and longer reaction times increased the conversion to zinc ferrite [15]. While roasting for the retort process could be performed at high temperature with excellent productivity and zinc extraction, roasting for the electrolytic zinc process required roasting at a lower temperature to avoid zinc ferrite production. Choosing the roasting temperature requires balancing the production of zinc sulfate and zinc ferrite with the conversion of zinc sulfide.

More recent studies [16, 17], using pure zinc oxide and iron oxide have shown that increased contact between the oxides increases the ferrite production rate. This explains why marmatitic zinc concentrates produces large quantities of zinc ferrites. Marmatite is a zinc sulfide that contains a significant amount of iron dissolved within the zinc sulfide matrix.
1.2.3 Flash or suspension roasting

During the 1920s and 1930s, a significant breakthrough in the roasting of sulfide ores occurred at the Consolidated Mining and Smelting Company of Canada. Engineers developed a plant to effectively recover and utilize sulfur dioxide off-gas in a contact acid plant. This plant requires a sulfur dioxide concentration higher than that can be obtained from the Wedge roaster. Inspired by pulverized coal combustion, they modified the existing Wedge roaster by removing all the hearths except for the top and bottom ones and installed a concentrate burner. The productivity improved so dramatically that sufficient roasting capacity was available after modifying 8 of the 25 Wedge roasters. The remaining 17 unmodified roasters were then permanently shut down.

![Flash roasting furnace diagram](image)

*Figure 1.3: Flash roasting furnace [14]*

Figure 1.3 presents the original flash roasting furnace of the Consolidated Mining and Smelting Company of Canada. Moist zinc concentrate entered the roaster on the top hearth where the concentrate dried. After drying, the concentrate left the roaster and entered a ball mill where the lumps were pulverized. After grinding, the dried concentrate was fed into the combustion chamber through the burner. The concentrate heated up rapidly and reacted to form calcine and sulfur dioxide. The calcine fell onto the bottom of the combustion chamber where it was pushed by a rabble into a chute. A significant portion of the calcine was carried with the gas
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to the boiler and the solids collection system. A portion of the calcine could be returned to the bottom hearth of the roaster for further reaction with sulfur dioxide to produce additional zinc sulfate.

The new roaster was so energy efficient that a waste-heat boiler could be installed to recover the heat from the effluent gases. The suspension roaster was the first roaster equipped with a waste-heat boiler.

In 1937, the roasting productivity was further increased by enriching the combustion air with oxygen [18]. The flash roaster was later redesigned to eliminate the central shaft within the combustion chamber by relocating the drying hearth beneath the roasting hearth [18]. In comparison to the Wedge roaster, the suspension roaster had a greater capacity, better heat utilization and recovery, produced a rich SO$_2$ gas and less zinc ferrite (because of shorter particle residence times). In view of these advantages, most plants in the electrolytic zinc and copper industries adopted the flash roaster.

1.2.4 Introduction of fluidized bed roasting

The fluidized bed technology was the next advance and is still the dominant roasting technology. Although Robinson patented the basis of a fluidized bed roaster in 1879 [19], it was not until the petrochemical industry mastered fluidized bed technology that it became attractive to the metallurgical industry. In 1944, Dorr-Oliver acquired the rights to Exxon’s fluidization knowledge for applications outside the petroleum industry [20]. It developed the FluoSolids system for roasting of sulfide ores. In 1947, the first roaster was built in Ontario for roasting arsenopyrite to produce a calcine suitable for gold extraction by cyanidation. In 1952, a unit was installed in New Hampshire to produce SO$_2$ from sulfide ores. Alcan (Arvida, Québec) pioneered the Dorr-Oliver fluidized bed roaster for zinc concentrates [21, 22], roasting 150 tons of zinc concentrate per day to produce sulfuric acid for the aluminum industry. The zinc calcine was shipped to electrolytic zinc plants. In Japan, numerous electrolytic zinc plants adopted the FluoSolid roaster [23].
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In 1945, the German company Badische Anilin und Soda-Fabrik (BASF) developed a fluidized bed roaster based on experience from the Winkler gas producer. Their first commercial roaster, with a capacity of 30 tons/day, went online in 1950, followed, two years later, by a 120 tons/day unit. The BASF roaster operates with a pelletized feed, a relatively shallow bed (0.6 m) and a high superficial gas velocity (1.3-2.3 m/s) [20].

Allied Chemical [24], St-Joseph Lead [25], New Jersey Zinc [25] and Metallurgie Hoboken-Overpelt [26, 27] have all developed different zinc fluidized bed roasters for their own use. The zinc industry uses primarily the Lurgi/Vielle-Montagne roaster. During the early 1960s, the Société de la Vieille-Montagne in Balen, Belgium, built its own fluidized bed roasters [28], before Lurgi [29, 30] (now a division of Outokumpu Technology [31]) acquired the rights. The Lurgi/Vieille Montagne roaster was also called the turbulent layer roaster, not to be confused with the turbulent fluidization flow regime. The Lurgi roaster offers the advantages of minimal concentrate preparation prior to feeding and excellent heat recovery through steam production (mainly because the concentrate is not fed as a slurry).

Types of fluidized bed roasters

Zinc fluid bed roasters can be classified into three general types (Table 1.1), the second of which is most widely used. The first two types mainly differ by their concentrate feeding system. The first type comprises mostly Dorr-Oliver roasters where the concentrate is fed as a slurry. The Lurgi/Vieille-Montagne roaster is the most popular roaster of the second type. The moist concentrate is fed directly to the furnace. The third type generally uses a dried, pelletized feed, utilizes a higher superficial velocity, and can operate at higher temperatures than the other two. Several designs fall within the third type, but none is widely used. This work focuses on Lurgi fluidized bed roasters.

Description of a typical fluidized bed roaster

Figure 1.4 shows the principal features of a typical Lurgi fluidized bed roaster. Concentrate feed is introduced by side ports with the help of slinger belt feeders. The number of feeders varies depending on the bed area. To improve the distribution of the feed over the entire bed
Table 1.1: Types of fluidized bed roasters used in the zinc industry

<table>
<thead>
<tr>
<th>Type</th>
<th>Feed System</th>
<th>Superficial Gas Velocity</th>
<th>Typical Roaster</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Slurry (20-25 wt% H₂O)</td>
<td>0.3-0.8 m/s</td>
<td>Dorr-Oliver</td>
</tr>
<tr>
<td>2</td>
<td>Moist concentrate (6-10 wt% H₂O)</td>
<td>0.3-0.8 m/s</td>
<td>Lurgi / Vieille-Montagne</td>
</tr>
<tr>
<td>3</td>
<td>Pelletized and dried concentrate</td>
<td>1-3 m/s</td>
<td>BASF Metallurgie Hoboken-Overpelt</td>
</tr>
</tbody>
</table>

area, a new feeding system for the Lurgi roasters has recently been developed and is currently under testing [31]. No details of the new system have been published. The very large freeboard helps reduce elutriation and increases the residence time of entrained particles. The calcine is recovered in the bed overflow and by the gas treatment system, usually consisting of a waste-heat boiler, cyclones and an electrostatic precipitator. The bed overflow height is often adjustable [30, 32]. Some roasters use a bed underflow discharge port to remove oversized, settled particles [33]. During startup, the roaster is preheated using oil and/or gas burners that can be inserted through burner ports located on the side of the roaster, just above the bed surface. The waste-heat boiler generates steam using heat liberated by the roasting reactions. Heat is recovered by tubes located in the fluidized bed, on the wall of the boiler and suspended in the boiler. Spraying water onto the bed or increasing the feed moisture content can be used to cool the bed. To ensure the safety of the operators, the roaster is usually operated under a slight vacuum [31]. Conversion of the zinc concentrate, based on residual sulfide sulfur, typically ranges from 98 to 99.9% [34, 35]. Using industrial data from a 32 m² Lurgi roaster, Avedesian [33] calculated the residence time distribution of various particle sizes. The mean residence time varied between 0.4 and 13.6 hours depending on the particle size. A radioactive tracer test provided experimental verification of the results for the smallest particles [33]. The difference in residence times is due to the fact that fine particles can leave the roaster by two output streams (entrainment and overflow), whereas the larger particles only exit via the overflow stream.
Figure 1.4: Typical fluidized bed roaster and associated streams [36].
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Advantages and disadvantages of fluidized bed roasters

The fluidized bed occupies only a small volume of the roaster shown in Figure 1.4. It is, however, responsible for several very important phenomena:

- Distribution of the concentrate feed (Efficient solids mixing)
- Heating the concentrate particles until they reach ignition (High heat transfer)
- Cooling the particles after they ignite (High heat transfer)
- Maintaining a uniform bed temperature (Isothermal)
- Bringing oxygen required for reaction to the particles (Efficient gas-solid contacting).

Satisfactory control of these phenomena depends on the reliability of the fluidized bed to ensure rapid mixing and heat transfer between the reacting particles and the calcine particles. Without the bed to distribute the concentrate and redistribute the heat, particles would sinter into an unmanageable heap. Therefore, the characteristics and the stability of the bed are critical to the operation of the roaster. Because the fluidized bed consists almost entirely of calcine particles, these define the behaviour of the bed.

Fluidized bed roasters have no internal moving parts. This reduces maintenance costs and make them mechanically more reliable than multi-hearth or suspension roasters. The fluidized bed roaster has excellent heat recovery and produces a gas with a high sulfur dioxide content, suitable for acid production while maintaining good temperature uniformity and control. While there are many advantages, fluidized bed roasters also suffer from disadvantages. Successful operation relies on the stability of the fluidized bed, and on particle growth to reduce carry-over [37]. Smooth operation of fluidized bed roasters involves a delicate balance between sufficient growth of the calcine and complete reaction of the concentrate, while minimizing the risk of defluidization. Even after 50 years, there is very limited knowledge of the mechanisms and rates of agglomeration, sintering and particle growth in fluidized bed roasters. A large portion of the literature on roasting focuses on zinc sulfide oxidation, and the formation of zinc sulfate and zinc ferrite because of their effects on downstream processes. Agglomeration and defluidization
in fluidized bed roasters have received little attention. These problems have been left to be solved by plant operators.

1.2.5 New roasters

In recent years, new types of roasters have been developed. Circulating fluidized bed technology developed by Lurgi for calcination of alumina and for coal combustion has been applied to the roasting of refractory gold ores (pyrite) [38, 39]. The Torbed reactor, invented during the early 1980s, has recently been used to roast zinc concentrates at the pilot scale [40]. The Torbed reactor has an unconventional geometry where a toroidal bed of coarse fluidized particles is used as a heat transfer medium into which the fine concentrate particles are injected [41]. Neither of these technologies has yet been applied industrially to the roasting of zinc sulfide concentrates. Due to the availability of proven technologies and to uncertainty associated with implementing a new unit process, it may be several years before these technologies are adopted by the zinc industry.

1.3 Brief introduction to fluidized beds

When a gas flows upward through a bed of particles at a low flowrate, the gas simply percolates through the bed and no movement of the particles occurs. This describes a fixed bed (see Figure 1.5). If the upward flow of gas is increased, a point is reached where the pressure drop counterbalances the buoyed weight of the particles. The particles then become fluidized and the bed behaves like a liquid. When the gas flowrate is further increased, large instabilities are observed and bubbling occurs, as in a violently boiling liquid. The fluidized bed is then commonly described as being composed of two phases: bubbles (lean or low-density phase) and a particulate phase (also called dense phase, high-density phase or emulsion). The bubbles are gas voids containing few particles. The dense phase consists of closely-spaced particles supported by the relative motion of interstitial gas. Gas entering the bed through a gas distributor therefore divides into two phases: interstitial gas in the dense phase, and flow through and carried by the bubbles. As an approximation, called the “two-phase theory of fluidization”, the amount of gas entering the dense phase is equal to that required for minimum fluidization. Bubbles
form at the gas distributor, rise, coalesce and finally burst at the surface of the bed. During their ascension, they entrain particles in their wakes and therefore engender solid mixing. If the bubbles reach a diameter similar to that of the reactor, the bed enters the slug flow regime. If the gas velocity is increased beyond the bubbling regime, the bed enters the turbulent regime where voids are unstable and transient in nature. In the fast fluidization regime, the solid particles now move in clusters surrounded by a relatively dilute suspension.

![Gas-solid flow regimes](image)

Each flow regime has unique characteristics that differentiate it from other regimes. Unless special attention is taken, modelling of a reactor within one flow regime should not be extended to another regime. Fluidized bed roasters typically operate in the bubbling fluidization regime.

### 1.4 Review of operating knowledge

Before reviewing some of the issues related to the operation of fluidized bed roasters, the materials present during roasting are described.
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Table 1.2: Published composition of some zinc sulfide concentrates and pure zinc sulfide (wt%).
Blank where amount not specified.

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>S</th>
<th>Fe</th>
<th>Pb</th>
<th>Cu</th>
<th>Cd</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cominco Customs [44]</td>
<td>55</td>
<td>4.4</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sullivan [44]</td>
<td>51</td>
<td>9.5</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red Dog [44]</td>
<td>52</td>
<td>8</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cominco FB Feed [45]</td>
<td>54</td>
<td>32</td>
<td>7</td>
<td>4.2</td>
<td>0.3</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Kiddcreek [43]</td>
<td>52.48</td>
<td>31.87</td>
<td>9.59</td>
<td>0.56</td>
<td>0.76</td>
<td>0.24</td>
<td>2.13</td>
</tr>
<tr>
<td>American Zinc [46]</td>
<td>54.55</td>
<td>30.65</td>
<td>5.64</td>
<td>0.68</td>
<td>0.58</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Gordonsville [47]</td>
<td>65.7</td>
<td>32</td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ZnS</td>
<td>67.1</td>
<td>32.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1.4.1 Feed: Zinc concentrate

Zinc concentrates are flotation products of milled ores containing various minerals and impurities. The compositions of several zinc concentrates are shown in Table 1.2. For reference purposes, the composition of pure zinc sulfide is also provided. The zinc concentrates are usually composed of zinc sulfide associated with other sulfidic and gangue minerals such as galena (PbS), iron sulfides, copper sulfides, silica (SiO₂), alumina (Al₂O₃) and lime (CaO). The reaction of each sulfide requires different amounts of oxygen to produce different compounds and for complete oxidation.

Some impurities are dissolved within the zinc sulfide matrix and cannot be separated by grinding and flotation. For example, zinc sulfide often contains appreciable amounts of dissolved iron. This iron-rich zinc sulfide mineral is called marmatite and is represented as (Zn,Fe)S. Cadmium present in the concentrate has also been found to be dissolved in sphalerite [43].

Most impurities contained in zinc concentrates are unlikely to affect agglomeration. However, lead, copper, arsenic and iron have been reported to contribute to agglomeration. The review of Krauss [48] presents in detail the effect of many elements on the electrolytic zinc process.
1.4.2 Feed: Gases

The fluidizing gas, air or oxygen-enriched air, enters the roaster through the distributor and reacts in the bed. In the non-ferrous metallurgical industries, the term oxygen enrichment is often used to indicate the oxygen concentration of the gas. For instance, 25% oxygen enrichment would mean that oxygen is added to air until the oxygen concentration reaches 25vol% rather than the 21% in standard air.

Oxygen enrichment is used to increase the productivity of fluidized bed roasters [49]. Oxygen enrichment has been found to significantly affect the particle size distribution of several fluidized bed roasters [35]. With oxygen enrichment, an unstable fluidized bed (low bed pressure, significant amount of fine particles < 56 μm and few particles of size 100-400 μm) became stable (high bed pressure, few fine particles and significant 100-400 μm fraction) within a few days [35]. The increase in bed pressure drop appears to have been caused by increasing particle density and size. A dense oxidized layer coated the sulfide core of calcine particles [35]. Oxygen enrichment has also been observed to affect the dust and sulfate formation in process gas lines [35].

In addition to the metered fluidizing gas, air is believed to leak into the roaster freeboard, boiler and associated piping and equipment. This leakage, present because the roaster is operated under a slight vacuum, can affect the reactions occurring in the freeboard and the boiler. There is no published information on the amount of leakage present.

Gases leave the roaster to the waste-heat boiler, cyclones and electrostatic precipitator where calcine particles are separated. After cooling, the gases are treated for mercury in a mercury removal plant before the production of sulfuric acid.

1.4.3 Product: Zinc calcine

Zinc calcine is extracted from the roaster via the bed overflow and through carry-over. The carryover material may constitute 70% of the calcine obtained from the process [33, 34]. It is a material of fine size (overall 70%<44μm), collected from the waste-heat boiler (67%<44μm),
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the cyclones (83%<44μm) and the electrostatic precipitator (99%<44μm) [33].

The calcine is formed of zinc oxide, zinc ferrite (ZnOFe₂O₃) and relatively small amounts of lead sulfate and zinc silicate (Zn₂SiO₄) [50]. Other studies corroborate these findings [51, 43, 52, 53, 54]. The entrained material contains a larger proportion of zinc sulfate. Zinc sulfate obtained in the boiler, cyclones and electrostatic precipitator originates from the reaction of zinc oxide with sulfur trioxide.

The entrainment in a fluidized bed roaster is of two categories: entrainment of particles from the bed and entrainment of feed material prior to joining the bed. Entrainment from the bed is zinc calcine. The entrained feed, however, is mainly zinc concentrate which may react in the freeboard to form zinc calcine. Both type of entrained solids are collected in the boiler, cyclone and electrostatic precipitator as zinc oxide, zinc ferrite, zinc sulfate and unreacted zinc sulfide. It is therefore impossible to differentiate between the two types when analyzing samples of entrained material. The effect of various variables on the entrained material, freeboard and boiler must therefore be analyzed carefully. The distinction between the two streams is very important because the entrained feed cannot contribute to agglomeration in the bed while the feed which mixes into the bed can. Some observations regarding each stream:

**Feed entrainment:** An increase in feed entrainment is associated with a decrease of the feed entering and mixing into the bed. This may be indicated by a decrease in bed temperature [35] and an increase in freeboard temperature [30, 35]. The moisture content of the concentrate and its size distribution affect the proportion of entrained feed. The feeding system geometry and velocity also influence feed entrainment.

**Bed entrainment:** Entrainment has been studied in many fluidized bed systems. Variables that typically affect entrainment include the superficial gas velocity, entrained particle size and density, and the entrainable particle concentration in the bed. There is large scatter among the numerous published empirical correlations. Because there is practically no zinc sulfide in these particles, negligible heat is generated by combustion in the freeboard. Therefore, the freeboard temperature cannot increase above the bed temperature because of increased bed entrainment.
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Any change in the entrainment rates may alter the residence time of particles in the bed, affecting the amount of unburned sulfide in the bed calcine (affecting the solids conversion). For example, in one study, increasing the amount of feed entering the bed reduced the amount of entrained material collected (increasing the bed calcine production), increased the mean particle size of the bed and increased the sulfide content of the bed calcine [35]. Because the mass of the fluidized bed is relatively constant (imposed by the weir height), an increase in the bed calcine production rate necessarily causes a decrease in particle residence time. The increase in the amount of sulfide in the bed calcine observed industrially [35], may have been compounded by increases in both bed particle size and bed calcine production.

Accretions and cake wall as well as bed-set material build up in the roaster. Bed-set material is made of very large particles that settle within the fluidized bed. Entrained material forms accretions on the freeboard and the waste-heat boiler walls composed of zinc sulfates [30, 35] and zinc oxide, zinc ferrite, minor amounts of zinc silicate and lead zinc silicate (PbZnSiO₄) [50].

1.4.4 Controlling bed particle size

Fluidized bed roasting is similar to fluidized bed coal combustion in that very few particles are in the process of reacting relative to the total number present. Typically only 0.1 to 1.0 % wt of particles in bubbling fluidized bed (BFB) coal combustion are reactive [55]. The particle size of the inert material (usually sand or partially sulfated limestone) governs the fluidization characteristics. In fluid bed roasting, the amount of unburned sulfide within the bed is small (<3 wt%). The size of the bed particles (mainly zinc oxide), not the feed material (zinc sulfide) governs the fluidization characteristics of the roaster. Unlike combustion where sand or limestone of the appropriate size is periodically added and removed to refresh the bed material and/or capture sulfur, the bed in the roaster is in continuous renewal through the reaction of zinc sulfide. The particle size of the zinc concentrate is generally much finer than that of the bed. Some degree of agglomeration is desirable to produce sustainable fluidization.

It is also important to distinguish the concentrate, feed and calcine particle size distributions.
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The particle size of industrial zinc concentrates is usually optimized for the flotation process. Zinc concentrates where more than 80% of the particles are smaller than 20 to 40 μm (d_{50}) are now common. The bed calcine particle size (10 μm to 30 mm [35]) is always much larger than the concentrate particle size. While as much as 25 wt% of the bed particles may be smaller than 105 μm, as much as 35 wt% can be larger than 1.1 mm [56].

Elutriation – the tendency for very fine particles to be preferentially entrained – and attrition – the reduction of particle size due to the break-up of particles – also affect the bed particle size distribution. No results on attrition in fluidized bed roasters have been published. However, its importance must not be neglected.

1.4.5 Agglomeration in industrial fluidized bed roasters

Agglomeration in fluidized bed roasters was reported early in the history of the process. For example, Fisher indicated in a patent that agglomeration occurred during the roasting of zinc concentrate containing significant levels of copper and lead [57]. According to industrial experience [30], feed moisture, concentrate particle size and lead content, temperature, and bed agitation all influence agglomeration, bed particle size and accretion formation. Moisture and agglomerated or pelletized feed have been said to be very important [37]. Several studies on agglomeration [58, 59] concluded that low melting point phases were present. Higher temperatures and lower air velocity were also found to favour agglomeration.

Industrial experience indicates that at 900 to 950°C some agglomeration occurs. The bed may sinter within 30 minutes after sudden defluidization without cooling [60]. If the bed were to defluidize before cooling, any residual sulfide could react with the oxygen contained in the interstitial gas space between particles (about 50 vol%). As a result of the poorer heat transfer in a packed bed, the heat generated would locally increase the temperature, resulting in bed sintering.

Little is known about agglomeration in fluidized bed roasters. The concentrate behaviour depends on its mineralogy, composition, size distribution, pre-treatment (filtration, micro-
agglomeration and handling) and moisture content [61]. Empirical guidelines have been set to minimize the risk of catastrophic defluidization. The amounts of copper and lead are limited because they promote agglomeration. For example, Cu is kept to less than 0.8% and Pb to less than 2% [60]. Others maintain Cu below 1.2%, especially if arsenic is present [48]. Pilot studies have shown that a generally accepted rule, i.e. Pb + Cu + SiO₂ < 5% for no defluidization to occur may only apply to some concentrates but not to others [61].

Several papers and patents refer to various methods to control or alter the bed particle size distribution. Depending on the methods, the goals are to promote larger bed particle sizes, reduce the amount of carryover, decrease agglomeration or decrease the build-up of settled particles. Measures reported are:

- Recycling properly sized calcine and conditioning the concentrate to obtain particles of proper size (pelletizing) [62].

- Compacted or agglomerated concentrate as a feed to a roaster such that decrepitation leads to an appropriate bed particle size [63].

- Blending to obtain a feed with a specified amount of agglomerating agent and pelletization of the feed [56].

- Cyclic temperature variation to cause partial sintering [64].

- Increasing the fluidizing gas velocity if excessive agglomeration occurs due to fusion [57].

- Provide a locally increased oxygen concentration by additional localized introduction of oxygen-containing gas into the bed to produce local partial agglomeration [65].

- Pelletizing with a binder, optionally followed by drying [66, 67, 68], compacting or briquetting the moist concentrate [69, 68] or creating structured pellets [70]

- Controlling the amount of feed, oxygen and water fed to the roaster such that fusion occurs during roasting, thereby forming agglomerated calcine particles of controlled size and shape [71].
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- Adjusting the amount of oxygen fed to the furnace using continuous or occasional in-bed oxygen measurements [72].

- Increasing the oxygen content of the gas fed near the feed point using a feed gas distributor [73]. The feed gas distributor is above the main distributor and directs the gas horizontally, promoting horizontal mixing [74].

- An overflow gas distributor can be used to modulate the overflow calcine output rate and control the bed particle size distribution [75].

1.4.6 Concentrate moisture content and concentrate agglomeration

Moisture in the concentrate reduces dusting during shipping and handling [76]. During handling, moisture contributes to the natural formation of small pellets and lumps of up to 1 to 2 mm. Moisture in the concentrate is thought to be a binding agent, thereby assisting agglomeration of the concentrate [33, 30]. In another study, an increase in feed moisture content reduced the feed entrained, and increased the mean particle size of the bed [35].

In their study of the decrepitation of concentrate filter cakes, Carey and Hall [77] found that the moisture content influenced the size of decrepitated cakes. They reported that very little entrainable dust was generated during decrepitation. Aging of the filter cake also reduced decrepitation. They attributed this finding to the production of zinc sulfate, which promotes salt bridging. They also measured the strength of fresh, aged and dried filter cakes. Capillary forces were responsible for approximately 90% of the strength of a fresh compact. Aging increased the strength threefold. Heating tests on the cakes showed that as a result of sintering, the strength was more than 10 times higher following exposure to high temperatures (>800°C). However, it is unclear how much time was required to achieve this strength increase.

Aging of zinc concentrates in a “last in, first out” storage facility has been said to contribute to defluidization due to the presence of large lumps [36]. During aging, oxidation of zinc sulfide produces higher proportions of zinc sulfate. Also during aging, large hard lumps are formed. These lumps may pass through the screening and crushing plant to enter the roaster [36].
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The formation of lumps or pellets cannot explain entirely the fact that bed particles are much larger than zinc concentrate particles. There is evidence that when the concentrate is fed as a slurry (i.e., no pellets in the feed), the particle size of a roaster bed is also much larger than the concentrate particles [78]. Therefore, other mechanisms must also contribute to the enlargement of the particle size distribution.

1.4.7 Low-melting-point phases during roasting

Zinc concentrates are generally impure zinc sulfides. Numerous reactions may therefore take place, generating various compounds, some of which may be molten and contribute to agglomeration. The proportion of low-melting-point phases present in the roaster depends on the feed composition and operating temperature. Agglomeration depends on the adhesive properties, area of contact and particle momentum [79]. Agglomeration caused by low-melting-point phases therefore depends on the properties of the phase in question and on the operating conditions, such as temperature and superficial gas velocity.

The presence of low-melting-point phases may be intentional (additives) or accidental (impurities). In one study, a sodium-iron sulfate eutectic mixture added to the feed reduced dust entrainment and increased the particle size [58].

The reaction of pyrite (FeS₂) may contribute to agglomeration [80] by the formation of a Fe-S-O liquid phase during the reaction of zinc concentrate [81, 82, 53]. The Fe-S-O liquid eutectic is present only during partial oxidation of the sulfide. With further reaction, the liquid would solidify and possibly act as a binder.

Oxidation of lead sulfide can produce numerous low-melting-point compounds. Condina et al. [83] found that alumina, silica and calcine particles can be agglomerated by monobasic lead sulfate (PbO-PbSO₄) on the surface of the particles. The deposit originated from the gaseous oxidation of lead sulfide. In their experiments, a single, large pellet (1 pellet per experiment) of pure lead sulfide was suspended in an inert fluidized bed. Since the fluidizing medium was air, oxidation of the lead sulfide pellet occurred rapidly and the tests ended after
only 2 minutes. Their experimental conditions differed from those in a continuously operating roaster. However, their test shows that basic lead sulfate can contribute to agglomeration of inert particles. In a study on the effects of lead and copper concentrations in the feed [59], several compounds were identified in agglomerated calcines: lead sulfate, basic lead sulfate, lead silicate and copper sulfate. Lead oxide and silica have been linked to defluidization in fluidized bed roasters [36]. Analysis of defluidized bed material has shown that lead tends to segregate to the coarse fractions of bed material [36]. Two types of particles were observed in the defluidized material: “globular” and “radiating globular”. The globular particle “is a more rounded particle that may have been formed by several spherical particles attaching themselves and joined by a binder phase. The radiating globular has clearer growth lines.” [36] Zinc oxide particles containing thin concentric layers of lead oxide and zinc silicate were found within the coarse fraction of the roaster bed material [36].

1.5 Fundamentals of agglomeration in fluidized beds

Agglomeration and defluidization occur in many other fluidized bed systems such as granulation, chemical vapour deposition [84], coal combustion, biomass gasification and pyrolysis. Previous studies on defluidization have focused on the sintering temperature of various materials and the effect of agglomeration on defluidization [85].

High speed photography was used by Siegell [86] to observe the mechanism of agglomeration and defluidization. Two opposite phenomena influenced the agglomerate size: adhesion of single particles to each other, and break-up of particle agglomerates as they collide. If the fluidization velocity was increased, the break-up rate increased. If the temperature increased, the average size of the agglomerates increased. Recent fundamental studies have looked at agglomeration of fine cohesive powders [87, 88], liquid bridge forces [89, 90, 91], sintering [92, 93, 90] and Van der waals forces [90]. Liquid bridges between particles are significant in drying, granulation and three-phase fluidization. The strength of a liquid bridge depends on the surface tension and viscosity of the liquid. In one study [91], the addition of liquids modified the behaviour of a fluid bed from a Geldart group B (bubbling) to a group A (aeratable), an eventually to group.
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C (cohesive).

Sintering is a time-dependent process in which material migrates to the region of contact to form a neck. Surface diffusion, volume diffusion, viscous flow and vaporization-condensation contribute to sintering. The predominant mechanism depends on the material in question. The use of characteristic times [90] appears to be a promising approach for modelling sintering in fluidized beds.

Fundamental approaches such as force balances and characteristic times have been used to predict agglomeration and defluidization. Fundamental models may provide useful insights, but are very difficult to apply to industrial roasters and other commercial reactors. The composition, quantity and properties of various phases present during fluidized bed roasting are uncertain and are likely to change over time and with changes in operating conditions and/or charge composition.

1.6 Agglomeration in other fluidized bed systems

Relevant information is available from fluidized bed reactors used to pyrolyse waste polymers particles. These reactors suffer from agglomeration and defluidization [94]. In this process, the polymer particles are fed to a hot bed of sand (450-500°C) under inert or oxidizing conditions. The polymer then decomposes and volatilizes. Upon entering the reactor, the polymer pellets quickly reach the polymer softening temperature and become very sticky. Layers of sand may attach to pellets, effectively forming polymer-sand aggregates which may crumble if there is insufficient polymer to bind the sand particles and withstand the agitation of the bed. Aggregates grow quickly, leading to severe defluidization. The time to achieve defluidization was found to depend on the bed temperature and on the ratio of initial bed weight to the polymer fed. This indicates that this is an unsteady-state process where the pyrolysis kinetics define the steady-state processing capacity. Feeding of polymer beyond that capacity causes accumulation in the reactor until the polymer concentration reaches a point where defluidization occurs. A similar defluidization process may occur in a fluidized bed roaster if the agglomeration rate
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exceeds the rate of solids removal.

Because particle growth is a main goal of the granulation process, published research on fluidized bed granulation is of relevance. Granulation is used to produce granules or dry powder (continuously or batchwise) from a liquid, which may be a melt, solution or slurry. Two types of granules have been observed: agglomerates formed from several bed particles “glued” together by feed material, and layered or “onion-ring” granules consisting of single particles coated with successive rings of deposited material [95, 96]. During granulation, a spray nozzle injects the liquid above or below the bed surface. If the liquid droplets solidify before reaching particles, they form fine particles, which may be elutriated or act as seeds for growth. If the droplet reaches a particle before solidifying, it may wet it (if the liquid wets the solid material) and, depending on the size of the droplet relative to the particles, engulf one or more particles or coat part of a particle. If a newly coated particle collides with another, a liquid bridge may form. On solidification, the liquid bridge forms a solid bridge. Depending on the strength of the bridges, two types of granules can be formed [97]. Growth models have been formulated for both the these “glued” and “onion-ring” particles [98].

Fluidized bed combustors are often used for power generation. In these combustors, coal or another fuel is distributed onto a bed of inert particles. Manzoori [99] observed that agglomerated sand particles were coated with a sulfated ash layer transferred from coal particles by random collisions. Depending on the fuel, the ash may contain low melting point compounds and eutectics. The transfer of ash to the inert particles caused the particles to grow, agglomerate and eventually defluidize. It was later verified that the deposition mechanisms proposed by Manzoori apply to various bed materials [100]. The growth of the sulfated layer can be modelled using a layered growth model (onion-ring model) [101].

Four types of agglomerates have been observed in fluidized bed coal combustors [102]:

- “Glued” or “raspberries” particles
  The first stage of creating “glued” or “raspberries” particles is through the deposition of a sticky ash layer onto bed particles. The ash layer builds up by the deposition of fine-
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grain liquid minerals and through heterogeneous condensation of vapour-phase species such as Na, K and S.

When the particles have a thick coating, e.g. with a thickness of approximately 10% of the particle diameter, they are able to stick to other coated particles. As a result of continued deposition, sintering between particles occurs. Additional particles stick and sinter to the joined particles and a "raspberry"-shaped agglomerate is formed.

- "Egg" particles
  The egg-types agglomerates are hollow particles that formed as a coating on a burning coal particle. The coating consists of coated bed particles that stick to the surface of the coal particle. Ash formed during combustion of the particle interacts with the particle and contributes to their sintering as a shell. When the coal particle is completely burned out, a hollow shell remains. Coating of a coal particle depends on the type of coal (swelling index, ash quantity, composition) and its size.

- Sintered fly ash
  These very fine dense particles consist mainly of fly ash sintered with sorbent material. They are found in regions of low or stagnant flow.

- High-temperature molten alumina-silicate agglomerates
  The fourth type of agglomerates is associated with the melting of alumina-silicate material due to process upsets. Operational problems or oversized agglomerates may cause poor fuel-air mixing leading to localized hot spots. In these hot spots, melting of an alumina-silicate-based phase occurs, accelerating the formation and growth of agglomerates. These agglomerates appear as sintered lumps showing obvious signs of melting [102].

The first two types of agglomerates are predominantly found in combustors. With the exception of the fourth type of agglomerate, all are formed during normal operation of fluidized bed combustors. The "egg"-type of agglomerates is directly related to coal combustion. Therefore, "egg"-agglomerates are not expected in fluidized bed roasters.
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1.7 Research objectives

The research reported in this thesis seeks to provide a better understanding of particle growth processes in zinc concentrate fluidized bed roasting. The objectives of the project were to:

- Investigate particle growth in a laboratory scale fluidized bed roaster.
- Identify particle growth mechanism(s) and quantify the rate(s) of different mechanisms for pure zinc sulfide and industrial concentrates.
- Identify the operating parameters influencing each mechanism.
- Develop a fundamental model, applicable to both pure zinc sulfide and industrial concentrates, describing the particle growth in a fluidized bed.
- Determine the applicability of the results to an industrial fluidized bed roaster.

The longterm objective of this research is to improve the understanding of industrial fluidized bed roasters and to provide tools to predict their behaviour and improve their operation. Using mechanistic models, the optimization of the operation and modification to the roasters or their operation can be considered and evaluated.

1.8 Thesis outline

Chapter 2 focusses on the chemical aspects of roasting zinc concentrates. The chapter first looks at the thermodynamics of the Zn-S-O system, followed by the kinetics of zinc sulfide oxidation. Next, the thermodynamics of the Fe-O-S, Pb-O-S, Cd-O-S and Cu-O-S systems are briefly presented. The vapour pressures of the metallic species are presented. The chapter concludes with an overview of phase diagrams which apply for zinc concentrates, zinc calcine and any other transient phases which may occur during roasting.

The first sections of Chapter 3 describe thoroughly the experimental roaster set-up, accessories, and data acquisition and control systems. Additional technical specifications and drawings are assembled in an appendix. The next sections report the physical and chemical properties of
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the concentrates and bed material tested, the factors studied, the description of the operating, shutdown, and cleaning procedures, and, finally, chemical and microscopic assays performed on the bed and carry-over samples. The instrument calibrations and a description of the data acquisition software are attached in appendix.

Chapter 4 presents the experimental results and their analysis. The various results are compared as a function of bed temperature, superficial gas velocity, base case, inlet oxygen concentration, excess oxygen and initial bed material and size. Results include the evolution of the particle distribution, rates of bed mass increase, overall mass balances, elemental balances, an analysis of the composition of bed samples as a function of the particle size, SEM images of coated and agglomerated bed particles as well as assays of carryover particles. The chapter concludes with a discussion of the mechanisms for the coating and agglomeration of particles in the laboratory roaster.

A generalized slugging-bubbling fluidized bed reactor model (GSBM) is developed in Chapter 5. This model can be used for both the bubbling and slugging flow regimes and transition between them. To model a fluidized bed roaster, the GSBM model is coupled to an isothermal single-particle reaction model. To help verify the validity of the assumption of perfect mixing, the times required for dispersing particles into the bed are briefly described.

Results of the models are presented in Chapter 6. With the help of a non-isothermal single-particle reaction model, the chapter describes the conditions where the assumption of isothermality is valid. Next, the generalized slugging-bubbling fluidized bed reactor model (GSBM) is compared to previous fluidized bed reactor models. Some of the experimental results presented in Chapter 4 are fitted with the complete gas-solid fluidized bed reactor model. A sensitivity analysis finally compares the laboratory fluidized bed roaster to the industrial roaster for different conditions.

The thesis concludes in Chapter 7 with a summary of the conclusions as well as recommendations regarding laboratory and industrial roasters and future work.
Chapter 2
Thermodynamics and Kinetics of Roasting

This chapter describes the chemistry of the roasting process from a thermodynamic and kinetics viewpoint. The thermodynamics and kinetics of the relevant zinc species are first reviewed, followed by the thermodynamics of iron and lead, copper and cadmium species. A number of studies have looked at the recovery or effect of minor elements such as magnesium [103, 104, 105], germanium [47], silver [106, 43] and other minor elements [107]. The focus of this thesis being agglomeration and related phenomena, only the major compounds and those shown to contribute to agglomeration are reviewed.

2.1 Zinc

2.1.1 Thermodynamics

The zinc-sulfur-oxygen system is a relatively simple system where zinc sulfide is only found as ZnS, zinc oxide as ZnO, zinc sulfate as ZnSO₄ and only one basic zinc sulfate (ZnO·2ZnSO₄) exists. Table 2.1 presents the crystalline structures as well as the theoretical densities and molar volumes, all calculated from the crystallographic data contained within the powder diffraction files [108]. The number of significant digits for the densities and the molar volumes reflects the accuracy of the crystallographic data for the different compounds.

At room temperature, the stable form of zinc sulfide is sphalerite. Upon heating, it transforms into wurtzite, the hexagonal form of zinc sulfide. The transformation temperature is 1019°C [109]. The difference between the sphalerite and wurtzite molar volumes is negligible. It is very unlikely that the phase transform would significantly affect the structure of zinc sulfide.
Table 2.1: Theoretical density and molar volume of zinc species calculated from crystalline structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>Density ( g/cm^3 )</th>
<th>Molar volume ( cm^3/mol )</th>
<th>Powder diffraction file</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS (sphalerite)</td>
<td>4.0966</td>
<td>23.789</td>
<td>5-566</td>
</tr>
<tr>
<td>ZnS (wurtzite)</td>
<td>4.0903</td>
<td>23.826</td>
<td>36-1450</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.6752</td>
<td>14.341</td>
<td>36-1451</td>
</tr>
<tr>
<td>( \alpha )-ZnSO(_4)</td>
<td>3.884</td>
<td>41.57</td>
<td>8-491</td>
</tr>
<tr>
<td>( \beta )-ZnSO(_4)</td>
<td>2.90</td>
<td>55.7</td>
<td>32-1477 (700°C)</td>
</tr>
<tr>
<td>ZnO(_2)-2ZnSO(_4)</td>
<td>3.8796</td>
<td>104.21</td>
<td>32-1475</td>
</tr>
<tr>
<td>ZnO(_2)-2ZnSO(_4)</td>
<td>3.85</td>
<td>105</td>
<td>32-1476 (850°C)</td>
</tr>
</tbody>
</table>

particles. The phase transform may, however, affect the reactivity of the particles.

Zinc sulfate exists in two crystalline forms. \( \alpha \)-ZnSO\(_4\) transforms into \( \beta \)-ZnSO\(_4\) above 734°C [110]. The crystalline structure information for the high temperature cubic form of zinc sulfate was measured at 700°C [108]. Similarly, the crystallographic information for the high temperature form of the basic zinc sulfate was obtained at high temperature.

When comparing the molar volumes of the different compounds, all on the basis of 1 mole of zinc, only the reaction of zinc sulfide to zinc oxide would potentially create a porous structure i.e. one mole of zinc sulfide is larger than one of zinc oxide. The reaction to create any of the sulfates from the sulfide or the oxide will create a product more voluminous than the starting material. The blocking of pores may therefore be caused by reactions to produce sulfates.

The thermodynamics of the oxide, sulfate and basic sulfate were first studied by measuring the SO\(_3\) equilibrium pressures [110, 111] and later using high-temperature electrochemical cells [112, 113]. The thermodynamics of the system can be graphically represented as predominance diagrams. A predominance diagram is a graphical representation of which solid phase is the most stable when in equilibrium with a given gas composition. Because predominance diagrams...
do not account for liquid and solid solutions, they represent a simplified system. They are, however, very useful to evaluate the effect of temperature and gas composition. The reader is referred to the articles of Bale [114, 115] for the theory of predominance diagrams and their calculation. Figures 2.1 to 2.3, as well as all other predominance diagrams presented in this thesis, were created using the thermodynamic data of HSC v4.0 [116]. FACTSage [117], a different thermodynamic package, could also have been used. The two software packages use similar sources for the thermodynamic data of pure inorganic compounds (JANAF [118], Barin [119], etc) and therefore give very similar predominance diagrams. However, FACTSage can generate higher order predominance diagrams (multi-metal or larger number of independent gaseous species) or take into account liquid and solid solutions. Since this thesis only considers simple predominance diagrams, FACTSage is not required here. HSC is therefore sufficient for the thermodynamic calculations of pure compounds in this thesis. To allow rapid and automatic thermodynamic calculation for any $O_2$ and $SO_2$ partial pressure, the required thermodynamic information was exported, and the method of creating higher-order predominance diagrams, described by Bale [114, 115], was implemented using Matlab. The code was verified by means of numerous test cases. All predominance diagrams (standard and modified) shown in this thesis were created using this code.

The upper temperature limit for the thermodynamic data for the basic zinc sulfate is 1200K. This temperature is not very far from the roasting temperature. If this phase was to be removed from the calculations, the ZnO - ZnSO$_4$ equilibrium line would fall within the ZnO·2ZnSO$_4$ stability area. Note that there is a discrepancy in the thermodynamic data for basic zinc sulfate (ZnO·2ZnSO$_4$) between FACTSage and HSC. The upper temperature limit for basic zinc sulfate is approximately 800K within FACTSage. For HSC, the limit is 1200K. Since it is not clear which source is the more authoritative, the HSC data, which has a higher temperature limit, was assumed to be correct. Using the FACTSage thermodynamic data for ZnO·2ZnSO$_4$ within HSC, the ZnO·2ZnSO$_4$ stability area at 850 °C virtually disappeared. Since basic zinc sulfate is not produced under typical roasting conditions, except in the boiler and downstream equipment, this uncertainty with respect to the basic zinc sulfate stability is of little concern.
Chapter 2. Thermodynamics and Kinetics of Roasting

for this thesis. However, if a sulfation study were to be initiated, the thermodynamics of the zinc-oxygen-sulfur system should be clarified.

The diagrams also present a family of lines representing different zinc partial pressure in equilibrium with the solid. The line where point A is located represents the gas composition in equilibrium with a mixture of zinc sulfide and zinc oxide. However, as discussed in section 2.8, point A on the predominance diagram represents the gas composition in equilibrium with a mixture of zinc sulfide and zinc oxide also in equilibrium with their zinc vapour pressures, i.e. vaporization from both zinc oxide and zinc sulfide. These additional lines and points are discussed in section 2.8 below.

As the diagrams show, for a given temperature (see Figure 2.2), the sulfate phases are stable at higher sulfur dioxide and oxygen concentrations (upper right). However, when comparing different temperatures, the sulfates cannot be stable at atmospheric pressure, at high temperature even at 1 atmosphere SO₂ (log(P_{SO₂}) ≈ 0). In order for the sulfate to be stable at 1050°C, the required oxygen pressure is beyond one atmosphere. However, the sulfates are stable at lower temperature and high sulfur dioxide concentration (log(P_{SO₂}) ≈ 0). These trends apply to many other systems.

The sulfation of zinc oxide occurs significantly in the gas handling equipment where the lower temperature and high SO₂ content of the gas enhance the stability of zinc sulfate. The sulfation of zinc oxide proceeds very slowly when oxygen and sulfur dioxide are present. The reaction is much faster once the O₂-SO₂ mixture contacts a V₂O₅ catalyst to produce SO₃ [120]. The catalyst can also be contained within the zinc oxide sample. In such a case, the sulfation rate of zinc oxide increased with increasing amount of V₂O₅ catalyst present [121]. Iron oxide also catalyses the production of SO₃. Because iron oxide is omnipresent in zinc calcine, its presence affects the sulfation of calcine occurring within the boiler.
Chapter 2. Thermodynamics and Kinetics of Roasting

Figure 2.1: Zn-O₂-SO₂ Predominance diagram at 850°C

Figure 2.2: Zn-O₂-SO₂ Predominance diagram at 950°C
2.1.2 Kinetics of zinc sulfide oxidation

The oxidation of zinc sulfide has been studied using relatively pure natural sphalerite crystals, synthetic powders and zinc concentrates. While the goal of most studies was to understand the oxidation of zinc sulfide for metallurgical processes, more recent studies have been concerned with the regeneration of zinc oxide for gas desulfurization processes.

