MODELING THE KINETICS OF THE ZINC PRESSURE LEACHING PROCESS – OXIDATIVE SPHALERITE LEACHING IN SULPHURIC ACID MEDIA

by

Devy Alexander William Dyson

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Abstract

In the field of hydrometallurgy, the industrial uptake of leaching models has been overlooked partially due to the lack of universal models. A model developed for one plant cannot easily be transferred for the application of a different plant without redesigning the leaching kinetics in the code. The Multiple Convolution Integral (MCI)-based model developed in this thesis has the ability to be universally applied by user-controlled inputs. Chemical reactions can be selected while the modeling software calculates the mass and energy balances. Residence times, operating conditions, and the rate-limiting reagents can also be defined to calculate a precise fraction reacted (leach extent) for sulphide minerals. The ability of the using the MCI model for predicting sphalerite leaching is examined in comparison to hydrometallurgical plant data collected from a Canadian pressure leach operation. The results are promising, showing that the model can predict plant Zn extraction data to within an error of 1.5 %. The model is further verified through bench scale pressure leaching experiments where 94 % of the zinc is extracted within 90 minutes using a concentrate sample from the same industrial plant. The effect of temperature is analyzed and the activation energy is calculated to be 40.8 kJ/mol. Interesting discoveries with respect to the reagent concentrations and their effect on the overall fraction reacted are also explored from the model results. In addition, the limitations of the MCI model are explained along with suggestions for improvement.
Lay Summary

Metal content in ores are declining globally, making metal extraction more difficult. Increased plant efficiencies are required to keep the process profitable while maintaining an affordable metal price for the market.

Process control is a major contributor to plant efficiency. Computer simulation is a useful tool that can improve the process control by predicting plant performance; it can be used as a job aid and enhance the knowledge of the operators. In this thesis, the model developed predicted how much zinc could be dissolved in an acidic solution. Data taken from an industrial plant verified the model results along with additional experiments performed in a laboratory setting. Variables that affect the dissolving rate were investigated to give the industry better quality control. The accuracy of the results allows the industry to benefit economically.
Preface

This thesis is the result of the original, independent and unpublished work by the author, Devy Alexander William Dyson.
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Dedication

This thesis is dedicated to my parents for their unconditional support.
Chapter 1: Background and Introduction

Modeling Background
Oxidative leaching is a critical step in the processing of ores, and it is necessary to include both the thermodynamics and kinetics of this process in a model to optimize the leaching conditions. Such a model can evaluate the parameters inside a leaching reactor and can determine the impact of many variables within this complex process. In the past, many researchers have focused on developing leaching models. Among them, Dixon introduced a new method for modeling multistage continuous leaching reactors known as the multiple convolution integral (MCI) in 1996. However, the industrial uptake of these leaching models has been slow for the following reasons:

i) Interpretation of model results and their implications can be difficult and

ii) Leaching models have been coded for a specific plant and cannot be applied easily for other plant conditions without reprogramming the code.

As leaching is a critical step in metal extraction, there is a need for accurate models to describe the chemical phenomena in order to produce an efficient design and operation of a hydrometallurgical plant (Crundwell, 1995). Process control can be improved with an accurate model simulation, giving operators the capability to respond to upsets with more precision. Producing an accurate model also benefits capital planning, as the scale up of equipment from a pilot plant to a full industrial plant can be predicted more easily. The complexity of the model is also critical for determining the sensitivity of the leach extractions to the ore particle size distributions and the reagent concentrations. Utilizing a simpler model would not allow for accurate extraction predictions with fluctuating parameters and the overall process would not be as well understood. A fundamental model is necessary: the ore particle size distribution, the residence time distribution, the particle kinetics and thermodynamics must all be included, which is demonstrated by the MCI model developed in this study. Accurate is defined in this thesis as a predicted model result within a 5% error of the industrial or experimental data.
The benefit of utilizing the MCI model is that it allows for accurate leach extractions to be calculated with relative ease. The population balance model also provides excellent predictions of leach extents in hydrometallurgy (Baldwin et al., 1995; Crundwell, 1995; Crundwell & Bryson, 1992). However, they are more difficult to implement due to increased complexity, and can lead to more difficult interpretation of results. The more basic segregated flow model is also a suitable option for modeling the leaching kinetics, but the simplicity hinders the accuracy of the model. The segregated flow model assumes that the individual compartments or tanks of a leaching system are treated as an entire reactor. Any conditions changing between compartments are unaccounted for, which is problematic and affects the accuracy of the model predictions considerably. The MCI model is different from the segregated flow model because it uses the convolution integral to solve for the fraction reacted with conditions varying in each compartment. Therefore, the MCI incorporates the advantages of both the population balance and segregated flow models. The precision of the MCI model predictions compare well with the population balance models while maintaining the ease of application associated with segregated flow models (Dixon, 1996).