Gaseous zinc sulfide oxidation can significantly influence the reaction rates [122, 123]. The oxidation of gaseous zinc sulfide, observed in several studies [124, 122, 123, 125, 126, 127] was not discussed in the review on the oxidation of zinc sulfide by Dimitrov [128]. In most cases, the evaporation of zinc sulfide, followed by oxidation to produce zinc oxide, depended on the temperature and on the oxygen concentration in the gas. Oxidation in the gas phase has been observed at temperatures as low as 900°C and in environments containing very little oxygen. This indicates that zinc sulfide vaporization and gaseous oxidation could occur if the oxygen concentration is low. The gaseous oxidation of zinc sulfide may deposit zinc oxide on the surface of the bed particles, as in chemical vapour deposition. This is partly supported by Chen et
al. [52] who characterized the mineralogy of calcine samples from an industrial roaster. They proposed that the morphology of product calcine particles may indicate vapour-phase deposition or repeated cycling of the particles into and out of the fluidized bed.

Graydon and Kirk [82, 129] studied the oxidation mechanism of zinc sulfide and the formation of zinc ferrite. They concluded that solid state iron diffusion, melting of the Fe-S-O eutectic and gaseous zinc species are important phenomena during zinc concentrate roasting. Gaseous oxidation of zinc sulfide may deposit zinc oxide on the surface of the bed particles, as in chemical vapour deposition, thereby contributing to the growth of calcine particles.

**Modelling, rate expressions and activation energy**

Numerous studies have quantified the oxidation kinetics of zinc sulfide and derived rate expressions from experiments. Table 2.2 summarizes the studies containing quantitative results applicable to a rate expression. The type of experiment and the method used to follow the progress of the reactions and the sample material are described in the first columns. The experimental conditions varied from fluidized bed, suspended pellets to powders in crucibles. The measurement method usually depends on the experimental conditions used. Gas analysis is performed either by SO₂ neutralization and measurement of the solution conductivity or titration or by infra-red measurement. The extent of oxidation of solid samples is monitored using chemical analysis or by measuring the oxide layer thickness. For suspended pellets and suspended crucibles, the most common method of monitoring the extent of reaction is by thermo-gravimetric analysis (TGA) i.e. continuously weighing the reacting sample.

Various methods have been used to analyze the reaction rates. The initial reaction rates (Dembigh and Beveridge (1962) [122], Prabhu et al. (1984) [130], Sanchuan et al. (1985) [125], Kim and Themelis (1987) [131] and Sofekun and Doraiswamy (1996) [132]), the overall measured rates (Ong et al. (1956) [133]), the overall modelled rates and the “settled” rates (rates once the model predicts the reaction rate) (Piskunov et al. (1981) [134]) have all been used to determine the activation energy. The models are briefly described below. The variability among the analysis methods contribute to the variability in the measured activation energies. For
instance, Rao et al. (1982) [135] considered both the initial rates and the modelled rates and obtained very different activation energies for the same experiments (87 and 160 kJ/mol). It is important to note that the activation energy also depend on the analysis of the effect of oxygen concentration. For instance, the oxygen concentration (mol/m$^3$) varies with temperature for a constant oxygen partial pressure. This effect is much smaller than the scatter in activation energies in Table 2.2, but must be accounted for.

The apparent activation energy and its applicable temperature range and the reaction order with respect to the oxygen concentration are shown in the table for each study. The range of maximum conversions ($X$) is indicated where available. In most studies the kinetic rate equation is of the form:

$$-r = kC^n_{O_2} \quad (2.1)$$

where $k$ is the reaction rate constant, $C_{O_2}$ is the oxygen concentration (mol/m$^3$) and $n$ is the reaction order with respect to the oxygen concentration. The assumed or measured reaction orders are shown in the table where given. Natesan and Philbrook (1969) [136], Sachdev and Mann (1980) [137], Prabhu et al. (1984) [130] and Sanchuan et al. (1985) [125] determined the reaction order to be 1. Agarwal and Gupta (1976) [138], Agarwal and Mohanty (1976) [139], Fukunaka et al. (1976) [140] and Rao (1984) [141] have assumed that the reaction order is 1. Cannon and Denbigh (1957) [124], Denbigh and Beveridge (1962) [122] and Kimura et al. (1983) [142] have measured the reaction order to be 1/2, and Takamura et al. (1974) [143] mentioned 1/2 but used first order for their modelling. Allay et al. [144, 145] observed a reaction order of 2/3. Piskunov et al. (1981) [134] measured different fractional reaction orders as a function of the controlling mechanism. Some studies (Ong et al. (1956) [133], Cannon and Denbigh (1957) [124], reference 10 of [128] or Gerlach of [132], Conrad and Wuth (1970) [146] and Sofekun and Doraiswamy (1996) [132]) have found that the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model for adsorption of reactant could be applied to the oxidation of zinc sulfide. The LHHW rate model is of the form:

$$-r = \frac{kK_A C_{O_2}}{1 + K_A C_{O_2}} \quad (2.2)$$

where $K_A$ is the adsorption equilibrium constant.
Table 2.2: Summary of zinc sulfide oxidation kinetic studies. Blank when information not available or not applicable

<table>
<thead>
<tr>
<th>Reference</th>
<th>Experimental conditions</th>
<th>Experimental method</th>
<th>Material</th>
<th>Temperature range (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Gas reaction order</th>
<th>Model used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 4 of [128] (1953)</td>
<td>Fluidized bed</td>
<td>Gas analysis</td>
<td>Sphalerite</td>
<td>800-900</td>
<td>118.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ong et al. (1956) [133]</td>
<td>Suspended sample</td>
<td>TGA Gas analysis (Titration)</td>
<td>Sphalerite single crystals plates</td>
<td>700-870</td>
<td>252.3</td>
<td>LHHW</td>
<td>none</td>
</tr>
<tr>
<td>Cannon and Denbigh (1937) [124]</td>
<td>Suspended sample</td>
<td>Oxide thickness and weight</td>
<td>Sphalerite single crystals (110) faces</td>
<td>680-830</td>
<td>209.2</td>
<td>LHHW</td>
<td>Shrinking-core for plates</td>
</tr>
<tr>
<td>Wada and Niwa (1957) [132]</td>
<td>Fluidized bed</td>
<td>Gas analysis</td>
<td>Sphalerite</td>
<td>600-700</td>
<td>184.2-192.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference 8 of [128] (1959)</td>
<td>Fluidized bed</td>
<td>Gas analysis</td>
<td>Sphalerite</td>
<td>900-1000</td>
<td>12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denbigh and Beveridge (1962) [122]</td>
<td>Suspended pellet</td>
<td>Gas analysis (Conductivity)</td>
<td>ZnS Powder 9.5-15.8 mm spheres</td>
<td>550-675</td>
<td>259.41</td>
<td>0.5</td>
<td>Initial rates</td>
</tr>
<tr>
<td>Reference 11 of [128] (1964)</td>
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<td>Chemical analysis of solid product</td>
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<td>121.4</td>
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<td>TGA</td>
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<td>301.5</td>
<td>LHHW</td>
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<tr>
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<td>Stationary bed</td>
<td>DTA</td>
<td>Amorphous ZnS 75-90 μm</td>
<td>530-600</td>
<td>67</td>
<td>238.7</td>
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<tr>
<td>Rao and Abraham (1965) [147]</td>
<td>Pellet in horizontal tube furnace</td>
<td>Oxide Thickness</td>
<td>ZnS 15 mm cylinders</td>
<td>750-900</td>
<td>12.13</td>
<td>none</td>
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<tr>
<td>Reference 12 of [128] (1967)</td>
<td>Fluidized bed</td>
<td>Gas analysis</td>
<td>Sphalerite 295-471 μm 57.9%Zn 5.2%Fe 2.26%Pb 31.1%S</td>
<td>&lt; 850</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td>850-930</td>
<td>209.4-251.2</td>
<td>104.7-125.6</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>930-1020</td>
<td>41.90</td>
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<table>
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<tr>
<th>Reference</th>
<th>Experimental conditions</th>
<th>Experimental method</th>
<th>Material</th>
<th>Temperature range (°C)</th>
<th>( E_a ) (kJ/mol)</th>
<th>Gas reaction order</th>
<th>Model used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 13 of [128] (1969)</td>
<td>Fluidized bed 295-471 ( \mu )m</td>
<td>Gas analysis</td>
<td>Sphalerite 57.9%Zn 5.2 %Fe 2.25%Pb 31.1%S</td>
<td>910-930 930-970 970-1020</td>
<td>50.20 25.10 37.70</td>
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<tr>
<td>Natesan and Philbrook (1969) [136]</td>
<td>Suspended pellet</td>
<td>TGA</td>
<td>Pretreated zinc concentrate 4-16 mm sphere</td>
<td>700-1030</td>
<td>12.55</td>
<td>1</td>
<td>Shrinking core: Chemical control ( X = 0.4 - 0.9 )</td>
</tr>
<tr>
<td>Conrad and Wuth (1970) [146]</td>
<td>Fluidized bed</td>
<td>Gas analysis (titration)</td>
<td>99% ZnS</td>
<td>650-800</td>
<td>215.89</td>
<td></td>
<td>LHHW</td>
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<tr>
<td>Dimitrov and Vanyukov (1970) [148]</td>
<td>Fluidized bed</td>
<td>Isothermal DTA</td>
<td>Amorphous ZnS Cubic ZnS Hexagonal ZnS Sphalerite Marmatite</td>
<td>505-700 625-900 650-850 740-860 710-870</td>
<td>153 190 205 196 233</td>
<td></td>
<td>Homogenous model ( X = 0.15 - 1 )</td>
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<tr>
<td>Reference 15 of [128] (1970)</td>
<td>Fluidized bed 208-246 ( \mu )m</td>
<td>Gas analysis</td>
<td>Sphalerite 64.1%Zn 3.68%Fe 31.78%S</td>
<td>650-800</td>
<td>208.9</td>
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<tr>
<td>Natesan and Philbrook (1970) [149]</td>
<td>Fluidized bed</td>
<td>Chemical analysis of solid samples</td>
<td>Pretreated zinc concentrate</td>
<td>690-960</td>
<td>168.41</td>
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<td>Shrinkin-core ( X = 0.8 - 0.96 ) 1-phase F.B. model</td>
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<tr>
<td>Reference 19 of [128] (1972)</td>
<td>Fluidized bed</td>
<td>Gas analysis</td>
<td>Sphalerite 65.5%Zn 1.6%Fe 33.4%S</td>
<td>760-840 840-900</td>
<td>252.1 76.6</td>
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<tr>
<td>Gokarn and Doraiswamy (1971,1973) [150, 151]</td>
<td>Suspended pellet</td>
<td>Gas analysis (Titration)</td>
<td>ZnS powder 17 mm sphere, plates and cylinders</td>
<td>600-670 720-780</td>
<td>31.61 8.04</td>
<td></td>
<td>Diffusion Model ( X = 1 )</td>
</tr>
<tr>
<td>Takamura et al. (1974) [143]</td>
<td>Suspended pellet</td>
<td>TGA</td>
<td>Zinc powder 9.5-11.5 mm spheres</td>
<td>560-690</td>
<td>145.6</td>
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<td>Assumed 1 in model</td>
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<table>
<thead>
<tr>
<th>Reference</th>
<th>Experimental conditions</th>
<th>Experimental method</th>
<th>Material</th>
<th>Temperature range (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Gas reaction order</th>
<th>Model used</th>
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<tbody>
<tr>
<td>Rayakar and Dixit (1975) [152]</td>
<td>Fluidized bed -100+300 mesh</td>
<td>Gas analysis</td>
<td>Sphalerite concentrate</td>
<td>800-950</td>
<td>43.72 110.46</td>
<td></td>
<td>Homogeneous model</td>
</tr>
<tr>
<td>Agarwal and Gupta (1976) [138]</td>
<td>Fluidized bed of 1.435, 1.84 and 2.19mm pellets</td>
<td>Chemical Analysis of solid samples</td>
<td>Zinc concentrate 200-300 mesh</td>
<td>700-800</td>
<td>114.27 127.82</td>
<td>assumed 1</td>
<td>Shrinking-core: Chemical control $X = 0.9$</td>
</tr>
<tr>
<td>Agarwal and Mohanty (1976) [139]</td>
<td>Suspended pellet</td>
<td>TGA</td>
<td>ZnS powder -325 mesh 20 mm pellet</td>
<td>700-800</td>
<td>138.62</td>
<td>assumed 1</td>
<td>Shrinking-core Chemical control $X = 0.6 - 0.9$</td>
</tr>
<tr>
<td>Fukunaka et al. (1976) [140]</td>
<td>Fluidized bed 60 to 100 mesh</td>
<td>Gas analysis</td>
<td>Zinc concentrate</td>
<td>800-910</td>
<td>313.82</td>
<td>assumed 1</td>
<td>Shrinking-core $X = 0.9 - 0.95$ 2-phase F.B. model</td>
</tr>
<tr>
<td>Hattori et al. (1980) [123]</td>
<td>Fluidized bed 60 to 100 mesh</td>
<td>IR Gas analysis and solid samples</td>
<td>Zinc concentrate</td>
<td>900</td>
<td>0.0009-0.02 atm O$_2$</td>
<td>Shrinking core Gaseous High T. $X = 0.7 - 0.95$</td>
<td></td>
</tr>
<tr>
<td>Sachdev and Mann (1980) [137]</td>
<td>Suspended pellet</td>
<td>TGA</td>
<td>99.9% ZnS 20mm H X 10mm D cylinder (open to flat face only)</td>
<td>565-665</td>
<td>95.40</td>
<td>Measured 1</td>
<td>Initial rates</td>
</tr>
<tr>
<td>Piskunov et al. (1981) [134]</td>
<td>Fluidized bed 160-520 microns</td>
<td>Gas analysis</td>
<td>Zinc concentrate 55.4%Zn 2.1%Pb 2.1%Fe 29.9%S 2.9%CaO 1.2%MgO</td>
<td>700-875</td>
<td>105.5</td>
<td>46.1</td>
<td>0.32 0.44</td>
</tr>
<tr>
<td>Rao and Kumar (1982) [135]</td>
<td>Suspended pellet</td>
<td>Gas analysis</td>
<td>1 sided pellet 1.25 cm diameter</td>
<td>600-744</td>
<td>159.58 model 86.61 initial rates</td>
<td>Structural model</td>
<td></td>
</tr>
<tr>
<td>Dimitrov and Boyanov (1983) [128]</td>
<td>Fluidized bed 125-160 microns</td>
<td>DTA and Gas analysis</td>
<td>Amorphous ZnS Cubic ZnS Hexagonal ZnS Sphalerite Marmatite</td>
<td>500-800</td>
<td>63.1</td>
<td>111.6</td>
<td>104 84.4 161.4 118.3</td>
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<tr>
<th>Reference</th>
<th>Experimental conditions</th>
<th>Experimental method</th>
<th>Material</th>
<th>Temperature range (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Gas reaction order</th>
<th>Model used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kimura et al. (1983)</td>
<td>Differential tube reactor</td>
<td>Gas analysis</td>
<td>99.9% ZnS 5.9-7.1 mm pellets</td>
<td>680-840</td>
<td>244</td>
<td>0.5</td>
<td>Grain model: Shrinking core grains with size distribution</td>
</tr>
<tr>
<td>Allay and Ablitzer (1984,1985)</td>
<td>TGA and Gas analysis</td>
<td></td>
<td>99.99% ZnS powder, sintered or fused</td>
<td>517-740</td>
<td>325.97</td>
<td>2/3</td>
<td>Shrinking-core: chemical control $X = 0.1 - 0.95$</td>
</tr>
<tr>
<td>Prabhu et al. (1984)</td>
<td>Suspended pellet</td>
<td>TGA</td>
<td>97.4% ZnS very porous pellets 9.5 mm D X 7-15 mm H</td>
<td>480-560</td>
<td>353±41</td>
<td>1</td>
<td>Initial rates</td>
</tr>
<tr>
<td>Rao (1984)</td>
<td>Suspended pellet</td>
<td>Gas analysis</td>
<td>99.9% ZnS Thin pellets 44-77 μm thick</td>
<td>602-734</td>
<td>159.70</td>
<td>Assumed 1</td>
<td>Structural model</td>
</tr>
<tr>
<td>Sanchuan et al. (1985)</td>
<td>Suspended pellet</td>
<td>TGA and Gas analysis</td>
<td>Marmatite 10.26 mm D X 8-10 mm H</td>
<td>450-505</td>
<td>263.43</td>
<td>1</td>
<td>Initial rates</td>
</tr>
<tr>
<td>Kim and Themelis (1987)</td>
<td>Suspended pellet</td>
<td>Gas analysis</td>
<td>ZnS pellets, 12.9 mm D X 7.3 mm H</td>
<td>577-1027 ≤577</td>
<td>17.57</td>
<td>158.99</td>
<td>Initial rates</td>
</tr>
<tr>
<td>Bagajewicz (1988) of</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kimura (1989)</td>
<td>Differential tube reactor</td>
<td>IR Gas analysis</td>
<td>very fine ZnS powder 0.5 mm pellet</td>
<td>715-808</td>
<td>230</td>
<td></td>
<td>Grain model</td>
</tr>
<tr>
<td>Sofekun and Doraiswamy (1996)</td>
<td>Suspended sample in TGA crucible</td>
<td>TGA</td>
<td>ZnS powder</td>
<td>548-609</td>
<td></td>
<td>LHHW</td>
<td>Initial rates only tested for chemical reaction control and ash layer control</td>
</tr>
<tr>
<td>Zivkovic et al. (1998)</td>
<td>Sample in DTA crucible</td>
<td>DTA</td>
<td>Pure marmatite Marmatite concentrate</td>
<td>69 and 86 187 and 194</td>
<td></td>
<td></td>
<td>Kissinger and Ozawa methods</td>
</tr>
<tr>
<td>Dimitrov et al. (2000)</td>
<td>Sample in TGA crucible</td>
<td>TGA</td>
<td>Marmatite powder</td>
<td>750-1000</td>
<td>80</td>
<td></td>
<td>Shrinking-core: chemical control $X = 0.6 - 1$</td>
</tr>
</tbody>
</table>

Figure 2.4: Intrinsic reaction rate of various kinetic studies. Rate expressions from references\[124, 143, 140, 135, 142, 130, 144, 145\]. Dashed line corresponds to fitted kinetics (equation 2.3) discussed in text.

The activation energy does not give a complete representation of the kinetics of the system. In addition to the activation energy, the pre-exponential constant from the Arrhenius equation, as well as the rate expression used to obtain the rate constant, must all be considered when comparing kinetic information from various authors. Figure 2.4 presents the rate information from several of the studies summarized in Table 2.2 which offer a complete rate expression. Note that since the rate expressions differ (reaction order and use of concentration or partial pressure for oxygen) from one study to another, comparison must be made on a reaction basis. With the exception of studies A and B, there is relatively little scatter among the different studies. The study of Takamura et al.\[143\] (line B) clearly stands out as aberrant. That of Fukunaka et al.\[140\] (line A) does not directly extend the clustered group of studies, but may represent an adequate upper bound to the kinetics. The dashed line represents the least-squares fit of the end-points of all the studies except those of Takamura et al.\[143\] and Fukunaka et al.\[140\]. Note that the slope of the line gives the negative value of the activation energy.
Since the Fukunaka et al. [140] kinetic study is the only study with a complete rate expression at high temperature and since the data are from a fluidized bed, this study is not dismissed as aberrant, but used to provide a probable upper-limit for the kinetics. Fukunaka et al. [140] obtained their kinetics by fitting their fluidized bed model to their experimental data, while the other kinetic studies obtained their rate information directly from kinetic experiments. The dashed line shown in Figure 2.4 and given by the kinetic rate expression:

\[ r_{O_2} = 6.28 \cdot 10^{12} \exp\left(\frac{-288kJ/mol}{RT}\right)C_{O_2} \]  

provides a reasonable fit to most of the kinetic studies and may be considered as a reasonable lower limit to the kinetic rates. The Fukunaka et al. [140] rate expression:

\[ r_{O_2} = 2.96 \cdot 10^{15} \exp\left(\frac{-314kJ/mol}{RT}\right)C_{O_2} \]

provides an upper limit. Until a better kinetic rate expression is available to calculate the reaction rate at high temperature, it is recommended that both of these kinetic rate expression be considered in sensitivity analyses. These two rate expressions are used in the remainder of this thesis.

Numerous approaches have been used to model the oxidation of zinc sulfide. The early works did not use models to predict the conversion with time. They often measured the reaction rates with the measured oxide thicknesses and assumed that the chemical reaction was rate-limiting.

The shrinking-core model was the first comprehensive model applied successfully to the oxidation of zinc sulfide. In the shrinking-core model, the solid reactant is assumed to be impervious to the gas, while the solid product is porous. The solid reactant is present as a core, which shrinks as the reaction proceeds. The core is surrounded by a porous ash layer. In the complete model, the effect of the chemical kinetics, the mass transport through the product layer and the effects of transport from the bulk gas phase to the surface of the particles are taken into account. Very simple equations are obtained from the shrinking-core model for the cases of chemical kinetics control, product layer mass transfer control and external mass transfer control. For the case where external mass transfer is rate-controlling, the conversion (X) increases
Chapter 2. *Thermodynamics and Kinetics of Roasting*

linearly with time (t):

\[ X = Kt \]  \hspace{1cm} (2.5)

When mass transfer through the product layer is rate-controlling:

\[ 1 - 3(1 - X)^{1/3} + 2(1 - X) = Kt \]  \hspace{1cm} (2.6)

When the chemical reaction is rate-controlling:

\[ 1 - (1 - X)^{1/3} = Kt \]  \hspace{1cm} (2.7)

Under conditions of chemical control, the thickness of the product layer increases linearly with time (proven by replacing the conversion by \( X = 1 - (r_c/R)^3 \) where \( r_c \) is the core radius and \( R \) is the particle radius). Note that these equations apply to the reaction of spherical particles. The equations are different for geometries other than spheres i.e. cylinders and flat plates. For flat plates under conditions of chemical kinetics or film diffusion control, both the conversion and the product layer thickness increase linearly with time. For a complete discussion of the model, the reader is referred elsewhere [156, 157]. The shrinking-core model is described further in chapter 5.

Several studies have modelled the oxidation of zinc sulfide with the spherical shrinking-core model (equations 2.6 and 2.7). These equations are often used with experimental data to identify the rate-controlling step. To obtain the activation energy of the process, the fitted rate constant (K) is plotted as a function of temperature in an Arrhenius plot.

Among the studies who have used the shrinking core-model, only Natesan and Philbrook (1970) [149], Takamura *et al.* (1974) [143] and Agarwal and Gupta (1976) [138] truly considered cases where product layer diffusion affected the reaction rates. The other studies only considered chemical kinetics control (equation 2.7).

Jander's equation has also been used to model the oxidation kinetics (Piskunov *et al.* (1981) [134]).

\[ 3(1 - (1 - X)^{1/3})^2 = Kt \]  \hspace{1cm} (2.8)
Chapter 2. Thermodynamics and Kinetics of Roasting

Jander's equation is valid only for slab-like particles or for the initial stages for other geometries [156]. Therefore, Jander's equation should not be used in place of the shrinking-core model. Hence, the analysis of Piskunov et al. (1981) [134], where only the experimental data between 20% and 97% conversion were able to fit Jander's equation, is questionable. The Crank-Ginstling-Brounshtein equation, proposed to model the reaction when diffusion through the product layer of a spherical particle is controlling [128, 158] is equivalent to equation 2.6. Its use is therefore acceptable.

The diffusion model of Gokarn and Doraiswamy [150, 159, 151] is another formulation of the shrinking-core model. By neglecting chemical kinetics, they obtained an equation similar to equations 2.5 and 2.6, including both diffusive resistances (external and ash-layer).

The grain model was also applied to the oxidation of zinc sulfide [135, 141, 142, 153, 160]. In the grain model, the porous solid reactant consists of a large number of small non-porous grains, each treated as shrinking-core. One advantage of the grain model is that it can effectively treat homogeneous reaction throughout a pellet as well as shrinking-core reaction. In fact, these two opposite phenomena are extremes of the grain model.

Figure 2.5 represents the grain model and its extremes. When the chemical kinetics are slow compared to the diffusion of species through the pores, (Figure 2.5, left), the gas concentration...
throughout the pellet is constant. Each grain of the pellet is surrounded by fluid of the same composition. At a given time, the conversion of every grain is the same and equal to the overall conversion. This is described as homogeneous reaction. This type of homogeneity must not be confused with the typical 1-phase homogenous reaction i.e. reactions of two species within the same fluid. For conditions where the resistance due to chemical kinetics is comparable to diffusional resistance through the pores (Figure 2.5, center), there is a concentration gradient through the pellet. For a given overall conversion (or time), the gas composition around each grain varies as a function of its position within the pellet. The reaction interface of the pellet is very diffuse. The grains located closer to the periphery of the pellet are more converted than those near the center. For conditions where the chemical kinetic resistance is much less than diffusion resistance through the pores (Figure 2.5, right), the reaction occurs within a very narrow reaction zone separating an unreacted core from a reacted shell. The entire pellet then reacts as a shrinking-core.

Takamura et al. (1974) [143] observed that the oxidation in air of 10 mm zinc sulfide spherical pellets occurred homogenously below 600 °C. Above 690 °C, the reaction proceeded in a topochemical matter (shrinking-core). Between these temperatures (600-690 °C), the reaction did not occur homogenously, but as a widespread reaction zone. Instead of using the grain model, Takamura et al. [143] used the simpler shrinking-core and homogenous models. However, they only used the extrapolated initial rate for the calculation of their activation energy. The final equation of the homogenous model is:

\[ X = 1 - e^{-Kt} \]  
(2.9)

Two studies (Dimitrov and Vanyukov(1970) [148] and Rayakar and Dixit(1975) [152]) used the homogenous model to analyze their experimental results.

Prasannan et al. [161] verified the applicability of the zone model of Mantri et al. [162] for the oxidation of sintered zinc sulfide pellets at 600°C. The zone model is similar to the shrinking-core model except that the reaction interface is replaced by a reaction zone. In this model, the reaction zone first expands into the pellet. Once a critical thickness is reached, the reaction
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zone moves into the pellet, leaving a product layer behind. As with the grain model described previously, the zone model combine the characteristics of the shrinking-core and homogenous models. Prasannan et al. [161] observed that the width of the reaction zone increases with pellet porosity.

A model for the gaseous oxidation of zinc sulfide was proposed by Denbigh and Beveridge [122], who assumed that the process occurs as a double diffusion layer where gaseous zinc sulfide diffuses out and oxygen diffuses toward the particle.

Gaseous oxidation of zinc sulfide in a fluidized bed was modelled by Hattori et al. [123] by combining the 2-phase fluidized bed model of Fukunaka et al. [140] and the gaseous oxidation model of Denbigh et al. [122].

2.1.3 Fluidized bed experimental studies

Table 2.3 summarizes the roasters used in various experimental studies. Most laboratory roasters were used for batch experiments and had diameters between 35 and 100 mm. Most of these studies have looked at the oxidation kinetics of zinc sulfide or of zinc concentrates. The first study on fluid bed roasting of zinc sulfide, published by Yagi et al. [163], presented valuable information (bed expansion, conversions, feed rates, residence times) for the design of fluid bed roasters. Although agglomeration has been observed in some studies [164, 59, 37], only Paik and Park [59] specifically studied agglomeration in a fluid bed roaster. The gaseous oxidation of zinc sulfide in a fluidized bed has only been considered in the work of Hattori et al. [123] where the kinetics of zinc sulfide oxidation were studied for low oxygen concentrations.

2.2 Iron

The iron-oxygen-sulfur system is very complex. Only a brief overview is presented here. Due to the existence of two oxidation states (ferric and ferrous), there are many compounds in the iron system. Several sulfides and oxides exist, both with significant non-stoichiometric compounds.

As Figure 2.6 shows, a number of forms of iron oxide may exist. Magnetite (Fe₃O₄) is a spinel
### Table 2.3: Details of experimental and pilot-scale roasters. Where blank, not specified.

<table>
<thead>
<tr>
<th>Authors or Company</th>
<th>Type of study</th>
<th>Batch/Continuous</th>
<th>DxH (mm)</th>
<th>Temperature (°C)</th>
<th>Velocity (m/s)</th>
<th>Carryover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Queiroz et al. [165]</td>
<td>Kinetics</td>
<td>Batch</td>
<td>45 x 700</td>
<td>780 - 930</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Yagi et al. [163]</td>
<td>Kinetics, New process</td>
<td>Batch / Continuous 0.5 - 5 g/min</td>
<td>50 x 500</td>
<td>700 - 900</td>
<td>0.19 - 0.34</td>
<td></td>
</tr>
<tr>
<td>Sanchuan et al. [125]</td>
<td>Kinetics</td>
<td>Continuous</td>
<td>34</td>
<td>950</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paik and Park [59]</td>
<td>Agglomeration</td>
<td>Batch</td>
<td>35 x 500</td>
<td>850 - 950</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Danilin et al. [164]</td>
<td>Kinetics</td>
<td>Batch</td>
<td>50 x ?</td>
<td>920 - 1020</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Fukunaka et al. [140]</td>
<td>Kinetics</td>
<td>Batch 1.5 g ZnS in 200 g Al₂O₃</td>
<td>53 x 600</td>
<td>800 - 910</td>
<td>0.1 - 0.57</td>
<td></td>
</tr>
<tr>
<td>Hattori et al. [123]</td>
<td>Kinetics, Gas phase oxidation</td>
<td>Batch 0.5 - 4 g ZnS in 200 g Al₂O₃</td>
<td>53 x 600</td>
<td>900</td>
<td>0.272</td>
<td></td>
</tr>
<tr>
<td>Yazawa et al. [107]</td>
<td>Behaviour of minor elements</td>
<td>Continuous 16.5 - 26.5 g/min</td>
<td>100 x 1100</td>
<td>980</td>
<td>0.3</td>
<td>50 %</td>
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<tr>
<td>Natesan and Philbrook [149]</td>
<td>Kinetics</td>
<td>Batch</td>
<td>101 x 533</td>
<td>690 - 960</td>
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<td>Sanchuan et al. [125]</td>
<td>Kinetics</td>
<td>Continuous</td>
<td>150 x ?</td>
<td>900 - 950</td>
<td></td>
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<tr>
<td>Pasminco Research [37]</td>
<td>Concentrate comparison</td>
<td>Continuous</td>
<td>300 x ?</td>
<td>825 - 1050</td>
<td>20 - 60%</td>
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<tr>
<td>Sulphide Corp. [166]</td>
<td>New process</td>
<td>Continuous 100 - 136 kg/hr</td>
<td>300 x ?</td>
<td>975 - 1000</td>
<td>8.2 - 16 %</td>
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<tr>
<td>Torbed, Canada [40]</td>
<td>New process</td>
<td>Continuous</td>
<td>400 x 800</td>
<td>620 - 950</td>
<td>3.1</td>
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<tr>
<td>Allied Chemical, Canada [24]</td>
<td>New process</td>
<td>Continuous 49 - 58 kg/hr</td>
<td>1520 x 15200</td>
<td>847 - 943</td>
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<td>Continuous 10-36 g/min</td>
<td>100 x 1170</td>
<td>875 - 975</td>
<td>0.25 - 0.5</td>
<td>37 - 84%</td>
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Figure 2.6: FeO-Fe₂O₃ phase diagram [167]

Figure 2.7: Fe-O₂-SO₂ Predominance diagram at 850°C
Figure 2.8: Fe-O₂-SO₂ Predominance diagram at 950°C

Figure 2.9: Fe-O₂-SO₂ Predominance diagram at 1050°C
formed of hematite ($\text{Fe}_2\text{O}_3$) and iron oxide ($\text{FeO}$). Wustite, often designated $\text{FeO}$, is clearly a distinct high-temperature oxide phase. Non-stoichiometric iron oxide also exists as $\text{Fe}_{1-x}\text{O}$. It is important to note that magnetite ($\text{Fe}_3\text{O}_4$) and zinc ferrite ($\text{ZnO}\cdot\text{Fe}_2\text{O}_3$) are two spinels that form extensive solid solutions [168].

A number of iron sulfides exists: marcasite and pyrite, two crystalline forms of FeS$_2$, FeS and pyrrhotite a non-stoichiometric sulfide Fe$_{1-x}$S. Upon heating in air, pyrite decomposes into porous pyrrhotite and elemental sulfur. Iron sulfide may also be present dissolved within zinc sulfide. The predominance diagrams in figures 2.7 to 2.9 assume pure stoichiometric compounds (no non-stoichiometric compounds and no solid solutions).

### 2.3 Lead

The lead-sulfur-oxygen system is a complex system where many compounds exist. Lead sulfate can form many intermediate compounds with lead oxide including the basic lead sulfates $\text{PbO} \cdot \text{PbSO}_4$, $2\text{PbO} \cdot \text{PbSO}_4$ and $4\text{PbO} \cdot \text{PbSO}_4$. $3\text{PbO} \cdot \text{PbSO}_4$ is a basic lead sulfate that can only be synthesized by wet methods. It can be neglected in pyrometallurgical studies. The oxidation kinetics of lead sulfide have recently been reviewed by the author [169]. Therefore, only the thermodynamics are reviewed here. Predominance diagrams are presented in Figures 2.10 to 2.12. As mentioned above, predominance area diagrams do not account for solid or liquid solutions. Each of these figures contain the predominance diagram and the partial pressures of the different gaseous lead species. The gaseous species are discussed in section 2.8.

When comparing the zinc and lead systems, one can see that, for the same temperatures, the stability areas of lead sulfates are at lower sulfur partial pressures than those of zinc sulfates. Also, unlike the zinc system, lead sulfide and lead oxide cannot co-exist in equilibrium with the gas. Instead they react to form lead and sulfur dioxide in a reaction called the roast reaction [170].

Note that the valid temperature range for the thermodynamic data for the basic lead sulfates is limited to 1200K ($\text{PbO} \cdot \text{PbSO}_4$), 1000K ($2\text{PbO} \cdot \text{PbSO}_4$) and 1168K ($4\text{PbO} \cdot \text{PbSO}_4$). These
Figure 2.10: Pb-O$_2$-SO$_2$ Predominance diagram at 850°C
Chapter 2. Thermodynamics and Kinetics of Roasting

![Figure 2.11: Pb-O₂-SO₂ Predominance diagram at 950°C](image)

(a) Predominance diagram
(b) Pb Partial pressures
(c) PbS Partial pressures
(d) PbO Partial pressures

Figure 2.11: Pb-O₂-SO₂ Predominance diagram at 950°C
Figure 2.12: Pb-O$_2$-SO$_2$ Predominance diagram at 1050°C
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Sulfates melt congruently or incongruently to form lead oxide - sulfate melts (see Figure 2.24). To allow some indication of the liquid composition, all three basic lead sulfates were kept in the calculation of the predominance diagram.

At 850°C, there are no liquid phases formed unless the gas composition is on the PbO-4PbO-PbSO₄ equilibrium line where one may expect some liquid since there is a eutectic between these two phases at 835°C. At 950°C, lead oxide is molten, and 4PbO-PbSO₄ decomposes into 2PbO-PbSO₄ and a liquid melt. Beyond 975°C, the basic lead sulfates are replaced by an extensive lead oxide-sulfate liquid phase.

2.4 Cadmium

Figure 2.13: Cd-O₂-SO₂ Preeminence diagram at 850°C

Cadmium is usually found as an impurity within zinc ores. Cadmium has been observed to be dissolved in the zinc concentrate (i.e. no distinct cadmium rich phases were found) and in the product within zinc ferrites and zinc and lead silicates [43]. Cadmium species have not been implicated in agglomeration problems within the fluidized roaster. However, they may have a significant effect on the leaching process [171]. Figures 2.13 to 2.15 presents predominance
Figure 2.14: Cd-O₂-SO₂ Predominance diagram at 950°C

Figure 2.15: Cd-O₂-SO₂ Predominance diagram at 1050°C
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diagrams for the Cd-O-S system. Since the partial pressure of cadmium reaches 1 for conditions beyond the metallic stability area, liquid metallic Cd cannot exist at atmospheric pressure for the temperatures shown here. Point A and the cadmium partial pressures lines are discussed in section 2.8.

Note that the basic cadmium sulfate \((\text{CdO})_2\text{CdSO}_4\) is well beyond its validity range (298-717K). Since there is no other information available, it was retained.

2.5 Copper

![Figure 2.16: Cu-O_2-SO_2 Predominance diagram at 850°C](image)

The Cu-O-S system is very complex, and only a brief overview is presented here. Figures 2.16 to 2.18 present predominance diagrams for the Cu-O-S system. The copper system is more complicated than indicated in these diagrams. For instance, in the presence of iron, copper and iron form 2-metal phases such as chalcopyrite and copper ferrite. Therefore a 2-metal predominance diagram is more appropriate [115].

Copper has been found to contribute to agglomeration in zinc fluidized bed roasters [59, 172].
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Figure 2.17: Cu-O₂-SO₂ Predominance diagram at 950°C

Figure 2.18: Cu-O₂-SO₂ Predominance diagram at 1050°C
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The exact mechanism or molten phases were not clearly identified. However, copper sulfate was identified in agglomerated zinc calcines [59]. The probable presence of a ternary eutectic between Cu$_2$S, Cu$_2$O and CuSO$_4$ around 400 °C was confirmed by Rosenqvist [173]. Additional studies are required to clearly identify the liquidus.

### 2.6 Water

The effect of water on concentrate lumps and pellets during roasting has been discussed in section 1.4.6. Here, we focus on its chemical aspects.

Sohn and Kim observed that zinc sulfide can react with water to form zinc oxide and hydrogen sulfide [174]. This reaction is not favoured thermodynamically and can only occur if the hydrogen sulfide concentration is very small. In their system, calcium oxide was used to capture hydrogen sulfide, allowing the oxidation reaction to proceed [175]. The reaction kinetics are first order with respect to the steam concentration. The effect of hydrogen sulfide was not studied, but the authors suggest that the H$_2$O/H$_2$S equilibrium be included in the analysis. Sohn and Kim [174] obtained a kinetic rate expression, applicable between 1023 and 1160K for steam concentrations between 3.94 and 9.84 mol/m$^3$.

Because oxygen is omnipresent in a roaster, hydrogen sulfide formation may be possible only in regions of very low oxygen concentration. Hydrogen sulfide would be very localized within the roaster, rapidly reacting with oxygen to form steam and sulfur dioxide. Therefore H$_2$S should not be detectable.

The reaction of zinc oxide with hydrogen sulfide to produce zinc sulfide was investigated for the desulfurization of gases from gasifiers [176]. Under reducing conditions, hydrogen sulfide can react with zinc oxide to form zinc sulfide and steam. However, at high temperature, zinc oxide was reduced to gaseous zinc and then reacted to zinc sulfide. Zinc oxide was stabilized by zinc titanates [177]. The regeneration of the desulfurization media was achieved by reoxidizing the zinc sulfide, releasing sulfur dioxide. Sasaoka et al. [178] have recently shown that steam plays a role in the oxidation of zinc sulfide. Using an oxygen isotope as a tag and a mass spectrometer,
they found that without oxygen, steam reacts with zinc sulfide to produce tagged sulfur dioxide and hydrogen, but when oxygen was present, the tagged steam still reacted with zinc sulfide to produce tagged sulfur dioxide. When no steam or small amounts of steam were present, oxygen reacted directly with the sulfide.

2.7 Effect of roasting conditions on stable phases

During roasting, zinc concentrate is contacted with air or oxygen-enriched air to produce zinc calcine. The equilibrium composition of the products may be calculated by minimizing the Gibbs free energy of the system. Thermodynamic calculations can be performed for a number of conditions of varying temperature and composition (amount of zinc concentrate and air). This would give an impressive list of compounds and concentrations. However, a simpler approach may be suitable, based on predominance diagrams.

Because zinc sulfide is the major compound in zinc concentrates, the reaction of oxygen to sulfur dioxide is governed by the oxidation of zinc sulfide. Assuming that reactions of other sulfides do not significantly affect the gas composition, their end product may be predicted with the help of the final gaseous composition of the zinc oxidation reaction:

$$\text{ZnS} + x\text{O}_2 + y\text{N}_2 \rightarrow \text{SO}_2 + \text{solid product} + y\text{N}_2 \tag{2.10}$$

The solid product may be ZnO, ZnSO₄ or ZnO·2ZnSO₄. The final gaseous composition of the zinc oxidation reaction depends on the initial amount of oxygen present. The resulting sulfur dioxide and any excess oxygen end up in the gaseous product. To help predict the final gaseous composition, assuming the reaction of zinc sulfide to zinc oxide, we define the stoichiometric excess of oxygen by:

$$Excess_{O_2} = \frac{n_{ZnS} n_{O_2}}{n_{O_2} n_{ZnS}} - 1 \tag{2.11}$$

where $n_i$ is the number of moles of species $i$ and $\nu_{ZnS}$ and $\nu_{O_2}$ are the stoichiometric coefficients for the reaction of zinc sulfide to zinc oxide. An excess oxygen value of 0 ($\log(Excess_{O_2}) = -\infty$)
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indicates that there is exactly a sufficient amount of oxygen for complete oxidation of zinc sulfide to zinc oxide (1.5 moles of oxygen for each mole of zinc sulfide). An excess oxygen value of 1 \((\log(Excesso_2) = 0)\) indicates that there is twice the sufficient amount of oxygen required for complete oxidation of zinc sulfide to zinc oxide (3 moles of oxygen for each mole of zinc sulfide). With this definition, a negative excess oxygen may exist for conditions where there is less oxygen than the stoichiometric requirement.

Equation 2.11 may be considered a stoichiometric model where the resulting gas composition after reaction depends on the input gas composition, the excess oxygen and the stoichiometry of the reaction. As for a standard predominance area diagram, the most stable compound in equilibrium with the resulting gas composition can be determined by calculating the \(\Delta G\) for each compound considered and selecting the one with the lowest \(\Delta G\). The most stable compound is then shown on the predominance diagram. However, instead of using the gas concentrations for the axes, as in the standard predominance diagram, we can create a new type of diagram by using excess oxygen to dictate the gas composition (using the stoichiometric model), with temperature as the other axis.

Equation 2.11 must be used carefully. Assuming a given reaction is acceptable, if the most stable compound is the same as the product of the reaction. However, the reaction must be changed if the assumption proves to be invalid. To calculate the equilibrium gas composition, one mole of zinc sulfide is completely reacted with the stoichiometric number of moles of oxygen and any excess as given by \(Excesso_2\). If the calculated gas composition is in equilibrium with zinc oxide, the gas composition is valid. If it is not, zinc sulfide reacts to produce a mixture of zinc oxide and basic zinc sulfate, pure basic zinc sulfate or a mixture of basic zinc sulfate and zinc sulfate. (Note that pure zinc sulfate cannot be produced since it requires that a given amount of sulfur dioxide be present to be stable.) Once the equilibrium gas composition is calculated, the reaction products of the other compounds are those which are in equilibrium with the gaseous products.

Figure 2.19 presents the predominant phases for various elements assuming the reaction of
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Figure 2.19: Excess oxygen - Temperature Predominance diagram for gaseous feed of air (21% O₂). Calculated from thermodynamic data and equation 2.11
Figure 2.20: Gas concentrations for excess oxygen - temperature predominance diagram for gaseous feed of air (21% O₂). Calculated using thermodynamic data and equation 2.11
air with zinc sulfide. The shape of these diagrams can be understood when considering the trajectory of the resulting gas composition on a typical \( \log(P_{SO_2}) - \log(P_{O_2}) \) predominance diagram as the amount of excess oxygen is increased. When the amount of excess oxygen is very small, the resulting sulfur dioxide concentration is large and the oxygen concentration is very small. Any change in the amount of excess oxygen dramatically changes the resulting oxygen concentration, but not the sulfur dioxide, i.e. the gas composition moves horizontally on the \( \log(P_{SO_2}) - \log(P_{O_2}) \) predominance diagram. When the amount of excess oxygen is very large, the resulting oxygen concentration is still very large and effectively dilutes the resulting sulfur dioxide i.e. the gas composition moves vertically on the \( P_{SO_2} - P_{O_2} \) predominance diagram.

This analysis is complicated by the fact that under some conditions, the predominant zinc compound after reaction to zinc oxide is not zinc oxide. In such cases, the gas composition moves along the \( \text{ZnO-ZnO-2ZnSO_4} \) equilibrium lines and enters the \( \text{ZnO-2ZnSO_4} \) stability area once there is sufficient oxygen for sulfation.

Figure 2.20 presents the gas composition related to Figure 2.19. The oxygen concentration is very small for small excess oxygen and increases with excess oxygen. The sulfur dioxide concentration is 15% for low excess oxygen, and slowly decreases with increasing excess oxygen. When the excess oxygen passes 100% (0 on Figures 2.19 and 2.20) the sulfur dioxide concentration rapidly decreases due to the dilution effect of additional gas.

The system is very sensitive to excess oxygen between an exact stoichiometric amount of oxygen and twice that amount \((-\infty < \log(\text{ExcessO}_2) < 0)\). Any major departure from the operating conditions (typically 10-20 % excess oxygen) has dramatic effects. Major departures from the operating conditions may arise from inefficient feed distribution and mixing. This is best shown by the lead species.

These diagrams are similar to the constant total pressure predominance diagrams presented by Kusano et al. [179]. Their diagrams were three-dimensional surfaces at a constant total partial pressure representing a cross-section of the three-dimensional \( (P_{O_2},P_{SO_2},T) \) predominance diagram. The main difference from the diagrams presented here is that the graph is transposed.
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to 2 dimensions by adopting the operating condition (excess oxygen) instead of the gas partial pressures ($P_{O_2}$ and $P_{SO_2}$) for a constant total partial pressure.

In section 6.3.4, the stoichiometric model will be replaced by a complete fluidized bed roasting reactor model, and its output will be used to create a diagram similar to Figure 2.19. As kinetic modelling will show, the use of thermodynamics for fluidized bed roasters may result in erroneous conclusions. However, thermodynamics show very clearly that excess oxygen may significantly affect the reaction products of the impurities.

2.8 Gas phase reactions

Various elements and compounds are volatile during the roasting of zinc concentrates. For example, due to their volatile nature, halides, mercury and arsenic species are separated from the calcine during roasting. The mercury and arsenic species are gaseous at roasting temperatures and are not discussed here. Cadmium, lead and zinc species are not usually gaseous at roasting temperatures. However, under some conditions, their partial pressures are relatively high and this may affect their volatilization. For example, various researchers have studied cadmium volatilization during the roasting of zinc concentrates, either to increase [180, 181, 182] or reduce [183, 184] its removal from the calcine.

Vaporization chemistry has received very little attention in the roasting literature. However, an early review [185] has shown that it is more complex than one would expect. Depending on the metal in question, oxides and sulfides species have been found to exhibit different features such as simple vaporization, dissociative vaporization and polymeric gas species.

Zinc and cadmium volatilize very similarly. The vapour pressures of zinc and cadmium for the oxygen or sulfur systems are shown in Figure 2.21. Both their oxide and sulfide dissociate to form $Zn(g)$, $Cd(g)$ and $O_2(g)$, $S_2(g)$. Because vaporization produces a non-metal species, any change in its concentration affects the metal vapour pressure. This has been experimentally observed by measuring the vapour pressure of cadmium over cadmium oxide as a function of oxygen partial pressure [185]. The analysis of the metal vapour partial pressure is very similar.
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to that of the solubility of salts in aqueous solutions where a solubility product is used to establish the equilibrium ionic concentrations. In the gaseous state, the partial pressure of the non-metal species is used with the equilibrium constant to obtain the equilibrium metal vapour pressure.

The volatility of the oxide or sulfide in vacuum or inert atmosphere is represented by points A in Figure 2.21. The volatility of zinc in retorting or slag fuming is enhanced by using a reducing atmosphere i.e. moving to the left of point A. Below a critical level, the condensed metal is stable and its partial pressure reaches a constant value.

The zinc and cadmium partial pressures and the interaction of sulfur and oxygen in the ternary systems are presented with their respective predominance diagrams (see Figures 2.1 to 2.3 and 2.13 to 2.15). Point A in these diagrams represents the composition of the gas in equilibrium with a mixture of sulfide and oxide. Point A is a point because of the following equilibria:

\[ MS + 2MO = 3M(g) + SO_2 \]  
\[ \frac{1}{2}S_2 + O_2 = SO_2 \]

The metal partial pressure in equilibrium with the oxide-sulfide mixture is higher than that in equilibrium with oxide or sulfide (Points A on Figure 2.21).

One of the zinc sulfide oxidation mechanisms is its reaction in the vapour phase. As Figure 2.21 suggests, under conditions of high temperatures and/or very low oxygen concentrations, the sulfide may sublimate and, once the oxygen concentration is sufficiently high, react at a distance from the sulfide particle. Such a mechanism has been observed in various studies. It has been shown that the oxidation of zinc sulfide at very high temperature (1800-2200K) proceeds by dissociative vaporization and reaction in the gas phase [186]. However, typical roasters operate far from these temperatures. The same gas phase reaction has been observed at lower temperatures [122].

The vaporization chemistry of lead species is very different from that of zinc and cadmium species. For instance, lead species form polymeric vapour compounds (Pb$_2$S$_2$, Pb$_2$O$_2$, etc
Figure 2.21: Zinc and cadmium partial pressures. Points A represents the partial pressure in equilibrium with pure oxide or sulfide.
[185]) and do not dissociate. The exact compounds present in the gaseous state depend on the oxygen and sulfur partial pressures. However, unlike the zinc and cadmium systems, the total metal vapour pressure does not change as significantly with changing oxygen or sulfur partial pressure (see Figure 2.22).

![Figure 2.22: Lead partial pressures](image-url)
Similar to the zinc and cadmium systems, the partial pressures of the lead species are presented on the predominance diagram of the lead system (see Figures 2.10 to 2.12). However, to simplify the representation of more than one predominant gaseous species, the partial pressures of the oxide, sulfide and metal are shown as different sub-figures.

The vapour pressures in equilibrium with zinc concentrates will mainly be governed by the predominant sulfide phase i.e. zinc sulfide. Therefore, under equilibrium conditions, the concentrate, a mixture of zinc, iron, lead and cadmium sulfides, generates a gaseous mixture close to point A on the zinc diagram. The gas composition at point A on the zinc diagram (Figures 2.1 to 2.3) falls within the cadmium sulfide stability area (Figures 2.13 to 2.15). The cadmium partial pressures in this area are relatively high compared to those at higher oxygen concentrations. The gas composition at point A on the zinc diagram is located within the lead stability area, close to the lead-lead sulfide equilibrium line (Figures 2.10 to 2.12). The region near this equilibrium line is where the total lead partial pressure is a maximum, Because it is near the equilibrium line, the most important lead gaseous species is lead sulfide, even within the metallic lead area.

In summary, all three systems discussed here (Zn, Cd and Pb) have their highest partial pressures at low oxygen partial pressures. For conditions near point A on the zinc system (Figure 2.2), the metal partial pressures rank as follows:

\[
P_{\text{Cd}} > P_{\text{PbS}} > P_{\text{Zn}}
\]

Therefore, significant transport of cadmium and lead would occur prior to the gaseous mass transport of zinc. Very low oxygen concentrations are required for the gaseous transport of metal species. If the oxygen partial pressure increases, “precipitation” from the gas phase would occur.

### 2.9 Low-melting-point phases during roasting

In addition to predominance area diagrams, phase diagrams are graphical representations of the thermodynamics of the system. They represent the solids, liquids and solutions present
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in a given system, for different compositions and temperatures. Unlike the predominance area diagram, their generation is very complex requiring difficult experimental measurements.

Several phase diagrams are presented in this section, both for the products and the reactants. These diagrams give information on the possible molten phases present during roasting. Because of the number of impurities present in a typical concentrate, the melting point of the calcine or concentrate may be well below that of its main constituents. The phase diagrams may indicate which impurity and phase contribute to agglomeration.

Low-melting-point compounds can be classified in three general types: reactant, product and reacting. The reactant low-melting-point compounds are those present in the concentrate. The eutectics in the ZnS-FeS-PbS system fall into this category. Because the reactants react in the roaster, these compounds have a finite life.

The product low-melting-point compounds are those present in the zinc calcine product. The eutectics in the PbO-PbSO₄ and PbO-SiO₂ systems belong to this category. These are compounds stable in the roaster gas and should always be present during roasting. A summary of the melting temperatures of various phases is shown below, in Table 2.4.

2.9.1 Phase diagrams - product type

The first phase diagram, shown in Figure 2.23, presents the zinc oxide silica phase diagram. Due to its effect on downstream processes, the production of zinc silicate during roasting has received some attention. Because the silica contained in zinc silicate is acid soluble, the presence of zinc silicate does not affect zinc recovery, but does affect the amount of silica in solution. Dissolved silica can polymerize, produce colloidal silica, gelify and cause severe filtering problems [187]. Zinc silicate is only found as Zn₂SiO₄. From the diagram, two eutectics are present, but both are much higher than typical roaster operating temperatures (~950°C). Therefore, any pure zinc silicate would likely be formed by a solid-state diffusion process. Liu et al. [188] have studied the kinetics of formation of zinc silicate from high silica-containing sphalerite concentrate. They have observed that the process could be modelled by the shrinking core
model and that solid-state diffusion controls the process. They obtained an activation energy of 406 kJ/mol.

In the lead system, there is a significant solubility amongst some of the species. For instance, Pb(l) and PbS(l) can be described as a single liquid solution [195]. As shown in Figure 2.24, the lead oxide-lead sulfate system has numerous phases and eutectics.

Figure 2.24 is the PbO-PbSO₄ phase diagram refined by Billhardt [190]. As seen in the diagram, no solid solutions exist in this system. However, the lowest temperature at which a liquid phase can exist is 835°C corresponding to the PbO-4PbO-PbSO₄ eutectic. All the phases melt congruently except tetrabasic lead sulfate which melts incongruently at 895°C. 2PbO·PbSO₄ is metastable below 640°C.

Figure 2.25 presents the lead oxide silica phase diagram. There are three lead silicates and three eutectics, all molten above 760°C. The lead oxide zinc oxide phase diagram, shown in Figure 2.27, has one eutectic melting at 861°C. The PbO-ZnO-SiO₂ system was recently optimized [196] such that a complete thermodynamic representation of the system is available in the FACT thermodynamic database computing system. The alumina-lead oxide phase diagram is shown in Figure 2.26. Similarly to the zinc oxide-lead oxide system, the alumina system only has one eutectic.

2.9.2 Phase diagrams - reactant type

Impurities in the zinc concentrate may contribute to the presence of low-melting-point phases. The phase diagrams presented in Figures 2.29 to 2.31 are needed when considering the effect of impurities on the melting temperature of zinc concentrates. Note that these diagrams neglect solid solutions and were created to represent the liquidus and solidus lines.

The minimum melting temperatures for the three binary systems are 1160°C (FeS-ZnS, Figure 2.29), 1041°C (PbS-ZnS, Figure 2.30) and 1130°C (Cu₂S-ZnS, Figure 2.31). However, the addition of FeS to the PbS-ZnS system produces a ternary eutectic which melts as low as 717°C [81]. Figures 2.32 and 2.33 present the FeS-PbS and Cu₂S-PbS phase diagrams. Both
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Figure 2.23: ZnO–SiO₂ phase diagram. [189], Temperature in °C

Figure 2.24: PbO–PbSO₄ phase diagram [190]
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Figure 2.25: PbO–SiO₂ phase diagram [191]. Composition in wt%, Temperature in °C

Figure 2.26: PbO–Al₂O₃ phase diagram [192] Temperature in °C
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Figure 2.27: PbO–ZnO phase diagram [193] Temperature in °C

Figure 2.28: PbO–Fe$_2$O$_3$ phase diagram [194] Temperature in °C
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Figure 2.29: FeS–ZnS phase diagram [109]

Figure 2.30: PbS–ZnS phase diagram [109]
Figure 2.31: Cu₂S–ZnS phase diagram [109]

Figure 2.32: FeS–PbS phase diagram [197]
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Figure 2.33: Cu$_2$S–PbS phase diagram [197]

Figure 2.34: Quaternary ZnS–FeS–PbS–Cu$_2$S phase diagram [198] Temperature in °C
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are relatively simple phase diagrams with eutectics at 863 (Figure 2.32) and 517°C (Figure 2.33), respectively. It is clear that it is the interaction of impurities that may lead to low-melting-point phases within zinc concentrates.

A complete ternary or quaternary phase diagram is therefore helpful in evaluating the effect of the main impurities on the melting temperatures of zinc concentrates. Figure 2.34 presents the liquidus surface of the ZnS-FeS-Cu₂S-PbS quaternary system (shown as 4 ternary systems). Note that the liquidus surface represents the composition and temperature of complete melting. Since roasting involves predominantly solid phases and agglomeration may be promoted by very small amounts of liquids, the solidus surface (surface of the conditions where a liquid phase first appears) offers the most useful information. However, a quaternary (or ternary) section (phases at a given temperature) or solidus surface phase diagram is not available.

Analysis is therefore limited to the quaternary phase diagram and to the binary diagrams presented previously. Zinc concentrates may, depending on their mineralogy and their extended exposure to high temperatures within the roaster, form liquid phases with compositions near the FeS-PbS and Cu₂S-PbS eutectics. Note that amongst these phases, PbS is the most volatile under roasting conditions. Its presence within liquid phases would likely be influenced by vaporization.

2.9.3 Phase diagrams - reacting type

The last type of phase diagram represents the reacting low-melting-point liquid formed from reactant and products. The ternary eutectic in the Fe-S-O system, shown in Figure 2.35, is a good example. The ternary eutectic in the FeS-FeO-ZnS system at 920°C [201] also falls within this category. A liquid phase would only be present for a short time during the reaction. The initial reactant and final product may be solid, but the intermediate may pass near the eutectic composition and become liquid until it resolidifies as the reaction proceeds. Such a low-melting-point phase would be transient and would depend on the reaction path and the kinetic conditions. Such a reactive solidification has been observed in the copper system [173]. A Cu₂S-CuSO₄ mixture was molten at 450°C under an atmosphere of SO₂, but solidified at
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Figure 2.35: Region of the Fe–S–O ternary phase diagram [199] Temperature in °C

Figure 2.36: FeO–FeS–Cu₂S ternary phase diagram [200] Temperature in °C
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550°C after loss of SO₂.

A eutectic melting at temperatures below typical roasting temperatures is also present in the Cu₂S-FeS-FeO system (Figure 2.36). This phase diagram clearly shows that the melting temperature may be lowered by adding a third component to where a ternary eutectic is present.

Table 2.4: Melting temperature of various phases

<table>
<thead>
<tr>
<th></th>
<th>Type</th>
<th>Melting Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS-ZnS</td>
<td>Binary Eutectic</td>
<td>1041°C from Figure 2.30</td>
<td>[197]</td>
</tr>
<tr>
<td>PbS-FeS</td>
<td>Binary Eutectic</td>
<td>842°C from Figure 2.32</td>
<td>[197]</td>
</tr>
<tr>
<td>FeS-ZnS</td>
<td>Binary Eutectic</td>
<td>1160°C from Figure 2.29</td>
<td>[109]</td>
</tr>
<tr>
<td>Cu₂S-PbS</td>
<td>Binary Eutectic</td>
<td>517°C from Figure 2.33</td>
<td>[197]</td>
</tr>
<tr>
<td>FeS-ZnS-PbS</td>
<td>Ternary Eutectic</td>
<td>717°C</td>
<td>[81]</td>
</tr>
<tr>
<td>Product type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>Pure</td>
<td>880°C</td>
<td></td>
</tr>
<tr>
<td>PbO-PbSO₄</td>
<td>Binary Eutectics</td>
<td>835°C from Figure 2.24</td>
<td>[190]</td>
</tr>
<tr>
<td>PbO-SiO₂</td>
<td>Binary Eutectics</td>
<td>720°C from Figure 2.25</td>
<td>[191]</td>
</tr>
<tr>
<td>PbO-ZnO</td>
<td>Binary Eutectic</td>
<td>861°C from Figure 2.27</td>
<td>[193]</td>
</tr>
<tr>
<td>PbO-Fe₂O₃</td>
<td>Binary Eutectic</td>
<td>730°C from Figure 2.28</td>
<td>[194]</td>
</tr>
<tr>
<td>Reacting type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-S-O</td>
<td>Ternary Eutectic</td>
<td>915°C from Figure 2.35</td>
<td>[199]</td>
</tr>
<tr>
<td>FeS-FeO-ZnS</td>
<td>Ternary Eutectic</td>
<td>920°C</td>
<td>[201]</td>
</tr>
<tr>
<td>Cu₂S-Cu₂O-CuSO₄</td>
<td>Ternary Eutectic</td>
<td>&lt;450°C</td>
<td>[173]</td>
</tr>
<tr>
<td>Cu₂S-FeS-FeO</td>
<td>Ternary Eutectic</td>
<td>850°C from Figure 2.36</td>
<td>[200]</td>
</tr>
</tbody>
</table>

The low-melting-point phases discussed and shown in the various phase diagrams are summarized in Table 2.4. Zinc sulfide, zinc oxide or zinc silicates are not molten at typical roaster operating temperatures (~950°C). Therefore, any roasting of pure zinc sulfide would not produce
any low-melting-point phases, even if silica was present. Agglomeration caused by low-melting-point phases would therefore be impossible in a pure ZnS roasting system. However, once impurities are present, as it is the case for zinc concentrates, a large number of low-melting-point phases can be produced. Depending on the temperature, liquid lead oxide can dissolve various amounts of lead sulfate (Figure 2.24), zinc oxide (Figure 2.25), iron oxide (Figure 2.28) and silica (Figure 2.25), all of which are present during roasting of zinc concentrates.

### 2.10 Conclusions and recommendations

Predominance diagrams are readily available for most metals. However, they usually assume pure solid compounds. Current thermodynamic data are relatively limited when considering sulfates, especially with respect to the thermodynamics of molten sulfates. The decomposition temperatures of sulfates may be estimated using current data. However, most of their melting temperatures are unknown. Except for the PbO-PbSO$_4$ system (Figure 2.24), no binary or ternary sulfate, oxide-sulfate or sulfide-sulfate phase diagrams were found in the literature. Research on these systems may uncover new avenues for industrial extraction processes.

Little is known on how to treat solid-liquid phase transforms during isothermal gas-solid reactions. Liquid products behave very differently from solid products. The diffusion of species between the solid and the gas-liquid interface becomes important. There is also the possibility of ionic and electrochemical reactions and frothing of the melt if there are gaseous reaction products.

Since it is the interaction of various impurities that lead to various low-melting-point phases, a complete ZnS-FeS-PbS-Cu$_2$S quaternary phase diagram would be helpful in determining the melting temperatures of various concentrates. Zinc was recently included into the matte, slag and blister copper databases of the FACT thermodynamic database computing system [109]. The FeS-ZnS, PbS-ZnS and Cu$_2$S-ZnS phase diagrams were calculated from the database. It is not clear whether the database for copper matte would apply and if there are sufficient data in the database to create this ternary diagram. Attempts to recreate the binary diagrams using
Chapter 2. Thermodynamics and Kinetics of Roasting

FactSage 5.1 [117] were not successful when FeS was involved. Equilibrium calculations of matte against solid sulfides is currently limited to zinc and copper sulfide solid solutions. Equilibrium calculations of the matte with other solid sulfide phases is currently not recommended. It is likely that the database will allow calculations within a relatively near future.

The most common compound contributing to low-melting-point phases is lead oxide (PbO). Pure lead oxide is a liquid at typical roaster operating temperatures (∼950°C). Several compounds are soluble in lead oxide, and some create eutectics that melt at even lower temperatures.
Chapter 3
Experimental Methods

In the light of the complex features of industrial fluidized bed roasters, the process must be simplified in an experimental setup capable of evaluating agglomeration phenomena. For instance, unlike the feed to the industrial roaster, the feed to the experimental roaster consists of dried concentrate particles where no lumps are present. Also, since entrainment of concentrate particles prior to their entry into the industrial fluidized bed cannot be clearly separated from entrainment from the bed, the feed is directly injected into the experimental fluidized bed. Hence moisture, lumps and concentrate entrainment are absent in the experiments so that we can determine how the chemical phenomena influence the particle size distribution.

Most experiments used the same initial bed material and same industrial concentrate. Since the concentrate was the same and only the operating conditions varied from one experiment to another, the experiments focussed on how the operating variables affect the bed particle size distribution.

3.1 Experimental pilot plant

The pilot scale roaster used in the present study is similar to that of Yazawa et al. [107], requiring continuous feeding for experimental runs lasting several hours. However, because they studied the behaviour of minor elements during fluidized bed zinc roasting, Yazawa et al. [107] required a gas cleanup system similar to the industrial process. In this work, the focus is on the processes occurring in the fluidized bed. Therefore, a simplified gas treatment system was used. Figure 3.1 presents the experimental set-up.
Figure 3.1: Experimental apparatus. T: Thermocouple, P: Pressure transducer, A: Oxygen sensor.
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The gases fed are compressed air and nitrogen. Oxygen is also available for oxygen enrichment. The gases are metered using rotameters, mixed and sent to the gas preheater, built from 316 stainless steel pipe, 102 mm ID, 114 mm OD (4" pipe, schedule 40), 710 mm long with standard flanges at its ends. Pipe couplings for thermocouples and pressure transducers, gas inlet and oxygen sensors are located 90 mm from each end. The preheater is filled with alumina packing and preheats the gas before entering the roaster. The preheater can be bypassed if no preheating is required.

The roaster consists of a fluid bed at the bottom and freeboard above, enlarged to reduce elutriation. The fluid bed zone consists of a 316 stainless steel pipe, 102 mm ID, (4" pipe, schedule 40), 660 mm long. The freeboard zone was built with a 316 stainless pipe, 154 mm ID, (6" pipe, schedule 40), 365 mm long. A standard 4" x 6" (100 x 150 mm) reducer joins the two zones. Standard flanges are located at the bottom and top of the roaster. Temperature and pressure ports are located 90, 281, 435, 626, 799 and 1080 mm above the distributor, while the top cover is 1165 mm above the distributor. Larger couplings for the gas outlet, feed inlet and oxygen sensor are installed 90 mm from the ends. A removable gas distributor, made of a 6.3 mm (1/4") thick 316 stainless steel plate and drilled with thirty-seven 1.2 mm (3/64") holes evenly distributed on a hexagonal grid, is located between the preheater and the roaster. The entire reactor assembly is suspended from the top flange. To compensate for thermal expansion and help compress the copper gaskets at high temperature, the lower support is held using compression springs.

To minimize axial temperature gradients and to simplify modelling, the temperature of each zone is controlled independently using three furnaces (see Figure D in appendix D). The controllers are connected to a computer, which can remotely change their setpoints. The top furnace is suspended from the top of the reactor. The middle furnace is supported by the flange of the distributor plate. The lower furnace is held by the lower support. Insulation is added or removed between the fluidized bed and freeboard furnaces during heat-up and cool-down of the reactor. Zirconia-based automotive oxygen sensors (shown as component A in Figure 3.1) are located at three locations in the reactor. The lifetime of these sensors is mainly limited by the
electrical connections at the back of the sensor. Only the sensor located within the bed did not fail prematurely. The outputs of these sensors are proportional to the logarithm of the ratio of the oxygen pressures inside and outside the sensing element. Therefore, the output is sensitive to both the overall pressure of the system and the oxygen partial pressure.

The elutriated material is collected by a hot gas filter unit at the exit of the roaster. This is a chamber which functions like a high-temperature baghouse equipped with three porous ceramic candles [202]. To enhance particle capture and to minimize the loading of the candles, the particle-laden gas enters the filter “tangentially”. The candles are cleaned by a pulse system involving solenoid valves, with the timing and duration of the pulses controlled by the data acquisition computer. A chemical scrubber removes sulfur dioxide from the outlet gas stream. The scrubber consists of two 57 litre stainless tanks (beer kegs) filled with 16 wt% NaOH solution. The choice of the solution strength is discussed in appendix E. The draft through the entire system is created by an eductor-type vacuum pump (Vaccon CDF-200).

The feeding system (not shown in Figure 3.1) allows the roaster to be fed continuously. Solid additions to the fluidized bed are metered using a scale and a speed-controlled rotary valve. The concentrate is conveyed pneumatically and enters the bed through couplings near the distributor plate. A Kalman filter with integral control automatically controls the feeder motor speed to obtain the desired feedrate. Appendix A presents more details on the feeder.

A pressure switch and a safety manometer are connected to the bottom of the preheater to allow for overpressure and underpressure protection. If plugging occurs anywhere in the system, the system will pressurize up to the pressure switch limit. Once this limit has been reached, the system automatically stops the power to the furnaces and interrupts the flow of gases to the system. If the pressure still increases beyond the pressure switch limit, a second limit may be reached, set by the safety manometer. The safety manometer will drain and vent the gases to the building exhaust system. Underpressure protection is set by the safety manometer water height. If excessive underpressure occurs, the water will drain and air will enter the system. Once the safety manometer seal has been broken, an experiment cannot be continued until the
manometer is refilled with coloured water.

3.2 Description of materials

3.2.1 Zinc concentrates

The zinc concentrates used in this study were chosen because of the large experience of this project’s sponsor using with these concentrates. Their compositions are typical of most zinc concentrates. Approximately 200 kg of zinc concentrate were shipped to UBC by TeckCominco in June 2001 in 16 sealed 11 litres pails (concentrate 1(a) and concentrate 2). The pails were weighed, labelled, and stored outside in a covered, locked enclosure until required. Samples were gathered from a number of pails for assay of multiple elements (including total sulfur and silica) and sulfate sulfur. A second batch of 140 kg of zinc concentrate (Concentrate 1(b)), shipped in September 2002, was also assayed.

Table 3.1 presents the concentrates chemical compositions. These results were obtained from an independent laboratory (International Plasma Laboratory Ltd, Vancouver). Only the major elements are shown in the table; the complete assays are presented in Appendix F. The zinc, and sulfur assays were obtained by titration and gravimetric methods, while the other elements were obtained by multi-acid digestion followed by inductively coupled plasma (ICP) analysis.

Table 3.1: Weight composition of zinc concentrates (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentrate 1(a)</th>
<th>Concentrate 1(b)</th>
<th>Concentrate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>53.22</td>
<td>54.28</td>
<td>51.12</td>
</tr>
<tr>
<td>S_{Total}</td>
<td>30.51</td>
<td>31.19</td>
<td>29.83</td>
</tr>
<tr>
<td>S_{SO_4^{2-}}</td>
<td>1.76</td>
<td>1.38</td>
<td>1.48</td>
</tr>
<tr>
<td>Fe</td>
<td>4.47</td>
<td>4.57</td>
<td>8.1</td>
</tr>
<tr>
<td>Pb</td>
<td>3.5</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Cd</td>
<td>0.34</td>
<td>0.34</td>
<td>0.14</td>
</tr>
<tr>
<td>Cu</td>
<td>0.15</td>
<td>0.14</td>
<td>0.05</td>
</tr>
</tbody>
</table>

X-Ray diffraction of one of the concentrate 1(a) samples confirmed the presence of sphalerite.
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Silica and lead sulfide may have accounted for some of the very small peaks detected, but their presence is inconclusive. Electron microscopy and X-Ray spectroscopy could not detect any sulfide phases other than sphalerite. Some gangue mineral inclusions, mainly composed of silica, were observed.

The solid density are 4170 kg/m$^3$ and 4040 kg/m$^3$ for concentrates 1 and 2, respectively, based on the wet picnometer method. Electron microscopy indicated that there is little or no porosity present within the concentrate particles.

The particle size distributions were obtained using a Malvern Mastersizer 2000 equipped with a Scirroco 2000 dry feeder. This instrument uses laser diffraction to measure particle size distributions ranging from 0.02 to 2000 $\mu$m. The dry feeder was operated with a dispersion pressure of 2.5 bar. Particle size distribution analyses of concentrate 1 and of concentrate 2 are shown in Figure 3.2 and Table 3.2. The two batches of concentrate 1 have, for all practical purposes, the same particle size distribution. The particle size distribution of a pure zinc sulfide is also shown in Figure 3.2. Since pure zinc sulfide has a much finer particle size distribution than that of the concentrates, no fluidized bed roasting experiment was attempted with pure ZnS. Note that $d_p$ is the area averaged particle size and $d_v$ is the volume averaged particle size. They are calculated from the average size ($d_{pi}$) and the mass fractions ($x_i$) of each size fractions, using the following equations:

$$d_p = \frac{\sum x_i}{\sum d_{pi}} \quad (3.1)$$

$$d_v = \sum x_i d_{pi} \quad (3.2)$$

Approximately one week before an experiment, the contents of one pail were transferred into stainless steel and glass containers that were then placed in an 50°C oven until they reached a constant weight (after approximately 6 days). The dried concentrate was then sieved through a 63 $\mu$m screen and the oversize fraction was rejected. The screened concentrate was also assayed for the same elements as listed in Table 3.1.
3.2.2 Bed material: silica sand and alumina

To determine whether agglomeration occurred on the surfaces of the particles initially present in the bed, or alternatively from newly-formed zinc calcine seeds, the typical zinc calcine bed material was replaced with silica sand or alumina particles, because of their relative inertness at high temperatures. Furthermore, the large difference between the molecular weights of silica and zinc oxide enhanced the visual differentiation between these phases in backscattered electron microscopy.

50 kg each of 50 mesh and 125 mesh Lane Mountain silica sand, (≥ 99 wt% SiO₂), were obtained in 25 kg bags from Target Products (Burnaby, B.C.). Upon reception, the silica sand was stored in pails and sampled for chemical analysis. Similarly, a 25 kg bag of 100 mesh brown alumina was purchased from Manus Abrasives.
Table 3.2: Particle size distribution of zinc concentrates

<table>
<thead>
<tr>
<th></th>
<th>Concentrate</th>
<th>Pure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1(a)</td>
<td>1(b)</td>
</tr>
<tr>
<td>Surface/Volume average:  d_p (µm)</td>
<td>3.67</td>
<td>3.71</td>
</tr>
<tr>
<td>Volume average: d_v (µm)</td>
<td>14.6</td>
<td>14.8</td>
</tr>
<tr>
<td>d_{10} (µm)</td>
<td>1.49</td>
<td>1.49</td>
</tr>
<tr>
<td>d_{50} (µm)</td>
<td>9.53</td>
<td>9.58</td>
</tr>
<tr>
<td>d_{80} (µm)</td>
<td>23.4</td>
<td>24.1</td>
</tr>
<tr>
<td>d_{90} (µm)</td>
<td>32.9</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Table 3.3 presents the sand chemical composition. The metals are shown in their oxide form. The reader is referred to appendix F for the complete assay in metal form. The particle size distributions are shown in Figure 3.3 and the Sauter mean size of the various sands are reported in Table 3.4. The measured solids densities of silica and alumina are 2650 kg/m³ and 3960 kg/m³ respectively. Electron microscopy of cross-sections have shown that both silica and alumina are non-porous.

Table 3.3: Weight composition of initial bed materials (wt%). Silica sand assays performed by multi-acid digestion and ICP. Alumina assay performed by fusion and ICP.

<table>
<thead>
<tr>
<th>Element</th>
<th>SiO₂ 50 mesh</th>
<th>SiO₂ 125 mesh</th>
<th>Al₂O₃ 100 mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.21</td>
<td>0.30</td>
<td>92.34</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.033</td>
<td>0.048</td>
<td>0.23</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.056</td>
<td>0.077</td>
<td>0.14*</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.019</td>
<td>0.021</td>
<td>0.043*</td>
</tr>
<tr>
<td>SiO₂</td>
<td>balance</td>
<td>balance</td>
<td>1.1+</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>2.94</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.029</td>
<td>0.010</td>
<td>0.103*</td>
</tr>
</tbody>
</table>

*:Multi-acid digestion may be incomplete
+: Fusion and ICP laboratory 2
Between 3 and 3.5 kg of silica (5 kg for alumina) were taken from any pail before an experiment. A sample was assayed for the same elements as listed for the concentrates. The silica and alumina compositions differed slightly, during the course of the experimental program (SiO$_2$: average=95.5wt%, $\sigma$=3.9wt%, Al$_2$O$_3$: average=88wt%, $\sigma$=2.2wt%).
Chapter 3. Experimental Methods

3.2.3 Gases

The gases used were air, nitrogen and oxygen. Nitrogen was used as a purge gas for the various pressure transducers and as the carrier gas for the pneumatic concentrate feeder. Air and oxygen were the main reaction gases. Nitrogen and oxygen were supplied in compressed gas cylinders by Praxair. Table 3.5 presents the purities guaranteed by the supplier. The relative humidity of the air supplied by the building compressor was measured on June 10, 2003 to be 8.6% at a temperature of 23.6°C. At this relative humidity, air contains approximately 0.25 vol% water. Similar humidity readings were measured in December 2003.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Nitrogen</td>
<td>Praxair</td>
<td>99.995 vol%</td>
</tr>
<tr>
<td>Medical Oxygen</td>
<td>Praxair</td>
<td>99.0 vol%</td>
</tr>
</tbody>
</table>

3.3 Roasting experiments: Experimental conditions

3.3.1 Experimental program

The experimental runs tested the effects of temperature, superficial gas velocity, stoichiometric excess oxygen, inlet oxygen concentration, bed material and size distribution. Table 3.6 presents the range of conditions of each factor. The superficial gas velocity is the velocity of the fluidizing gas at the roasting temperature and one atmosphere pressure. The maximum temperature is the maximum safe temperature which can be sustained by the reactor material without excessive oxidation. The experimental conditions were chosen by setting the bed temperature, gas velocity, inlet oxygen concentration and, knowing the concentrate composition, calculating the required feedrate for a chosen stoichiometric excess oxygen.

Table 3.7 lists the experiments performed during the experimental program. In experiments 5, 6, 11 and 12, where oxygen enrichment (higher oxygen concentration) was used, the gas velocity was chosen so that the same feedrate as without oxygen enrichment could be used for a given
stoichiometric excess oxygen. For experiments 25 and 26, the freeboard oxygen concentration was measured for different feed rates and inlet oxygen concentrations. Experiment 27 is identical to experiment 23 except that additional oxygen was inserted into the freeboard to provide an additional 10% excess oxygen (total: 20% excess oxygen). This experiment was performed to evaluate whether the freeboard affects the bed particle behaviour.

### 3.3.2 Operating procedure

The day prior to an experiment, the zinc concentrate was sieved, 24 kg of 16 wt% sodium hydroxide (NaOH) solution were prepared, transferred to the scrubber tanks, and allowed to cool before use, and the bed sand was pre-weighed. On the day of an experiment after the three zones of the roaster had been preheated to roughly 600 to 700°C, the pre-weighed sand was loaded into a hopper and discharged through the sampling port at the top of the roaster. Dry air supplied by the building compressor was simultaneously blown at a rate of 20 to 25 l/min (STP) to prevent particles from falling through the distributor plate. The temperature in the three zones was then allowed to reach the roasting temperature before the oxygen, nitrogen, and air flow rates were adjusted to their set levels. Preheating and bed material loading typically required 3 hours.

The feeder hopper was filled with 2 kg of concentrate, enough to last for 1 to 2 h. Grab samples for chemical analysis were occasionally taken from the prepared feed prior to refilling the hopper. The feeder was activated by first specifying the desired feed rate on the display screen of the data acquisition and control software, and then pressing the start key. Together with the furnace controllers, the data acquisition system monitored and logged periodically (1 s intervals) temperatures, pressures, oxygen concentrations, at several locations throughout the set-up, including the preheater, bed, freeboard, filter, cooler, and outlet. The concentrate feed rate and feeder weight were also recorded. The hopper was refilled periodically over the course of an experiment.

Bed and carry-over samples were typically collected every 30 min. The bed sampling device consisted of a 3 m long, 6.3 mm (1/4 inch) wide stainless steel 316 tube connected at one end to
### Table 3.6: Range of experimental variables

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>875°C</td>
<td>975°C</td>
</tr>
<tr>
<td>Feed gas oxygen concentration</td>
<td>21%</td>
<td>30%</td>
</tr>
<tr>
<td>Superficial gas velocity</td>
<td>0.25 m/s</td>
<td>0.5 m/s</td>
</tr>
<tr>
<td>Inert bed mass</td>
<td>3 kg</td>
<td>5 kg</td>
</tr>
<tr>
<td>Inert bed material</td>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Bed material size</td>
<td>81 μm</td>
<td>223 μm</td>
</tr>
<tr>
<td>Concentrate</td>
<td>Concentrate 1</td>
<td>Concentrate 2</td>
</tr>
<tr>
<td>Dry concentrate feed rate</td>
<td>10 g/min</td>
<td>36 g/min</td>
</tr>
<tr>
<td>Excess Oxygen</td>
<td>0 %</td>
<td>80 %</td>
</tr>
</tbody>
</table>

### Table 3.7: Summary of experimental conditions for each experiment

<table>
<thead>
<tr>
<th>Run</th>
<th>Bed Material</th>
<th>Concentrate</th>
<th>Feed rate</th>
<th>Temperature</th>
<th>Sup. gas velocity</th>
<th>Gas composition</th>
<th>Excess Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 SiO$_2$</td>
<td>C. 1 + 125 SiO$_2$</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>2</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>3</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>4</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>5</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.22 m/s</td>
<td>25% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>6</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>10 g/min</td>
<td>940 °C</td>
<td>0.22 m/s</td>
<td>25% O$_2$</td>
<td>80 %</td>
</tr>
<tr>
<td>7</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>17.5 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>0 %</td>
</tr>
<tr>
<td>8</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>17.5 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>0 %</td>
</tr>
<tr>
<td>9</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>10</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>11</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>17.5 g/min</td>
<td>940 °C</td>
<td>0.22 m/s</td>
<td>25% O$_2$</td>
<td>0 %</td>
</tr>
<tr>
<td>12</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>15 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>20 %</td>
</tr>
<tr>
<td>13</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>15 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>20 %</td>
</tr>
<tr>
<td>14</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>15 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>20 %</td>
</tr>
<tr>
<td>15</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>15 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>16</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>975 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>17</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>905 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>18</td>
<td>50 SiO$_2$</td>
<td>Conc. 2</td>
<td>14.85 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>19</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>36 g/min</td>
<td>940 °C</td>
<td>0.5 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>20</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>23.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>30% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>21</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>26.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>22</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>19.8 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>25% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>23</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>24</td>
<td>100 Al$_2$O$_3$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>975 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 %</td>
</tr>
<tr>
<td>25</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>Varies</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21 and 25% O$_2$</td>
<td>varies</td>
</tr>
<tr>
<td>26</td>
<td>125 SiO$_2$</td>
<td>Conc. 1</td>
<td>Varies</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>varies</td>
</tr>
<tr>
<td>27</td>
<td>50 SiO$_2$</td>
<td>Conc. 1</td>
<td>16.25 g/min</td>
<td>940 °C</td>
<td>0.25 m/s</td>
<td>21% O$_2$</td>
<td>10 % + 10 %</td>
</tr>
</tbody>
</table>
Chapter 3. Experimental Methods

a 150 mm long, 25.4 mm (1 inch) wide strainless steel 316 tube (cup) using a Swagelok fitting, hand-tightened with Rock and Roll ceramic anti-seize (for details, see appendix D). The fitting was screwed into a plug welded at one end of the wider tube. The other end was also sealed with a plug. Four 9.5 mm (3/8”) wide, 12.5 mm (1/2”) long slots were machined into this tube as openings for capturing particles. A longer version of this sampler is capable of capturing about twice as much solids.

The sampling valve was opened to lower the sampling device into the bed, until it reached the level of the distributor plate. The sampler was continuously purged with nitrogen gas, injected through the tube to “quench” reactions of particles which had been collected. The device was quickly retracted and removed 5 s later and allowed to cool before discharging the solids (60-140 g, sampler-dependent) into a metal cup standing in a water bath. After cooling, the samples were bagged and labelled.

The carry-over particles accumulated at the bottom of the filter were collected according to the following method. After opening the filter outlet valve, the bottom of the filter was hammered to dislodge adhering particles into the hopper. The filter outlet valve was closed before unscrewing the cap below the hopper and discharging the solids (60-600 g, average 100 g) into a Pyrex dish. These solids were at ambient temperature and did not require further cooling. The solids were bagged and labelled.

During some experimental runs, the gas was analyzed for oxygen. The analysis train consisted of an inline cooler, a solids collection tube, an inline gas filter (Swagelok SS-2F-0.5μm), a small sulfur dioxide scrubber (two 1 litre Erlenmeyer containing 500 ml 16wt% NaOH solution) and a gas dryer. The sampling train effectively removed particles and SO$_2$ from the sampled gas prior to analysis. A Horiba ES-510 sampling unit and a Horiba PG-250A portable gas analyzer terminated the sampling train. The sampling unit pumped the necessary gas volume required for analysis through the sampling train.

The feeder was turned off after supplying the available concentrate (typically 8 to 10 h). Samples were collected during the next hour, after which the electrical heaters, as well as the nitrogen
and oxygen gas supplies, were shut off, leaving only a flow of air. Sampling continued during the next hour. The fluidizing gas delivery was discontinued when the temperatures dropped to between 700 and 800°C. During cooling, the scrubber by-pass valve was opened, while the eductor maintained a slight vacuum within the roaster.

When the temperatures in the three zones were near ambient (approximately 36 hours later), a tube was inserted through the sampling valve to extract the bed particles by vacuum cleaning. The solids were then weighed. The roaster was disassembled and cleaned. A metal wire brush was used to scrub the inside walls for particulates and accretions which were collected and weighed. The particles in the pre-heater, outlet pipe, and filter were also collected.

The scrubber tanks, containing a spent solution of sodium hydroxide, a mixture of sodium sulfite and sodium bisulfite, were emptied. The solutions were disposed in waste drums. Some samples of the solutions were assayed. With the exception of sulfur, which exceeded the ICP detection range, all assayed elements were in negligible amounts.

For further details of the experimental procedures, see Appendix B.

3.4 Sintering tests

To determine the sintering tendency of the materials during roasting, static sintering tests were performed in Vicor tubes (96% SiO₂ glass). A number of tubes were prepared by sealing one end of the tube and filling with zinc concentrate. The filled tubes were dried in air at 105°C and sealed. The sealed tubes were placed in a cold muffle furnace, heated to the sintering temperature (950°C), and held at that temperature for 1 hour. The muffle furnace was then turned off and the sample was furnace cooled. After cooling, the tube was broken to access the sample and prepare it for electron microscopy.

3.5 Analysis of solid products

Either the solids collected during the last bed sampling or the leftover bed solids were split and then sieved on 16 (1.18 mm), 40 (425 μm), 70 (210 μm), 140 (105 μm), and 230 (63 μm)
mesh screens. Except where the weight of the solids collected on a given screen was negligible, the solids of each size fraction were packaged and assayed. Similarly, some of these solids were prepared for electron microscopy.

### 3.5.1 Chemical analyses

The bed samples required for analysis were riffled three times and split. This procedure was repeated, if needed, until the halves weighed about 30 g. Grab samples of about 60 g were taken from the required carry-over samples. The 3-4.5 kg of solids left in the roaster were also riffled, split, and sampled. These samples were packaged in plastic bags, labelled, and shipped to the analytical laboratory for chemical analysis. Typical analyses, performed by the TeckCominco Analytical Laboratory according to the methods described in Table 3.8, comprised: ICP scan (including sulfur and silicon reported as silica), sulfate sulfur, ferric iron, chlorides, and fluorides.

#### Table 3.8: Methods used for chemical analysis of solid samples

<table>
<thead>
<tr>
<th>Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)</th>
<th>Fuse samples in NaOH/Na₂O₂ over flame. Button dissolved in HCl. Dilute to 10% HCl. Simultaneous multi-element analysis by ICP-AES.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄/S</td>
<td>Digest samples to dryness with HCl. Dissolve residue in Na₂CO₃ and filter. Neutralize and add BaCl₂. Filter off BaSO₄ precipitate and ash in muffle furnace.</td>
</tr>
<tr>
<td>Fe⁺⁺/Fe⁺⁺⁺</td>
<td>Digest samples in HCl. Redox Titration with Na₂Cr₂O₇.</td>
</tr>
<tr>
<td>Loss on ignition (LOI)</td>
<td>Weigh samples before and after ashing at 800°C for one hour.</td>
</tr>
</tbody>
</table>

### 3.5.2 Scanning electron microscopy and X-ray diffraction

Less than 0.5 g of sieved solids was placed into a silicone rubber crucible over which was poured a viscous epoxy solution, comprised of 2 parts of epoxy resin and 1 part of hardener (Cold Cure resin and Jet Cure Hardener from Industrial Formulators Burnaby, B.C.), previously stirred thoroughly for approximately 3 min. The solution was gently mixed to disperse the particles and to ensure good contact between particles and epoxy. The epoxy mount was allowed to harden at room temperature, then ground with silicon carbide paper, and finally polished using alumina slurries from 6 down to 1 μm. After rinsing with water and ethanol, and allowing the samples
Chapter 3. Experimental Methods

to dry, the mount was carbon-coated. Qualitative analysis and imaging were performed using a Hitachi S-2300 scanning electron microscope (SEM) equipped with an X-ray energy dispersion spectrometer (EDS), operated with an accelerating voltage of 20 kV, and a working distance of 23 mm. Backscattered and secondary electron images were simultaneously acquired and stored on a PC computer for later analysis.

For the samples observed without epoxy mounting, the samples were laid on an electrically conductive double-sided adhesive pad. The samples were than carbon-coated prior to observation.

X-ray diffraction was performed on a few samples. The samples were ground to a fine powder using a mortar and pestle prior to mounting in the sample holder. The diffractograms were obtained from a Philips PW1830 X-Ray generator equipped with a copper source (operated at 35 kV and 20 mA) and a diffractometer. The scanning angle, $2\theta$, usually ranged from 20 to 90°.
In this chapter, the experimental results are presented for different operating conditions. Table 4.1 summarizes the comparisons to be made for the different experimental conditions.

The evolution of the bed particle size distribution and the rate of bed mass increase are first described. These two variables are similar to monitoring the bed size distribution and the amount of bed overflow over time in industrial fluidized bed roasters. This laboratory study has the advantage that many other variables are monitored and a complete mass balance can be performed on the metallic species. For instance, an overall mass balance is done to evaluate the overall proportion of carryover calcine. Elemental balances are used to determine if and which elements stay preferentially in the bed.

Bed samples were assayed by particle size fraction. Elemental mass balances over the samples were performed to determine if coating and agglomeration with the initial inert bed particles occurred and to evaluate if some elements preferentially segregated to some size fractions. The microstructure of bed and carryover particles are presented in scanning electron images for the key conditions. These images show coatings and agglomerates produced in the laboratory roaster.