**Zinc Pressure Leaching Background**
Zinc is a common base metal that is consumed around the world. Over the last 30 years, the world zinc consumption has grown by over 3 million tonnes per annum (R. Sinclair, 2005). The demand for zinc has increased through brass alloy production, diecasting alloy production, and steel galvanizing. Zinc oxide is also used in rubber production, fertilizers, and the pharmaceutical industry. With the increasing demand for zinc and the declining ore grades, metal extraction efficiency has become paramount in the industry. For this purpose, using pressure oxidative leaching at elevated temperatures inside an autoclave to dissolve the metals of interest has become increasingly common. In the case of zinc pressure leaching, autoclaves operate at an elevated pressure of 90 psi above the vapour pressure, or around a total pressure of 150 psi with a temperature of 150 °C. The elevated pressure serves two purposes: first, to allow the temperature of the solution to increase above the ambient boiling point; second, to aid the reaction kinetics by increasing the solubility of oxygen. The reaction of importance is the sphalerite
conversion to soluble zinc sulphate. This conversion can occur in two methods: the ferric leaching of zinc sulphide and the reaction of zinc sulphide with sulphuric acid. The former is kinetically favourable in comparison to the latter. Also, non-oxidative leaching can occur with the reaction of sphalerite and sulphuric acid alone. However, this reaction would not proceed as easily as the others due to the oxidative environment created within the vessel (Yan et al., 2010). These reactions occurring in the autoclave are listed in Equations (1-4) (Chalkley et al., 1993). Usually, the soluble iron is contained within marmatite [(Zn,Fe)S]. However, the source of iron for the concentrate in this study originates from pyrrhotite, pyrite and chalcopyrite. When sulphide minerals are oxidized, the temperature is critical as liquid sulphur becomes viscous when it undergoes phase changes at temperatures above 150 °C (Peters, 1992). However, an advantage of having sulphides in the feed is that the oxidation of these minerals provides heat, which helps to maintain reactor temperatures. The first compartment of the autoclave is usually extended in comparison to the remaining compartments to ensure adequate amounts of the sulphides are oxidized and to generate heat.

\[
\begin{align*}
ZnS + H_2SO_4 + \frac{1}{2}O_2 & = ZnSO_4 + S^0 + H_2O \quad (1) \\
2FeSO_4 + H_2SO_4 + \frac{1}{2}O_2 & = Fe_2(SO_4)_3 + H_2O \quad (2) \\
ZnS + Fe_2(SO_4)_3 & = ZnSO_4 + 2FeSO_4 + S^0 \quad (3) \\
ZnS + H_2SO_4 & = ZnSO_4 + H_2S \quad (4)
\end{align*}
\]

The solids exiting the autoclave consist of unleached material and precipitates, which are then separated from the remaining zinc metal ion solution before neutralization. It is more effective if the discharge solution is near neutral pH, as lower operating costs result from using less lime or limestone for neutralization. Industrial zinc plants can achieve this by installing a two-stage pressure leaching system, where a low acid leach (LAL) is utilized in the first autoclave followed by a high acid leach (HAL) in the second autoclave. The discharge from the HAL is thickened and the pregnant leach solution is re-circulated to the LAL where a lower acid concentration will be exiting the autoclave for neutralization and purification (Sinclair, 2005). Figure 1 shows an entire zinc processing flow sheet for
Hudbay Minerals Inc.’s Flin Flon plant modeled in this thesis (Mirzoev & Bodnarchuk, 2015). The unit operations are referred to frequently throughout this work. The operating conditions are important aspects of any leaching process as they play a vital role in the reaction kinetics and thermodynamics; they must be defined prior to calculating the leaching rate. In summary, there must be an understanding of the autoclave operating conditions, the inputs and outputs, and the reactions occurring to accurately model the reactor.
Figure 1: Zinc Plant Flow Sheet – the Flin Flon plant operations has a two-stage pressure leach with recirculating loads of the filtrate. The entire operations are shown to the end process of casting done on site (Mirzoev & Bodnarchuk, 2015). Printed in August 2015 Conference Proceedings. Reproduced with permission from the Canadian Institute of Mining, Metallurgy and Petroleum.