Assays of carryover samples for various experimental conditions are summarized as conversions, sulfate to sulfur ratios and ferric to total iron ratios.
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Table 4.1: Correspondence between run numbers and parameters studied. For operating conditions of each experiment, see Table 3.7

<table>
<thead>
<tr>
<th>Temperature</th>
<th>875°C</th>
<th>905°C</th>
<th>940°C</th>
<th>975°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment number</td>
<td>15</td>
<td>17</td>
<td>10 and 23</td>
<td>16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Superficial gas velocity</th>
<th>0.25 m/s</th>
<th>0.375 m/s</th>
<th>0.5 m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment number</td>
<td>10 and 23</td>
<td>21</td>
<td>19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base Run</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. 1(a)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Conc. 1(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conc. 1(b)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conc. 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment number</td>
<td>10</td>
<td>23</td>
<td>27</td>
<td>18</td>
</tr>
</tbody>
</table>

*: An additional 10% excess oxygen (pure oxygen) was added into the freeboard.

<table>
<thead>
<tr>
<th>Inlet oxygen concentration</th>
<th>21 vol%</th>
<th>25 vol%</th>
<th>30 vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment number</td>
<td>10 and 23</td>
<td>22</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Excess oxygen</th>
<th>0 %</th>
<th>10 %</th>
<th>20 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment number</td>
<td>7</td>
<td>10 and 23</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>(large particles, 21% inlet oxygen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment number</td>
<td>8</td>
<td>9</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(small particles, 21% inlet oxygen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment number</td>
<td>12</td>
<td>22</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>(large particles, 25% inlet oxygen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment number</td>
<td>11</td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>(small particles, 25% inlet oxygen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bed material</th>
<th>Silica Large particles</th>
<th>Silica Small particles</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment number</td>
<td>see above</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

4.1 Evolution of bed particle size distribution

The initial bed material for each experiment differs from any of the materials produced during the experiments. The initial bed size distribution is that of the initial bed material. Any changes in the size distribution and bed average particle size are attributed to agglomeration, elutriation and reaction of zinc concentrate. Figure 4.1 presents the average bed particle sizes for the samples taken during each experiment. The initial and final particle sizes are highlighted. Except for experiments at higher superficial gas velocity (Figure 4.1(b)), or with very fine initial bed material (Figure 4.1(f)) all experiments produced a smaller average bed particle size than the initial size. The decrease in size for most experiments is simply due to the presence of very
Chapter 4. Experimental Results

fine calcine particles. Since few fine particles were initially present, the presence of very fine calcine particles (new particles) shifts the average to smaller sizes. For the experiments with small initial average particle size at low excess oxygen (0 and 10%) (Figure 4.1(f)), the bed particle size was larger than that of the initial bed material. However, for large excess oxygen, there was little change in the average bed particle size. Note that the average bed particle size does not give any information on whether agglomeration occurs, or to what extent.

4.2 Rate of bed mass increase

The laboratory roaster does not have an overflow or underflow exit stream, and material entrained is not returned to the bed. Material accumulating in the bed leads to an increase in bed mass. In the industrial roaster, there is a weir whose height is constant. Therefore, any material accumulating in the industrial roaster bed is balanced by material overflowing from the bed. Since there is no exit stream in the laboratory roaster other than the entrained material, material not entrained stays in the bed. The bed mass increase rate in the laboratory roaster should therefore be related to the overflow rate in the industrial roaster.

The rate of bed mass increase is calculated from the bed pressure drop recorded during the experimental run. Sampling caused a small reduction in bed pressure drop, therefore, the bed pressure drop data between bed samples is used for the calculation of the rate of bed mass increase. The bed sampling frequency was adjusted to keep the average bed pressure drop relatively constant. Figure 4.2 presents rates of bed mass increase. The calculation of each data point is done by fitting one slope and multiple origins to the logged bed pressure drops. The error bars correspond to ± one standard deviation of the rate of bed mass increase for consecutive 15-30 minutes intervals during a given run. It is not known why the variability (error bar range) of some runs is very small, while the variability of others is very large.

The rate of bed mass increase increases with temperature and decreases with excess oxygen. It also increases with superficial gas velocity because of the increasing concentrate feed rate (constant excess oxygen).
Figure 4.1: Evolution of the surface/volume average particle size for various experimental conditions. ×: initial conditions, o: during experiment at different times, *: final conditions. (a): Temperature, (b): superficial gas velocity, (c): Base run number, (d): Inlet oxygen concentration, (e): Excess oxygen for large inert particles, (f): Excess oxygen for small inert particles.
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The rate of bed mass increase does not offer information on whether agglomeration occurred, nor to what extent, i.e. there is no information on whether the new particles are small or large non-elutriable particles. Therefore, a more detailed analysis is required.

4.3 Assays and mass balances

The validity of the assay and mass information collected during the experimental runs is evaluated by means of an overall mass balance. Table 4.2 summarizes the overall mass information gathered for all the experiments. The five last columns of the table give masses of the samples collected during cleaning of the laboratory roaster after an experiment. The preheater contained some solids that fell through the distributor plate holes. After removing the bed of particulate material at the end of a run, the distributor plate (grid) was still covered with some solids. Accretions were scraped from the walls of the roaster. The pipe connecting the roaster to the filter contained some entrained solids. Note that the first two experiments lack the final bed mass information. The amount of calcine produced is calculated using the total mass of samples collected (collected from carryover (C.O.), bed, preheater, grid, walls, pipe), the initial and final bed mass:

\[ \text{Calcine Produced} = \text{Samples collected} + \text{Final Bed} - \text{Initial Bed} \]  

This calculation subtracts the mass of the initial bed, consisting of a different material, from the total mass of collected material.

Table 4.3 presents the overall mass balance results. All the final samples, in addition to those collected during each experiment, are used to calculate the amount of calcine produced. The proportion of calcine collected as carryover is shown. The mass conversion ratio ($\beta$), i.e. ratio of mass of zinc calcine produced to mass of zinc concentrate fed, is shown in the last column. For complete conversion of pure zinc sulfide to pure zinc oxide, $\beta$ would have a value of 0.835. The theoretical value of $\beta$ for zinc concentrate 1, calculated from the concentrate assays, is 0.801. With some exceptions, the values of $\beta$ in Table 4.3 agree well with the theoretical value. The calculated value of $\beta$ is influenced by the extent of conversion as well any inaccuracy in
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Figure 4.2: Rate of bed mass increase (g/min). Calculated from bed pressure drop measurements for various experimental conditions. ○ 21 vol% inlet oxygen concentration, • 25 vol% inlet oxygen concentration, Lines correspond to ± standard deviation from experimental data over durations of 15-30 minutes. (a): Temperature, (b): superficial gas velocity, (c): Base run, (d): Inlet oxygen concentration, (e): Excess oxygen for large inert particles, (f): Excess oxygen for small inert particles.
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Table 4.2: Summary of total masses of samples used for the overall mass balance. Blank when unavailable.

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial bed (g)</th>
<th>Feed samples (g)</th>
<th>Bed samples (g)</th>
<th>Carryover samples (g)</th>
<th>Final bed (g)</th>
<th>Preheater Grid (g)</th>
<th>Grid Walls (g)</th>
<th>Pipe (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3000</td>
<td>6000</td>
<td>1728.8</td>
<td>5295.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3502.8</td>
<td>6221.6</td>
<td>772.4</td>
<td>4405.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3000.1</td>
<td>6484.4</td>
<td>811.4</td>
<td>3912.2</td>
<td>2854.4</td>
<td>242.7</td>
<td>0</td>
<td>198.3</td>
</tr>
<tr>
<td>6</td>
<td>3501</td>
<td>6458.1</td>
<td>474.5</td>
<td>3151.2</td>
<td>2942.4</td>
<td>422.8</td>
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<td>199.9</td>
</tr>
<tr>
<td>7</td>
<td>3303</td>
<td>8972.5</td>
<td>1492.1</td>
<td>4513.2</td>
<td>3869.9</td>
<td>126.8</td>
<td>360.7</td>
<td>9.4</td>
</tr>
<tr>
<td>8</td>
<td>3307</td>
<td>6357.7</td>
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<td>3560.1</td>
<td>3300.7</td>
<td></td>
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<td>103.8</td>
</tr>
<tr>
<td>9</td>
<td>3306.6</td>
<td>9456.6</td>
<td>1261</td>
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<td>198.6</td>
<td>53.5</td>
<td>54.4</td>
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<td>1669</td>
<td>3543.6</td>
<td>3059.3</td>
<td>216.6</td>
<td>47.7</td>
<td>37.2</td>
</tr>
<tr>
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<td>3301.1</td>
<td>9631</td>
<td>1639.5</td>
<td>5178.8</td>
<td>3835.4</td>
<td>138.8</td>
<td>169.5</td>
<td>109.7</td>
</tr>
<tr>
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<td>3304.3</td>
<td>9972.9</td>
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<td>620.6</td>
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<td>88.3</td>
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<td>3023.6</td>
<td>588.7</td>
<td>196.9</td>
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</table>

the mass of concentrate fed. Inaccuracies are mainly caused by the loss of some concentrate during feeder upsets.

The proportion of calcine collected as carryover varied between 37 and 84%. The experimental conditions which influenced these proportions are discussed below.

4.3.1 Conversion and sulfur balance

The method used to calculate the conversion uses the residual sulfur left as sulfide. Both sulfate and sulfide sulfur are unwanted in the calcine. However, because sulfide sulfur does not typically
Table 4.3: Results of overall mass balance: Proportion of calcine as carryover and calcine to concentrate mass ratio ($\beta$)

<table>
<thead>
<tr>
<th>Run</th>
<th>Total Calcine (g)</th>
<th>Carryover (%)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5004.4</td>
<td>78.1</td>
<td>0.771</td>
</tr>
<tr>
<td>6</td>
<td>3689.8</td>
<td>85.4</td>
<td>0.571</td>
</tr>
<tr>
<td>7</td>
<td>7172.9</td>
<td>62.9</td>
<td>0.799</td>
</tr>
<tr>
<td>8</td>
<td>4577.6</td>
<td>77.7</td>
<td>0.720</td>
</tr>
<tr>
<td>9</td>
<td>7512.4</td>
<td>72.8</td>
<td>0.794</td>
</tr>
<tr>
<td>10</td>
<td>5392.5</td>
<td>65.7</td>
<td>0.709</td>
</tr>
<tr>
<td>11</td>
<td>7909.4</td>
<td>65.4</td>
<td>0.821</td>
</tr>
<tr>
<td>12</td>
<td>7879</td>
<td>59.1</td>
<td>0.790</td>
</tr>
<tr>
<td>14</td>
<td>7339.6</td>
<td>79.1</td>
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<td>15</td>
<td>6876</td>
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<tr>
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<td>7690</td>
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<tr>
<td>27</td>
<td>6819</td>
<td>65.2</td>
<td>0.829</td>
</tr>
</tbody>
</table>

leach in downstream processes, this method of calculating the conversion is usually preferred.

Because the scrubbing efficiency is not known and no sulfur analysis was performed on the scrubbing solutions, a complete sulfur mass balance cannot be calculated. However, the proportion of sulfur leaving in the gas may be estimated from the solid sample masses and compositions. The converted sulfur is therefore taken as the ratio of unaccounted sulfur in the solid at the end of the run to the amount of sulfur fed to the roaster. In general, 90-95% of the sulfur was not accounted for in the solid product. Therefore 90-95% of the sulfur fed to the roaster was assumed to be converted to sulfur dioxide, with the remainder collected in the carryover and bed material.
4.3.2 Base cases

The base cases can be used to estimate the variation from one experiment to another when no experimental conditions changed. The base case runs are runs 10, 23, 27 and 18 (labelled base cases 1, 2, 3 and 4 respectively, below and in Figures 4.1 (c) and 4.2 (c)). All base cases were operated at 940°C, at a superficial gas velocity of 0.25 m/s, at 10% excess oxygen. They differ only in the concentrate used (base case 4) and, for base case 3, by additional injection of oxygen into the freeboard (equivalent to an additional 10% excess oxygen, for a total of 20% excess oxygen). All four base cases had an overall proportion of carryover between 61 and 65% (see Table 4.3).

Figure 4.3 presents the time-variation of some parameters used in the mass balance for experimental run 10. The instantaneous mass of the bed is estimated from the instantaneous bed pressure drop. The sharp variations in apparent bed mass may be due to adjustments in purge gas flowrate, port blocking or other related factors affecting pressure drop measurement. Some experiments showed significant variations while others did not. The assays of the bed samples clearly show an accumulation of zinc and other elements, while the assays for the carryover material suggest that the composition did not vary significantly with time.

Figure 4.4 presents the elemental mass balance results for the four base cases runs. In general, approximately 50% of the iron and zinc stayed within the bed while the remainder left with the carryover. The proportion staying within the bed was slightly higher (60-70%) for copper and cadmium. For lead, the proportion staying in the bed was 75 to 80%. The differences between the overall and elemental proportion in carryover comes from the assumption of the same calcine composition for the overall mass balance.

A closer analysis of bed samples reveals that the compositions of the different sizes of bed particles (see Figure 4.5) differed very little. The only exception is that the proportion of lead in the fine particles (+230 mesh) of the experimental run with concentrate 2 (base case 4) was much larger than for the other sizes and base cases. The assays do not add up to 100% since oxygen is not determined in the analyses. The large variability of the silica assays is likely the
cause of some summations exceeding 100% (Figure 4.5 (a), +70 mesh)

Analysis of the assays of the carryover samples and the mass balance reveals that there was approximately 3 to 4% sulfur left in the carryover calcine, 20 to 40% of which was in the form of sulfate. The carryover conversion, based on the remaining sulfide sulfur, ranged from 90 to 95%. This conversion is much smaller than observed industrially. However, in industrial roasters, the very large freeboard leads to a much longer residence time than could be achieved in the present equipment. Approximately 94 to 95% of the sulfur could not be accounted for in the solid product. This sulfur is expected to have reacted to sulfur dioxide and escaped to the scrubbers.

In general, differences between the base cases are small. The injection of additional oxygen in the freeboard did not have any significant effect. This may be due to the relatively small freeboard of the equipment. The origin of the large difference in the fraction of iron as ferric iron (Figure 4.7(d)) between base case 1 and the other base case runs is unknown.

Even if the amount of zinc and iron staying within the bed was slightly higher for concentrate 2 (Figure 4.4), the proportion of calcine (zinc, iron and lead) reporting to the very small particles was much larger for concentrate 2 than concentrate 1 (Figure 4.6). As much as 50% of the calcine staying within the bed was present within the very fine particles (-230 mesh or pan). This indicates that concentrate 2 appears to have a lower agglomeration tendency. In summary, by changing to concentrate 2 (base case 4), less agglomeration occurred and more zinc reported to the very small particles.
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(a) Bed samples assays. •:Zn, ○:SiO₂, ×:Pb, +:Fe
(b) Carryover samples assays. •:Zn, ○:SiO₂, ×:Pb, +:Fe

(c) Input and output masses
(d) Bed mass

Figure 4.3: Assays of bed and carryover samples, masses of feed, bed samples, carry-over and bed for run 10, base case 1
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Figure 4.4: Variation in proportion of key elements based on mass balance for base cases. 1: Concentrate 1(a), 2: Concentrate 1(b), 3: Concentrate 1(b), freeboard oxygen injection, 4: Concentrate 2. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
Figure 4.5: Assays of different bed particle size fractions for four base case runs. 1: Concentrate 1(a), 2: Concentrate 1(b), 3: Concentrate 1(b), freeboard oxygen injection, 4: Concentrate 2. Bottom to top: SiO$_2$, Zn, Fe, Pb.
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Figure 4.6: Distribution of mass of key elements with bed particle size fractions for four base case runs. 1: Concentrate 1(a), 2: Concentrate 1(b), 3: Concentrate 1(b), oxygen injection in freeboard, 4: Concentrate 2. Bottom to top: pan, +230, +140, +70, +40
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Figure 4.7: Comparison of assays of carryover of base cases. 1: Concentrate 1(a), 2: Concentrate 1(b), 3: Concentrate 1(b), freeboard oxygen injection, 4: Concentrate 2. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
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Figures 4.8 to 4.12 present the microstructures of sieved bed particles for base case 1 (experimental run 10). The larger bed particles clearly consist of a silica core with a coating. Two other type of particles are present within the smaller +230 mesh and -230 mesh particles: unagglomerated and agglomerated calcine particles. The unagglomerated particles mainly appear in the carryover and the -230 mesh fraction (pan). A few agglomerated particles appear in the upper right portion of Figure 4.11. Figure 4.13 presents such an agglomerated particle. X-ray spectroscopy on several locations within this type of particle shows that such agglomerated particles are very rich in lead. Since X-ray spectroscopy does not give accurate results for oxygen, the oxygen peak was not used to quantify the composition of the particle, even when an oxygen peak was present. The core of the particle contains approximately 73 wt% Pb, 17 wt% Zn, 8 wt% S and small amounts of Fe and Ca (approximately 1 wt% each). At the periphery, higher concentrations of zinc (25-46 wt%Zn) and iron (2-3.5 wt%Fe) were found. This may indicate that calcine particles adhere to the surface of these agglomerated particles.

Figure 4.14 shows an intermediate size (+140 mesh) particle. Particles of this type usually present a silica core, with a “coherent” lead-rich coating (up to 65 wt%Pb, 7.5 wt%Cd, 10.5 wt%Zn and 16 wt%Si) in some locations and a detached coating rich in zinc, iron and silica (up to 81 wt%Zn, 2-10 wt%Fe, 9-15 wt%Si). The coherent coating is very thin and directly on the surface of the silica particle.

Figure 4.15 portrays carryover particles. Figure 4.16 shows an incompletely reacted particle found in the entrained calcine. This particle, like other similar particles, has a core of zinc concentrate (66 wt% Zn, 26 wt%S, 7.5 wt%Fe, 0.5 wt%Pb) and a product layer of zinc calcine (89 wt% Zn, 8 wt% Fe, 1.3 wt%S, 0.6 wt% Pb and 0.4 wt% Si). The particles may not be spherical or have a uniform product layer. However, it is reasonable to assume that they react according in a shrinking-core manner.

X-ray diffraction on the bed particles detected silica and zinc silicate. The carryover is composed of zinc oxide, zinc ferrite, and zinc silicate. A few peaks were unidentified for both the carryover and bed samples. One of the peaks found on both samples is probably zinc sulfide.
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Figure 4.8: SEM micrograph for product particles of run 10, +40 mesh, Secondary electrons image

Figure 4.9: SEM micrograph for product particles of run 10, +70 mesh, Secondary electrons image
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Figure 4.10: SEM micrograph for product particles of run 10, +140 mesh, Secondary electrons image

Figure 4.11: SEM micrograph for product particles of run 10, +230 mesh, Secondary electrons image
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Figure 4.12: SEM micrograph for product particles of run 10, -230 mesh (pan), Secondary electrons image

Figure 4.13: SEM micrograph for product particles of run 10, -230 mesh (pan), Secondary electrons image of agglomerated particle
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Figure 4.14: SEM micrograph for product particles of run 10, +140 mesh, Secondary electrons image of coated particle

Figure 4.15: SEM micrograph for product particles of run 10, carryover, Secondary electrons image
Figure 4.16: SEM micrograph for product particles of run 10, carryover, Secondary electrons image of partially reacted particle
4.3.3 Effect of superficial gas velocity

The effect of superficial gas velocity is explored in experimental runs 10, 23 (U= 0.25 m/s), 21 (U=0.375 m/s) and 19 (U=0.5 m/s). It is important to note that as the superficial gas velocity increased, the concentrate feed rate also increased to keep the excess oxygen constant. However, the proportion of calcine leaving as carryover increased to 83.9% at the highest superficial gas velocity. The intermediate velocity did not see a significant increase in carryover over the lower velocities.

Figure 4.17 presents the mass balance results. As for the base cases, cadmium and copper stayed within the bed in slightly larger proportion (50-60%) than zinc and iron (25-50%). Lead remained within the bed in similar proportions as for the base cases.

Increasing the superficial gas velocity decreased the proportion of zinc and iron staying within the bed. This trend is less clear for cadmium, copper and lead. The superficial gas velocity had a similar effect on the sulfur leaving with the gas.

The compositions of the different sizes of bed particles (see Figure 4.18) did not differ significantly for different superficial gas velocities. However, as the superficial gas velocity increased, the proportion of very fine particles (pan or -230 mesh) decreased (See Figure 4.19). The effect of superficial velocity on the bed particle size distribution can also be observed in Figure 4.1. It is well known that elutriation from a fluidized bed increases strongly with increasing superficial gas velocity. Not surprisingly, increasing the superficial gas velocity led to a smaller proportion of fines in the bed and a larger proportion of calcine leaving in the carryover.

The superficial gas velocity did not have significant effects on the quantity of sulfur, the form of sulfur (sulfate to total sulfur ratio), the conversion or the proportion of ferric iron in the carryover(See Figure 4.20).
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Figure 4.17: Variation in proportion of key elements based on mass balance for different superficial gas velocities. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
Figure 4.18: Effect of superficial gas velocity on assays for different bed particle size fractions. Bottom to top: SiO₂, Zn, Fe, Pb
Figure 4.19: Effect of superficial gas velocity on distribution of mass of key elements with bed particle size fraction. Bottom to top: pan,+230,+140,+70,+40
Figure 4.20: Comparison of assays of carryover for different superficial gas velocities. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
4.3.4 Effect of temperature

Experimental runs 10, 23 (940°C), 15 (875°C), 17 (905°C) and 16 (975°C) allow the effect of the roasting temperature to be examined. Run 24 was also performed at 975°C, but used brown alumina particles instead of silica sand as the initial bed material. The overall carryover (Table 4.3) varied from 84% at 875 °C to 56% at 975 °C for the silica sand. For the alumina, however, the proportion leaving the roaster as carryover was 38%, a further decrease from the silica.

When comparing the proportion of key elements reporting to the bed for the experimental runs with silica sand, see Figure 4.21, there is a clear upward trend of the material staying within the bed with increasing temperature. For example, the proportion of lead staying within the fluidized bed increased from approximately 40% at 875°C to more than 80% at 975°C. For iron and zinc, the increase was not as dramatic as for lead. However, it nevertheless increased from approximately 20 to 40-50%. The mass balance on sulfur, however, does not show any clear trend.

The effect of temperature on the constitution of the bed samples is shown in Figures 4.22 and 4.23. As the bed temperature increased, the proportion of fine particles in the bed decreased, while the proportion of zinc reporting to the small particles was also much lower. The assays also indicate that as the temperature increased, the particles contained a much larger proportion of zinc. This suggests that agglomeration increases with temperature.

Figure 4.24 presents the assays of the carryover. With the experiment with alumina excluded, the proportion of sulfur as sulfate within the carryover calcine decreased with temperature. However, if the run with alumina particles is included, this trend may disappear.

The microstructures of sieved particles collected during the experimental run at 975°C are shown in Figures 4.25 to 4.30. These particles appear to be denser and have a much coarser microstructure than for particles formed at lower temperature (Figures 4.8 to 4.12).

Figure 4.26 portrays the microstructure of the coating of a 70 mesh particle. This figure clearly shows that the coating consists of two-phases, akin to a lead-zinc silicate eutectic. Table 4.4
Figure 4.21: Variation in proportion of key elements based on mass balance for different temperatures. o: Silica sand, +: Alumina. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
Figure 4.22: Effect of temperature on assays of different bed particle size fractions. Bottom to top: SiO₂, Zn, Fe, Pb
Figure 4.23: Effect of temperature on distribution of mass of key elements with bed particle size fractions. Bottom to top: pan, +230, +140, +70, +40
Figure 4.24: Comparison of assays of carryover for different temperatures. •: Silica sand bed, +: Alumina bed. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
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presents the results of X-ray spectroscopy at different locations on 140 mesh particles. The white phases within the coating are rich in lead, and the dark phases are rich in zinc. Both contain a significant proportion of silica. The coherent coating on the surface of the silica particles is much more omnipresent for particles roasted at 975°C than for those shown previously (roaster at 940°C). Cadmium was detected in non-negligible amounts in the coherent coating and the white phase. Iron appears to be in relatively small amounts in the coherent coatings and dark phases (compared to the initial iron concentration within the concentrate).

Table 4.4: X-ray spectroscopy analysis of particle coatings obtained after roasting at 975°C. Blank when not detected. Detection limit is typically 0.5 wt% or less and vary with elements detected

<table>
<thead>
<tr>
<th></th>
<th>Pb wt%</th>
<th>Zn wt%</th>
<th>Fe wt%</th>
<th>Si wt%</th>
<th>Cd wt%</th>
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<td>1.3</td>
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<tr>
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<td>2</td>
<td>11</td>
<td>1.8</td>
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<tr>
<td>White phase</td>
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<td>35</td>
<td>1.7</td>
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</table>

The +230 mesh particles are predominantly of agglomerated type. When compared with the +140 mesh particles, one can clearly see that the silica cores are smaller and the coatings are thicker for particles formed at higher temperature. This indicates that these particles have grown.

The microstructures of particles (not shown) formed at lower temperatures (875, 905°C) have a much thinner coating on the silica particles, indicating negligible agglomeration.

The compounds within the bed and carryover particles produced at 975°C were identified using
Figure 4.25: SEM micrograph for product particles of run 16, +70 mesh, Secondary electrons image

Figure 4.26: SEM micrograph for product particles of run 16, +70 mesh, Backscattered electrons image of particle coating
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Figure 4.27: SEM micrograph for product particles of run 16, +140 mesh, Secondary electrons image

Figure 4.28: SEM micrograph for product particles of run 16, +230 mesh, Secondary electrons image
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Figure 4.29: SEM micrograph for product particles of run 16, -230 mesh (pan), Secondary electrons image

Figure 4.30: SEM micrograph for product particles of run 16, Carryover, Secondary electrons image
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X-ray diffraction. The bed particles consisted of zinc silicate and silica. The carryover samples were composed of zinc oxide, zinc ferrite and some zinc silicate. Again, some peaks could not be identified. The unidentified peak locations were at the same positions as those for the samples produced at lower temperature. One of these peaks may be due to zinc sulfide.

4.3.5 Effect of inlet oxygen concentration

Experimental runs 10, 23 (21%), 22 (25%) and 20 (30%) allow the effect of oxygen enrichment or inlet oxygen concentration to be investigated. The overall proportion of calcine as carryover decreased marginally as the inlet oxygen concentration increased: from 66 and 62 % to 60% at 25 vol% to 56% at 30 vol% oxygen (Table 4.3).

As shown by Figures 4.31 to 4.34, there is no significant difference for most variables among the different inlet oxygen concentrations. However, as indicated by Figure 4.33, the proportion of lead in the very fine particles (-230 mesh or pan) of the runs with oxygen enrichment was smaller than that of iron or zinc, indicating that lead may segregate to larger particles.

4.3.6 Effect of excess oxygen

The effect of excess oxygen was studied in combination with two other factors: oxygen enrichment and bed particle size. Two bed particle sizes and two inlet oxygen concentrations were considered. Experimental runs 7 (0%), 10, 23 (10%), 14 (20%) and 2 (80%) used 50 mesh silica sand, with air as the fluidizing gas. Experimental runs 12 (0%) and 5 (80%) also used 50 mesh silica sand, but the fluidizing gas was oxygen-enriched air (25 vol% O₂). Experimental runs 8 (0% excess oxygen), 9 (10%) and 4 (80%) used 125 mesh silica sand and air. Experimental runs 11 (0%) and 6 (80%) employed 125 mesh silica sand and oxygen-enriched air (25 vol% O₂).

Table 4.5 summarizes the overall proportion of carryover from the various experimental runs for different excess oxygen and oxygen inlet concentrations. In general, increasing excess oxygen increased the proportion of calcine leaving the roaster as carryover. Higher excess oxygen led to a smaller coating than for the base case, a decrease in the amount of zinc on the large particles, and a decreased rate of bed mass increase.
Figure 4.31: Variation in proportion of key elements based on mass balance for different inlet oxygen concentrations. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
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Figure 4.32: Effect of oxygen concentration on assays of different bed particle size fractions. Bottom to top: SiO₂, Zn, Fe, Pb

Table 4.5: Overall proportion of carryover as a function of excess oxygen, inlet oxygen concentration and initial bed particle size. Blank when no experiment, N.A. when information is not available. Initial bed material: 125 mesh: small particles, 50 mesh: large particles.

<table>
<thead>
<tr>
<th>Excess Oxygen</th>
<th>125 mesh</th>
<th></th>
<th>50 mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21 %</td>
<td>25 %</td>
<td>21 %</td>
</tr>
<tr>
<td>0</td>
<td>78</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>10</td>
<td>73</td>
<td>62, 66</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>80</td>
<td>N.A.</td>
<td>85</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

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Figure 4.33: Effect of oxygen concentration on distribution of mass of key elements with bed particle size fraction. Bottom to top: pan, +230, +140, +70, +40
Figure 4.34: Comparison of assays of carryover for different inlet oxygen concentrations. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
The experiments at 0% excess oxygen gave different results depending on the original average bed particle size. For a larger mean particle size, the large particles had negligible calcine coating. For the coarse initial bed, very little agglomeration occurred. For the fine silica sand (125 mesh), the effect of excess oxygen was similar, except for the 0% excess oxygen case where large calcine particles were created. The calcine particles adhered excessively to very large particles, causing defluidization to occur due to segregation. Lead again preferentially segregated to larger particles.

For both particle sizes (see Figures 4.38 and 4.42), increasing the excess oxygen led to increased conversion of carryover calcine, a higher proportion of sulfur as sulfate, and an increased proportion of iron as ferric iron. Overall, the effect of oxygen enrichment was less important than the effect of excess oxygen (Figures 4.43 to 4.46). The elemental mass balances do not show any clear trend (Figures 4.44 and 4.46).
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Figure 4.35: Variation in proportion of key elements based on mass balance for different excess oxygen and 50 mesh silica sand. o: Silica sand, •: Silica sand with 25% O₂ in the fluidizing gas. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
Figure 4.36: Effect of excess oxygen on assays for different bed particle size fractions with 50 mesh silica sand. Bottom to top: SiO$_2$, Zn, Fe, Pb
Figure 4.37: Effect of excess oxygen on distribution of mass of key elements with bed particle size fraction for 50 mesh silica sand. Bottom to top: pan,+230,+140,+70,+40
Figure 4.38: Comparison of carryover assays for different excess oxygen for 50 mesh silica sand. ○: Silica sand, ◦: Silica sand with 25% O₂ in the fluidizing gas. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
Figure 4.39: Variation in proportion of key elements based on mass balance for different excess oxygen and 125 mesh silica sand. o: Silica sand, •: Silica sand with 25% O₂ in the fluidizing gas. (a) Cadmium, (b) Copper, (c) Iron, (d) Lead, (e) Zinc, (f) Sulfur.
Figure 4.40: Effect of excess oxygen on assays of different bed particle size fractions for 125 mesh silica sand. Bottom to top: SiO$_2$, Zn, Fe, Pb
Figure 4.41: Effect of excess oxygen on distribution of mass of key elements with bed particle size fraction for 125 mesh silica sand. Bottom to top: pan,+230,+140,+70,+40
Figure 4.42: Comparison of carryover assays for different excess oxygen for 125 mesh silica sand. o: Silica sand, ●: Silica sand with 25% O\textsubscript{2} in the fluidizing gas. (a) Total sulfur, (b) Fraction of sulfur as sulfate, (c) Conversion based on remaining sulfide sulfur, (d) Fraction of iron as ferric iron.
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Figure 4.43: Effect of excess oxygen and oxygen enrichment on assays of bed particle of different size fractions with 50 mesh silica sand. Bottom to top: SiO₂, Zn, Fe, Pb
Figure 4.44: Effect of excess oxygen and oxygen enrichment on distribution of mass of key elements with bed particle size for 50 mesh silica sand. Bottom to top: pan, +230, +140, +70, +40
Figure 4.45: Effect of excess oxygen and oxygen enrichment on assays of different bed particle sizes for 125 mesh silica sand. Bottom to top: SiO₂, Zn, Fe, Pb
Figure 4.46: Effect of excess oxygen and oxygen enrichment on distribution of mass of key elements with bed particle size for 125 mesh silica sand. Bottom to top: pan,+230,+140,+70,+40
4.3.7 Effect of bed material and size

Figures 4.49 to 4.54 show the microstructures of the sieved bed (product) particles for the experiment with fine bed particles and 0% excess oxygen (run 8). As mentioned previously, excessive agglomeration led to very large particles that segregated and defluidized.

Some silica particles are embedded within the agglomerates. There is essentially no coating on the silica particles. It is important to note that the particles are relatively porous and that, because of their relatively large size, some particles were not able to be adequately truncated. Therefore, the apparent cavities within the particles were caused by polishing.

As previously shown in Table 4.5, the proportion of calcine as carryover is larger for the fine bed material than for the coarser material.

One experiment was performed with brown alumina at 975°C. As Figures 4.55 to 4.60 portray, no significant coating was present on the alumina particles after the experiment. The larger particles were created by agglomeration of smaller particles with a lead-rich phase that contained some titanium (checked by X-ray spectroscopy). The PbO-TiO₂ phase diagram, calculated from the FACT thermodynamic database, indicates that some titanium dioxide may dissolve within liquid lead oxide. Since the alumina particles contained a small portion of titanium, it is possible that the titanium within the lead-rich phase originated from the bed particles. The morphology of the alumina particles differs from that of the silica particles, possibly due to their different reactivities with PbO. The lead-rich phase may wet the silica particles more readily than the alumina particles.

X-ray diffraction of the bed and carryover samples indicate that both consist mainly of zinc oxide. The carryover sample also contained detectable quantities of zinc ferrite. The same peaks as for the two other set of silica samples could not be identified. Note that there were fewer unidentified peaks for the alumina samples. This suggests that the compound(s) related to some of the unidentified peaks is/are silica-based.
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Figure 4.47: Effect of bed material on assays for different bed particle size fractions. Bottom to top: SiO₂ or Al₂O₃, Zn, Fe, Pb
Figure 4.48: Effect of bed material on distribution of mass of key elements with bed particle size fraction. Bottom to top: pan,+230,+140,+70,+40
Figure 4.49: SEM micrograph for product particles of run 8, +16 mesh, Secondary electrons image

Figure 4.50: SEM micrograph for product particles of run 8, +40 mesh, Secondary electrons image
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Figure 4.51: SEM micrograph for product particles of run 8, +70 mesh, Secondary electrons image

Figure 4.52: SEM micrograph for product particles of run 8, +140 mesh, Secondary electrons image
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Figure 4.53: SEM micrograph for product particles of run 8, +230 mesh, Secondary electrons image

Figure 4.54: SEM micrograph for product particles of run 8, -230 mesh (pan), Secondary electrons image
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Figure 4.55: SEM micrograph for product particles of run 24, +40 mesh, Secondary electrons image

Figure 4.56: SEM micrograph for product particles of run 24, +70 mesh, Secondary electrons image
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Figure 4.57: SEM micrograph for product particles of run 24, +140 mesh, Secondary electrons image

Figure 4.58: SEM micrograph for product particles of run 24, +230 mesh, Secondary electrons image
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Figure 4.59: SEM micrograph for product particles of run 24, -230 mesh (pan), Secondary electrons image

Figure 4.60: SEM micrograph for product particles of run 24, carryover, Secondary electrons image
4.4 Gas and solid conversions

Experimental runs 25 and 26 differed from the other experiments. In these experiments, the concentrate feedrate was varied and the freeboard gas was sampled, scrubbed to remove sulfur dioxide, dried and sent to a portable gas analyzer. The solids collected in the sampling train were collected and sent for assay. Figure 4.61 presents the freeboard oxygen concentration as a function of the concentrate feedrate and initial bed particle size. The oxygen concentration clearly decreased with increasing feedrate. The oxygen concentration was slightly higher for the 125 mesh silica sand for a similar concentrate feedrate, probably due to increased gas bypassing caused by the bubbles. As expected, for a given concentrate feedrate, the outlet oxygen concentration was higher when oxygen enrichment was used.

The solid conversion corresponding to the data in Figure 4.61 is shown in Figure 4.62. Oxygen enrichment increased the solids conversion for a given feedrate. Again, this is expected because for a given concentrate feedrate, an increase in the inlet oxygen concentration simply increased the excess oxygen. The bed particle size does not seem to have had a significant effect. The data in Figures 4.61 and 4.62 are used in chapter 6 to fit the fluidized bed reactor model.

Figure 4.63 presents the averaged output of the oxygen sensor within the fluidized bed. The output of the sensor is proportional to the log of the ratio of outside to inside oxygen partial pressures. A small output signal indicates a high in-bed oxygen concentration, while a large output value indicates a small in-bed oxygen concentration. An interesting feature observed in Figure 4.63 is that the oxygen concentration within the bed was not significantly affected by the oxygen enrichment, but was significantly influenced by the average bed particle size.

By increasing the concentrate feedrate from 10 to 20 g/min, the NO concentration in the sampled freeboard gas increased from approximately 15 to 30 ppm. No NO was present when no concentrate was fed to the roaster. This indicates that the NO may originate from the combustion of the concentrate. However, it is not clear whether the NO production rate depends upon the excess oxygen, in-bed oxygen concentration or just the concentrate feedrate.
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Figure 4.61: Freeboard oxygen concentration (SO$_2$ scrubbed,dry) as a function of feedrate. o: 50 mesh silica sand, 21%O$_2$, +: 50 mesh silica sand, 25%O$_2$, x: 125 mesh silica sand, 21%O$_2$.

Figure 4.62: Solids conversion as a function of feedrate. o: 50 mesh silica sand, 21%O$_2$, +: 50 mesh silica sand, 25%O$_2$, x: 125 mesh silica sand, 21%O$_2$. 
Figure 4.63: In-bed oxygen sensor mean output as a function of feedrate. o: 50 mesh silica sand, 21%O₂, +: 50 mesh silica sand, 25%O₂, ×: 125 mesh silica sand, 21%O₂. Note: Higher measured output, lower oxygen concentration.
4.5 Sintering test for zinc concentrate

The raw unsintered concentrate is shown in Figure 4.64. A careful search using the electron microscope did not reveal any significant phases other than zinc sulfide.

Sealed ampoules of dried zinc concentrate (concentrate 1(b), approximately 1g) were submitted to a ramp-up to 950°C, and held for an hour at that temperature, and then cooled slowly to room temperature. Since the ampoules could not be sealed under vacuum or a nitrogen atmosphere, a small amount of air was initially present within the ampoules. The number of moles of oxygen contained within the air in the ampoules was smaller than 1% of the ZnS in the concentrate.

After the sintering cycle, the concentrate had formed a porous elongated rod of diameter slightly smaller than the tube diameter. The rod showed some signs of oxidation near the end where the bulk of the air was present. A sample of the rod was taken from the opposite end and prepared for electron microscopy. An image of the sintered concentrate is presented in Figure 4.65. The lighter-coloured cube is composed of pure lead sulfide. Several of these cubes appeared on the periphery of the sintered “cylinder”. Note that the cube is much larger than any of the original concentrate particles.

The lead sulfide cubes probably originate from deposition of lead sulfide from the gaseous phase during cooling. The gaseous composition of a mixture of zinc sulfide and zinc oxide is located at point A on Figure 2.2. This location is valid because the concentrate is mainly composed of zinc sulfide, but, as the assays show, a small fraction of the sulfur is present as sulfate. Also, the ampoule could not be vacuum-sealed nor nitrogen-purged. Therefore, the small amount of oxygen remaining when the ampoule was sealed would react to form zinc oxide and sulfur dioxide. The equilibrium gas composition of a mixture of zinc sulfide and zinc oxide, represented by point A on Figure 2.2, is adequate to represent the gas composition of the sealed ampoule. When transposing point A of Figure 2.2 onto Figure 2.11, the gas composition falls within the lead stability area, very close to the lead sulfide area. When considering the gaseous lead species, lead sulfide is still the most predominant gaseous lead species, even though it falls
Chapter 4. Experimental Results

Figure 4.64: SEM micrograph for dried, unsintered, zinc concentrate 1(b), Secondary electrons image.

Figure 4.65: SEM micrograph for dried, zinc concentrate 1(b) sintered for 1 hour at 950°C, Secondary electrons image. Cube is pure lead sulfide.
within the lead stability area. Note in Figure 2.11 that if the oxygen concentration is increased, the lead sulfide partial pressure decreases. Even though the lead oxide partial pressure increases with oxygen partial pressure, it remains much lower than that of lead sulfide at lower oxygen partial pressures. During cooling, lead sulfide “precipitated” from the gaseous phase to form lead sulfide cubes.

From this simple experiment, it is clear that lead sulfide can evaporate from zinc concentrate. However, this experiment does not offer any information on the vaporization kinetics.

### 4.6 Growth mechanism in the laboratory roaster

A probable growth mechanism may now be suggested from the experimental observations. Prior to formulating a growth mechanism, let us summarize the most relevant observations:

- From the sample mass balances, we have observed that larger particles contain a larger proportion of lead than smaller particles.

- Temperature has a significant effect on the thickness and morphology of the coating. Temperature also affects the proportion of calcine leaving the roaster as carryover.

- Excess oxygen also affects the coating and the proportion of calcine leaving the roaster as carryover.

- From the electron microscope observations, the silica particles were observed to be coated with a two-phase coating, one rich in lead, the other zinc-rich, while the inner silica was coated with a thin “coherent” layer of lead-rich compound. All have silicon (silica) present. Alumina particles were not coated with any zinc. However, some of the alumina particles were agglomerated with a lead-rich phase.

- Lead sulfide sublimates from zinc concentrate when exposed to roasting temperatures and oxygen-deficient atmospheres.

The mechanism may now be postulated as follows:
• When process conditions are such that low oxygen concentrations and high sulfur dioxide concentrations are favoured, excess oxygen is one of the most important factors. Under such conditions, the lead partial pressure is maximized, with lead predominantly present as lead sulfide.

• Lead sulfide vaporizes from the zinc concentrate.

• Gaseous lead sulfide is transported to regions of the bed where higher oxygen concentrations are present. It then reacts with oxygen to produce lead oxide.

• Since the lead oxide partial pressure is lower than for the lead sulfide, lead oxide precipitates out.

• Lead deposits onto the bed particles to form a very thin lead-oxide-based coating. The reactivity of the particles with lead oxide affects whether or not a significant coating appears on the surface of the particles.

• Lead oxide is liquid at roasting temperatures. It can dissolve an increasing amount of various compounds with increasing temperature. Since it is liquid, it is sticky.

• The sticky particle surface can trap other very small particles. The momentum of these particles is insufficient to break up the viscous liquid lead oxide bridges upon contact. Larger particles, however, have sufficient momentum to remain separate. Conditions that may influence the momentum of particles such as the gas distribution and the vigour of fluidization (superficial gas velocity) affect coating and agglomeration.

• Rapid sintering of the coated particles is favoured by liquid lead oxide.

This mechanism is consistent with the observations of Condina et al. [83] (see section 1.4.7) where monobasic lead sulfate was observed in alumina, silica and calcine agglomerates. Condina et al. [83] observed agglomerates, but did not observe growth of single particles. In their experiments, they used a "caged" lead sulfide source, immersed in a bed of inert particles. After a few minutes the particles started to agglomerate outside the cage, due to gaseous lead species. Since their experiments lasted only a few minutes, no lead silicates were observed in
Chapter 4. Experimental Results

the agglomerates. It is important to note that the experimental conditions of Condina et al. [83] differed from those expected in a continuously operating fluidized bed roaster. Air was used to fluidize the inert bed material, and no material other than the pure lead sulfide pellet could react with the fluidizing gas. Also, in their experiments no zinc sulfide was present to form zinc oxide. Condina et al. [83] did not consider the effect of different particles sizes on agglomeration, growth or attrition nor did they indicate the effect of the oxygen concentration.

It is not known whether this coating mechanism would apply to calcine particles since their reactivity with lead oxide is unknown. However, considering the solubility of the particles in PbO in the PbO-ZnO, PbO-SiO₂ and PbO-Al₂O₃ phase diagrams (Figures 2.25 to 2.27), it is likely that the reactivity of calcine particles lies between that of silica and alumina.

Since vaporization and deposition kinetics are not known, it is premature to model the coating of particles. However, since the partial pressures are strongly dependent on the oxygen concentrations, it would be beneficial to evaluate the effect of various process parameters on the oxygen concentration experienced by the particles in the fluidized bed. Assuming that coating depends on the relationship between the oxygen concentration and the transport of metallic species through the gas phase, modelling the oxygen concentration within the fluidized bed would give important insights on the coating of particles.

4.7 Agglomeration mechanism in the laboratory roaster

Since only one experiment generated catastrophic agglomerates (defluidization due to segregated agglomerates), there are insufficient data to clearly formulate an agglomeration mechanism. However, since lead strongly segregated to these agglomerates, it is probable that lead species play a strong role in the agglomeration mechanism. Some small agglomerates were found in the fine particles of other experiments (see Figures 4.13). These agglomerates were also rich in lead. It is possible that these agglomerates are formed in a similar manner to the catastrophic agglomerates produced during run 8 (see Figure 4.49 to 4.54). Other agglomerates were formed during the experiment with alumina as the inert bed material (see Figures 4.57
The following agglomeration mechanism may be suggested:

- Transport of lead from the concentrate particles to the bulk of the bed occurs in a manner similar to the growth mechanism described previously.

- However, for the conditions of catastrophic agglomeration, the roaster operated with no excess oxygen. Under these conditions, very low oxygen concentrations are present around the concentrate particles. This lower oxygen concentration enhances the transfer of lead to other particles. This may produce a larger amount of liquids within the bed.

- A larger amount of liquid may contribute to the formation of agglomerates through liquid bridging.

- Attrition limits the agglomeration rate and possibly the maximum agglomerate size. Since catastrophic agglomeration only occurred for the experiment with a fine bed particle size, it is possible that attrition of the agglomerates depends on the bed particle size. Large bed particles would limit the size of agglomerates while fine bed particles would not have sufficient momentum to break up the agglomerates into smaller ones.

This agglomeration mechanism is very similar to that observed by Condina et al. [83]. As mentioned above, Condina et al. [83] neither varied the particle size nor the oxygen concentration. Similarly to the coating of particles, there is still too much information missing for the modelling of agglomeration with the mechanism described here. Therefore, assuming that agglomeration is related to the coating mechanism, any important insights on the coating of particles may be useful to predict agglomeration.

The next chapter describes a fluidized bed reactor model applicable to the laboratory and industrial roasters. The results of this model will be used to evaluate the conditions when the coating and agglomeration mechanisms can be extended to the industrial roaster.
Chapter 5
Model Development

A gas-solid fluidized bed reactor model is formulated in this chapter in order to evaluate the effect of excess oxygen, oxygen enrichment, temperature and other operating parameters on the oxygen concentration close to reacting particles. The important issue of scale-up of the results from a slugging fluidized bed to a bubbling fluidized bed must be addressed to apply the results from the laboratory roaster to industrial fluidized bed roasters.

Any fluidized bed gas-solid reactor model requires that the gas reaction model be coupled to the solids reaction model. The gas reaction model accounts for the hydrodynamics of the fluidized bed reactor. The solids reaction model requires that a single-particle reaction model be selected and used in conjunction with a model for the mixing of the solids within the fluidized bed.

This chapter proposes a new generalized slugging-bubbling fluidized bed reactor model. The reaction and mixing of solids within a fluidized bed is presented next. Finally, an unsteady-state model for the reaction of single particles is described.

The model assumes that the entire fluidized bed, as well as the reacting particles, are isothermal. The model also assumes that the particles are well-mixed, axially and radially within the fluidized bed. Elutriation, attrition and agglomeration are not considered. Reactions in the freeboard of the roaster are neglected. The time for complete reaction, the mixing times and the single particle unsteady-state model are used in the next chapter to verify some of these assumptions.
5.1 Steady-state fluidized bed reactor model: Gas reaction

The steady-state fluidized bed reactor model accounts for the fluidized bed hydrodynamics, gas reactions, and solids reactions. The model extends the generalized bubbling, turbulent and fast fluidization reactor model of Abba et al. [203, 204, 205], which accounts for variable gas density and bulk flow in the interphase mass transfer. This model, consisting of a single set of steady-state differential equations, can be applied across several flow regimes from the bubbling regime to the fast fluidization regime by using a probabilistic approach to specify the parameters. Contrary to the generalized bubbling, turbulent, fast fluidization model, the model developed in this chapter ignores the turbulent and fast fluidization flow regimes. Instead, the model is extended from bubbling into the slugging flow regime. Also, the approach used to model changes in total gas molar flow differs from the generalized model of Abba et al. [203, 204, 205].

Figure 5.1 represents the two phases of the model, named the L- and H-phases for low-density and high-density phases respectively. In the bubbling fluidized bed, the L-phase represents the bubbles, while the H-phase represents the dense phase or emulsion. The gas enters at the bottom of the fluidized bed where it is distributed between the L- and H-phases. The gas then rises in each phase and reacts with the solids present. Exchange occurs between the two phases. Axial and radial dispersion could be included within each phase, and the former would need to be incorporated to extend the model to the turbulent flow regime.

5.1.1 Phase balances

The fluidized bed is divided into the L- and H-phases (Figure 5.1). The bed volume fractions of these phases ($\psi_L$ and $\psi_H$) add up to one:

$$\psi_L + \psi_H = 1 \quad (5.1)$$

Each phase volume is composed of particles and void space occupied by the gas. The particle volume fraction ($\phi$) and gas volume fraction ($\epsilon$) within each phase also add up to one. The total gas molar flowrate ($F_T$) through the reactor equals the sum of the molar flowrates through
Each phases \(F_L\) and \(F_H\), i.e.:

\[ F_T = F_{LT} + F_{HT} \]  \hspace{1cm} (5.2)

According to the ideal gas law, for a given total pressure \((P)\) and temperature \((T)\), the total concentration \((C_T)\) (sum of all gaseous species) is constant \((C_T = \frac{P_T}{RT})\). Therefore, for a given reactor area \((A)\), the gaseous molar flowrates are related to the superficial gas velocities \((U, U_L\) and \(U_H)\) by:

\[ F_T = AC_TU \]  \hspace{1cm} (5.3)
\[ F_{HT} = \psi_H AU_H C_T \]  \hspace{1cm} (5.4)
\[ F_{LT} = \psi_L AU_L C_T \]  \hspace{1cm} (5.5)

Similarly, the molar flowrate of gaseous species \(i\) in the H- and L-phases are:

\[ F_{Hi} = \psi_H AU_H C_{Hi} \]  \hspace{1cm} (5.6)
After replacing the molar flowrates into equation 5.2 and simplifying, we obtain:

\[ U = \psi_L U_L + \psi_H U_H \]  

(5.8)

These volume and gas flow balances are summarized in Table 5.1.

Table 5.1: Volume and gas flow balances

<table>
<thead>
<tr>
<th></th>
<th>( \psi_L + \psi_H = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed volume</td>
<td>( \phi_L + \epsilon_L = 1 )</td>
</tr>
<tr>
<td>L-phase volume</td>
<td>( \phi_H + \epsilon_H = 1 )</td>
</tr>
<tr>
<td>Gas flow</td>
<td>( U = \psi_L U_L + \psi_H U_H )</td>
</tr>
</tbody>
</table>

5.1.2 Gas mole balances for H- and L-phases

Referring to Figure 5.1, the gas mole balance over the control volume for an increment of time is, in general terms:

\[
\left\{ \text{number of moles entering minus those exiting}\right\} \left\{ \text{number of moles entering minus those exiting}\right\} \left\{ \text{number of moles transferred to the control volume by interphase mass transfer}\right\} + \\
\left\{ \text{number of moles produced minus those consumed by reaction within the control volume}\right\} \left\{ \text{number of moles flowing into the control volume due to bulk interphase mass transfer}\right\} = \left\{ \text{number of moles accumulating within the control volume}\right\} \tag{5.9}
\]

Assuming steady-state conditions and neglecting axial and radial dispersion, i.e. assuming that the accumulation and dispersion terms are zero, the mass balance over the low-density phase (L) leads to (terms are explained below):

\[
\left\{ F_{Li} - \left( F_{Li} + \frac{dF_{Li}}{dz} \Delta z \right) \right\} + \{0\} + \left\{ A\Delta z \psi_L k_{LH} \alpha I \left( \frac{F_{Hi}}{A\psi_H U_H} - \frac{F_{Li}}{A\psi_L U_L} \right) \right\} + \\
\left\{ A\psi_L \Delta z k_r \phi_L \nu \left( \frac{F_{LO2}}{A\psi_L U_L} \right) \right\} + \left\{ A\psi_H \Delta z k_r \phi_H \Delta \nu \left( \frac{F_{HO2}}{A\psi_H U_H} \right) \left( \frac{F_{Li}}{F_{LT}} \right) \right\} = \{0\} \tag{5.10}
\]
Chapter 5. Model Development

For the high-density phase (H), the same development leads to:

\[
\left\{ F_{Hi} - \left( F_{Hi} + \frac{dF_{Hi}}{dz} \phi_H \Delta z \right) \right\} + \{0\} + \left\{ A \Delta z \psi_H k_{LH} \alpha_i \left( \frac{F_{Li}}{A \psi_H U_L} - \frac{F_{Hi}}{A \psi_H U_H} \right) \right\} + \\
\left\{ A \psi_H \Delta z k_r \phi_H \nu_i \left( \frac{F_{HO2}}{A \psi_H U_H} \right) \right\} - \left\{ A \psi_H \Delta z k_r \phi_H \Delta \nu \left( \frac{F_{HO2}}{A \psi_H U_H} \right) \left( \frac{F_{Li}}{F_{LT}} \right) \right\} = \{0\}(5.11)
\]

The interphase mass transfer and reaction terms in equations 5.10 and 5.11 require some clarification. The interphase mass transfer coefficient \(k_{LH}\) is defined as the volumetric rate of transfer per unit bubble surface area. The interphase mass transfer exchange area \(a_I\) is the interfacial bubble area per unit bubble volume. Multiplying the two \((k_{LH} \cdot a_I)\) gives the volumetric rate of transfer per unit bubble volume. To obtain the number of moles transferred, we need to multiply by the bubble volume within the control volume \((A \Delta z \psi_L)\) and by the concentration difference between the L- and H-phase. The concentration of each species within each phase is given by equations 5.6 and 5.7. Note that the interphase mass transfer terms are identical in equation 5.10 and 5.11, except for their signs.

The reaction is first order with respect to the oxygen concentration. The reaction rate constant \(k_r\) is based on the particle volume. To obtain the number of moles reacted within the L-phase of the control volume per unit time, the reaction rate constant \(k_r\) is multiplied by the particle volume within the phase \((A \psi_L \Delta z \phi_L)\), the stoichiometric constant for species i \((\nu_i)\), and the oxygen concentration \(\frac{F_{HO2}}{A \psi_L U_L}\). Similarly, for the H-phase, the reaction rate constant \(k_r\) is multiplied by the particle volume within the phase \((A \psi_H \Delta z \phi_H)\), the stoichiometric constant for species i \((\nu_i)\), and the oxygen concentration \(\frac{F_{HO2}}{A \psi_H U_H}\).

Bulk interphase mass transfer is required when a change in gas volume occurs within the H-phase. According to the two-phase fluidization theory, a given flow of gas, \(U_{mf} A\) is required for fluidization of the high-density phase. Any excess gas enters the low-density phase to create bubbles. In a reacting system, the requirement for the high-density phase is still present. However, if there is a volume change, it must be balanced by bulk interphase transfer. The bulk interphase mass transfer terms in equations 5.10 and 5.11 are very similar to the reaction term of the H-phase (equation 5.11). However, the required stoichiometric coefficient is now the change in the total number of gaseous moles \((\Delta \nu)\) multiplied by the gas molar fraction of
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the L-phase \( \frac{F_{Li}}{F_{LT}} \). The direction of the bulk flow and the required gas molar fraction depends on the sign of \( \Delta \nu \). In this case, it is negative since, in the reaction of zinc sulfide with oxygen to produce zinc oxide and sulfur dioxide, 1.5 moles of gas on the left-hand side of the roasting reaction produce only 1 mole of gaseous product on the right-hand side. If \( \Delta \nu \) were positive, any excess gas produced in the dense phase would go to the bubble phase. Therefore, the gas molar fraction would become \( \frac{F_{Hi}}{F_{HT}} \). For zinc sulfide roasting, the bulk flow term is described by equations 5.10 and 5.11.

After simplification, the mole balance equations for the L- and H-phases are:

\[
-\frac{dF_{Li}}{dz} + k_{LH} a_l \left( \frac{\psi_L F_{Hi}}{\psi_H U_H} - \frac{F_{Li}}{U_L} \right) + k_r \phi_L \nu_i - \frac{F_{LO2}}{U_L} = 0 \quad (5.12)
\]

\[
-\frac{dF_{Hi}}{dz} + k_{LH} a_l \left( \frac{F_{Li}}{U_L} - \frac{\psi_L F_{Hi}}{\psi_H U_H} \right) + k_r \phi_H \nu_i - \frac{F_{HO2}}{U_H} = 0 \quad (5.13)
\]

These equations are solved using an initial value solver and the boundary conditions:

\[
F_{Li} = F_{Li,in} = \psi_L A U_L C_{i,in} \quad \text{at} \quad z = 0 \quad (5.14)
\]

\[
F_{Hi} = F_{Hi,in} = \psi_H A U_H C_{i,in} \quad \text{at} \quad z = 0 \quad (5.15)
\]

These boundary conditions originate from the fact that the inlet flow is distributed among the H- and L-phases.

5.1.3 Superficial gas velocities and phase volume fractions

The superficial gas velocities \((U_L, U_H)\) and the phase volume fractions \((\psi_L, \psi_H)\) are calculated at a series of vertical positions in the bed including the boundary surface. The superficial gas velocity \((U)\) is first calculated from the gaseous molar flowrates \((F_{HT}, F_{LT})\). The low-density phase superficial gas velocity \((U_L)\) is calculated using equation 5.53 (i.e. \(U_L = U_v\)). This calculation requires the bubble size correlations described in section 5.1.7.

The low-density phase volume fraction \((\psi_L)\) is calculated using [206]:

\[
\psi_L = \frac{U - U_{mf}}{U_L} \quad (5.16)
\]

The superficial gas velocity and phase volume fraction of the high-density phase are then calculated by means of equations 5.1 and 5.8.

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5.1.4 Expanded bed height

Since the set of differential equations is solved from the distributor (z = 0) to the surface of the expanded bed (z = H), the expanded bed height (H) must be known, or first estimated and then calculated iteratively. Since it is only the volume occupied by the bubbles (L-phase) that contributes to the expansion of the bed, the relationship between the expanded bed height (H), the bed height at minimum fluidization velocity \( (H_{mf}) \) and the L-phase volume fraction \( \psi_L \) is relatively simple:

\[
H - H_{mf} = \int_0^H \psi_L \, dz \quad (5.17)
\]

Similarly, if the H-phase fraction is integrated over the expanded bed height, we obtain \( H_{mf} \):

\[
H_{mf} = \int_0^H \psi_H \, dz \quad (5.18)
\]

The bed height at minimum fluidization \( (H_{mf}) \) depends on the bed mass \( (M_{bed}) \), bed cross-sectional area \( (A) \), particle density \( \rho_p \) and void space \( (\epsilon_{mf}) \).

\[
H_{mf} = \frac{M_{bed}}{\rho_p(1 - \epsilon_{mf})A} \quad (5.19)
\]

For industrial zinc roasters, the expanded bed height is limited by the weir overflow height. Therefore, \( H \) is known and constant while \( H_{mf} \) may vary. For the laboratory roaster, on the other hand, the expanded bed height is unknown. However, the bed mass can be be used to calculate \( H_{mf} \). In this case, the calculation of the expanded bed height proceeds iteratively (since we need to integrate from 0 to \( H \) and \( H \) is not known at first).

5.1.5 Gas conversion and average gas compositions

The overall gas conversion, i.e. the oxygen conversion \( (X_{O2}) \), is calculated as follows:

\[
1 - X_{O2} = \frac{F_{LO2, out} + F_{HO2, out}}{C_{O2, in} AU} \quad (5.20)
\]

Similarly, the number of moles of oxygen reacted per unit time is given by:

\[
\Delta F_{O2} = C_{O2, in} AU - (F_{LO2, out} + F_{HO2, out}) \quad (5.21)
\]

The number of moles of oxygen reacted per unit time must be coupled to the solids reaction. With the freeboard neglected, \( F_{i, out} \) is equal to \( F_{i,z=H} \).
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The solids reaction model assumes that the particle reaction times are long compared to their vertical mixing times. Therefore, the solids composition is assumed to be independent of the vertical position in the bed. The solids model therefore uses the average gas composition seen by the solid particles to calculate their conversion. The gas reaction model calculates the particle-averaged gas concentrations as:

\[
\overline{C_i} = \frac{\int_0^H \phi_H \psi_HC_{Hi} \, dz + \int_0^H \phi_L \psi_L C_{Li} \, dz}{\int_0^H \phi_H \psi_H \, dz + \int_0^H \phi_L \psi_L \, dz} \tag{5.22}
\]

\[
\overline{C_{ji}} = \frac{\int_0^H \psi_j C_{ji} \, dz}{\int_0^H \psi_j \, dz} \quad (j = L \text{ or } H) \tag{5.23}
\]

Assuming that the solid volume fractions (\(\phi_L\) and \(\phi_H\)) do not change with height and using the volume balances (equations in Table 5.1) and the bed expansion calculation (equations 5.17 and 5.18), these equations reduce to:

\[
\overline{C_i} = \frac{\phi_L (H - H_{mf}) \overline{C_{Li}} + \phi_H (H_{mf}) \overline{C_{Hi}}}{\phi_L (H - H_{mf}) + \phi_H (H_{mf})} \tag{5.24}
\]

\[
\overline{C_{Li}} = \frac{\int_0^H \psi_L C_{Li} \, dz}{H - H_{mf}} \tag{5.25}
\]

\[
\overline{C_{Hi}} = \frac{\int_0^H \psi_H C_{Hi} \, dz}{H_{mf}} \tag{5.26}
\]

The solid reaction model uses the particle-averaged oxygen concentration to calculate the solids reaction rates. Since the gas concentrations and the solids volume fractions differ between the L- and H-phases, averaging the oxygen concentration over the particles within each of the two phases allows a simple coupling between the fluidized bed and the solids reaction model while accounting for the effect of particles within the L-phase.

5.1.6 Minimum fluidization velocity

Most minimum fluidization velocities correlations are of the form:

\[
Re_{mf} = \sqrt{C_1^2 + C_2Ar - C_1} \tag{5.27}
\]

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where \( C_1 \) and \( C_2 \) are constants. The Archimedes number \( (Ar) \) is given by:

\[
Ar = d_p^* = \frac{\rho_g (\rho_p - \rho_g) g d_p^3}{\mu^2} \tag{5.28}
\]

The dimensionless particle size \( (d_p^*) \) is the cubic root of the Archimedes number. The form of the correlation was developed by equating the pressure drop calculated from the Ergun equation to the buoyed weight of the bed per unit area. The values recommended by Grace [207] are \( C_1 = 27.2 \) and \( C_2 = 0.0408 \).

The choice of the average particle size \( (d_p) \) is important. For fluidization calculations, the Sauter mean size (mean surface/volume size) is commonly used, with:

\[
d_p = \frac{1}{\sum \frac{x_i}{d_{pi}}} \tag{5.29}
\]

where \( x_i \) is the weight fraction of particles in each size range and \( d_{pi} \) is the average of adjacent sieve apertures. Note that this definition gives more weight to smaller particles than larger ones.

### 5.1.7 Bubbling fluidized bed

The industrial roaster is operating in the bubbling fluidized bed regime. Since bubble velocities depend on their size, the effective bubble size \( (D_e) \) must be calculated as a function of the vertical position in the bed. In this work, the bubble size is calculated using the correlations in Table 5.2. Most bubble size correlations require the bed diameter \( D \), and the distributor surface area per orifice \( (A_d) \). The Mori and Wen [208] correlation also gives an initial bubble size \( (D_{e,0}) \) and a maximum bubble size due to bubble coalescence \( (D_{e,\infty}) \).

The concept of maximum bubble size, first introduced by Harrison et al. [210], is of critical importance in evaluating bubble diameters in fluidized beds of fine (Geldart Group A) particles. The maximum bubble size is obtained by using the terminal velocity \( (U_t^*) \) of spherical particles of \( 2.7d_p \) [207, 211]:

\[
D_{e,\max} = 2.0 \frac{U_t^*}{g} \tag{5.32}
\]
Table 5.2: Correlations for bubble sizes

<table>
<thead>
<tr>
<th>Reference</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darton et al. [209]</td>
<td>( D_e = 0.54(U - U_{mf})^{0.4}(z + 4\sqrt{A_d})^{0.8}g^{-0.2} ) (5.30)</td>
</tr>
</tbody>
</table>
| Mori and Wen [208] | \[
\begin{align*}
D_e &= D_{e,\infty} - (D_{e,\infty} - D_{e,0})e^{-0.3z/D} \\
D_{e,\infty} &= 1.49\left(D^2(U - U_{mf})\right)^{0.4} \\
D_{e,0} &= 1.38g^{-0.2}(A_d(U - U_{mf}))^{0.4}
\end{align*}
\] (5.31) |

The factor 2.7 was obtained empirically to better predict the maximum stable bubble diameter observed experimentally. The dimensionless terminal velocity \( U_t^* \) of spherical particles can be estimated from the dimensionless particle diameter \( d_p^* \) [20]:

\[
U_t^* = \left( \frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^{*0.5})} \right)^{-1}
\] (5.33)

To estimate parameters that depend on the effective bubble size, it is common to use the bubble size correlation at 40% of the bed height, i.e. at \( z = 0.4H \). The isolated bubble rise velocity \( U_{b\infty} \) can be obtained by:

\[
U_{b\infty} = 0.71\sqrt{gD_e}
\] (5.34)

The isolated bubble rise velocity \( U_{b\infty} \) is the rise velocity of a single bubble injected in a fluidized bed operated at the minimum fluidization velocity.

For freely bubbling beds, the bubble rise velocity \( U_b \) is given by:

\[
U_b = U_{b\infty} + (U - U_{mf})
\] (5.35)

The bubble rise velocity cannot be used to calculate the superficial gas velocity in the L-phase. According to the two-phase theory of fluidization, all the gas enters the H-phase at minimum fluidization velocity. However, at minimum fluidization, equation 5.35 predicts that the superficial gas velocity is \( U_{b\infty} \) and not 0. The expression for the bubble rise velocity is
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therefore modified so that \( U_b \to 0 \) as \( U \to U_{mf} \) [212]:

\[
U_b = (U - U_{mf})(1 + \frac{0.711}{U} \sqrt{gD_e})
\]  

(5.36)

The bed expansion \( (E) \) can be estimated from:

\[
E = \frac{H - H_{mf}}{H_{mf}} = \frac{U - U_{mf}}{U_{\infty}}
\]  

(5.37)

Equation 5.37 results from the two-phase theory of fluidization and assumes that the bed expansion is caused by any gas flow beyond \( U_{mf} \), i.e. by \( (U - U_{mf}) \). This calculation also assumes an average bubble size for the entire fluidized bed. Because \( H \) is usually unknown, an iterative procedure is used. In the present model, the bubble size is not set at an average value, but is varied along the vertical position in the bed. The values of other dependant parameters also change as the bubble size varies within the bed.

For three-dimensional bubbles, the interphase mass transfer coefficient [213] and area are obtained from:

\[
k_{LH} = \frac{U_{mf}}{3} + 2 \left( \frac{D_g \rho_{mf} U_{\infty}}{\pi D_e} \right)^{1/2}
\]  

(5.38)

\[
a_I = \frac{6}{D_e}
\]  

(5.39)

These two parameters were briefly discussed in section 5.1.2. The interphase mass transfer coefficient is composed of a throughflow (convection) component and a diffusion component. The diffusion component varies with gas diffusivity \( (D_g) \), bubble velocity \( (U_{\infty}) \) and bubble diameter \( (D_e) \).

### 5.1.8 Slugging fluidized bed

A slugging fluidized bed is similar to a bubbling fluidized bed. However, bubble growth is restricted by the reactor walls and bubbles travel through the bed as slugs (elongated bullet-shaped bubbles constrained by the walls). Three conditions are necessary for slugging. The superficial velocity \( (U) \) must be higher than the minimum slugging velocity \( (U_{ms}) \); the bed
height \( H \) must be greater than the minimum slugging height; and the maximum bubble size \( D_{e,\text{max}} \) must be at least of the order of the column diameter \( D \). The minimum slugging velocity \( U_{ms} \) is calculated using [214]:

\[
U_{ms} = U_{mf} + 0.07 \sqrt{gD} \quad \text{if} \quad H_{mf} > 1.3D^{0.175} \tag{5.40}
\]

\[
U_{ms} = U_{mf} + 0.07 \sqrt{gD} + 0.16(1.3D^{0.175} - H_{mf})^2 \tag{5.41}
\]

Equation 5.40 and 5.41 apply for shallow beds and deep beds respectively. The maximum bed height \( H_{\text{max}} \) during slugging can be estimated from [215, 216]:

\[
\frac{H_{\text{max}} - H_{mf}}{H_{mf}} = \frac{U - U_{mf}}{U_{\infty}} \tag{5.42}
\]

The velocity of a single slug \( U_{\infty} \) is given by:

\[
U_{\infty} = 0.35 \sqrt{gD} \tag{5.43}
\]

For a continuously slugging bed, the slug velocity \( U_s \) is:

\[
U_s = U_{\infty} + (U - U_{mf}) \tag{5.44}
\]

With the exception of the single slug velocity, the last three equations are similar to those for bubbling fluidized beds, but with \( s \) (slug) in place of \( b \) (bubble).

Comparing the Hovmand slugging model [217] to the Orcutt “piston-flow” fluidized bed model [218, 219] shows that the derivations are identical. The interphase mass transfer coefficient \( k_{LH} \) and area \( a_I \) can be expressed in a form similar to that of the bubbling case:

\[
k_{LH} = U_{mf} + \frac{16 \varepsilon_{mf} I}{1 + \varepsilon_{mf}} \left( \frac{Dg}{\pi} \right)^{1/2} \left( \frac{g}{D} \right)^{1/4} \tag{5.45}
\]

\[
a_I = \frac{1}{D f_s} \tag{5.46}
\]

The surface integral \( I \) (shown in Table 5.3) and the slug shape factor \( f_s \) are functions of the slug length-to-diameter ratio \( \frac{L}{D} \):

\[
f_s = \frac{4V}{\pi D^3} = \left( \frac{L}{D} \right) - 0.495 \left( \frac{L}{D} \right)^{1/2} + 0.061 \tag{5.47}
\]
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Table 5.3: Values of the surface integral ($I$) for various slug length to diameter ratio ($L/D$)

<table>
<thead>
<tr>
<th>$L/D$</th>
<th>0.3</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>0.13</td>
<td>0.21</td>
<td>0.39</td>
<td>0.71</td>
<td>0.98</td>
<td>1.24</td>
<td>1.48</td>
</tr>
</tbody>
</table>

The slug length to diameter ratio ($\frac{L}{D}$) can be obtained by solving the quadratic equation [217]:

$$\frac{L}{D} - 0.495\left(\frac{L}{D}\right)^{\frac{1}{2}}\left(1 + \frac{U - U_{mf}}{0.35\sqrt{gD}}\right) + 0.061 - \frac{(T/D - 0.061)(U - U_{mf})}{0.35\sqrt{gD}} = 0 \quad (5.48)$$

where $T$ is the slug-to-slug spacing (tail-to-nose spacing).

5.1.9 Transition from bubbling to slugging

Slugging may be considered as a special case of bubbling fluidization where the bubble size is physically restricted by the walls of the reactor. In a bubbling fluidized bed, bubbles coalesce as they rise through the bed causing their average diameter to increase with increasing height vertical position. As the bubble diameter approaches the reactor diameter, slugging takes over. As the mean bubble size increases, the effect of the walls becomes greater and one expects a smooth transition from bubbling to slugging fluidization.

Modelling the transition to slug flow may be attempted in various ways:

- One could use two separate models, one for bubbling and one for slugging, applying a bubbling model below a given criteria, then switch to the slug flow model. The problem with this approach is that there would be a discontinuity at the point where the switch is made, while in practice the transition occurs gradually. Moreover, there is uncertainty in characterizing the regime transition.

- One could use the results from the two models and interpolate or average their results. A probabilistic average could be used and would better characterize the uncertainty of the regime transition. The probabilistic average would be the weighted sum of the results where the weights are based on the probability of being in a given regime. A problem
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with this approach is that the interpolated results are not necessarily consistent with the physics of the system, especially where there are non-linearities.

- A better method is to combine the two models into a single model which predicts results similar to the two limiting models outside the transition range. In the transition region between two flow regimes, the model uses the probabilistic average of the parameters (not the final predictions) for each regime. This approach has been used previously to model the transition from the bubbling to the turbulent fluidization regime and from turbulent to fast fluidization [212, 220, 203, 205]. In that case, relatively simple Re vs Ar correlations describe the transitions from bubbling to the turbulent fluidization regime and from turbulent to fast fluidization [205]. The probabilities were related to the root-mean-square deviations from these correlations [205].

Currently, the transition from bubbling to the slugging fluidization regime is only described by the minimum slugging velocity \( U_{ms} \), the necessary conditions for slugging (see section 5.1.8) and the criterion [216]:

\[
\frac{U_{ms} - U_{mf}}{0.35\sqrt{gD}} = 0.2
\]

(5.49)

This criterion does not quantify the probability of slugging and bubbling, nor does it allow for a transition within the fluidized bed, i.e. bubbling near the distributor and slugging above.

The bubble rise velocity as a function of the bubble-to-column-diameter ratio is used in the next section to characterize the transition from bubbling to the slugging fluidization flow regime. The regime probabilities are then obtained. These probabilities are then used to calculate probabilistic averages of the parameters required by the model.

**Void velocity**

In order to bridge the bubbling and slugging fluidization regimes, the void (bubble or slug) rise velocities \( U_v \) are described as a function of the Froude number:

\[
\text{Fr} = \frac{U_v}{\sqrt{gD}} \quad v = b \text{ or } s
\]

(5.50)
Using the Froude number, equations 5.34 and 5.43 may be converted to:

\[
\begin{align*}
\text{Bubbling} & \quad \text{Fr} = 0.71 \sqrt{\frac{De}{D}} \\
\text{Slugging} & \quad \text{Fr} = 0.35
\end{align*}
\] (5.51) (5.52)

The modified bubble rise velocity (from equation 5.36) can be written:

\[
U_v = (U - U_{mf})(1 + \frac{\text{Fr}}{U} \sqrt{gD})
\] (5.53)

As for several other aspects of the hydrodynamics of fluidized bed systems, the transition to slug flow in fluidized bed systems is analogous to that in gas-liquid systems. The experimental data from fluidized bed systems presents a similar trend as in the water system. However, the scatter is much larger [216]. Figure 5.2 shows that the velocities at the two extremes are described by equations 5.51 and 5.52. The transition between the two extremes is smooth and occurs for \(\sqrt{De/D}\) between about 0.38 and 0.7 [216].

The behaviour at each end of the transition interval clearly approaches the two limiting cases. In other words, the slopes at each end of the interval are equal to each of the limiting cases. The fit of the experimental data must also approach the limiting cases similarly with a sigmoidal fit in-between to express the probability of slugging passing from 0 to 1 as \(\sqrt{De/D}\) goes from small values to values approaching unity. To simplify the fitting for the transition region, a transformation is used such that the bubbling-to-slugging transition interval \((X)\) goes from 0 to 1 and the corresponding Froude numbers \((Y)\) also passes from 0 to 1. Here:

\[
X = \frac{\sqrt{De/D} - DD_0}{DD_1 - DD_0}
\] (5.54)

where \(DD_0\) and \(DD_1\) are the lowest and highest values of \(\sqrt{De/D}\) in the transition interval, i.e. the endpoints of the transition interval. Similarly, \(Y\) is taken as:

\[
Y = \frac{\text{Fr} - 0.71DD_0}{0.35 - 0.71DD_0}
\] (5.55)

so that it represents a fraction departure from the wall-effect free bubble velocity. By imposing the values and the slopes at the end points, the following third order polynomial is obtained:
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Figure 5.2: Bubble rising velocity in water. Experimental points obtained from Hovmand and Davidson [216]

\[ Y = KX + (3 - 2K)X^2 + (K - 2)X^3 \]  

(5.56)

where \( K \) is the required slope at \( X = 0 \). The slope, obtained from equation 5.51 and transformed into \( X,Y \) coordinates is:

\[ K = \frac{0.71(DD_1 - DD_0)}{0.35 - 0.71DD_0} \]  

(5.57)

Note that once this initial slope is set, there are no degrees of freedom to set any other parameters in the transformed coordinates. Therefore, the only fitting parameters are the endpoints of the interval, i.e. the values of \( \sqrt{D_e/D} \) at which one sets \( X = 0 \) and \( X = 1 \) (\( DD_0 \) and \( DD_1 \)).

The Froude number is described for the three ranges as follows:

- For \( \sqrt{D_e/D} < DD_0 \)

\[ Fr = 0.71 \sqrt{D_e/D} \]  

(5.51)
• For $DD_0 \leq \sqrt{D_e/D} \leq DD_1$

$$Y = KX + (3 - 2K)X^2 + (K - 2)X^3$$  \hspace{1cm} (5.56)

• For $\sqrt{D_e/D} > DD_1$

$$Fr = 0.35$$  \hspace{1cm} (5.52)

The optimum transition interval is obtained by minimizing the squares of the difference between the fitted function and the experimental data. An excellent fit of the experimental data is obtained by using a transition interval ($\sqrt{D_e/D}$) between 0.319 and 0.714. This interval is only slightly larger than suggested by Hovmand and Davidson [216] who employed 0.38 to 0.7. With these values, $K$ is equal to 2.27.

**Probability of slugging**

The fit in Figure 5.2 cannot directly represent the probability of slugging or the probability of bubbling. For instance, the probability of slugging should not increase proportionally to the void velocity, i.e. rapidly at first then more slowly. Outside the transition interval, the probability of slugging is taken as 0 for $\sqrt{D_e/D} < DD_0$ and 1 for $\sqrt{D_e/D} > DD_1$. In the transition interval, the probability of slugging increases from 0 to 1 in an appropriate manner.

A reasonable way of estimating the probability from the fit of the Froude numbers was obtained by considering the growing deviation of the void velocity (equation 5.56) from the corresponding wall-effect independent bubble rise velocity (equation 5.51) in the lower part of the transition interval, and then considering the shrinking difference between the void velocity (equation 5.56) and the slug flow (equation 5.52) limit in the upper section of the transition interval. The condition ($\sqrt{D_e/D} = 0.35/0.71 = 0.493$) when the velocities are equal (equal Fr from equation 5.51 and 5.52) defines the point where the probabilities of slugging and bubbling are equal, i.e. $P_{slugging} = P_{bubbling} = 0.5$. Hence the probabilities are assigned as follows, with the transition interval being $DD_0 \leq \sqrt{D_e/D} \leq DD_1$:

• For $\sqrt{D_e/D} < DD_0$

$$P_{slugging} = 0$$  \hspace{1cm} (5.58)
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\[ P_{\text{bubbling}} = 1 \]  

(5.59)

- For \( DD_0 \leq \sqrt{D_e/D} \leq 0.493 \)

\[ P_{\text{slugging}} = \frac{KX - (KX - (3 - 2K)X^2 + (K - 2)X^3)}{2 \left[ \text{value of numerator at } \sqrt{D_e/D} = 0.493 \right]} \]  

(5.60)

\[ P_{\text{bubbling}} = 1 - P_{\text{slugging}} \]  

(5.61)

- For \( 0.493 \leq \sqrt{D_e/D} \leq DD_1 \)

\[ P_{\text{bubbling}} = \frac{1 - (KX - (3 - 2K)X^2 + (K - 2)X^3)}{\text{same numerator as in equation 5.60 above}} \]  

(5.62)

\[ P_{\text{slugging}} = 1 - P_{\text{bubbling}} \]  

(5.63)

- For \( \sqrt{D_e/D} > DD_1 \)

\[ P_{\text{slugging}} = 1 \]  

(5.64)

\[ P_{\text{bubbling}} = 0 \]  

(5.65)

Figure 5.3 presents the resulting probability of slugging as a function of \( \sqrt{D_e/D} \). The probability of slugging first increases proportionally to the deviation of equation 5.56 from equation 5.51, reaches 50%, then increases at a decreasing rate as the deviation of equation 5.56 from equation 5.52 decreases. The equations describing the probability of slugging as well as other equations required to describe the transition regime are summarized in Table 5.4. Note that the suggested procedure allows a smooth transition between pure bubbling (\( P_{\text{bubbling}} = 1 \)) and pure slugging (\( P_{\text{slugging}} = 1 \)) as \( \sqrt{D_e/D} \) increases from \( DD_0 \) to \( DD_1 \). While this is conceptually similar to the probabilistic transitions introduced in the generalized fluidized bed reactor model [212, 220, 203, 205], one must note that in the current case, the transition takes place over height as \( \sqrt{D_e/D} \) grows due to coalescence, whereas in the bubbling/turbulent/fast fluidization transitions of the generalized fluidized bed reactor model [212, 220, 203, 205], the transitions are only functions of the superficial velocity.

The generalized bubbling-slugging interphase mass transfer coefficient and area are calculated using the equations in Table 5.5.

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5.2 Steady-state fluidized bed reactor model: Reaction of solids

So far, the model has described the fluidized bed dynamics and the gas reaction. This is sufficient for catalytic fluidized bed reactors. However, for gas-solid reactions, the fluidized bed reactor model must be coupled to a solid reaction model such that the number of moles consumed and produced in the gas are balanced with the number of moles consumed and produced in the solid. The model assumes the reaction:

$$\text{ZnS}^{(\text{solid})} + \frac{3}{2} \text{O}_2^{(\text{gas})} = \text{ZnO}^{(\text{solid})} + \text{SO}_2^{(\text{gas})}$$  \quad (5.66)

To obtain an overall solids conversion, the solids reaction model must include assumptions on the mixing of the solids within the fluidized bed, the single particle reaction model and the residence times of the solids within the fluidized bed.
Table 5.4: Summary of equations describing the transition from bubbling to slugging fluidization

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{D_e/D}$ to $X$</td>
<td>$X = \frac{\sqrt{D_e/D} - DD_0}{DD_1 - DD_0}$ or $\sqrt{D_e/D} = DD_0 + X(DD_1 - DD_0)$</td>
</tr>
<tr>
<td>Fr to $Y$</td>
<td>$Y = \frac{Fr - 0.71DD_0}{0.35 - 0.71DD_0}$ or $Fr = Y(0.35 - 0.71DD_0) + 0.71DD_0$</td>
</tr>
</tbody>
</table>

**Bubble velocity**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{D_e/D} &lt; DD_0$</td>
<td>$Fr = 0.71\sqrt{D_e/D}$</td>
</tr>
<tr>
<td>$DD_0 \leq \sqrt{D_e/D} \leq DD_1$</td>
<td>$Y = 2.27X - 1.54X^2 + 0.27X^3$</td>
</tr>
<tr>
<td>$\sqrt{D_e/D} &gt; DD_1$</td>
<td>$Fr = 0.35$</td>
</tr>
</tbody>
</table>

**Probability**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{D_e/D} &lt; DD_0$</td>
<td>$P_{slugging} = 0$</td>
</tr>
<tr>
<td>$DD_0 \leq \sqrt{D_e/D} \leq 0.493$</td>
<td>$P_{slugging} = 2.79X^2 - 0.490X^3$</td>
</tr>
<tr>
<td>$0.493 &lt; \sqrt{D_e/D} \leq DD_1$</td>
<td>$P_{slugging} = -0.813 + 4.12X - 2.79X^2 + 0.490X^3$</td>
</tr>
<tr>
<td>$\sqrt{D_e/D} &gt; DD_1$</td>
<td>$P_{slugging} = 1$</td>
</tr>
</tbody>
</table>

Interval: $DD_0 = 0.319$, $DD_1 = 0.714$

5.2.1 Mixing of solids within the fluidized bed

In this model, the solids are assumed to be well mixed axially and radially, as implied in the gas model. If mixing were not perfect, some regions of the fluidized bed would contain higher concentrations of reacting solids than others. The gas reaction is formulated in terms of solids volume fraction within each phase which are constant ($\phi_H = 1 - \epsilon_{mf}$ and $\phi_L = \text{constant}$) for the entire reactor and does not differentiate the type of solids (reacting or inert). Therefore, any difference in the concentration of reacting solids (i.e. insufficient mixing) affects the reactivity of the solids mixture.

To account for variations in the concentration of reacting particles, a solids mixing and flow model should be coupled to the gas reaction model. This approach has been used to model shallow fluidized beds [221, 222, 223, 224, 225] where radial mixing is accounted for, while axial mixing is assumed to be perfect.
Table 5.5: Summary of the bubbling, slugging and generalized model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bubbling</th>
<th>Slugging</th>
<th>Generalized</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bubble</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size ($D_e$)</td>
<td>Calculated from bubble size correlations. See section 5.1.7.</td>
<td>$D$</td>
<td>Calculated from bubble size correlations. See section 5.1.7.</td>
</tr>
<tr>
<td>Velocity ($U_{v\infty}$)</td>
<td>$0.71\sqrt{g,D_e}$</td>
<td>$0.35\sqrt{g,D}$</td>
<td>Calculated using Froude number.</td>
</tr>
<tr>
<td>Froude Number (Fr)</td>
<td>$0.71\sqrt{\frac{D_e}{D}}$</td>
<td>$0.35$</td>
<td>Calculated using equations in Table 5.4</td>
</tr>
<tr>
<td>Velocity ($U_v$)</td>
<td>$(U - U_{mf}) + 0.71\sqrt{g,D_e}$</td>
<td>$(U - U_{mf}) + 0.35\sqrt{g,D}$</td>
<td>$(U - U_{mf})(1 + \frac{Fr}{U\sqrt{g,D}})$</td>
</tr>
<tr>
<td><strong>L-Phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume fraction ($\psi_L$)</td>
<td></td>
<td>$\frac{U-U_{mf}}{U_v}$</td>
<td></td>
</tr>
<tr>
<td>Superficial gas velocity ($U_L$)</td>
<td></td>
<td>$U_v$</td>
<td></td>
</tr>
<tr>
<td>Bed expansion</td>
<td>$\frac{H - H_{mf}}{H_{mf}} = \frac{U - U_{mf}}{U_{v\infty}}$</td>
<td>$\frac{H_{max} - H_{mf}}{H_{mf}} = \frac{U - U_{mf}}{U_{v\infty}}$</td>
<td>$H - H_{mf} = \int_0^H \psi_L , dz$</td>
</tr>
<tr>
<td><strong>Interphase mass transfer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coefficient ($k_{LH}$)</td>
<td>$\frac{U_{mf}}{3} + 2\left(\frac{D_g \epsilon_{mf} U_{v\infty}}{\pi D_e}\right)^{1/2}$</td>
<td>$U_{mf} + \frac{16 \epsilon_{mf}}{1 + \epsilon_{mf}} \left(\frac{D_g}{\pi}\right)^{1/2} \left(\frac{D}{D_e}\right)^{1/4}$</td>
<td>$(1 - P_{slugging}) k_{LH, bubbling} + (P_{slugging}) k_{LH, slugging}$</td>
</tr>
<tr>
<td>Exchange area ($a_I$)</td>
<td>$\frac{6}{D_e}$</td>
<td>$\frac{1}{D g s}$</td>
<td>$(1 - P_{slugging}) a_I, bubbling + (P_{slugging}) a_I, slugging$</td>
</tr>
</tbody>
</table>

$I$: Slug surface integral, $f_s$: Slug shape factor, See section 5.1.8
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To verify if the assumption of perfect mixing is valid, mixing times will be compared to the reaction and residence times of the reacting particles. Solids mixing in a fluidized bed must be considered separately in the two important dimensions. Axial mixing may be characterized by the turnover time, the time required for the bubbles to displace the entire mass of the bed. The solids turnover time is calculated using the axial solids flux \( J \), bed mass \( M_{\text{bed}} \) and cross-sectional area \( A \) [226]:

\[
J = \rho_p (1 - \epsilon_{mf}) (U - U_{mf}) Y (\beta_w + 0.38 \beta_d)
\]

\[
t_{\text{turnover}} = \frac{M_{\text{bed}}}{AJ}
\]

To calculate the solids flux, the values suggested by Baeyens and Geldart [226] for rounded sand are used: \( \beta_w = 0.32, \beta_d = 0.7, Y = 0.82 \). Complete axial mixing can be achieved in 2 to 3 turnover times. For a complete discussion on axial mixing and turnover time, see [226].

The solids are also assumed to be well mixed radially. Radial mixing is usually quantified using a dispersion model [227, 228, 229, 230]. The radial diffusion coefficient of solids \( D_{\text{radial}} \) in a bubbling fluidized bed may be expressed [227] as:

\[
D_{\text{radial}} = 3.66 \cdot 10^{-4} \frac{U - U_{mf}}{U_{mf}^{1/3}}
\]

By considering radial diffusion in a cylinder, a characteristic time may be obtained [231].

\[
t_{\text{radial}} = \frac{D^2}{4 \times 5.78 D_{\text{radial}}}
\]

The constant 5.78 is the square of the root of the Bessel function of zero order.

The most important difference between industrial and laboratory roasters is the radial mixing time. The assumption of a perfectly mixed bed is verified by comparing the particle residence time and reaction times to the two mixing times described above.

5.2.2 Solid residence times

The solids mean residence time characterizes the average time spent by particles in the fluidized bed. The solids mean residence time is required in section 5.2.4 to calculate the average solids
conversion. For non-reacting mono-sized particles, the mean residence time is related to the space-time:

\[ \tau = \frac{M_{\text{bed}}}{F_{\text{Feed}}} \]  

(5.71)

However, since a fluidized bed roaster has reacting particles of different sizes, this calculation is not valid. To evaluate the mean residence time of different particle sizes we formulate an overall mass balance and a mass balance by-size over the reactor:

\[ \beta F_{\text{Feed}} - F_{\text{Overflow}} - F_{\text{Carryover}} = 0 \]  

(5.72)

\[ \beta F_{\text{Feed}} p_{\text{Feed}} - F_{\text{Overflow}} p_{\text{Overflow}} - F_{\text{Carryover}} p_{\text{Carryover}} = 0 \]  

(5.73)

where \( p_{\text{Feed}}, p_{\text{Overflow}} \) and \( p_{\text{Carryover}} \) are the particle size distribution functions of the feed, overflow and carryover respectively. These mass balances assume steady-state, complete conversion and no changes in particle sizes. The mass conversion ratio, \( \beta \), was briefly discussed for the overall mass balance of the experimental results in section 4.3. The constant \( \beta \) is used to convert the concentrate feedrate into a calcine feedrate. For pure zinc sulfide and oxide, \( \beta \) is simply the ratio of the molar masses i.e. \( \beta = \frac{M_{\text{ZnS}}}{M_{\text{ZnO}}} = \frac{81.379 \text{g/mol}}{97.44 \text{g/mol}} = 0.835 \).