Objectives

The significance of this study is of great industrial relevance. Operators and engineers are searching for improved process control and plant efficiency. This thesis focuses on the low acid zinc pressure leaching conditions, and it also examines the ability of utilizing the MCI model to predict the leach extents. The goal is to enable the important parameters to be selected by the user while the leach code solves the kinetics. Accurately modeling the leaching kinetics is also a challenge, as the chemical system is complicated and requires a substantial understanding before attempting to mathematically represent the process. The MCI model developed in this work allows the user to define a set of input parameters that can account for different plant conditions and various types of leaching phenomena, hence, creating a workable universal model that can accurately predict industrial data. Improving the workability would hopefully encourage further applications of leaching models that could contribute strongly to higher extraction targets and thus positively affect the revenue generated by the plant. Industrial data from a Canadian hydrometallurgical plant was compared to the simulated predictions from the MCI model for validation of the results. In addition, bench scale pressure leaching experiments were also performed to further verify parameters in the model. This MCI model was constructed using the CADSIM simulation software provided by Aurel Systems Inc. The software enables the user to select the reactions occurring in the vessel and calculates the mass and heat balances of the MCI model while solving for the leach extractions simultaneously.
Chapter 2: Literature Review

Zinc Processing History
Zinc was first produced in China and India around the 14th century using pyrometallurgy to reduce zinc oxide with carbon. The vaporized zinc metal was then collected via condensation. This same process started in Europe around the 18th century and was continually improved. It was not until the beginning of the 20th century that the hydrometallurgical processing of zinc was developed. The hydrometallurgical process is now well established producing over 80% of the world’s zinc. Depending on the ore, different hydrometallurgical routes have been developed for the production of zinc. The majority of zinc found in ores is present as zinc sulphide (ZnS) (Sinclair, 2005).

A typical processing route for zinc sulphide ores is the Roast, Leach, Electrowin (RLE) process. Zinc sulphide is oxidatively roasted at 900-1000 °C to form a zinc oxide and sulphur dioxide gas. The latter can be converted to sulphuric acid for leaching. The zinc oxide can be leached to soluble zinc sulphate in downstream processing.

\[
ZnO + H_2SO_4 = ZnSO_4 + H_2O
\]  

(5)

Unfortunately, this roasting process also converts any iron sulphides to oxides and these may form compounds with zinc producing a zinc ferrite. These zinc ferrites are difficult to leach; atmospheric leaching requires strong sulphuric acid solutions and elevated temperatures. More aggressive leaching stages are required and an additional iron removal stage is useful in eliminating any iron present that could interfere with other downstream processes.

The zinc sulphide can also be leached directly using an autoclave at an increased temperature and pressure, converting the zinc sulphide into elemental sulphur and soluble zinc sulphate. The elemental sulphur can be recovered and used for sulphuric acid production as well. The advancements in technology to reproduce sulphuric acid while minimizing the production of gases that are environmentally damaging have increased
the overall use of pressure leaching (declining ore grades have also contributed to this). No roasting stage is required in the autoclave direct leaching method. However, the leaching kinetics are more complicated and harder to control, as the temperature must be regulated precisely. This creates an incentive to model the process accurately, as there is a potential for a greater economic gain and overall efficiency of metal extraction through pressure leaching (Crundwell, 1995). Before modeling the overall leaching kinetics, experimental data is utilized to compare against certain micro models for leaching. These micro models can describe the particle leaching kinetics if the data fits well. Once a micro model is determined, a complete leaching model can be developed. The shrinking sphere micro model often describes the pressure leaching kinetics of reactions in autoclaves (Levenspiel, 1972). However, there are many proposed micro models to describe leaching, some of which will be described in the following sections.

**Shrinking Core**

This model assumes that the surface of the particle is reacting to form a product layer while the unreacted core continues to shrink with time. The leaching rates are dependent on the mass transport through the film layer to the particle surface, the transport through the product layer and the rate of reaction on the surface of the unreacted core.
Leaching reactions can be activation controlled or diffusion controlled depending on which phenomena is limiting. If the two phenomena are equal in magnitude, then the reaction is said to be under mixed control. The rate controlling process is important and dictates which model the leaching follows.