The mean residence time for a given size is calculated from the carryover and overflow mass flowrates, in addition to the size distributions and bed mass:

\[ \tau = \frac{M_{\text{bed}} p_{\text{Overflow}}}{F_{\text{Overflow}} p_{\text{Overflow}} + F_{\text{Carryover}} p_{\text{Carryover}}} \]  

(5.74)

Because of elutriation, the residence time of a given size of particles depends on the particle size in question. Very small particles have a short mean residence time in the bed, while larger particles spend much longer in the roaster. This is because fine particles can leave the roaster by two output streams, whereas larger ones only exit via the overflow stream. It has been shown theoretically that the average residence time of carryover and overflow particles of the same diameter is the same [232].

The elutriation constant is related to the carryover mass flowrate and size distribution, by:

\[ \kappa = \frac{F_{\text{Carryover}} p_{\text{Carryover}}}{M_{\text{bed}} p_{\text{Overflow}}} \]  

(5.75)
which can be used to obtain:

\[ \tau = \frac{1}{\frac{F_{\text{overflow}}}{M_{\text{bed}}} + \kappa} \]  \hspace{1cm} (5.76)

Use of equation 5.76 requires appropriate information on the elutriation constant. Elutriation in commercial fluidized bed roasters has not been characterized, and predictions from available correlations vary widely [233]. Therefore, accurate prediction of the particle residence time is not possible without direct measurements.

A more adequate representation of equation 5.71 when considering reacting particles and a wide size distribution may be obtained from equations 5.73 and 5.74:

\[ \tau = \frac{M_{\text{bed}}P_{\text{Bed}}}{\beta F_{\text{Feed}}P_{\text{Feed}}} \]  \hspace{1cm} (5.77)

The effective size distribution of the industrial feed is very difficult to characterize since concentrate particles form lumps due to the presence of water. However, the feed particle size distribution of the laboratory roaster can be measured using particle size analyzers.

Some particles of the feed may be smaller than the smallest particle in the bed. In such cases, equation 5.77 results in mean residence times equal to 0. For these particles, a minimum mean particle residence time is required. This minimum mean particle residence time is set to be equal to the mean residence time of the gas in the fluidized bed:

\[ \tau_{\text{minimum}} = \frac{H_{mf}A(1 - \phi_H) + (H - H_{mf})A(1 - \phi_L)}{UA} = \frac{H_{mf}(1 - \phi_H) + (H - H_{mf})(1 - \phi_L)}{U} \]  \hspace{1cm} (5.78)

### 5.2.3 Single-particle reaction model

This section briefly describes a transient non-isothermal solid reaction model and its simplified pseudo-steady-state isothermal version for the reactions of solids within the fluidized bed. The transient non-isothermal particle reaction model is used to verify that the assumption of isothermality is valid and to estimate under which conditions it is not. The fluidized bed reactor model assumes that the particles are isothermal, at the same temperature as the fluidized bed and uses the simplified solids reaction model described at the end of this section.
The single particle reaction model is a transient model aimed at predicting the gas concentrations at the reaction site, the particle temperature and the evolution of conversion with time. As summarized by Wen and Wang [234] the model accounts for thermal and diffusional effects in noncatalytic solid gas reactions. The model, based on the unreacted-shrinking-core model, includes temperature predictions and uses effectiveness factors to describe the effects of diffusion and heat generation. The resulting model can predict various phenomena such as ignition, extinction, geometric instability and abrupt changes in the controlling mechanism.

The nomenclature of the equations is the same as in Wen and Wang [234] with minor changes to allow for the calculation of gaseous product concentrations. The model applies to the following general reaction:

$$aA(gas) + S(solid) = gG(gas) + cC(solid)$$  \hspace{1cm} (5.79)

For the roasting of zinc sulfide, A is O$_2$, S is ZnS, G is SO$_2$ and C is ZnO. As for the fluidized bed model, the stoichiometric coefficients, $\nu_i$, are positive for products and negative for reactants.

The rate of reaction can be represented as:

$$r_A = \nu_A r_S = \nu_A k_s C_S^m C_A^n$$  \hspace{1cm} (5.80)

where $m$ and $n$ are the orders of the reaction with respect to the solid and the gaseous reactants concentrations, respectively. The reaction rate constant, $k_s$ is per unit reacting surface area. The temperature dependency of the reaction rate constant is assumed to be of Arrhenius type, i.e.:

$$k_s(T_c) = k_s^0 \exp\left(-\frac{E_a}{RT_c}\right)$$  \hspace{1cm} (5.81)

where $k_s^0$ is the pre-exponential constant and $E_a$ is the activation energy. Figure 5.4 presents the geometry of the model as well as typical concentration and temperature profiles.
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Figure 5.4: Concentration and temperature profiles of a single reacting particle [234]

Mole balances

In terms of gas mole fractions ($x_i$), the steady-state gas mole balance over the reacted layer ($r_c < r < R$) of a spherical reacting particle can be described as:

$$
\frac{d^2 x_i}{dr^2} + \frac{2 dx_i}{r \, dr} = 0
$$

(5.82)

where $i$ can either be the gaseous reactant (A) or product (G). Although equimolar counter-diffusion is assumed, the following treatment can be applied to the zinc roasting system when the reactant and resulting product gas concentration is small, which is assumed to be the case. The boundary condition at the surface ($r = R$) is:

$$
(CD_{ei})T_o \frac{dx_i}{dr} \bigg|_{r=R} = (k_{mi} C)T_o (x_{io} - x_{is})
$$

(5.83)

The product of the total gas concentration (sum of all gaseous species) times the diffusivity ($CD_{ei}$) is assumed to be temperature-independent. The boundary condition at the core surface ($r = r_c$) is

$$
(CD_{ei})T_o \frac{dx_i}{dr} \bigg|_{r=r_c} = -\nu_i k_s(T_o) C_S^m C_{Ac}^n
$$

(5.84)

where $\nu_i$ is the stoichiometric coefficient for component $i$. The evolution of the core radius with time is described by:

$$
(CD_{ei})T_o \frac{dx_i}{dr} = \nu_A C_S \frac{dr_c}{dt}
$$

(5.85)
with the initial condition, \( r_c = R \) when \( t = 0 \). The subscripts \( T_o \) and \( T_c \) indicate that the quantities are evaluated at the bulk conditions or at the reaction interface conditions, respectively.

### Heat balance

The energy balance in the ash layer is given by:

\[
\frac{\partial T}{\partial t} = \frac{k_e}{C_{pe}} \left( \frac{\partial^2 T}{\partial r^2} + \frac{2 \partial T}{r \partial r} \right)
\]

where \( k_e \) and \( C_{pe} \) are the effective thermal conductivity and volumetric heat capacity of the ash layer respectively. The boundary condition at the surface (\( r = R \)) is:

\[
-k_e \frac{\partial T}{\partial r} = h_C(T_s - T_o) + h_R(T^d_s - T^d_w)
\]

Note that radiation is included using a radiative heat transfer coefficient. The radiative heat transfer coefficient (\( h_R \)), includes the emissivity of the particle (\( \varepsilon_{\text{particle}} \)), the Stefan-Boltzmann constant (\( \sigma = 5.67 \times 10^{-8} \text{ W m}^2 \text{ K}^{-4} \)) and view factors, if applicable. The first right-hand term is the heat transfer by convection, while the second term allows for the radiation from the particle surface to a wall surface. For a particle in a fluidized bed, the wall surface consists of other bed particles. The boundary condition at the unreacted core surface (\( r = r_c \)), assuming that the core is at a uniform temperature (\( T_c \)), is:

\[
4\pi r_c^2 k_e \frac{\partial T}{\partial r} - 4\pi r_c^2 \nu A_k s T_c C_{pm} C_{Ac}(\Delta H) = \frac{4}{3} \pi r_c^3 \rho_c C_{pe} \frac{dT_c}{dt}
\]

### Solution

The reader is referred to Wen and Wang [234] for more details on the solution of the mass and heat balances. The equations can be rewritten in dimensionless form. The solution of the mass balance for the gaseous reactant (A) is given by:

\[
\omega_{cA} = \omega_{sA} + Sh_A(1 - \omega_{sA}) \left( 1 - \frac{1}{\xi_c} \right)
\]

\[
\frac{Sh_A(1 - \omega_{sA})}{\phi_s \xi_c^2} = \left( \frac{\omega_{cA}}{U_c} \right)^n \exp \left( \frac{E_a}{RT_o} \left( 1 - \frac{1}{U_c} \right) \right)
\]
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The solution of the mass balance for the gaseous product (G) is given by:

\[ \omega_{cG} = \omega_{sG} + \text{Sh}_G (1 - \omega_{sG}) \left( 1 - \frac{1}{\xi_c} \right) \]  

(5.91)

\[ \frac{\text{Sh}_G(1 - \omega_{sG})}{\phi_s \xi_c^2} = \left( \frac{\omega_s A}{U_c} \right)^n \exp \left( \frac{E_a}{RT_o} \left( 1 - \frac{1}{U_c} \right) \right) \left( \frac{\nu_G D_e \Delta T_o X_A}{\nu_A D_e \Delta T_o X_G} \right) \]  

(5.92)

The position of the reaction front (\( \xi_c \)) can be calculated by integration:

\[ \frac{\text{Sh}_A(1 - \omega_{sA})}{\phi_s \xi_c^2} = -\frac{d\xi_c}{d\theta} = \eta_s \]  

(5.93)

The solution of the heat balance is given by:

\[ U_s = U_c + \left( 1 - \frac{1}{\xi_c} \right) \left( \text{Nu}_C (U_s - 1) + \text{Nu}_R (U_s^4 - U_{\theta}) \right) \]  

(5.94)

\[ \frac{dU_c}{d\theta} = -\frac{6 \beta \left( \frac{E_a}{RT_o} \right) \xi_c^2 \eta_s - (U_s - U_c) \left( \frac{6}{\phi_s (1 - \xi_c)} + A_{sp} \eta_s (1 + 2 \xi_c) \right) + \frac{A_{sp} \eta_s (2 + \xi_c)}{\xi_c (1 - \xi_c) (\text{Nu}_C + 4 \text{Nu}_R U_s^3)} \} \]  

(5.95)

where

\[ \beta = \frac{C_A D_e \Delta T_o (-\Delta H) R}{k_e E_a} \]  

(5.96)

\[ A_{sp} = -\frac{C_A D_e \Delta T_o C_{pc}}{\nu_A C_s k_e} \]  

(5.97)

\[ G = -\frac{\rho_e C_{pc} T_o}{\nu_A C_s (-\Delta H)} \]  

(5.98)

The last two dimensionless numbers originate from the transient analysis of the heat balance.

Several parameters are grouped into dimensionless numbers such as the Thiele modulus

\[ \phi_s = -\frac{\nu_A R_p k_s \Delta T_o C_{A}^{n-1} C_s^{m}}{D_e \Delta T_o} \]  

(5.99)

and the modified Sherwood number (Sh):

\[ \text{Sh} = \frac{R_p k_m}{D_e \Delta T_o} \]  

(5.100)

The Thiele modulus accounts for mass transfer resistance within the product layer, while the modified Sherwood number accounts for the external mass transfer resistance.
Equations 5.89 to 5.95 must be solved simultaneously by integrating over dimensionless time ($\theta$). If steady-state is assumed, there is no energy accumulation in the ash layer ($A = 0$) or the unreacted core ($G = 0$). The equations thus simplify to the results of Ishida and Wen [235].

To obtain the solids conversion from the reaction interface position, the following relationship is used:

$$ X = 1 - \xi_c^3 $$

(5.101)

**Isothermal solid reaction model**

The isothermal solid reaction model assumes that the particle has no internal temperature gradient and reacts at a constant temperature, equal to the environment (or bulk) temperature. For such an isothermal system, there are no heat effects. The effectiveness factor ($\eta_s$) and the reaction interface position ($\xi_c$) are given by:

$$ \eta_s = \frac{1}{1 + \phi_s \xi_c (1 - \xi_c) + \frac{\phi_s}{\text{Sh}} \xi_c^2} $$

(5.102)

$$ \theta = 1 - \xi_c + \frac{\phi_s}{2} \left(1 - \xi_c^2\right) + \frac{\phi_s}{3} \frac{1}{\text{Sh}} - 1 \left(1 - \xi_c^3\right) $$

(5.103)

where $\theta$ is the dimensionless time. The dimensionless time required for complete reaction ($\theta_{cr}$) is obtained by setting $\xi_c$ to 0 in equation 5.103.

The time for complete reaction of the solid particles is required for calculating the overall conversion of the solids in the fluidized bed. To obtain the (dimensional) time for complete reaction, we note that:

$$ t_{cr} = \frac{R_p \theta_{cr}}{k_s T_0 C_A^n C_s^{m-1}} $$

(5.104)

A dimensionless time of 1 ($\theta_{cr} = 1$) signifies that the reaction is controlled by chemical kinetics only. The reciprocal of the dimensionless time for complete reaction may be viewed as the overall effectiveness factor. For an isothermal system, the effectiveness factor varies between 0 and 1. When heat effects are accounted for and the reaction is exothermic, the effectiveness factor can exceed 1.
Equations 5.102, 5.103 and 5.104 are used in the gas-solid fluidized bed reactor model to calculate the overall solids conversion, as discussed in the next section.

5.2.4 Conversion of solids

Assuming that the bed solids are perfectly mixed, the solids reactions are modelled in similar fashion to the reaction of a macro-fluid where the solid conversion is integrated over the age distribution. For mono-sized particles reacting as shrinking cores under chemical control, the solids conversion in a well-mixed fluidized bed is a function of the mean solids residence time \( \tau \), and the time required for complete conversion of a single particle \( t_{cr} \) \[232, 157\] is given by:

\[
1 - X = \int_0^{t_{cr}} \left( 1 - \frac{t}{t_{cr}} \right)^3 \frac{e^{-t/\tau}}{\tau} \, dt
\]

(5.105)

After integration, the overall solid conversion is:

\[
X = 3 \left( \frac{\tau}{t_{cr}} - 2 \left( \frac{\tau}{t_{cr}} \right)^2 + 2 \left( \frac{\tau}{t_{cr}} \right)^3 (1 - e^{-t_{cr}/\tau}) \right)
\]

(5.106)

Due to numerical instability at high \( \frac{t}{t_{cr}} \), the exponential is expanded using the Taylor series.

If a wide size distribution is modelled, the overall solids conversion of a given stream (carryover, overflow) may be calculated as the size-distribution-weighed sum of the conversions of the different sizes \[232\]:

\[
\bar{X} = \int_0^{d_{p,\text{max}}} \bar{X}(d_p) p_{\text{stream}} \, dd_p
\]

(5.107)

where \( p_{\text{stream}} \) is the particle size distribution function of the stream, the sum of which equals 1.

The calculation of the conversion for a given particle size is the same as in equation 5.106, but uses the average residence time for this given particle size. Each particle size will therefore have different average conversions \( \bar{X}(d_p) \) due to different residence time \( \tau(d_p) \) and different times to complete conversion \( t_{cr}(d_p) \). Unlike the calculation of the average particle size (equation 5.29), the calculated average conversion weighs the larger unconverted particles equally to the smaller particles.
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5.3 Solution method

Prior to solving the model, the reactor geometry, the operating conditions, particle properties and other model parameters must be set.

The model is implemented assuming pure zinc sulfide as solid input. The zinc sulfide feedrate is calculated by setting the superficial gas velocity \((U)\), inlet oxygen concentration \((C_{O_2,in})\) and excess oxygen \((Excess_{O_2})\) and using the equation:

\[
F_{Feed,ZnS} = \frac{\nu_{ZnS} M_{ZnS}}{\nu_{O_2}} \frac{1}{1000} \frac{1}{1 + Excess_{O2}} C_{O_2,in} U
\]  
(5.108)

Similarly, the zinc concentrate feedrate is calculated by replacing the zinc sulfide molar mass \((M_{ZnS})\) by its concentrate equivalent \((M_{concentrate})\) i.e.:

\[
F_{Feed,concentrate} = \frac{\nu_{ZnS} M_{concentrate}}{\nu_{O_2}} \frac{1}{1000} \frac{1}{1 + Excess_{O2}} C_{O_2,in} U
\]  
(5.109)

The excess oxygen is calculated for a given experiment using equation 5.109 (by isolating \(Excess_{O2}\)).

Two additional parameters are required prior to fitting the experimental data shown in section 4.4. \(M_{concentrate}\) is the mass of zinc concentrate equivalent to a mole of zinc sulfide for the reaction:

\[
ZnS + \frac{3}{2} O_2 = ZnO + SO_2
\]  
(5.110)

A value of \(M_{concentrate}\) larger than the molar mass of zinc sulfide (97.456 g/mol\(ZnS\)) indicates that more concentrate is required than pure zinc sulfide to react with 1.5 moles of oxygen. \(M_{concentrate}\) can be calculated by adding the oxygen requirement for each element in the concentrate assuming complete conversion to \(ZnO\), \(SO_2\), \(Fe_2O_3\), \(PbSO_4\) and accounting for the presence of oxygen in sulfates in the concentrate. The proportion of each element in the concentrate is obtained from the zinc concentrate assays. For the same operating conditions, i.e. inlet oxygen concentration, superficial gas velocity and excess oxygen, equations 5.108 and 5.109 can be combined to relate the concentrate and \(ZnS\) molar masses and feedrates:

\[
\frac{F_{Feed,ZnS}}{M_{ZnS}} = \frac{F_{Feed,concentrate}}{M_{concentrate}}
\]  
(5.111)
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$M_{\text{concentrate}}$ is only used when a concentrate feedrate must be converted to an equivalent pure zinc sulfide feedrate.

The second parameter, the particle mean residence time factor ($f$) is used to adjust the residence time of the reacting particles to account for the change in particle mass ($\beta$) and for the fact that the mass of zinc concentrate fed differs from the pure zinc sulfide assumed in the model:

$$f = \frac{M_{\text{ZnS}}}{\beta M_{\text{concentrate}}}$$

The particle residence time is therefore:

$$\tau = \frac{f M_{\text{bed}} P_{\text{Bed}}}{F_{\text{Feed}} P_{\text{Feed}}}$$

The experimental data shown in section 4.4 are fitted by adjusting the solids reaction rate constant ($k_s$).

Once the parameters are set, the model is solved following these steps:

- Guess initial values for $k_r$, and $H$ or $H_m f$. Note that once either $H$ or $H_m f$ is known, the other one can be estimated.

- Integrate the fluidized bed mole balance equations (equations 5.12 and 5.13) over the height.

- If the calculated bed expansion (equation 5.17) does not agree with the initial values of $H$ or $H_m f$, adjust their values using the calculated bed expansion and repeat the previous step. Convergence is obtained when the difference between the bed expansions is less than $5 \times 10^{-4}$ (0.5 mm).

- Calculate the gas conversion using equation 5.20.

- Calculate the average gas concentrations seen by the solids (equation 5.23).

- Using the gas concentrations from the previous step, calculate the time for complete reaction (equations 5.102, 5.103 and 5.104) and the average solids conversions (equations 5.106 or 5.107).
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- Compare the gas to the overall solids conversions. If the number of moles reacted do not balance, adjust the effective gas reaction rate constant \( (k_r) \) and return to the second step. If they balance, the model has converged to the desired solution. The effective gas reaction rate constant \( (k_r) \) in the fluidized bed model is an adjustable parameter chosen so that the moles of reactant balance according to the stoichiometry:

\[
residual = \frac{F_{\text{Feed}}X_{ZnS}1000}{M_{ZnS} \nu_{ZnS}} - \frac{\Delta F_{O2}}{\nu_{O2}} \tag{5.114}
\]

The model finds the value of \( k_r \) for which the residual (equation 5.114) is zero. The iterative procedure searches for the zero by narrowing the interval where the sign of the residual changes. To constrain the solver, the log of \( k_r \) is used to ensure that \( k_r \) is never negative. The initial \( k_r \) interval is \( 10^{-8} \) to \( 10^8 \). Convergence is obtained when the interval, on a log scale, is smaller than \( 2 \times 10^{-4} \). The effective gas reaction rate constant is adjusted such that the fluidized bed reactor model consumes the correct amount of oxygen.
Chapter 6
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The mechanism, proposed in chapter 4, assumes that lead species assist agglomeration through lead sulfide vaporization and deposition onto bed particles. Since the partial pressure of lead sulfide depends strongly on the oxygen partial pressure, it seems that increased agglomeration through this mechanism would occur when the bed particles experience a low average oxygen partial pressure. Therefore, modelling looks at the average oxygen concentration surrounding the particles through the simple reaction of pure zinc sulfide to pure zinc oxide. No other components are modelled, e.g. lead, silica, iron, copper and cadmium.

The unsteady-state single particle reaction model is first used to evaluate the conditions under which the particle temperature can exceed the environment temperature. This model is used to evaluate the assumptions of isothermality (no temperature gradients inside the particles and constant particle temperature equal to the fluidized bed temperature). Next, the generalized slugging-bubbling fluidized bed model (gas only) is compared with the previous slugging and bubbling fluidized bed models. The scale-up of fluidized beds is briefly discussed. The complete gas-solids model is then used to fit experimental laboratory roaster data. With the aid of the estimated parameters, the model is then employed to evaluate the effect of various model parameters and operating conditions on the average oxygen partial pressure around the particles.
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6.1 Unsteady-state single particle reaction

The unsteady-state single particle reaction model is used to evaluate the conditions under which the particle temperature exceeds the temperature of its surroundings. Since the fluidized bed model assumes that the particles are isothermal and at the same temperature as the fluidized bed, the conditions where the unsteady-state model predicts excessive temperatures will therefore be conditions which require more complex modelling to replace the isothermality assumptions.

6.1.1 Model parameters

The model requires a number of kinetic, heat and mass transfer parameters as inputs. The values used here are also employed for the solids reaction of the fluidized bed model. Both kinetic expressions suggested in chapter 2 are used for the model. The sulfur dioxide concentration is taken to be constant at 17 vol%, a value similar to that obtained below for the fluidized bed modelling. The sulfur dioxide concentration does not influence the reaction kinetics in any way. Both the bulk oxygen concentration and the particle size are varied.

The effective diffusivity in the ash layer is based on the gas diffusivity of oxygen in sulfur dioxide (obtained using Chapman-Enskog theory [231, 236]), a porosity of 0.4 and a tortuosity factor of 3. These values are similar to those obtained by Gokarn and Doraiswamy [150, 159] where they measured the diffusivity within an ash layer of reacted zinc sulfide pellets. Gokarn and Doraiswamy [150, 159] obtained gas diffusivities which are 38-47% of the bulk diffusivity. A smaller value is chosen here because the pellets of Gokarn and Doraiswamy were initially porous, while the single particles modelled here were initially non-porous. The effective thermal conductivity was estimated from those of ceramic materials with similar porosities [231]. The heat capacities and the heats of reaction were obtained from HSC [116]. Since the particle temperature is assumed to be the same as the temperature of the surroundings, there is no net heat transfer by radiation. Radiation is therefore neglected. However, once a temperature difference occurs, radiation should be taken into account. For an exothermic reaction, such as zinc sulfide roasting, radiation would simply reduce the overheating.
Table 6.1: Summary of single particle model parameters and their values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical kinetics</strong></td>
<td></td>
</tr>
<tr>
<td>Fitted kinetics</td>
<td></td>
</tr>
<tr>
<td>Pre-exponential constant $k^\circ_s$ (cm/s)</td>
<td>$6.28 \times 10^{12}$</td>
</tr>
<tr>
<td>Activation energy $E$ (kJ/mol)</td>
<td>288</td>
</tr>
<tr>
<td>Fukunaka et al. [140] kinetics</td>
<td></td>
</tr>
<tr>
<td>Pre-exponential constant $k^\circ_s$ (cm/s)</td>
<td>$2.96 \times 10^{15}$</td>
</tr>
<tr>
<td>Activation energy $E$ (kJ/mol)</td>
<td>314</td>
</tr>
<tr>
<td><strong>Reaction orders</strong></td>
<td></td>
</tr>
<tr>
<td>Oxygen $n$ (-)</td>
<td>1</td>
</tr>
<tr>
<td>Solids $m$ (-)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Particle properties</strong></td>
<td></td>
</tr>
<tr>
<td>Reactant (core) density $\rho_c$ (kg/m$^3$)</td>
<td>4100</td>
</tr>
<tr>
<td>Reactant (core) molar weight $M_c$ (g/mol)</td>
<td>97.4</td>
</tr>
<tr>
<td>Product (ash layer) density $\rho$ (kg/m$^3$)</td>
<td>5600</td>
</tr>
<tr>
<td>Product (ash layer) molar weight $M$ (g/mol)</td>
<td>81.4</td>
</tr>
<tr>
<td><strong>Mass transfer</strong></td>
<td></td>
</tr>
<tr>
<td>Effective gas diffusivity in ash layer $D_{eA(T_o)}$ (m$^2$/s)</td>
<td>$D_{O2-SO2} \times 0.4/3$</td>
</tr>
<tr>
<td>Modified Sherwood number $Sh$</td>
<td>1</td>
</tr>
<tr>
<td><strong>Heat generation and transfer</strong></td>
<td></td>
</tr>
<tr>
<td>Effective thermal conductivity of ash layer $k_e$ (W/(m K))</td>
<td>0.3</td>
</tr>
<tr>
<td>Heat capacity of ash layer $C_{pe}$ (J/(mol K))</td>
<td>54</td>
</tr>
<tr>
<td>Heat capacity of unreacted core $C_{pc}$ (J/(mol K))</td>
<td>56.8</td>
</tr>
<tr>
<td>Heat of reaction $\Delta H$ (kJ/mol)</td>
<td>-448</td>
</tr>
<tr>
<td>Modified Nusselt number for convection $Nu_C$ (-)</td>
<td>1</td>
</tr>
<tr>
<td>Modified Nusselt number for radiation $Nu_R$ (-)</td>
<td>0</td>
</tr>
<tr>
<td>Initial dimensionless temperature $U_0$</td>
<td>1</td>
</tr>
<tr>
<td><strong>Environment conditions</strong></td>
<td></td>
</tr>
<tr>
<td>Temperature $T$ (°C)</td>
<td>940</td>
</tr>
<tr>
<td>Bulk $O_2$ concentration $x_{O2}$ (-)</td>
<td>1e-3 to 0.5</td>
</tr>
<tr>
<td>Bulk $SO_2$ concentration $x_{SO2}$ (-)</td>
<td>0.17</td>
</tr>
<tr>
<td>Particle diameter $d$ (μm)</td>
<td>1 to 10 000</td>
</tr>
</tbody>
</table>
Chapter 6. Modelling Results

6.1.2 Time for complete reaction

The time for complete reaction is the most important output for the fluidized bed model. It is used in conjunction with the residence time distribution to evaluate the average conversion.

Figure 6.1 presents the time required for complete conversion as a function of particle size and bulk oxygen concentration for both kinetic rate expressions. As expected from the pre-exponential constants, the fitted kinetics are slower by a factor of approximately 50 to 100 compared to values from the expression of Fukunaka et al. [140]. As expected, the time for complete conversion is reduced as the particle size is reduced and the bulk oxygen concentration is increased.

![Graph showing time to complete reaction vs. particle size and oxygen concentration](image)

(a) Kinetics from Fukunaka et al. [140]  
(b) Fitted kinetics (dashed line in Figure 2.4)

Figure 6.1: Unsteady-state particle model: Time to complete reaction in seconds.

6.1.3 Particle temperatures

The average particle temperatures (averaged over time) are shown in Figure 6.2. Both the core and surfaces temperatures are equal to the temperature of the surroundings (dimensionless temperature =1) for conditions of low oxygen concentrations. A dimensionless temperature of 1.01 is equivalent to a 12°C increase from the surroundings.
(a) Average core dimensionless temperature \( (U_c) \) (b) Average surface dimensionless temperature \( (U_s) \)

Fukunaka et al. [140] Kinetics

Figure 6.2: Unsteady-state particle model: Dimensionless temperatures.

(c) Average core dimensionless temperature \( (U_c) \) (d) Average surface dimensionless temperature \( (U_s) \)

Fitted kinetics

Fitted kinetics
For particles smaller than about 100 μm, the core and surface dimensionless temperatures are identical for most conditions. This indicates that thermal gradients are negligible. For larger particles, thermal gradients may be significant, especially for oxygen concentrations larger than 10 vol%. The assumption that the particles have no internal temperature gradients is acceptable for the concentrate particles in this study.

The kinetic results of Fukunaka et al. [140] suggest much higher temperatures than the fitted kinetics (equation 2.3). For instance, large particles (larger than 3 mm) may experience very large temperature excursions when the oxygen concentration exceeds 10% if the Fukunaka et al. kinetics apply. However, for the fitted kinetics, particle overheating is much smaller.

Regardless of the kinetics, any bulk oxygen concentration less than 5 vol% does not promote overheating. If the particles are within a bulk atmosphere containing 10% oxygen, the overheating would be limited to about 12°C for the largest particles. Since the experimental laboratory roaster did not have any feed particles larger than 100 μm, the assumption that the particle temperature is equal to that of the bed is reasonable. If the Fukunaka et al. kinetics apply, these particles may experience a small temperature increase of less than 10°C if they also encounter oxygen concentrations larger than about 10 vol%.

For the assumption to be valid for the industrial roaster, the large particles must not experience oxygen concentrations larger than about 5 to 10 vol%. However, calculations for the very large particles should be made with the grain model since the current model assumes that the initial solid is non-porous and that these large particles are likely to be lumps of smaller concentrate particles. Since lumps are created with smaller grains, the diffusion resistance through the bulk of the lump would be smaller than that for a similarly-sized particle. Lumps may therefore react faster than particles of the same size. Heat transfer limitations from a lump to the surroundings are likely to be similar to their particle counterpart. Therefore, lump overheating may be greater and occur for smaller lumps than for particles.

Temperature excursions for large particles have been documented previously [160, 237]. Patisson et al. [160] used 10 mm porous pellets in a thermogravimetric balance with an atmosphere of
pure oxygen and pellet temperatures up to 1100°C while the surrounding atmosphere was only at 550 to 650°C. Much less overheating was observed when air was used (740°C for a 600°C atmosphere). Natesan and Philbrook [237] obtained more modest overheating (+50 °C) in an 27 vol% oxygen atmosphere at 960 °C. Their smaller overheating may have been due to pre-sintering prior to exposing the pellet to the reactive gas.

6.1.4 Gas concentrations

The average concentrations at the core and at the surface of the particle are shown in dimensionless form in Figures 6.3 and 6.4. A core dimensionless concentration of 1 indicates that the mole fraction at the surface of the unreacted core is equal to that of the bulk. A dimensionless concentration lower than one indicates that the mole fraction is only a fraction of the bulk concentration while a dimensionless concentration higher than one, the mole fraction is larger than that of the bulk. The dimensionless oxygen concentration at the unreacted shrinking core of a particle is lower than that of the bulk. This is not unexpected since mass transfer limitations from the bulk to the surface of the unreacted core are present. However, the particle size for which the oxygen concentration at the core start to be smaller than 90% of the bulk \( (\omega_{c,O2} < 0.9) \) depends on the kinetics used. For instance, if the Fukunaka et al. [140] kinetics are used, particles larger than about 3 μm have less than 90% of the bulk oxygen concentration at their core. However, if the fitted kinetics are used instead, any particles smaller than about 125 μm will not have any significant oxygen concentration difference.

The sulfur dioxide concentrations follow a profile different from the oxygen concentration because only the bulk oxygen concentration is varied. The sulfur dioxide concentrations is governed by the dynamic equilibrium between the production of \( \text{SO}_2 \) and its transport to the bulk gas. This process is similar to the generation and transport of heat, and therefore, the \( \text{SO}_2 \) profiles are similar to the temperature profiles. As mentioned previously, the sulfur dioxide concentration does not affect the reaction rate.

In summary, the dimensionless gas concentrations at the outer surface and at the core surface depend greatly on the kinetics used. However, to calculate the predominant phase, a small
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(a) Average core dimensionless oxygen concentration ($\omega_{c, O_2}$)

(b) Average core dimensionless sulfur dioxide concentration ($\omega_{c, SO_2}$)

(c) Average surface dimensionless oxygen concentration ($\omega_{s, O_2}$)

(d) Average surface dimensionless sulfur dioxide concentration ($\omega_{s, SO_2}$)

Figure 6.3: Unsteady-state particle model: Dimensionless gas concentrations. Kinetics from Fukunaka et al. [140]
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Figure 6.4: Unsteady-state particle model: Dimensionless gas concentrations. Fitted Kinetics
deviation from the bulk concentration (dimensionless concentrations between 0.75 and 1.25) would not represent a significant shift (-0.12 to +0.09 on the log scale) on the predominance diagram (Figure 2.2). Since the concentrate particles are much smaller than 100 μm (80% of the concentrate particles are smaller than 23 μm, see Table 3.2), the concentrations in the bulk and the concentrations at the particle core do not differ significantly. This argument does not hold for large particles such as lumps present within the feed to the industrial roaster.

### 6.1.5 Effectiveness factors

Wen and co-workers utilized the concept of effectiveness factors for gas-solid reactions [238, 235, 234]. The effectiveness factor is the ratio of the predicted rate of reaction over the rate of reaction if the reaction sites were at the bulk composition and temperature. In isothermal systems, effectiveness factors are equal to or less than one, depending on the mass transfer limitations. For non-isothermal exothermic systems, the effectiveness factor can exceed one, due to self-heating of the reacting particles.

![Figure 6.5: Unsteady-state particle model: Effectiveness factors.](image)

Figure 6.5 shows effectiveness factors as a function of the bulk oxygen concentration and particle diameter.
size. It is important to note that the conditions for factors > 1 are not identical to the conditions that promote very high particle temperatures. The effectiveness factor is small for large particles (>1 mm), even if they reach very high temperatures. This is due to the large mass transfer limitation. The only conditions where the effectiveness factor > 1 is for small particles in oxygen-rich atmospheres. Because the mass transfer resistance is small for small particles, a small overheat increases dramatically the effectiveness factor leading to a higher reaction rate. This is observed on Figure 6.1 where the contour lines bend slightly around the location where the effectiveness factor is larger than 1. In general, the effectiveness factor is ≤ 1 for any particle with oxygen bulk concentrations less than 10 vol%.

The non-isothermal effectiveness factor (shown in Figure 6.5) does not portray adequately the extent of heat effects on the reaction rate. To better visualize the conditions where heat generation affects the reaction rate, a new factor is introduced. The heat enhancement factor \( H \) taken as the ratio of the non-isothermal effectiveness factor (equation 5.93) to the isothermal effectiveness factor (equation 5.102) i.e.

\[
H = \frac{\eta_{s,\text{non-iso}}}{\eta_{s,\text{iso}}}
\]

represents the deviation (as a ratio) of the non-isothermal model over the isothermal model. If heat effects are important, the heat enhancement factor will differ from one, regardless of the limiting steps. For exothermic systems, \( H \geq 1 \). For endothermic systems, \( H \leq 1 \). Since our system is exothermic, any conditions where the heat enhancement factor is significantly greater than one signifies that the isothermal model does not adequately represent the actual reaction rates.

Figure 6.6 presents the heat enhancement factors for the two kinetic expressions considered. A heat enhancement factor of 1.1 represent an increase of the non-isothermal reaction rate of 10% over the isothermal reaction rate. Unlike the effectiveness factor where no clear conclusion regarding the effect of heat on the reaction rate can be drawn for large particles in an oxygen-rich environment, the heat enhancement factor clearly shows that even if temperature deviations are large for the largest particles in an oxygen rich environment (see Figure 6.2, Fukunaka et
Figure 6.6: Unsteady-state particle model: Heat enhancement factors.

al. kinetics, 10 mm diameter particles, 21-50% oxygen), the reaction rate can be reasonably well represented by the isothermal model ($H = 1$). This is due to the low effectiveness factor caused by large mass transfer limitations.

From this analysis, it is clear that heat enhancement (faster reactions due to the effect of heat) and temperature deviation (particle temperature much higher than that of the environment) are two different phenomena. Both require use of a non-isothermal model for their detection. For the reaction of zinc concentrate, heat enhancement will affect the overall reaction rate, while temperature deviation will affect low-melting-point phases, product layer sintering and vapour phases.

The conditions where the heat enhancement factor exceeds 1 depend on the kinetics and particle size. However, for oxygen concentrations $\leq 1\%$, the heat enhancement factor is very close to 1, regardless of the kinetics or particle size. For oxygen concentrations $\leq 10\%$, the heat enhancement factor is $\leq 1.1$. If a deviation (or error) in reaction rate of 10% is acceptable ($H \leq 1.1$), the isothermal model may be used for any oxygen concentration below 10%.
In summary, the unsteady-state single particle reaction model has shown that particle overheating occurs only for large particles and high bulk oxygen concentrations. Effectiveness factors greater than one only occur for high bulk oxygen concentrations. The time for complete reaction depends greatly on the kinetics used. The gas compositions are not significantly different from the bulk when very small particles, similar to the concentrates used in this study, are reacting. It is unknown at this point which kinetic rate expression should be used. The assumption of isothermal particles within the fluidized bed is therefore reasonable if the particles do not experience oxygen concentrations larger than a few percent. The relatively simple isothermal single particle reaction model is used for the gas-solid fluidized bed reactor modelling that follows in this chapter.

6.2 Generalized slugging-bubbling model (GSBM)

This section presents some results of the generalized slugging-bubbling fluidized bed reactor model for gas catalytic reactions. Since no solid reaction occurs, the model is not coupled with a solid reaction model nor any solids mixing model.

6.2.1 Comparison with previous models

Prior to using the generalized slugging-bubbling fluidized bed model, it must be compared with the currently available fluidized bed models. Figure 6.7 presents conversions calculated from the Hovmand slugging bed model [216, 217], the Orcutt mixed-flow and plug-flow models [218, 219], the Grace two-phase bubbling bed reactor model [239] and the generalized slugging-bubbling model (GSBM), developed in Chapter 5 for pure slugging and pure bubbling with constant average bubble size and variable bubble size. The constant average bubble size case is considered because the Orcutt and Grace models use an average bubble size. Since previous models do not consider gas volume changes, the stoichiometry adopted for the generalized model is equimolar (1 to 1). For all models, the reaction is first order with respect to the oxygen concentration.

In general, the predictions for the bubbling fluidized bed models are higher than those of
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Table 6.2: Model parameters used to compare the generalized bubbling slugging model to the earlier slugging and bubbling models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U )</td>
<td>0.5 m/s</td>
</tr>
<tr>
<td>( U_{mf} )</td>
<td>0.02 m/s</td>
</tr>
<tr>
<td>( H )</td>
<td>1 m</td>
</tr>
<tr>
<td>( H_{mf} )</td>
<td>calculated</td>
</tr>
<tr>
<td>( \epsilon_{mf} )</td>
<td>0.45</td>
</tr>
<tr>
<td>Gas diffusivity: ( D_{gas} )</td>
<td>( 10 \cdot 10^{-5} , m^2/s )</td>
</tr>
<tr>
<td>Bubble correlation</td>
<td>Mori and Wen [208]</td>
</tr>
<tr>
<td>Initial bubble size: ( D_{eo} )</td>
<td>0.01 m</td>
</tr>
<tr>
<td>( \nu_{O_2} )</td>
<td>-1</td>
</tr>
<tr>
<td>( \nu_{SO_2} )</td>
<td>+1</td>
</tr>
<tr>
<td>( \Delta \nu )</td>
<td>0</td>
</tr>
</tbody>
</table>

the slugging models. Note that the fluidized bed models are applied without any allowance for slugging, even when the bubble size exceed the reactor diameter. For this reason, the predictions for small column diameters must be considered with caution.

There is very little difference between the results of the Hovmand slugging model and the GSBM model when the probability of slugging is imposed at 1. The GSBM can therefore adequately represent the Hovmand slugging model in the limit. When considering pure bubbling behaviour (\( P_{bubbling}=1 \)), the GSBM compares favorably with all the other models. However, there is a much larger scatter between the different models.

Since the generalized model compares well with the previous slugging and bubbling models for the conditions studied here, the GSBM is used below to evaluate the effects of the gas reaction rate constant and bed diameter on the predicted gas conversion.
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Figure 6.7: Comparison of the GSBM model to the Hovmand slugging model and to the Grace 2-phase and Orcutt bubbling models. For conditions, see Table 6.2
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Figure 6.8: Comparison of the conversions calculated using GSBM model and its limiting models as a function of gas reaction rate constant for different bed diameters. For conditions, see Table 6.2

(a) Bed diameter: 0.1 m, $\phi_L$: 0

(b) Bed diameter: 0.1 m, $\phi_L$: 0.005

(c) Bed diameter: 0.5 m, $\phi_L$: 0

(d) Bed diameter: 0.5 m, $\phi_L$: 0.005

(e) Bed diameter: 1 m, $\phi_L$: 0

(f) Bed diameter: 1 m, $\phi_L$: 0.005
6.2.2 Effect of effective gas reaction rate constant

The effect of the effective gas reaction rate constant ($k_r$) on the gas conversion ($X$) is presented in Figure 6.8 for different reactor diameters and with $\phi_L = 0.005$ and neglecting the solids present within the bubbles (i.e. $\phi_L = 0$). The figure presents the results of the complete generalized slugging-bubbling model, as well as the predictions when the probabilities of bubbling and slugging are set equal to one (entirely slugging or bubbling). When the probability of slugging equals one, no bubbling region is considered prior to slugging. When the probability of bubbling is one, the model either calculates a given bubble size for each vertical position or uses a constant average bubble size calculated at 40% of the expanded bed height ($x = 0.4H$).

The model parameters and conditions appear in Table 6.2.

For slugging beds (Figure 6.8,(a) and (b)), using a bubbling fluidized bed model clearly overpredicts the conversions. For small $k_r$, the generalized slugging-bubbling fluidized bed model predicts conversions similar to that when imposing pure slugging ($P_{slugging}=1$). However, for higher $k_r$, the generalized slugging-bubbling fluidized bed model predictions diverge from the pure slugging predictions due to the increasing importance of mass transfer from the bubbles to the dense phase. For such conditions, the bubbling region at the base of the bed before the onset of slugging is of critical importance to the conversion. The presence of particles within the bubbles ($\phi_L$) significantly augments the predicted gas conversions for large $k_r$.

For large beds where slugging does not occur (Figure 6.8,(e) and (f)), the GSBM model predicts the same conversions as for pure bubbling ($P_{bubbling}=1$). Using pure slugging to model a bubbling fluidized bed clearly underestimates the conversion. The use of an average bubble size also underestimates the gas conversion for large reaction rate constants. For large $k_r$, mass transfer from the bubbles to the dense phase is rate-controlling. There is a significant beneficial effect on interphase mass transfer from the small bubbles near the distributor. This effect is neglected when using an average bubble size. As for slugging beds, accounting for the presence of particles within the bubbles ($\phi_L$) is significant for large $k_r$.

For fluidized beds of intermediate sizes (Figure 6.8,(c) and (d)), the prediction of the GSBM
model diverge slightly from the predictions for pure bubbling due to the effect of walls on the larger bubbles causing a decrease in interphase mass transfer.

In summary, if one chooses to use a regime-specific model, choosing the appropriate model (pure bubbling or pure slugging) is critical to obtaining adequate results. For reactions where large values of the effective reaction rate constant \( k_r \) are expected, the model should not use an average bubble size to characterize the entire reactor and must include the effect of the solids within the bubbles. The generalized slugging-bubbling fluidized bed model allows the modelling of fluidized systems where a transition from bubbling to slugging occurs within the bed, or where there are appreciable wall effects.

### 6.2.3 Effect of reactor diameter

The effect of scale-up of a reactor may be evaluated from the gas conversions for different reactor diameters and different reaction rate constants. Figure 6.9 graphically presents the conversion for various rate constants.

For the condition considered, the GSBM model predictions depart from pure slugging for large reaction rate constants and for reactor diameters larger than about 0.1 m. The departure from pure slugging at high reaction rate constants results from the significance of the bubbling region near the distributor.

For the conditions studied, the predictions of the GSBM model converge to pure bubbling at diameters close to 1 m. This is the minimum reactor diameter for the system to be modelled as pure bubbling. This implies that results from small and large industrial fluidized beds must be compared with care. Note that this diameter applies only for reactors operating at the conditions in Table 6.2. The bubble sizes were calculated using the Mori and Wen bubble correlation [208]. Since this correlation is limited to reactor diameters smaller than 1.22 m, predictions for larger reactors must be treated with some caution.

In the transition region, the generalized model predicts conversions less than for pure bubbling and more than for pure slugging (See Figure 6.9). To understand how this can occur, one
Figure 6.9: Comparison of the conversions calculated using GSBM model and its limiting cases as a function of bed diameter for different gas reaction rate constants. For conditions, see Table 6.2
must consider the basic equation of the model (equation 5.12) and the interaction between the bubbling and slugging flow regimes. Figure 6.10 presents in more detail the values of the various variables which lead to such conversions.

We first consider the interphase mass transfer term of equation 5.12:

\[
\text{(Interphase mass transfer term)} = k_{LH} a_I \left( \frac{\psi_L F_{Hi}}{\psi_H U_H} - \frac{F_{LI}}{U_L} \right)
\]

The first part of the term is the mass transfer coefficient and interfacial area. These are directly related to bubbles and slug properties. The second part is the driving force i.e. the difference in gas concentrations. This driving force is a function of the gas concentrations within the bubbles (or slugs) and the dense phase. Unlike the mass transfer coefficient and area, it does not have any direct relationship with any of the bubble or slug properties.

We next consider the transition from bubbling to slugging by observing that the probability of slugging goes from 0 to 1 in the height interval between approximately 0.1 and 0.3 m for the conditions studied. The mass transfer coefficient and interfacial area \((k_{LH} \text{ and } a_I)\) both vary in this interval. Therefore, the interphase mass transfer coefficient (Figure 6.10 (b)) varies strongly within this interval. Note the logarithmic scale. The driving force for the interphase mass transfer (Figure 6.10 (c)) does not increase within this transition interval but over a much longer interval than the bubbling-slugging transition interval. The net effect is a rapid decrease followed by a slow increase in interphase flow. The bubbling region ensures good interphase mass transfer and low concentration differences between the bubbles and dense phase (small driving force). However, once the bubbles have grown and coalesced into slugs, the small driving force limits interphase mass transfer until the reaction within the dense phase increases the driving force to values closer to the pure slugging model. This shows that even for small reaction rate constants, interphase mass transfer may have significant effects. This effect may not be observed experimentally due to the small difference in overall conversions.

The same transition interval applies for a system with a large reaction rate constant (see Figure 6.11 (a)). More than 50% of the conversion is due to reaction within the bubbling regime. Since interphase mass transfer is very small within the slugging regime, the reaction proceeds slowly.
Figure 6.10: Comparison of the variable model parameters and output for the GSBM model and its limiting models as a function of height the vertical position in the bed for $k_r = 0.1 \text{s}^{-1}$, $D = 0.2 \text{m}$, $\star$: Bubbling, $\circ$: Slugging, $\cdot$: GSBM. For conditions, see Table 6.2.
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Figure 6.11: Comparison of the variable model parameters and output for the GSBM model and its limiting models as a function of the vertical position in the bed for $k_r = 10 \text{s}^{-1}$, $D = 0.2$ m, $\star$: Bubbling, $\circ$: Slugging, $\cdot$: GSBM. For conditions, see Table 6.2.
once the slugging flow regime is reached. The overall effect of including the bubbling region at the bottom is to increase the conversion.

In summary, when the generalized slugging-bubbling fluidized bed model is used for one of the limiting cases (pure bubbling or slugging), it closely matches the results of the earlier regime-specific models. For the transition between the slugging and bubbling regimes, the GSBM model adequately represents the system. In the transition, the model predicts conversions and evolution between the two limiting cases.

6.3 Fluidized bed roaster model

6.3.1 Model parameters

The fluidized bed reactor model requires the fluidized bed reactor geometry, operating conditions, kinetics of the reaction, as well as some parameters related to the fluidized bed. Table 6.3 summarizes the various parameters and their values used for the modelling of the industrial and laboratory fluidized bed roasters.

The industrial roaster geometry and conditions are taken from published information [33, 34]. The laboratory roaster column geometry is that of this study. The expanded bed height and the height at minimum fluidization are related to each other using the calculated bed expansion. Since the industrial bed height is limited to the weir overflow height, $H_{mf}$ is calculated while solving the model. Since there is no overflow weir for the laboratory roaster, $H$ is calculated from a known $H_{mf}$ which is related to the bed mass.

The void space at minimum fluidization was measured from the particle density and bulk density of the experimental material. The solids volume fraction in the L-phase ($\phi_L$) is taken as 0.005 as suggested by Kunii and Levenspiel [20] based on some experimental evidence. The solids reaction kinetics are as proposed in Chapter 2.
Table 6.3: Summary of the model parameters and their values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Industrial</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor geometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area $A$ (m$^2$)</td>
<td>84</td>
<td>0.00785</td>
</tr>
<tr>
<td>Diameter $D$ (m)</td>
<td>10.34</td>
<td>0.1</td>
</tr>
<tr>
<td>Expanded bed height $H$ (m)</td>
<td>1.2 variable</td>
<td></td>
</tr>
<tr>
<td>Bed height at minimum fluidization $H_{mf}$ (m)</td>
<td>variable</td>
<td>0.27</td>
</tr>
<tr>
<td>Distributor area per orifice $A_d$ (m$^2$)</td>
<td>.01</td>
<td>0.00021</td>
</tr>
<tr>
<td><strong>Fluidized bed model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bubble solids volume fraction $\phi_L$ (-)</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Void space at minimum fluidization $\epsilon_{mf}$ (-)</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td><strong>Solids reaction kinetics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fitted kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential constant $k_e$ (cm/s)</td>
<td>6.28·10$^{12}$</td>
<td></td>
</tr>
<tr>
<td>Activation energy $E$ (kJ/mol)</td>
<td>287.5</td>
<td></td>
</tr>
<tr>
<td>Fukunaka et al. [140] kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential constant $k_e$ (cm/s)</td>
<td>2.96·10$^{15}$</td>
<td></td>
</tr>
<tr>
<td>Activation energy $E_a$ (kJ/mol)</td>
<td>313.8</td>
<td></td>
</tr>
<tr>
<td>Reaction orders</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen $n$ (-)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Solids $m$ (-)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Effective gas diffusion coefficient in ash layer $D_eA(T_0)$ (m$^2$/s)</td>
<td>$D_{O_2-SO_2} \times 0.4/3$</td>
<td></td>
</tr>
<tr>
<td>Modified Sherwood number $Sh$ (-)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td><strong>Base operating conditions</strong> (Sensitivity analysis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature $T$ (°C)</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>Pressure $P$ (kPa)</td>
<td>101.3</td>
<td></td>
</tr>
<tr>
<td>Superficial gas velocity $U$ (m/s)</td>
<td>0.66</td>
<td>0.25</td>
</tr>
<tr>
<td>Excess Oxygen $ExcessO_2$ (%)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Inlet Oxygen Concentration (vol%)</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td><strong>Bed and concentrate properties</strong> (Sensitivity analysis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average bed particle diameter $d_p$ (µm)</td>
<td>65 or 150</td>
<td></td>
</tr>
<tr>
<td>Inert solids particle density $\rho_T$ (kg/m$^3$)</td>
<td>2650</td>
<td></td>
</tr>
<tr>
<td>Average concentrate particle diameter $d_{v,concentrate}$ (µm)</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Concentrate particle density $\rho_{concentrate}$ (kg/m$^3$)</td>
<td>4000</td>
<td></td>
</tr>
<tr>
<td>Particle mean residence time factor $f$ (-)</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
6.3.2 Fit of laboratory experiments

Two parameters of the model are still unknown. The first is the mass of concentrate equivalent to a mole of pure zinc sulfide ($M_{\text{concentrate}}$) while the second, $f$ is the residence time factor.

Preliminary fitting of the experimental data showed that the choice of the kinetic rate expression (Fukunaka et al. or fitted kinetics) has more influence on the predictions than either the residence time factor ($f$) or the equivalent molar mass of concentrate ($M_{\text{concentrate}}$). Therefore, the values of $f$ and $M_{\text{concentrate}}$ were chosen as 1 and 110. A value of 1 was chosen for the mean solids residence time factor since $1/\beta$ (which increases the residence time) is compensated by using concentrate as a feed, requiring additional feed mass for the same oxygen consumption (which decreases the residence time). $M_{\text{concentrate}}$ was calculated from the zinc concentrate assays assuming complete conversion to ZnO, SO$_2$, Fe$_2$O$_3$, PbSO$_4$ and accounting for the presence of sulfates in the concentrate. Since there is information for only one temperature, only a single value of the rate constant is fitted.

Fitting a model to experimental data involving two or more outputs requires multiple response non-linear regression [240]. Such a problem must be addressed using weighted least squares regression. The choice of weights is critical to obtain an adequate fit. The weights used for each observation is the reciprocal of its variance. The objective function for the weighted least squares is then:

$$\text{LeastSquares} = \sum_{j=\text{output}} \sum_{i=\text{data}} \frac{(y_{i,j} - \hat{y}_{i,j})^2}{\sigma_{i,j}^2}$$  \hspace{1cm} (6.3)

The variance of the experimental points was either obtained from the logged data (oxygen concentration) or estimated from the detection limits of the assays (solids conversions).

Preliminary fitting of the experimental data was not able to adequately fit any of the outlet oxygen concentrations using reasonable $M_{\text{concentrate}}$ values. To allow closer predictions of the oxygen concentrations, values of $M_{\text{concentrate}}$ around 90 were required. This is unacceptable since it is impossible that impure zinc sulfide (containing less sulfur and zinc than pure ZnS)
would require more oxygen than pure zinc sulfide.

It was noticed long after the experimental phase that the oxygen sensor in the gas analyser used for the measurement of the freeboard oxygen concentrations had failed. The failure was noticed approximately one year after the experiments. Since the analyzer was not used during this period, there is uncertainty in the measurement provided here. In addition, simple calculations show that oxygen concentrations should be higher than measured: Assuming complete solids conversion, 10% excess oxygen should give approximately 2 vol% oxygen. This value is measured for feedrates of approximately 14 g/min. Concentrate assays show that this value should be observed at a feedrate of approximately 16 g/min. Further fitting will not consider the freeboard oxygen concentrations. However, the data adequately represent the trend that outlet oxygen decreases with increasing feedrate and that additional feed can be used when oxygen enrichment is employed.

Figure 6.12 presents the experimental data and the model predictions for the parameters presented in Table 6.4. Since only one temperature was available from the experimental data, the reaction rate constant, shown in Table 6.4, does not allow the pre-exponential constant and the activation energy of the reaction rate equation to be separated. The fluidized bed model parameters are the same as those shown in Table 6.3. The operating conditions (temperatures, inlet gas concentrations and superficial gas velocities) used for fitting the experimental data are those used experimentally. The particle parameters are those described in chapter 3. Figures 6.12 and 6.13 present the model fit results. The predicted solids conversion predict relatively well the experimental conversions. The predicted scrubbed oxygen concentrations are different from the observed values (Compare Figures 6.13 and 4.61). Due to the incertitude in oxygen measurements (sensor failure, as discussed previously), these measurements are not fitted. Figure 6.14 compares the fitted kinetics with the kinetic rates obtained from the literature. The fitted rate is between the fitted kinetics (dashed line) and the Fukunaka et al. kinetics, close to Fukunaka et al. kinetics. The temperature of the experiments clearly exceeds the temperature range of all rate expressions shown. Since only one point was obtained from the fit of experiments, there is still some incertitude regarding the appropriate kinetic rate expression.
Table 6.4: Summary of fitted model parameters and their values. The chosen values are the best estimates from theory, literature, measurements or calculations. Only the reaction rate constant was fitted, see text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$ (-)</td>
<td>not fitted</td>
</tr>
<tr>
<td>$M_{Concentrate}$ (g/mol)</td>
<td>not fitted</td>
</tr>
<tr>
<td>Reaction rate constant (cm/s)</td>
<td>fitted</td>
</tr>
</tbody>
</table>

Figure 6.12: Gas-solid reactor model fit of the experimental conversion data. •: 50 mesh silica sand, 21%O$_2$, model, +: 50 mesh silica sand, 25%O$_2$, model, ×: 125 mesh silica sand, 21%O$_2$, model. Model predictions are joined by lines. ⊙: 50 mesh silica sand, 21%O$_2$, experiments, ⊙: 50 mesh silica sand, 25%O$_2$, experiments, ⊙: 125 mesh silica sand, 21%O$_2$, experiments
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Figure 6.13: Gas-solid reactor model predictions of the freeboard oxygen concentration (scrubbed). o: 50 mesh silica sand, 21%O₂, +: 50 mesh silica sand, 25%O₂, x: 125 mesh silica sand, 21%O₂.

Figure 6.14: Fitted intrinsic reaction rate compared with those of various kinetic studies. Rate expressions from references [124, 143, 140, 135, 142, 130, 144, 145]. Dashed line corresponds to fitted kinetics discussed in Chapter 2. o: Fitted intrinsic kinetics.
6.3.3 Roaster sensitivity analysis

A sensitivity analysis provides useful information on which process and model parameters are most important. The model calculates the gas compositions for the reaction of pure zinc sulfide. Differences between concentrates and pure zinc sulfide are taken into account by converting the oxygen demand of each concentrate to its equivalent for zinc sulfide (see section 5.3). Therefore the equivalent molar mass of zinc concentrate ($M_{Concentrate}$) is not required for the sensitivity analysis.

The sensitivity analysis uses mono-sized particles for the concentrate and the inert bed material (not size distributions). The actual mean residence time of particles depends on the concentration of particles of the same size in the bed (see equation 5.77). Since the two types of particles are of different sizes, equation 5.77 no longer holds mathematically. In a real system, the bed would be composed of mainly inert bed material containing an equilibrium amount of concentrate-sized particles. Since in this sensitivity analysis, the equilibrium amount of concentrate-sized particles is unknown, the residence times of the reacting concentrate particles are assumed to be equal to:

$$
\tau = \frac{fM_{bed}}{F_{Feed}}
$$

(6.4)

with $f$ as in Table 6.3. The volume-based average particle size ($d_v$) of the concentrates is used in the sensitivity analysis. The model parameters and operating conditions are summarized in Table 6.3. For this analysis, each parameter in Table 6.5 is varied one at a time.

Since there is incertitude in the choice of kinetic rate expression for the reaction of solids, both the fitted kinetics and the Fukunaka et al. [140] are used in the sensitivity analysis. These two rate expressions are considered as the two possible extremes in the reaction rates.
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Table 6.5: Parameter ranges for sensitivity analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excess Oxygen</td>
<td>0 - 100 %</td>
</tr>
<tr>
<td>Inlet Oxygen Concentration</td>
<td>21 - 100 vol%</td>
</tr>
<tr>
<td>Average particle size</td>
<td>50 - 250 μm</td>
</tr>
<tr>
<td>Superficial gas velocity</td>
<td>0.25 - 0.75 m/s</td>
</tr>
<tr>
<td>Temperature</td>
<td>800 - 1000 °C</td>
</tr>
<tr>
<td>Height at minimum fluidization (Laboratory)</td>
<td>0.25 - 1.25 m</td>
</tr>
<tr>
<td>Expanded bed height (Industrial)</td>
<td>0.5 - 2 m</td>
</tr>
</tbody>
</table>

Oxygen available to the particles

Since oxygen governs the vapour pressure of lead species, any significant variation in its concentration affects the transport of lead species to other particles where agglomeration can occur. Figures 6.15 to 6.18 present the predicted particle-averaged oxygen concentrations for the laboratory roaster for the fitted and Fukunaka et al. [140] kinetics for small (65 μm) and large (150 μm) particles. Except for the effect of temperature, there is very little effect of the kinetics or the average particle size on the oxygen available to the particles. The choice of kinetics changes the effect of temperature. However, its influence is small compared to the effect of excess oxygen or inlet oxygen concentration. The average bed particle size does not significantly affect the particle-averaged oxygen concentration. Overall, for the laboratory roaster, the particle-averaged oxygen concentration (which affects agglomeration) is mostly affected by the excess oxygen, followed by the inlet oxygen concentration. These observations are partly supported by the in-bed oxygen sensor measurements (See Figure 4.63) where the oxygen concentration was mostly influenced by excess oxygen, followed by bed particle size. Oxygen enrichment had a negligible effect. The discrepancy may originate from the fact that the sensor measures a localized oxygen measurement, close to the gas distributor as opposed to the model which calculates an average oxygen concentration. Bed height is the next most important factor. The trends of particle-averaged oxygen concentration with bed height are explained later.
Figure 6.15: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the laboratory reactor for the fitted kinetics and a 150 µm average bed particle size. For conditions, see Table 6.2.
Figure 6.16: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the laboratory roaster for the Fukunaka et al. kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2
Figure 6.17: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the laboratory roaster for the fitted kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2
Figure 6.18: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the laboratory roaster for the Fukunaka et al. kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2.
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Figures 6.19 to 6.22 present the predicted particle-averaged oxygen concentrations for the industrial roaster for the fitted and Fukunaka et al. [140] kinetics for small (65\(\mu\)m) and large bed particles (150\(\mu\)m). The effect of temperature again differs from one kinetic rate expression to the other. Contrary to the laboratory roaster, the average bed particle size is predicted to significantly affect the particle-averaged oxygen concentration. The sharp increase in predicted oxygen concentration for small particles (<70\(\mu\)m) is due to the maximum effective bubble size limit (equation 5.32) being reached. For 150 \(\mu\)m particles, there is only a small effect of any of the operating variables on the oxygen concentration. However, for 65 \(\mu\)m particles, excess oxygen and inlet oxygen concentration are predicted to have significant effects. Since the oxygen concentration affects the volatilization of lead sulfide, the mean particle diameter will affect the agglomeration behaviour of the industrial fluidized bed.

As Figures 6.15 to 6.22 show, the particle-averaged oxygen concentration increases with bed height in the laboratory roaster and for the industrial roaster with a mean particle size of 65 \(\mu\)m. When the particle size is large (150\(\mu\)m) in the industrial roaster, the oxygen concentration decreases slightly. Since these trends are counter-intuitive, a more detailed explanation is required.

It is commonly accepted that in fluidized bed reactors, as the expanded bed height is increased, for the same operating conditions (superficial gas velocity), additional gas conversion occurs which leads to a decreased particle-averaged oxygen concentration. This may be summarized as: “With deeper beds, the gas can reach higher conversions.” This reasoning originates from catalytic reactors where only the gas reacts and as such, additional particles simply increase gas conversion. In catalytic fluidized beds, the gas reaction rate constant \(k_r\) does not change. The gas conversion at a given vertical position in the bed is the same regardless of the expanded bed height. Additional height leads to higher gas conversions. When averaged, the additional conversion provided by increasing the expanded bed height (through increased solids inventory) lowers the overall gas concentration.

For gas-solid fluidized beds reactors, the assumption that the effective gas reaction rate constant
Figure 6.10: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the industrial roaster for the fitted kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2.
Figure 6.20: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the industrial roaster for the Fukunaka et al. kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2
Figure 6.21: Effect of process parameters, varied one at a time, on the predicted particle-averaged oxygen concentrations in the industrial roaster for the fitted kinetics and a 65 µm average bed particle size. For conditions, see Table 6.2.
Figure 6.22: Effect of process parameters, varied one at a time, on the predicted oxygen concentration available to the particles in the industrial roaster for the Fukunaka et al. kinetics and a 65 µm average bed particle size. For conditions, see Table 6.2
does not vary is flawed. Contrarily to catalytic reactors where the reaction proceeds as long as the gas is not completely converted and that it contacts active catalyst, the gas in gas-solid reactors only reacts to the same extent as the solids. Increasing the bed height does not necessarily increase the gas conversion. In fact, for all other parameters being constant, the effective gas reaction rate constant in gas-solid reactors decreases with increasing expanded bed height. This decrease in effective gas reaction rate constant is reasonable. Increasing the expanded bed height increases the number of inert particles while the number of reactive particles stays relatively the same (same solids feedrate, same superficial gas velocity). This dilutes the concentration of reactive particles in the bed and effectively lowers the effective gas reaction rate constant. This may be summarized as: “With deeper beds, the gas has more height to react with the reactive particles.” The gas conversion at a given vertical position will depend on the expanded bed height. Additional height does not directly lead to higher gas conversions since the gas conversion is tied to the solids conversions. The effect of increasing the expanded bed height (through increased solids inventory) on the overall gas concentration will be different in gas-solid fluidized bed reactors than in catalytic fluidized bed reactors.

First, we consider the effect of height on the average oxygen concentration for the laboratory roaster (Figures 6.15 to 6.18). As previously discussed, to reach a similar solids conversion, the reaction rate constant decreases when the bed height is increased (here, $H_{mf}$). This leads to a decreased reaction of the gas per unit volume of reactor. Also, the interphase mass transfer coefficient and area, governed by slugs, does not vary when the bed height is varied. Therefore, interphase mass transfer per unit volume of reactor is approximately the same (similar driving force). The combination of a decreased gas reaction and similar interphase mass transfer leads to an increased average oxygen concentration with increasing expanded bed height (increasing $H_{mf}$).

Next, we consider the effect of expanded bed height on the average oxygen concentration for the industrial roaster with a bed of 65 μm (small) particles (Figures 6.21 and 6.22). Similarly to the laboratory roaster, the reaction of gas per unit volume decreases as expanded bed height increases (due to decreasing reaction rate constant). The interphase mass transfer coefficient
and area is governed by the effective bubble size. Since the effective bubble diameter reached its maximum value somewhere in the bed, interphase mass transfer coefficient and area for the additional height are similar to most of the bed. Therefore, the net effect of decreasing the reaction of gas per unit volume and a similar interphase mass transfer is to increase the average oxygen concentration.

Finally, we consider the effect of expanded bed height on the average oxygen concentration for the industrial roaster for a bed of large particles (Figures 6.19 and 6.20). In this case, the maximum bubble size (which is very large) is never reached, significantly affecting the interphase mass transfer coefficient and area. Any additional bed height has smaller interphase mass transfer than any other upstream portion of the bed. The combination of decreased reaction rate (everywhere) and smaller interphase mass transfer (in additional height) leads to a small decrease in average oxygen concentration with increasing expended bed height. This decrease applies for the conditions modelled here. For other conditions, the decrease may be of a different magnitude or even be an increase.

In summary, changing the expanded bed height can affect the overall oxygen concentration by changing the relative importance of the gas reaction rate and interphase mass transfer. It is interesting to note that for conditions where the bubble size is limited (i.e. laboratory reactor and industrial reactor with small bed particles (particle diameter < 70 μm)) increasing the bed height increases the overall oxygen concentration. Such an increase reduces the time for complete conversion of concentrate particles. A reduced time for complete conversion combined with an increased residence time in the bed (larger bed mass) signifies that the average solids conversion is increased further than what would be expected by just increasing the residence time. For industrial fluidized beds with beds of large particles, only the increase in residence time positively affects the solids conversion.

In summary, for an industrial roaster with 150 μm particles, the particle-averaged oxygen concentration is low, regardless of the operating conditions. For the same roaster with 65 μm particles, excess oxygen significantly affects the oxygen concentration, thereby affecting the
agglomeration behaviour. This is due to the enhanced interphase mass transfer caused by the much smaller bubbles (with the maximum bubble size being reached). Oxygen enrichment (inlet oxygen concentration) also affects the particle-averaged oxygen concentration. However, since the practical range of oxygen enrichment is limited, changing the particle-averaged oxygen concentration using oxygen enrichment has little influence.

For the laboratory roaster, excess oxygen and oxygen enrichment both significantly affect the particle-averaged oxygen concentration, regardless of the particle size. This is explained by significant wall effects in the laboratory roaster. The interphase mass transfer for the laboratory roaster reaches a minimum, constant value once slugging is established. However, for the industrial roaster with 150 μm particles, the bubble diameter does not reach a limiting value (maximum bubble size or reactor diameter). Since interphase mass transfer decreases as bubbles grow larger, there is no lower limit on interphase mass transfer in the industrial roaster. For the laboratory roaster, the lower limit on interphase mass transfer is governed by the reactor diameter. Since particle size does not affect the slug diameter (diameter of the laboratory roaster), particle size has little influence on the particle-averaged oxygen concentration. For the industrial roaster, however, particle size significantly affects the particle-averaged oxygen concentration once the bubble size limit (equation 5.32) is reached.

Mixing in the laboratory and industrial roasters

In the previous chapter, we have seen that mixing in a fluidized bed must be characterized in its two main dimensions (axial and radial) independently. The fluidized bed roaster model assumes that perfect mixing applies to both the laboratory and the industrial roasters. To verify this assumption, the characteristic mixing times of the roasters are compared with the particle reaction times.

Table 6.6 summarizes the mixing times for both the industrial and laboratory roasters. The turnover time (calculated using equation 5.68) for both the laboratory and the industrial is of order 1 to 10 s. Radial mixing (equation 5.70), however, differs greatly between the laboratory and industrial roasters. For the laboratory roaster, the radial mixing time is approximately 1
Figure 6.23: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the laboratory roaster for the fitted kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2
Figure 6.24: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the laboratory roaster for the Fukunaka et al. kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2
Figure 6.25: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the laboratory roaster for the fitted kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2
Figure 6.26: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the laboratory roaster for the Fukunaka et al. kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2
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s or less. For the industrial roaster, on the other hand, the radial mixing time is much longer, ranging from 2000 to 11000 s, mainly depending on the particle size and gas velocity.

Figures 6.23 to 6.26 present contour plots of the solids reaction time with dimensionless vertical position in the bed and varying parameters, calculated using the local concentration in the H-phase for the laboratory roaster. The reaction times in these figures are calculated differently from those in the model: The model calculates a single particle-averaged oxygen concentration from which it calculates the time for complete reaction. The figures, however, are calculated for each vertical position in the bed. The Subfigures (f) in Figures 6.23 to 6.26 present the reaction time with dimensionless vertical position in the bed for a varying bed height at minimum fluidization. The expanded bed height increases as the bed height at minimum fluidization ($H_{mf}$) increases. Therefore, a dimensionless vertical position of 1 (bed surface) represents an increasing bed height as $H_{mf}$ is increased.

Table 6.6: Characteristic solids mixing times for laboratory and industrial roasters. For conditions, see Table 6.2. All times are given in seconds.

<table>
<thead>
<tr>
<th>Effect of f on $\rightarrow$</th>
<th>Laboratory</th>
<th>Industrial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radial time</td>
<td>Turnover time</td>
</tr>
<tr>
<td>Particle size (50 - 250 $\mu$m)</td>
<td>0.5-1.6</td>
<td>2.35-2.6</td>
</tr>
<tr>
<td>Velocity 65 $\mu$m particles</td>
<td>0.6-0.2</td>
<td>2.4-0.8</td>
</tr>
<tr>
<td>150 $\mu$m particles</td>
<td>1.1-0.35</td>
<td>2.4-0.8</td>
</tr>
<tr>
<td>Bed height 65 $\mu$m particles</td>
<td>0.6</td>
<td>2-11</td>
</tr>
<tr>
<td>150 $\mu$m particles</td>
<td>1.1</td>
<td>2-11</td>
</tr>
</tbody>
</table>

As for figures 6.15 to 6.18, the time for complete reaction within the H-phase does not differ greatly for the small (65 $\mu$m) and large (150 $\mu$m) particles. However, large differences appear when comparing the two reaction rate expressions from Chapter 2 (fitted and Fukunaka et al. [140]). Since the Fukunaka et al. rate expression gives much faster rates, the times for complete reaction are much smaller. Comparison of these times with the turnover and radial times for the laboratory roaster reveals that radial mixing is extensive. Axial mixing, however, may be incomplete if the Fukunaka et al. kinetics apply. This can be seen for conditions of high excess.
oxygen on Figure 6.24 (a). In this figure, a large portion of the contour plot gives reaction times of less than 10 s. Since the turnover time is of the order of 2.5 s, operation at excess oxygen larger than approximately 60% may not achieve perfect mixing. For other conditions, however, the region where the reaction time is less than the turnover time is relatively limited, generally to very close to the distributor. Since only a small area near the distributor has reaction times smaller than the turnover time, assuming that particles in the bed are perfectly mixed is reasonable. If the fitted kinetics apply, the assumption of radial and axial mixing is valid since the time for complete reaction is larger than any of the mixing times.

Figures 6.27 to 6.30 present contour plots of the solids reaction times calculated using the local concentration in the H-phase for the industrial roaster. As for the laboratory roaster, axial mixing may only be a concern if the Fukunaka et al. kinetics apply to the system. The turnover time is larger than the reaction time only when the inert particles are small and the excess oxygen is large.

In contrast to the laboratory roaster, radial solids mixing times in the industrial roaster are often larger than the corresponding reaction times. This may be of concern if the feed is unevenly distributed. The importance of radial mixing depends on the efficiency of the feeding system to distribute the zinc concentrate over the entire cross-section of the fluidized bed. If the feed is evenly distributed over the entire area, the importance of radial mixing may not be critical. However, if the feed is not distributed evenly, local differences in excess oxygen may occur and effective radial dispersion of the unreacted concentrate may be critical to the success of the process.

Note that the most favourable radial mixing conditions in the industrial roaster corresponds to large particles and low excess oxygen (see Figure 6.27 (a)). For industrial roasters containing very small average particle sizes (left of Figure 6.29 (c), <70μm), the reaction time decreases more quickly than the mixing time, due to the maximum effective bubble size (equation 5.32). For fluidized beds of fine particles, the bubble size is relatively small leading to enhanced interphase mass transfer. With faster interphase mass transfer, the oxygen concentration within
Figure 6.27: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the industrial roaster for the fitted kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2
Figure 6.28: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the industrial roaster for the Fukunaka et al. kinetics and a 150 μm average bed particle size. For conditions, see Table 6.2.
Figure 6.29: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the industrial roaster for the fitted kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2
Figure 6.30: Effect of process parameters varied one at a time, on the predicted reaction time (in s) of particles in the H-phase of the industrial roaster for the Fukunaka et al. kinetics and a 65 μm average bed particle size. For conditions, see Table 6.2.
the H-phase increases rapidly, causing a significant reduction in the time for complete reaction. This increase is seen on the particle-averaged oxygen concentration presented in Figure 6.21.

6.3.4 Model-based predominance-like diagrams

The figures presented in section 2.7 show that temperature and excess oxygen have a significant effect on the stable phases after complete reaction. Since the fluidized bed reactor model can more adequately predict the gas composition experienced by the particles, the results from the reactor model may be used to predict the most stable phases. The stoichiometry of the reaction is adjusted so that the reaction and the gas composition are consistent with the stable phase. Since the main reaction products for the oxidation of zinc sulfide are zinc oxide, basic zinc sulfate and zinc sulfate, the stoichiometric coefficients ($\nu_{O_2}$ and $\nu_{SO_2}$) for each reaction (oxidation and sulfation) are multiplied by the ratio of zinc oxide or zinc sulfate to converted zinc i.e. $\frac{n_{ZnO}}{n_{ZnS0_4} + n_{ZnS}}$ or $\frac{n_{ZnSO_4}}{n_{ZnS0_4} + n_{ZnO}}$ and added to obtain the overall stoichiometric coefficient. This allows for a variable stoichiometry from pure oxide to pure sulfate. Figure 6.31 presents the stable phases predicted from the gas composition from the fluidized bed reactor model using the model parameters for the laboratory fluidized bed. This Figure is calculated similarly as Figure 2.19 in section 2.7 with the exception that the gas composition is calculated using the GSBM model, coupled to a solids reaction model instead of a simple stoichiometric model (equation 2.11). In other words, the gas composition is first calculated using the reactor model. The most stable compound is then determined using this calculated gas composition.

Since the conversion is incomplete at low temperature, sufficient oxygen is available to produce basic zinc sulfate, even if it requires more oxygen. For the diagram calculated using the stoichiometric model, Figure 2.19, a mixture of zinc oxide and basic zinc sulfate is produced due to the complete conversion and to the insufficient amount of oxygen present to completely convert the zinc oxide to basic zinc sulfate.

When comparing Figures 2.19 and 6.31, it is clear that considering thermodynamics without considering reactor hydrodynamics and kinetics may yield erroneous results. The thermodynamics show that the lead system is highly sensitive to excess oxygen, especially near stoicho-
Figure 6.31: Excess oxygen - Temperature GSBM model-based predominance-like diagram for the experimental fluidized bed conditions shown in Table 6.3
Figure 6.32: Gas concentrations for excess oxygen - temperature GSBM model-based predominance-like diagram for the experimental fluidized bed conditions shown in Table 6.3
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metric operation. However, modelling clearly shows that the lead species are not sensitive to excess oxygen. Note that since the oxygen partial pressure is sensitive to excess oxygen, so will be the lead partial pressures.

Figure 6.32 presents the particle-averaged gas concentration related to Figure 6.31. The particle-averaged oxygen gas concentration increases with increasing excess oxygen. This is mostly observed between 1 and 100% excess oxygen (between -2 and 0 on Figure 6.32). The gas concentrations do not change appreciably below approximately 1% excess oxygen. The directions of the iso-concentration lines differ greatly from those presented in Figure 6.32. This is due to greater reactivity of the solids with increasing temperature.

The particle-averaged oxygen concentration is smaller than 1% for most conditions. It is larger than 1% only at lower temperatures were ZnO·2ZnSO₄ is produced. In this region, the kinetics and the model applied to the system probably no longer apply since the solid product is no longer ZnO and pore-blocking may occur (see Table 2.1).

Note that these calculations assume that the activities of a given species when it is stable is 1 and that the gas concentrations used averages for all particles within the fluidized bed. Since the activity of lead oxide within a lead oxide solution is less than 1, a liquid mixture of lead oxide with silica, zinc oxide or basic lead sulfate could exist, even for gas compositions where lead sulfate or basic lead sulfate is predicted. To correctly predict the appropriate stable phases for such conditions, the overall Gibbs free energy should be minimized, including gaseous phases and liquid solutions. This figure nevertheless demonstrates that thermodynamics alone and thermodynamics coupled to reactor modelling give very different results.

6.4 Discussion of key coating and agglomeration results

- **Effect of excess oxygen**

Excess oxygen had a significant effect on coating and agglomeration in the laboratory roaster. In addition, modelling of the laboratory roaster showed that the oxygen concentration surrounding the particles varies significantly with excess oxygen. Since the partial
pressure of lead sulfide varies with oxygen partial pressure (see Figure 2.11), these results are consistent with the mechanism proposed for coating and agglomeration.

For the industrial roaster, the model predicts that the effect of excess oxygen greatly depends on the mean bed particle size. For large average bed particle sizes, the effect of excess oxygen is small. However, for small average bed particle sizes (<70μm), excess oxygen has a significant effect on the average oxygen concentration surrounding the particles. This may imply that when the industrial roaster has a small average bed particle size, agglomeration and coating in the roaster may significantly vary with excess oxygen. When the average bed particle size is large, agglomeration and coating in the industrial roaster should not be significantly affected by the excess oxygen.

- **Effect of inlet oxygen concentration**

The experimental results do not show any significant effect of inlet oxygen concentration on the coating and agglomeration behaviour. Similarly, modelling predicts that the inlet oxygen concentration has a limited effect on the oxygen surrounding the particles, mainly because of the limited practical range of inlet oxygen concentrations.

Model predictions for the industrial roaster indicate that the average oxygen surrounding the particles does not vary significantly in the practical range of oxygen enrichment. This implies that coating and agglomeration should not be significantly affected by oxygen enrichment.

It was observed by operators of industrial fluidized bed roasters that changes in inlet oxygen concentration can affect the bed particle size distribution of the roasters [35]. Unfortunately, this study cannot explain the effect of changes in oxygen enrichment on the bed particle size distribution. One possibility may be that excess oxygen may have also been modified at the same time.

- **Effect of roasting temperature**

Temperature had a significant effect on coating and agglomeration in the laboratory roaster. Considering the proposed mechanisms, this observation is consistent with the increased lead partial pressures at higher temperatures (Figures 2.10 to 2.12 and 2.22)
and the more predominant liquid lead phases in the different phase diagrams (Figures 2.24 to 2.28).

The metal species partial pressures and the proportion of liquids within phase diagrams all increase with temperature. Considering that temperature has a similar effect on the particles regardless of the reactor geometry, it is reasonable that temperature affect coating and agglomeration in a similar manner in the industrial and laboratory roasters.

- **Effect of superficial gas velocity**

The superficial gas velocity did not have a significant effect on coating and agglomeration. This is consistent with model prediction of the oxygen concentration surrounding particles. For both the laboratory and industrial roasters, superficial gas velocity usually had little effect on the oxygen concentration.

It did, however, have an effect on the proportion of fine particles in the laboratory fluidized bed. This is consistent with the accepted knowledge of elutriation. One can also assume that attrition would be increased when the gas velocity is increased.

- **Effect of bed material**

The experiments have shown that the bed material has a significant effect on the coating and agglomeration behaviour. This can be explained by considering the phase diagrams of the main constituents of the particles, in particular with lead oxide.

For silica particles, the presence of extensive liquid phases in the phase diagram (Figure 2.25) indicates a significant reactivity of lead oxide with silica. Such a reactivity would manifest itself by significant “wetting” of the particles by a liquid layer which would contribute to the coating of such particles.

For alumina particles, the phase diagram (Figure 2.26) also presents a eutectic composition, liquid at typical roasting temperatures. However, the proportion of liquid is much smaller than for silica. The reactivity of lead oxide with alumina can therefore be assumed to be smaller, yet still existent. This smaller reactivity would be manifested by a different “wetting” behaviour. This was observed experimentally.
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For the calcine particles, one can assume from the phase diagrams (Figures 2.27 and 2.28) that the reactivity of calcine with lead oxide may be larger than for alumina yet smaller than silica. This implies that the coating and agglomeration behaviour of calcine particles would likely rank between the silica and alumina particle.

Modelling characterizes the effect of bed material only in terms of its density and size. It cannot predict the chemical effects of the bed material on the agglomeration and coating processes.

- **Effect of average bed particle size**

Differences in the behaviour of industrial fluidized bed roasters have been observed with changes in average bed particle size [35].

Modelling has shown that the average bed particle size significantly affects the behaviour of the industrial fluidized bed roaster. The span of particle-averaged oxygen concentrations for changes in excess oxygen strongly depends on the average particle size. For fine (Geldart Group A) particles, the bubble diameter is limited and the range of particle-averaged oxygen concentrations is greater than for larger (Geldart Group B) particles where bubble diameter is not limited. For the laboratory roaster, no significant changes were found.

Experimentally, the bed particle size affected the agglomeration behaviour in the laboratory roaster. When the laboratory roaster was operated with small particles under conditions of no excess oxygen, agglomeration was excessive and lead to defluidization. Under the same operating conditions for a bed of larger particles, agglomeration occurred but not excessively. Therefore, it is reasonable to assume that the average bed particle size affects the later steps of the agglomeration and coating mechanisms.

### 6.5 Implications for the industrial process

Excess oxygen and temperature were found to influence the agglomeration behaviour in the experimental fluidized bed. Since modelling has shown differences in behaviour between the laboratory and industrial roasters, and since there were significant difference in scale and moisture
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content of the feed, direct extrapolation of the results from the experimental to the industrial fluidized bed must be done cautiously.

The modelling results imply that the coating and agglomeration behaviour in the industrial roaster depend on the mean bed particle size. The strategy on how to affect and control the bed particle size will therefore depend on the mean bed particle size.

6.5.1 Effect of uneven spatial distribution of feed material

It is likely that the industrial fluidized bed roaster experience “feed-rich” and “feed-lean” regions due to the way slinger belts distribute feed onto the bed surface. For this discussion, assume that the feed-rich and feed-lean areas are equal (i.e. 50% of the bed area each). For a properly functioning gas distributor, the gas would be evenly distributed among the two areas (50/50%). Assume that the overall excess oxygen is 20%. If the feed is distributed among the feed-rich and feed-lean areas in a 60/40% proportion, the local excess oxygen of the two areas, neglecting lateral mixing of the solids, would be 0 and 50%.

Note that agglomeration could therefore proceed in the sector with no excess oxygen even though the overall proportion of oxygen is well above stoichiometric. Overall, agglomeration in the industrial fluidized bed roaster involves a balance between local agglomeration, which depends on local process conditions, lateral mixing of the feed and agglomerates, elutriation and attrition. Therefore, overall agglomeration would depend on the extent of the feed-rich and feed-lean areas and the proportion of feed delivered to each areas, as well as mixing and reaction kinetics.

Uneven feed distribution is clearly an issue which requires further attention, both from theoretical and industrial points of view.

6.5.2 Mean bed particle size too large

The model results presented in section 6.3.3 suggests that for a large mean particle size in the industrial roaster, the average oxygen concentration surrounding the particles is not significantly affected by most operating variables. Small changes in the operating conditions should
not therefore greatly affect agglomeration and coating. However, since the coating and agglomeration mechanisms require a source of lead sulfide, uniform distribution of zinc concentrate over the entire bed cross-section is beneficial to promoting uniform coating and agglomeration behaviour. Since the reaction time of the particles in beds of large mean particle size is much larger than for small mean particle size, lateral mixing is more likely to be sufficient to provide sufficient lead sulfide to areas not directly fed.

If there is too much agglomeration in the industrial fluidized bed roaster, the mean particle size of the bed would become very large. Since few parameters affect the oxygen in the bed (and therefore agglomeration) when the mean particle size is large (e.g. ≥100μm), temperature may be the main parameter affecting agglomeration due to the dependence of the lead partial pressure on temperature. The bed temperature is a consequence of the heat balance between the heat supplied by the reaction, the heat removed by the boiler tubes in the bed, the heat carried out by nitrogen and the heat used to generate steam from feed moisture. Therefore, a reduction in bed temperature through a decrease in concentrate feedrate may be appropriate. Increasing excess oxygen may also help to decrease agglomeration since the oxygen concentration leads to a smaller lead sulfide partial pressure and a shorter reaction time (decreased period where lead sulfide can volatilize).

If the feed is distributed unevenly over a bed of large particles, agglomeration would occur in the feed-rich areas and little or no agglomeration would occur in the feed-lean areas. There are no experimental results corresponding to the conditions in a fluidized bed containing large particles where bubble size is not limited by the reactor diameter. However, if the laboratory results apply, agglomeration in the feed-rich area may produce particles of an adequate size (for a bed of large particles).

6.5.3 Mean bed particle size too small

If conditions in the industrial roaster are such that the average particle size is small (<70μm), significant variations in average oxygen concentrations occur for changes in excess oxygen (see Figures 6.19 to 6.22). This is due to limited bubble diameter which increases interphase mass
transfer (compared to an unlimited bubble size system). Since the coating and agglomeration mechanisms rely on vapour-phase transport of lead, variations in average oxygen concentrations affect coating and agglomeration. Therefore, extreme care must be taken to ensure adequate excess oxygen and proper feed distribution over the entire bed cross-section. Improper feed distribution may lead to areas with very small, even negative excess oxygen (see equation 2.11), while other areas of the fluidized bed may experience excessive oxygen. The extent of variation in excess oxygen within the bed will depend on the degree of feed maldistribution and on lateral mixing. Note that the reaction time of concentrate particles in a bed of small mean particle size is much less than for large particles. This makes uniform excess oxygen and efficient lateral mixing more difficult to achieve. Therefore, it is even more important to ensure a uniform feed distribution.

If there is too little agglomeration in the industrial fluidized bed roaster, the mean particle size of the bed becomes small. Excess oxygen has a significant effect on the oxygen in the bed when the mean particle size is small ($\leq 70 \mu m$). Decreasing the overall excess oxygen is expected to increase agglomeration. However, feed-rich areas may experience excessive agglomeration (production of very large particles) while feed-lean areas have negligible agglomeration. This may lead to a bed where only small and very large particles exist (i.e. no intermediate sized particles). Such a bed may be susceptible to defluidization by segregation of sizes. Increasing temperature may also cause increased agglomeration. However, without even feed distribution it is possible that increasing temperature will exacerbate excessive agglomeration in the feed-rich areas. Uniform feed distribution is especially critical to achieve adequate agglomeration in beds of small mean particle size.

### 6.5.4 Recommendations with respect to industrial roasting

Overall excess oxygen should be strictly monitored to find the appropriate level for adequate agglomeration. Once the optimum excess oxygen level is found, excess oxygen must be carefully controlled, keeping in mind the significant difference in the average oxygen concentration for small and large mean particle sizes and the variations in feed composition.
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It is currently not known how uniformly the feed is distributed. Monitoring and improving the uniformity of feed distribution may allow better control of the bed behaviour. Feed distribution in an industrial fluidized bed roaster is possibly the most difficult variable to quantify and monitor. Changes in bed behaviour may be caused by even small changes in the feeding system. Any changes to the feeding system, due to maintenance or other reasons, should be recorded. Increasing the number of feed points and/or changing the method of feeding should be considered seriously to improve the uniformity of the bed, especially if the mean bed particle size is small.

If even feed distribution cannot be achieved economically, one should consider non-uniform gas distribution. This method has recently been proposed to control agglomeration in a fluidized bed roaster [73]. Appropriate gas distribution may allow better control of the excess oxygen within the feed-rich and feed-lean areas of the bed.
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Conclusions and Recommendations

7.1 Major contributions

- Coating and agglomeration mechanisms have been formulated. The main contribution is the coating mechanism. The second contribution is that the oxygen concentration of the surrounding gas is, for the first time, shown to play a significant role in the coating and agglomeration processes. Excess oxygen affects agglomeration, especially near stoichiometric (0% excess oxygen). Experimentally, agglomeration increased when excess oxygen approached 0%. This is an important contribution. This behaviour was explained using the mechanisms, their dependence on the oxygen concentration and the fluidized bed reactor model. In addition is has been verified that the zinc concentrate does not require that a lead sulfide phase be present in the concentrate for volatilization of lead sulfide to occur.

- A probabilistic fluidized bed reactor model has been formulated which can be used for both the bubbling and slugging fluidization flow regimes. The key contribution is the manner in which the bubbling-to-slugging transition has been handled.

- The last important contribution is the model confirmation that the mean bed particle size of an industrial fluidized bed roaster can strongly affect how the industrial roaster responds to changes in operating conditions. In particular, the model has shown that a change in excess oxygen affects the fluidized bed roaster differently depending on the average bed particle size.
7.2 Key conclusions

- The experimental results show that temperature and excess oxygen significantly affect agglomeration within the laboratory roaster. Excess oxygen was not previously thought to be a significant variable. Modelling indicates that excess oxygen can also be significant for the industrial roaster.

- Oxygen enrichment did not have a significant effect on coating and agglomeration in the laboratory roaster for the restricted range investigated. This is opposite to what is suggested in the literature [35]. Modelling suggests that oxygen enrichment is also of limited importance in the industrial roaster.

- A coating mechanism has been formulated, relying on the vaporization of lead sulfide from the zinc concentrate followed by deposition of lead oxide/sulfate onto bed particles. Lead oxide is a liquid at typical roasting temperatures. The liquid lead oxide/sulfate film can trap smaller particles onto the surface of larger particles.

- An agglomeration mechanism has been formulated. Similar to the coating mechanism, the agglomeration mechanism relies on vaporization of lead sulfide from the zinc concentrate, followed by deposition of liquid lead oxide/sulfate onto particles. The coated particles can then agglomerate to form larger particles.

- The first step of both mechanism, the vaporization of lead sulfide, is strongly affected by the oxygen partial pressure.

- Lead sulfide was observed to volatilize from zinc concentrate.

- The coating and agglomeration mechanisms formulated in this work are consistent with the observations of Condina et al. [83] and extend their work to both coating and agglomeration in fluidized bed roasting conditions.

- A sensitivity analysis indicates that there are significant differences between laboratory and industrial fluidized beds, the most significant being the effects of excess oxygen and bed particle size.
• The behaviour of the industrial roaster depends greatly on the average inert particle size. For a large average bed particle size (150 μm), the operating conditions have only minor effects on the oxygen concentration experienced by the reacting particles. However, for a small average particle size (65 μm), excess oxygen has a significant effect on the average oxygen concentration seen by the reacting particles. Inlet oxygen concentration also has an effect. However, the inlet oxygen concentration is usually varied over only a narrow range (e.g. 21 to 25-30 vol%), thereby limiting its influence.

7.3 Secondary conclusions

• Reactor modelling has shown that scale-up from laboratory to industrial scale reactors must be carried-out very carefully, accounting for the differences in interphase mass transfer and radial mixing. Experimental results are more scalable once the reactor diameter is sufficiently large such that wall effects are negligible on the bubbles. To reach such conditions, the minimum diameter must exceed approximately 1 meter in practice.

• The oxygen present within the fluidized bed, determined using an in-bed oxygen sensor, is a function of excess oxygen and bed particle size. Oxygen enrichment, however, does not have a significant effect for the limited range investigated. Prior to this study, there was no information on the effect of process parameters on the oxygen present within the fluidized bed. The measurements are consistent with the model predictions.

• Low-melting-point phases within zinc concentrates originate from the interaction of impurities. The main impurities are PbS, Cu₂S and FeS.

• A single compound, lead oxide, accounts for numerous low-melting-point phases. If lead oxide or any of the basic lead sulfates is produced, the likelihood of producing low-melting-point phases is high, especially for particles that spend long times within the roaster.

• The stable phases calculated using the fluidized bed reactor model differ considerably from those based on stoichiometry and thermodynamics. The identity of the stable phase varies much less for the reactor model than when predicted from pure thermodynamics.
7.4 Recommended future work

In light of the implications of the current work on the industrial process, more detailed modelling of industrial fluidized bed roasters is recommended:

- **Distribution, mixing and reaction of zinc concentrates in industrial fluidized beds**

  In this study, it was assumed that concentrates were introduced uniformly over the entire cross-section of the fluidized bed. For large industrial roasters, this is unlikely to be the case.

  The effect of non-uniform solids distribution in large industrial fluidized bed roasters should be evaluated. A non-uniform feed distribution could cause regions of the fluidized bed to experience very low or even negative local excess oxygen conditions (e.g. where the concentrate enters the bed), while other regions would experience high excess oxygen. Since it is the goal of fluidized bed roasting to efficiently react the concentrate with oxygen in the gas, maldistribution of the feed may affect the maximum achievable productivity from a given roaster. Since the effect of excess oxygen is greatest for roasters with small bed particles, any non-uniform feed distribution, beyond that which can be dissipated by radial dispersion, would significantly affect bed agglomeration.

  Modelling the distribution, mixing and reaction of zinc concentrates in industrial fluidized beds would allow evaluation of the effectiveness of increasing the oxygen content of the gas fed near the feed point using a feed gas distributor as proposed by Taskinen *et al.* [73]. The current model should be extended by accounting for lateral mixing using an approach used for shallow fluidized beds [221, 222, 223, 224, 225]. However, the model would not need to account for slugging since industrial fluidized bed roasters are too large to encounter slugging.

  In addition to the distribution of feed, the mixing of zinc concentrates within the fluidized bed roaster should be clarified. In this study, it was assumed that the mixing of the concentrates is rapid and that each concentrate particle can be treated individually. If
the concentrate particles tend to move in groups or clusters, macro-mixing would also need to be considered.

- **Particle size distribution modelling**
  The particle size distribution was only accounted for when fitting the model to experimental results. The experimental particle size distributions were used to calculate the residence times of the reacting particles. However, since the resulting bed particle size distributions are not predicted in this study, the sensitivity analysis did not consider the size distributions of the concentrate and inert bed particles.

To include the effect of the particle size distributions (concentrate and inert bed particles) a population balance should be coupled with the solids reaction model. Using a population balance, agglomeration, coating, attrition, elutriation can all be accounted for and the resulting bed particle size distribution can be predicted. The resulting bed distribution is then coupled to the solids mean residence time (see equation 5.113).

- **Reaction of concentrate lumps in industrial fluidized beds**
  Concentrate lumps were not studied in this research project. Such lumps should react similarly to the grain model. Using the shrinking-core model, we have seen that very large particles have the possibility of reaching temperatures greater than their environment. Since the two models are fundamentally different, concentrate lumps may behave differently from single particles.

This work has shed light on some gaps in current pyrometallurgical knowledge. Applied research could be initiated in the following areas:

- **Kinetics of zinc concentrate oxidation**
  The oxidation kinetics of zinc sulfide and zinc concentrates were reviewed. A number of studies have suggested rate expressions. Most of these expressions give similar rates. Fitting of the model to the experimental data obtained in this study indicated rates of reaction which are higher than predicted by most kinetic rate expressions, but slightly lower than those of Fukunaka *et al.* [140]. Since the rates obtained from the Fukunaka
et al. [140] kinetic rate expression were larger than almost all other rate expressions, further kinetic results are needed. In particular, most kinetic rate data were obtained at temperatures below those employed in industrial fluidized bed roasters. The intrinsic kinetics should be evaluated for typical roasting temperatures. Since the reaction rates can be enhanced by vaporization and oxidation of zinc sulfide in the gas phase [122, 123], both the vaporization and reaction kinetics must be included in the higher temperature reaction rate analysis.

- **Vaporization kinetics from zinc concentrates**
  No modelling of coating and agglomeration can be reliably performed until the lead vaporization kinetics from zinc concentrates are studied. Vaporization is likely to be influenced by the process conditions (temperature, oxygen and sulfur dioxide concentrations) and is probably influenced by the concentrate composition and mineralogy.

- **Coating and agglomeration in the fluidized bed roaster**
  Since different behaviour was observed for silica and alumina inert particles, it would be advantageous to evaluate whether the proposed coating and agglomeration mechanisms would apply to a bed of calcine particles.

  Further study on the agglomeration mechanism is required. Since catastrophic agglomeration occurred only during one of the experiments carried out in this work, limited insight was gained.

- **Melting point of zinc concentrates**
  The melting of zinc concentrates is discussed briefly in Chapter 2 on the basis of phase diagrams for various sulfides. Various low-melting-point phases were found. However, a complete ZnS-FeS-PbS ternary phase diagram would prove useful to determine the minimum temperature and composition of the liquid phases. Since copper also affects agglomeration, the complete quaternary diagram would also be useful.

  Contrary to what is proposed in the literature, agglomeration did not occur in this study by the melting of zinc concentrates [73, 72] (see section 2.9.2) or by the melting of a reactive
low melting point phase [80, 81, 82, 53] (see section 2.9.3). Evaluating the conditions where concentrate melting and reactive melting can occur would be beneficial to the industry. These low-melting-point phases may be concentrate-dependent. It is likely that the three major impurities (lead, copper and iron) contribute to agglomeration in industrial fluidized bed roasters according to different mechanisms. Therefore conclusions from one concentrate may not apply to another.

In addition to the applied pyrometallurgical research, fundamental fluidized bed research would be beneficial to the better understanding of the coating and agglomeration processes:

- **Generalized slugging bubbling fluidized bed reactor model**
  The generalized slugging bubbling fluidized bed reactor model should be tested against experimental data for catalytic reactions. If possible, these data should span both fluidization regimes and cover a wide range of reaction rate constants.
  
  The model should also be integrated into the current generalized fluidized bed reactor model [205]. However, the transition from slugging to turbulent must first be clarified and characterized.

- **Agglomeration behaviour of binary fluidized beds in the presence of liquids**
  Further study is required to elucidate the coating and agglomeration behaviour of fluidized beds containing different types and sizes of particles in the presence of liquids. The fluidized bed roaster of this study had very small concentrate and calcine particles in a bed of larger silica sand particles. The reactivity of lead oxide/sulfate melts may vary with the type of particles (concentrate, calcine, or inert sand). This difference in reactivity would cause different dynamic-wetting behaviour. The attrition behaviour may depend on the amount and composition of liquid present and the size of the initial bed material.
  
  A fundamental study on the agglomeration of very fine particles within a fluidized bed of coarser particles, in the presence of a liquid phase, may shed some light on the mechanism of agglomeration within the fluidized bed roaster. The effect of the quantity of liquid present within the bed and the attrition of agglomerates by larger particles may be studied.
in a controlled experiment. Such a study may also reveal information on the growth of particles. The study may reveal the conditions under which the fine particles are glued onto larger particles by a liquid film and the conditions to create agglomerates of fine particles held together by a liquid. The important variables to account for in such a study would include the amount of liquid, the size of the fine and large particles, their surface properties and the superficial gas velocity.

**Effect of particle stickiness on minimum fluidization velocities and average bubble diameters**

The fluidized bed roaster relies strongly on interphase mass transfer for the transport of oxygen from the bubbles to the reacting particles. The most important parameter for interphase mass transfer is the average bubble diameter. Evaluating how the bubble diameter varies as a function of particle stickiness would give insight whether or not particle stickiness improves interphase mass transfer.

### 7.5 Review of objectives

The research reported in this thesis has sought to provide a better understanding of particle growth processes in zinc concentrate fluidized bed roasting. We now conclude by relating the thesis results to the project objectives set forth in section 1.7.

**Investigate particle growth in a laboratory scale fluidized bed roaster.**

Particle growth and agglomeration were studied in a laboratory fluidized bed roaster (see Chapters 3 and 4). The temperature and excess oxygen were found to significantly affect entrainment and agglomeration within the laboratory roaster.

**Identify particle growth mechanism(s) and quantify the rate(s) of different mechanisms for pure zinc sulfide and industrial concentrates.**

Mechanisms for the growth and agglomeration of particles have been identified (see sections 4.6 and 4.7). Both mechanism rely on the transport of lead species to the inert bed particles. The rates for each mechanism have not been quantified. However, it is...
clear that the rates would depend greatly on the lead species partial pressure, their vaporization and deposition kinetics and the interaction of the deposited lead phase with the bed particles. Agglomeration in a pure zinc sulfide system also has not been studied because, as explained in Chapter 3, pure ZnS particles of the right size could not be found. In light of the proposed mechanisms, it is doubtful that significant coating and agglomeration would have been observed if such runs had been carried out.

- **Identify the operating parameters influencing each mechanism.**

  A number of operating parameters were varied experimentally to evaluate their influence on particle growth and agglomeration (see Chapters 3 and 4). Since catastrophic agglomeration occurred only during one experiment carried out in this work, limited insight on agglomeration was gained. The experiments showed that the temperature and excess oxygen have the greatest effects on particle growth, with bed material, its size distribution and superficial gas velocity also playing significant roles.

- **Develop a fundamental model, applicable to both pure zinc sulfide and industrial concentrates, describing the particle growth in a fluidized bed.**

  To model growth and agglomeration in a fluidized bed roaster, a population balance on the solids must be coupled to a fluidized bed reactor model incorporating a vaporization and deposition model. The fundamental model developed in this study predicted the effects of various parameters on the oxygen concentration in the bed. The model developed in this thesis provides the first step of a comprehensive model describing particle growth in a fluidized bed roaster. The relationship between the oxygen concentration in the bed, the vaporization and deposition kinetics and the growth and agglomeration of particles must first be quantified to complete the fundamental growth and agglomeration model.

- **Determine the applicability of the results to an industrial fluidized bed roaster.**

  Sensitivity analysis has allowed the laboratory results to be extended to the industrial scale. However, the applicability of the results to an industrial fluidized bed roaster still remains to be verified.
Chapter 7. Conclusions and Recommendations

This thesis is an important step in achieving the longterm objective of improving the understanding of industrial fluidized bed roasters and providing tools to predict their behaviour and improve their operation.
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Appendix A
Instrument Calibration

A.1 Thermocouples

All thermocouples used during the project were of type K i.e. Chromel-Alumel. The standard polynomial used for type K thermocouples [241], indicated in Table A.1 was used to calculate the temperatures.

In addition to using the polynomial, the thermocouples were verified with an ice bath and boiling water. The temperature reading of an ice bath was also recorded during the experiments.

A.2 Gas flowmeters (rotameters)

All rotameters in this study are installed with the control valve at the outlet of the rotameter tube. The main advantage of this type of installation is that the rotameter reading is insensitive to the outlet pressure. The calibration of the rotameter depends on the pressure inside the

<table>
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<tr>
<th>Coefficient</th>
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</tr>
<tr>
<td>a8</td>
<td>-6.33707 e+13</td>
</tr>
</tbody>
</table>
Appendix A. Instrument Calibration

rotameter i.e. inlet pressure. Early during the calibration of the rotameters it was observed that the typical equation used to describe the flow of a rotameter did not adequately describe the observed gas flow rate under various pressures. The typical rotameter equation in most catalogs only applies to rotameters operating in turbulent flow. It can easily be shown (force balance over float) that for a given height of the float, the volumetric flow rate \( F \) follows the following equation if the flow is viscous [242]:

\[
F = \alpha D_b^4 \frac{(\rho_b - \rho_{gas})g}{\mu_{gas}} \tag{A.1}
\]

where \( \alpha \) is a constant characteristic to the tube and float and \( D_b \) is the float diameter. Similarly the following equation applies in turbulent flow [242]:

\[
F = \beta D_b^{5/2} \sqrt{\frac{(\rho_b - \rho_{gas})g}{\rho_{gas}}} \tag{A.2}
\]

where \( \beta \) is a constant characteristic of the tube and float.

From these equations, it is clear that changing the operating pressure (gas density) of a rotameter operating in viscous flow will differ from that if the rotameter were operating in the turbulent regime. Because the rotameters used in this study were operating different flow regime (laminar, intermediate, turbulent), a general rotameter equation was developed and used to calibrate the flowmeters.

A.2.1 Development of general rotameter equation

At any time, the mass flowrate of the rotameter is governed by this equation:

\[
Q = AU\rho_g \tag{A.3}
\]

where \( A \) is the annular area between the tube and float, \( U \) is the gas velocity in this area and \( \rho_g \) is the gas density.

For steady state operation, the gas flows around the spherical float at the float terminal velocity. Using a force balance over a spherical float and the float friction factor \( (f) \), the following relationship between the float Archimedes number, and float terminal Reynolds number is found:

\[
Ar = \frac{3}{4} f Re^2 \tag{A.4}
\]
Combining equations A.3 and A.4 and isolating the terminal velocity, we obtain:

\[ Q = \frac{A\mu_g}{D_b} \sqrt{\frac{4Ar}{3f}} \]  \hspace{1cm} (A.5)

This equation clearly separates the rotameter tube geometry \( A \) from the factors affected by the gas conditions \( (\mu_g, Ar, f) \). By lumping the annular area with the constants, a general rotameter equation can be obtained:

\[ Q = \alpha(h)\mu_g\sqrt{\frac{Ar}{f}} \]  \hspace{1cm} (A.6)

where \( \alpha(h) \) is a polynomial used to fit the equation to the measured gas flowrates. Note that for a given rotameter, the float diameter \( (D_b) \) is constant. This equation was used to calibrate all the rotameters used in this study.

### A.2.2 Rotameter calibration fit

Each of the rotameter were calibrated by measuring the gas volume delivered for different gas pressures and float heights. The gas volume measuring device used to calibrate a given rotameter was either a 100 ml bubble column, a 3 l wet test meter or a 28.3 l dry test meter (gas meter). All the measurements were done by reading the height of the float in the tube at the bottom of the float. Tables A.2 and A.3 describe the rotameters and provide their calibration polynomials.

### A.3 Pressure transducers

The pressure transducers in this study were calibrated using a water manometer and a Vaccon CDF-200 air amplifier used as a vacuum pump. The constant for the calibration polynomials of the 4-20 mA transducers are shown in Table A.4.

\[ P = m_0 + m_1\text{reading} + m_2\text{reading}^2 \]  \hspace{1cm} (A.7)

The independent variable of the polynomial is the digital reading from the data acquisition system (12 bits). The pressure values obtained from the polynomial are in mm of water. To convert mm of water to Pa, multiply by 9.81.
Appendix A. Instrument Calibration

Table A.2: Rotameter description

<table>
<thead>
<tr>
<th>Rotameter</th>
<th>Material</th>
<th>Dia. (mm)</th>
<th>Dens. (g/cm³)</th>
<th>Reading</th>
<th>Factors at 103.4 kPa</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
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<tr>
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<tr>
<td>CHE3789E</td>
<td>Glass</td>
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<td>150</td>
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<tr>
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<td>16.6</td>
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A.4 Solids feedrate

The solids feedrate was originally thought to be sufficiently consistent that no feedback control was needed. The feedrate was calibrated by measuring the mass delivered for a given period at different motor speeds. However in run 2, it was realized that the calibration could not be relied upon because of variations in concentrate properties. An improved concentrate preparation method was therefore devised.

Manual feedback control was used for runs 3 through 9. A Kilo-Tech model LCS30 30 kg x 2 g scale was used to manually log the mass and to adjust the feedrate to the setpoint. The difference in mass for a given interval indicated the current feedrate, and the motor controller (Model HS20C-MD3 from G.K. Heller Corp.) was manually adjusted to obtain the desired feedrate. Manual feedback control ended with run 9 because it was difficult to keep the feedrate at the setpoint.
**Appendix A. Instrument Calibration**

Table A.3: Rotameter polynomial calibration fits

<table>
<thead>
<tr>
<th>Rotameter</th>
<th>Flow (std l/min) = (m₀ + m₁h + m₂h²)*factor</th>
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<tbody>
<tr>
<td>Cole Parmer Glass</td>
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<td>CHE3789E Glass</td>
<td>0.0003779</td>
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Table A.4: Pressure transducers - polynomial

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<th>m₂</th>
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</tr>
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<td>4</td>
<td>1.2963</td>
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<tr>
<td>5</td>
<td>1.3103</td>
<td>-3227</td>
<td></td>
</tr>
</tbody>
</table>
Appendix A. Instrument Calibration

Complete feedback control on the concentrate feedrate was implemented starting from run 10. The control loop consists of: feeder, motor controller, 20 kg x 1 g scale, data acquisition board with analog output and appropriate controller software.

![Diagram of Zinc concentrate automatic feedrate feedback control](image)

Figure A.1: Zinc concentrate automatic feedrate feedback control

The feeder is the same as used previously. However, a new motor controller was introduced. The DC motor controller consists of a Crydom proportional power controller model 10PCV2415 equipped with a bridge rectifier and a RC filter. The filter consists of two 8.2 ohm 10W power resistors in series and a 160V 820 μF capacitor. Because the input of the proportional power controller requires a 2 to 10 V control signal, an operational amplifier amplifies the 0-5V analog signal from the computer. The amplifier is adjusted so that the maximum voltage output does not exceed the motor rating. The input-output characteristic of the proportional power controller is non-linear. The computer can compensate for the non-linearity.

For the computer to obtain the current weight, a scale with a computer output was required. A 30 kg x 5 g scale (Ohaus model CH30R11) with a RS-232 output was modified by the supplier to give a 20 kg x 1 g output. The scale has a zero offset of 10 kg. Therefore, once the feeder
Appendix A. Instrument Calibration

(15 kg) is installed on the scale, the scale reads 5 kg, giving an effective 15 kg of payload. Note that the scale cannot be used without a dead weight of at least 10 kg.

The control algorithm is based on the papers of Kalata [243, 244] which implemented a stochastic controller for loss-in-weight machines using a Kalman filter to continuously compute the current solids feedrate and a integral control (integrator) for the control signal. Unannounced refills are accounted for by appropriately considering them as process noise.

The feeder and its controller do not require calibration. The scale was calibrated by Pacific Industrial Scale Co Ltd at the time of the purchase. The Kalman filter and the integral controller require that some parameters be tuned for an appropriate response of the system.

A.5 Solids mass flowmeter

In order to better diagnose problems with the feeder, a solids mass flowmeter was built using two pressure transducers and a loop in the pneumatic conveying line. One of the pressure transducer is a differential pressure transducer. It measures the pressure drop across a section of the pneumatic conveying line. It can be shown that the pressure drop across the line is the sum of the gas pressure drop and a contribution of the solids loading. For a constant gas flowrate, there is a minimum pressure drop which is essentially the gas contribution, and the pressure drop increases linearly with increasing solids loading. An absolute pressure transducer is located at the inlet of the line. This transducer indicates any plugging of the feed line. These transducers have not been calibrated to provide a mass flowrate since the mass flowrate can be determined more accurately from the weight loss of the feeding scale.
Appendix B
Laboratory Roaster Procedures

B.1 Experimental run

B.1.1 Startup

1. Turn on ventilation, blue panel on north wall, fan 5.
2. Turn on breakers(3) on bus bar
3. Start controllers (red button small panel).
4. Start furnaces/solenoids (start/stop on large panel).
5. Start air and water on wall.
6. Make sure vacuum valve is open.
7. Make sure scrubber bypass valve open.
8. Reboot computer.
   Note Filename.
10. Start preheating (run menu, preheat reactor).
    Furnaces temperature = 950 °C.
    This will change the controllers setpoint.
    This will also turn on the Air, N₂ and O₂ solenoids.
    Change setpoint of furnace 3 to 975°C. These are not the bed temperatures.
11. Adjust various rotameters to given settings.
    Use air only during preheat.
    Read bottom of rotameter floats.
12. Change ice point.
    Get ice from freezer.
    Fill with water.
    Put in insulating container.
    Insert thermocouple in ice bath - water side.
Appendix B. Laboratory Roaster Procedures

B.1.2 Feeder startup
1. Open scrubber inlet valve for tank 1.
2. Open scrubber outlet valves for both tanks.
3. Using nuts and bolts, lock scrubber outlet valves open for both tanks.
5. Change gas for all purges lines to nitrogen.
6. Change feeder pneumatic conveying line to nitrogen.
7. Fill feeder hopper as per next section
8. Turn on feeder motor controller. Put feeder motor controller on computer control.
9. Start feeder in software.
10. Enter desired feeder setpoint.

B.1.3 Feeder refill
1. Weigh concentrate bucket, note in log.
2. From software, place feeder on manual control.
3. Remove top flange of feed hopper.
4. Refill feed hopper.
5. Replace feed hopper top flange.
6. From software, place feeder on automatic control.
7. Weigh concentrate bucket and note in log.

B.1.4 Solid sampling - Bed samples
1. Make sure nitrogen flows through purge tube.
2. Open sampling valve.
3. Lower solids sampler until it reaches the gas distributor.
4. Wait 5 seconds.
5. Raise solids sampler.
6. Close sampling valve.
7. Let the sample in sampler cool for a minimum of 5 minutes.
8. Using small tube to "lock" the sampler, remove sampler from purge tube.
9. Pour solid sample into metal container.
Appendix B. Laboratory Roaster Procedures

10. Place metal container in water bath.
11. Let cool to room temperature.
12. Remove metal container from water bath.
13. Sponge out water from bottom of metal container.
14. Pour solids in plastic sample bag.
15. Label sample bag: run number, type of sample, time of sample.
17. Apply "Rock and Roll" anti-seize to thread.
18. Install sampler on purge tube, hand tight only.
19. Remove small tube to "unlock" the sampler.

B.1.5 Solid sampling - Carryover samples
1. Clean solids filter by pressing button "Clean Pulse" on main screen of roaster software.
2. Open valve at the bottom of the solids filter.
3. Hit several times on bottom of solids filter housing to dislodge particles.
5. Place collecting dish below the sample hopper.
6. Open the sample hopper by removing cap.
7. Hit a few times on bottom of solids hopper to dislodge particles.
8. Close solids hopper by reinstalling cap, hand tight only.
9. Using large stainless funnel, transfer the solids from the collecting dish to sample bag.
10. Label sample bag: run number, type of sample, time of sample.

B.1.6 Gas sampling
1. Install empty in-line filter and solids collecting tube in sampling line.
2. Turn on pump of sampling unit.
3. Once reading is at steady state, log time.
4. Once sampling flow is negligible on analyser unit, log time.
5. Turn off pump of sampling unit.
6. Remove, empty and clean in-line filter and solids collecting tube.
Appendix B. Laboratory Roaster Procedures

B.1.7 Scrubber switchover (To be done every hour)

1. Open closed scrubber inlet valve.
2. Close previously opened scrubber inlet valve.
3. Note switchover time and solution cumulative time.

B.1.8 Shutdown

1. Once feed has run out, keep feeding with reaction gas for approximately 30 minutes.
2. Change furnace setpoints to 25 °C.
3. Change nitrogen flows to air flows.
4. If necessary, reduce gas flow to 0.25 m/s.
5. Open scrubber bypass valve.
6. Once the bed temperature is below 800 °C, slowly turn down fluidization gas.
7. Stop data acquisition recording.
8. Close nitrogen and oxygen cylinder main valves.

B.1.9 Emergency shutdown

1. Turn off furnaces and gases by pressing STOP button on power panel.
2. Turn off feeder by turning off the motor controller.
3. Close nitrogen and oxygen cylinder main valves.
4. The vacuum pump and water cooling should still be on.
5. Note that sulfur dioxide may still be present within the roaster.

B.2 Disassembly and cleaning

1. Make sure furnaces 1, 2 and 3 breakers are turned off.
2. Verify that bed temperature is less than 50 °C.
3. Vacuum bed particles:
   Bring vacuum bucket on top of roaster.
   Open solid sampling valve.
   Insert copper tube.
   Attach garden hose to copper tube and bucket.
   Attach vacuum hose to bucket.
   Start vacuum cleaner.
   Remove entire bed with copper tube. When bed empty, disassemble vacuuming assembly, remove copper tube from roaster.
   Split bed using rifle splitter into 2 portions.
   Take 1 portion and divide into 200-300 g samples for sieving and assaying.
Appendix B. Laboratory Roaster Procedures

4. Disconnect thermocouples, tubes and other connections:
   Disconnect thermocouples from furnace 1 (preheater).
   Disconnect pressure transducer line from furnace 1 (preheater).
   Disconnect gas inlet tubes (2).
   Disconnect control thermocouple from furnace 1.
   Disconnect pressure switch tube (place protecting plug on switch).
   Disconnect safety manometer (place protecting plug and cap).
   Disconnect feeder gas supply.
   Disconnect feeder inlet on roaster.
   Disconnect oxygen probe on preheater.

5. Raise furnace 2:
   Remove insulation above furnace 2.
   Remove 4 bricks (grid level, top, 2 front and 2 back).
   Install tracks.
   Raise furnace 2.

6. Remove distributor bricks.
   Stack on table using same positions as on setup.

7. Remove top bricks.
   Stack on table using same positions as on setup.

8. Open preheater furnaces:
   Install shelves.
   Remove clamping strips (both front and back).
   Slide each furnace half.

9. Lower preheater:
   With pallet jack, pallet and wood blocks, hold the preheater section so that the grid bolts can be undone.
   With impact wrench, remove bolts from the distributor plate:
   Use the impact wrench on the nuts and a wrench on the bolts.
   This may take a while if the bolts are stuck.
   A Johnson bar is available and a pipe to slide it in is also available to increase the torque.
   It may require several seconds for the bolts to come loose with the impact wrench.
   It works better if the bolt is held back with a wrench.
   It is a very good idea to wear gloves, to attenuate the vibrations to the hands.
   Once everything is unbolted, lower the preheater:
   This is done in steps, by removing some pieces of wood between the pallet and the preheater.
   Last lowering step: pallet, 1 level of blocks and the plywood sheet.
   Pick up the preheater when the bolts are on the edge and remove the bolts.

10. Clean preheater:
    Using empty vacuum attachment, remove any solids that are collected at the bottom.

11. Put yellow catch bucket on top of preheater under the roaster.
    The distributor plate should stick to the roaster and hold in place without any help.

12. Remove roaster top:
    Place bolt catch plate under the bolts.
    Unbolt the top using the impact wrench.
    Unbolt the pipe using 2 3/4" wrenches.
    Pick up the flange extension and two 1" gaskets using pan.
Appendix B. Laboratory Roaster Procedures

Using the crane and the roaster top eye bolt, move the top to the table:
First lift the top (only vertically) until the gasket is clear, which may stick then move north to the table.

13. Clean roaster top.
Collect accumulated dust using empty vacuum attachment.

14. Remove pipe
Loosely hold the pipe using the following chain assembly:
1 lifting chain
3 3/8 shackles
1 1/4 shackle
1 hook shackle
Install 1 3/8 shackle in one of the bolt holes of the upper flange.
Install the remaining 3/8 shackles on the end of the chain.
Install the 1/4 shackle at the appropriate place on the middle of the chain.
Pass the hook shackle in the 1/4 shackle.
DO NOT lift the pipe with the pipe still attached. It would move the baghouse and may break its outlet.
The baghouse and cooler location would have to be readjusted (time consuming).
Undo the 1/2" bolts.
When the bolts are removed, lift the pipe vertically, making sure that the chain lifts it vertically.
Move the pipe onto the table.

15. Clean pipe.
Collect accumulated dust using empty vacuum attachment.

16. Collect roaster top and pipe dust into an appropriate container.
Label adequately for identification: run number, material type: top and pipe accumulation.

17. Remove distributor plate:
The distributor plate may be stuck to the roaster.
Using large flathead screwdriver, wedge out the distributor.
Be careful not to spill any dust. A clean empty bucket may be used underneath to catch the grid and any dust as it falls.

18. Clean Roaster:
Install a clean empty bucket under the roaster opening (distributor plate location).
Using the 6" sweep, clean the top portion of the roaster.
Using the 4" sweep, clean the bottom portion of the roaster.
Make sure that any scale is removed.
A small stainless brush may be used to intensity the scrubbing at some locations.
This small brush may also be used to clean the transition section.
Using the vacuum cleaner, clean the tubes and port (dust around oxygen-sensors).

19. Clean distributor plate:
Remove any dust, scale deposits from the distributor plate.
Using the large steel brush, scrub the distributor plate.
Holes may be cleared from dust using stainless wire.
Be sure that ALL holes are clean.
Note distributor top and bottom. The bottom has a broken drill bit stuck in it!
Using the steel brush, clean the flange of the distributor (roaster and preheater).

20. Final cleanup prior to assembly:
Clean with wire brush the flange faces (preheater (4" flange), roaster (4" and 6" flanges).
Appendix B. Laboratory Roaster Procedures

Vacuum flanges.
Vacuum distributor plate.
Vacuum preheater bottom.

B.3 Reassembly

1. Install distributor plate:
   Obtain 2 copper 4" gaskets.
   Apply ceramic anti-sieze (Rock and Roll) on both sides of gaskets.
   Install first gasket on preheater.
   Install distributor plate, lining up the bolt holes, making sure the gasket does not move.
   Install second gasket on distributor plate, making sure of the adequate position.
   Prepare 8 5/8" nuts washers and bolts with nickel antiseize (neverseez pure nickel special):
   Be very generous with the antiseize, apply to both bolt and nut on all threaded surfaces.
   Apply to bolt shoulder.
   Apply to both sides of washer.
   Drop bolts in flange, roaster side.
   Using pallet jack, wooden blocks and spring rods, lift preheater into position, taking care of not overlifting.
   Assemble bolts.
   Adjust the height of the preheater base.
   Using impact wrench, tighten the bolts up to a maximum setting of 3 (not 4 or undoing the bolts next time may be impossible).

2. Assemble Preheater furnace:
   Slide each half into position.
   Install both locking plates (front and back).

3. Open freeboard furnace to remove top bolts:
   Note: insulation between the roaster and freeboard furnaces may need to be removed or replaced.
   Undo the front and back locking plates.
   Pull out each half of the furnace to clear the bolts.
   Remove the bolts for cleaning and nickel anti-seize reapplication.

4. Reinstall roaster top.
   Obtain 6" copper gaskets.
   Apply ceramic anti-sieze (Rock and Roll) on both sides of gasket.
   Install gasket on top of 6" roaster flange.
   Using crane, lift cleaned roaster top to top of roaster.
   Taking care to not move the gasket, align the bolts holes and insert bolts from the bottom.
   Hand tighten the nuts.

5. Reinstall outlet pipe.
   Reinstall outlet pipe using crane.
   Hand tighten the bolts connecting the pipe to the filter inlet.
   Hand tighten the bolts connecting the pipe to the roaster top.

6. Tighten all nuts and bolts from roaster top and pipe:
   In the following order:
   Tighten the flange between the pipe and roaster top.
   Tighten the flange between the pipe and filter inlet.
   Using impact wrench, tighten the bolts up of the flange between the roaster and roaster top to a maximum setting of 3 (not 4 or undoing the bolts next time may be impossible).
Appendix C
Data Acquisition Software

The data acquisition software was written in Borland C++ Builder V.5.0. Due to its size, the source code is not included in the thesis. However, it is available from the author. This appendix is therefore limited to a brief description of the various sections of the software.

C.1 Data acquisition

The software generates a thread to handle the data acquisition. The software communicates to the thread, and the thread handles the communication with the driver and updates the values in the software through an event once the list of unprocessed requests is empty. Every second, a timer event is generated to create a list of required readings and is sent to the acquisition thread. Once the list has been sent, the software recalculates and displays the required data. This process is efficient for reading every second. However, for the fast single-channel data acquisition (100 Hz), the thread pauses and the main thread of the software handles the fast acquisition.

Note that the acquisition frequency of the fast acquisition is set at 100 Hz, calibrated using a frequency meter.

C.2 Database

The database file is a typical Borland Paradox file which is created using the database menu. Note that the file must be closed before turning the computer off. If the computer crashes, reboots or is turned off while recording, the entire database file (entire run) may be lost.
Appendix C. Data Acquisition Software

C.3 Thermocouples

C.4 Pressure transducers

There are currently two types of differential pressure transducers (4-20mA and 1-6V). The software does not distinguish between each type except by the calibration used. The output, converted into mmH2O, is saved to the database. Using the value of each pressure transducer and the configuration saved in the initialization file, the software calculates the various pressure drops and pressures. These values are also saved in the database file.

C.5 Oxygen sensors

The values in mV are recorded in the database file.

C.6 Gas analyzer

The Horiba gas analyzer outputs a 4-20mA signal for each gas analyzed ($O_2$, $SO_2$, $CO$, $CO_2$, $NO_x$). The signal is converted to volts using a 1% precision 250 $\Omega$ resistor. The second data acquisition board (DAS-8JR-AO) is used to digitalize the signal. The digitalized signal is converted to either ppm or $\%$, displayed and saved to the database.

C.7 Controllers

C.7.1 Temperature Controllers

The software communicates with the temperature controllers using a RS-485 line and the MOD-BUS protocol. Setpoint can be changed using the software menu or by double-clicking on the appropriate controller display. The software requests the current temperature, setpoint temperature and power output from each controller. This information is saved in the database. The current setup can be extended by additional controllers. However, the software requires the addition of controller display components and recompilation.

The software generates a thread to handle the RS-232 communications. The software commu-
データ収集ソフトウェア

インタフェースはスレッドと通信し、スレッドは通信を処理し、イベントを通じてソフトウェア内の値を更新します。

C.7.2 配管コントローラ

配管コントローラの基本的な説明は、Appendix Aで概説されています。

C.8 ソレノイドバルブ

現在のソフトウェアは、流化および洗浄ガスの主な緊急シャットオフバルブとして使用される3つのソレノイドバルブを制御し、ガスフィルタバックパルスの3つのソレノイドバルブを制御しています。緊急シャットオフバルブは、マニュアルにかかわらず自動的にソフトウェアを使用して開閉されます。これらのバルブは、電力障害、反応器オーバーパッキング（硬質プレススイッチを使用）または温度コントローラーの警告（ハードウェア）の発生時、自動的にオフになります。最後にスイッチされた出力は、配管コントローラにリンクされます。バルブは、主電源スイッチがローティングされている場合にオフにすることはできません。
Appendix D
Experimental Apparatus Schematics
Figure D.1: Experimental apparatus - Reactor
Next To Electrical Panel

From Building Water
To Building Water Drain
From Building Air

Gas Cooler

IN
OUT

Regulator

Solenoids (3)
Compressed Air
For Cleaning Pulse

To Ventilation Duct

Vacuum Pump
Vacuum Adjust Valve

Main Gas Panel

Sampler Purge
Pneumatic Feeder
Bed Purge Filter Purge
Non-Reactive Gas
Reactor Gas

Flexible Gas lines:
Between Rotameter and
Nitrogen or Air or Oxygen

Emergency Shutoff
Solenoids (3)

Nitrogen
Air
Oxygen

From Nitrogen Cylinder
From Oxygen Cylinder

Figure D.2: Experimental apparatus - Fluid connections
Appendix D. Experimental Apparatus Schematics

Figure D.3: Experimental apparatus - Pressure connections
Appendix D. Experimental Apparatus Schematics

Figure D.4: Experimental apparatus - Power connections
Material List (316 SS)

28" 4" Pipe Sch 40
2 4" 150 lbs Slip On Flanges
2 1/4" NPT Half couplings
2 1/2" NPT Half couplings
2 3/4" NPT Half couplings

Flange Holes - Coupling Orientation

Top Flange - Seen from pipe side

Bottom Flange - Seen from pipe side

Mini Roaster - Preheater Details

By: Pierre Constantineau - Ph.D. Student - (604)-822-2913
UBC Chemical Engineering, AMPEL, 2355 East Mall, Vancouver, B.C.

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<th>STATUS: Ready for Welding</th>
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Figure D.5: Fabrication drawing of preheater section
Appendix D. Experimental Apparatus Schematics

Material list (316 SS)
14.5" 6" Pipe Sch 40
26"  4" Pipe Sch 40
1  6" 150 lbs slip on flange
1  4" 150 lbs slip on Flange
1  6"x4" Reducer Sch 40 Concentric
6  1/4" NPT Half coupling
2  1/2" NPT Half coupling
2  3/4" NPT Half Coupling

Flange Holes - Coupling Orientation
Top Flange - Seen from pipe side
Bottom Flange - Seen from pipe side

Mini Roaster - Reactor Details
By Pierre Constantineau - Ph.D. Student - (604)-822-2913
UBC Chemical Engineering, AMPEL, 2355 East Mall, Vancouver, B.C.

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Figure D.6: Fabrication drawing of roaster section
Materials
End Plugs: 316 or 310SS
Tube: 1"x0.035" wall 316SS Tubing
Assembly
Insert Plugs in tube on side shown
TIG Weld the plugs on circumference

Sampling Cups (1 of each)
Zinc Fluidized bed Roaster
Pierre Constantineau (2-2913)

Figure D.7: Fabrication drawing of solid samplers
Figure D.8: Layout of distributor plate holes. 37 3/64" holes on a 0.6134" hexagonal grid. Material: 1/4" 316 stainless plate cut to 4" standard flange dimensions
Figure D.9: Fabrication layout of copper gaskets. 6": 8.5" OD, 6.5" ID; 4": 6.5" OD, 4.57" ID; 1": 2.5" OD, 1.367 ID.
Appendix E
Sulfur Dioxide Scrubbers

E.1 Overall scrubbing reactions

The sulfur dioxide (SO₂) scrubbers are based on the neutralization of a sodium hydroxide solution to produce sodium sulfide and bisulfite. The system is somewhat complex, but can be summarized by the reactions [116]:

\[
SO_2 + H_2O = H_2SO_3 \quad -26 \quad kJ/mol
\]
\[
2NaOH + H_2SO_3 = Na_2SO_3 + 2H_2O \quad -138 \quad kJ/mol
\]
\[
Na_2SO_3 + H_2SO_3 = 2NaHSO_3 \quad -8 \quad kJ/mol
\]

The first reaction produces sulfurous acid. This acid is neutralized with the sodium hydroxide already present in solution. This first neutralization produces sodium sulfite and is very exothermic. The complete neutralization of sodium hydroxide forms a solution of sodium sulfite which is still basic (pH>7). If more sulfur dioxide is introduced, the sodium sulfite reacts to produce sodium bisulfite. Once the sulfite is completely reacted to bisulfite, no more sulfur dioxide can be scrubbed from the gas.

The sulfite species are less thermodynamically stable than the sulfate species. The sulfites react with dissolved oxygen to produce sulfates. However, this reaction is very slow compared with the rate of SO₂ capture.

Assuming complete conversion to sulfur dioxide, each mole of zinc sulfide (32.9 wt% S) requires 1 mole of sodium hydroxide to produce sodium bisulfite. Therefore the minimum requirements are 411 g NaOH per kg of ZnS. Most zinc concentrates contain less sulfur than pure zinc.
Appendix E. Sulfur Dioxide Scrubbers

sulfide, therefore leading to excess scrubbing capacity.

It was observed that the first scrubbing step (production of Na$_2$SO$_3$) is very exothermic. To help control the evaporative losses of water, the gas is sent to one of the scrubbing tanks for an hour and switched to the second tank for the next hour while the first one cools. The flow is then alternated every hour until the end of the run.

### E.2 Strength of the caustic solution

The strength of the scrubbing solution must be chosen carefully so that operational problems are eliminated. If the solution is excessively diluted, a large volume of solution is required for a single run. If the caustic (NaOH) concentration is excessive, hydrated sodium sulfite may precipitate. This phenomena has been observed and was responsible for the catastrophic failure of run 3. X-ray diffraction on dried precipitates have shown that the precipitates were pure sodium sulfite.

In order to minimize the possibility of precipitation, the strength of the reacted sodium hydroxide solution must not exceed the solubility of the reaction products. Therefore, the maximum solution strength can be calculated using the solubilities of the various compounds formed during the reaction.

#### E.2.1 Solubilities of the various compounds

The solubilities of sodium sulfite and bisulfite were obtained from a manufacturer of sodium sulfite and bisulfite (Solvay Minerals). The solubility of sodium sulfate was obtained from the Kirk-Othmer Chemical Technology Handbook. Figure E.1 presents the solubilities of the reaction products as a function of temperature.

#### E.2.2 Solubilities expressed as caustic concentration

To find the appropriate sodium hydroxide concentration, the solubilities of sodium sulfite, bisulfite and sulfate can be expressed on a sodium hydroxide basis. Figure E.2 presents the NaOH concentrations required so that once it is completely reacted to the given compound,
Appendix E. Sulfur Dioxide Scrubbers

the solubility limit of that compound is reached. From this figure, one can see that if negligible sulfate is produced, the limiting compound, at room temperature would be sodium sulfite. Therefore, if one uses a sodium hydroxide concentration of less than 17 wt% NaOH (17g NaOH per 100g solution), no sodium sulfite would precipitate. 17% NaOH gives 24.5% Na₂SO₃.

The preparation of a sodium hydroxide solution is a very exothermic process. Therefore, very cold water should be used, the solid hydroxide must be added slowly to the solution, and adequate ventilation must be used. Thermodynamic calculations using HSC thermodynamic software [116] have shown that the temperature after dissolution of NaOH pellets in water to produce a 17 wt% NaOH solution is approximately 80°C.

E.3 Scrubbing efficiency

The scrubbing efficiency of the chemical scrubbers was not calculated. However, gas analysis of the scrubber outlet gas (10 l water, 2 kg NaOH, 1 tank) indicated at most 1500 ppm SO₂ during an entire experimental run. A small 2-l Erlenmeyer scrubber was used for gas sampling. The SO₂ content of the analyzed gas was negligible. No analysis was performed for sulfur trioxide. Sulfur trioxide, if present, would be scrubbed and form sodium sulfate. It is impossible to distinguish sodium sulfate formed from the scrubbing of sulfur trioxide or by the reaction of sodium sulfite with dissolved oxygen.
Appendix E. Sulfur Dioxide Scrubbers

Figure E.1: Solubility of compounds produced during SO$_2$ scrubbing using NaOH solutions

Figure E.2: NaOH concentration to reach maximum solubility of the compounds produced during SO$_2$ scrubbing
Appendix F
Detailed Experimental Results

F.1 Assay from independent laboratory

Table F.1 presents the assay of the three concentrates. Zinc was assayed by wet titration and the two sulfur assays were performed by a gravimetric method. Table F.2 presents the ICP assays of the concentrates, sands and a few samples that required assays for titanium. The samples were prepared by multi-acid digestion.

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<th>S(tot) (wt%)</th>
<th>S(SO4) (wt%)</th>
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<td>29.83</td>
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### Appendix F. Detailed Experimental Results

#### Table F.2: ICP Assay of zinc concentrates, sands and some experimental samples

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<th>As ppm</th>
<th>Ba ppm</th>
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325