If mass transport through the film layer is controlling the rate of reaction, the leaching reaction is diffusion controlled. The reagent concentration will essentially be zero at the surface of the core since most of it is taken up through the film layer. It is possible to express the leaching rate as the rate at which the solid particle $S$ disappears.

\[
-r_S = - \frac{1}{4\pi R^2} \frac{dN_S}{dt}
\]  

(6)

This rate of disappearance of the solid $S$ can be related to the rate of reagent use, as seen in Equations (7-10).
\[ -r_R = -\frac{S}{4\pi R^2} \frac{dN_R}{dt} \]  

(7)

\[ = -S \cdot j_R^\text{Surface} \]  

(8)

\[ = (S)k_i(c_\text{R}^\text{Solid} - c_\text{R}^\text{Surface}) \]  

(9)

\[ = (S)k_i c_\text{R}^\text{Solid} \]  

(10)

\[ = \text{Constant} \]  

(11)

\[ k_i : \text{mass transfer coefficient between the solid and liquid phases (m/s)} \]

Using the density of the solid and the core volume, it is possible to relate to the moles of the solid present.

\[ N_S = \rho_S V_{\text{core}} \]  

(12)

\[ -dN_S = -\rho_S dV_{\text{core}} \]  

(13)

\[ = -\rho_S d\left(\frac{4}{3} \pi r_{\text{core}}^3\right) \]  

(14)

\[ = -4\pi \rho_S r_{\text{core}}^2 dr_{\text{core}} \]  

(15)

\[ \frac{1}{4\pi R^2} \frac{dN_S}{dt} = -\frac{4\pi \rho_S r_{\text{core}}^2}{4\pi R^2} \frac{dr_{\text{core}}}{dt} \]  

(16)

\[ = -\rho_S \left(\frac{r_{\text{core}}}{R}\right)^2 \frac{d}{dt}(r_{\text{core}}) \]  

(17)
The left hand side of the equation is equal to a constant, \((S)k_iC_R^{solid}\). If the right hand side of the equation is collected in terms of \(r_{core}/R\), it is possible to simplify these units to a single variable \(\alpha\).

\[
(S)k_iC_R^{solid} = -\rho_s\alpha^2 R \frac{d\alpha}{dt}
\]  

(18)

Collecting like terms and integrating with respect to \(t\) and \(\alpha\), the resultant expression is shown in Equation (19).

\[
1 - \alpha^3 = \frac{3(S)k_iC_R^{solid} t}{\rho_s R}
\]

(19)

It is important to note that \(\alpha\) can relate to the fraction of the particle left, or the fraction unreacted.

\[
1 - X_S = \frac{V_{core}}{V}
\]

(20)

\[
= \left(\frac{r_{core}}{R}\right)^3
\]

(21)

\[
= \alpha^3
\]

(22)

\[
1 - \frac{3(S)k_iC_R^{solid} t}{\rho_s R} = \alpha^3
\]

(23)

\[
1 - \frac{3(S)k_iC_R^{solid} t}{\rho_s R} = 1 - X_S
\]

(24)

\[
1 - \frac{6(S)k_iC_R^{solid} t}{\rho_s D} = 1 - X_S
\]

(25)
\[ 1 - \frac{t}{\tau_t} = 1 - X_s \quad (26) \]

\( t \): time step (min)

\( \tau_t \): time required to completely leach a particle of size \( D \) (min)

\( D \): particle size diameter

Substituting \( \tau_t = \frac{\rho_s D}{6 k_t C_R^{\text{S\text{olid}}}} \) in Equation (26) allows for the calculation of the fraction unreacted at specific time steps \( t \) in comparison to the total time required to completely leach a particle of size \( D \) for leaching.

This derivation is useful in understanding how to relate the volume of a shrinking core and the leaching times required with quantitative resistances of mass transport. However, once the porous product layer develops, there is no chance of the reaction being diffusion controlled through the film layer, as there is much more resistance through the product layer as it thickens (Levenspiel, 1972).

**Parabolic Leaching**

In the case where the product layer is controlling the reaction by resisting diffusion, or diffusion controlled leaching through the product layer, then the reagent concentration does not change through the film layer. Instead, the reagent is taken up through the diffusion within the product layer. The concentration of the reagent at the surface of the core is essentially zero as the reaction on the surface is fast if diffusion is the limiting process. The leaching rate can be quantified by the disappearance of the reagent in a similar method to the last example. The final result is shown in Equation (29).

\[ 1 - \frac{\frac{6(S)k_t C_R^{\text{S\text{olid}}}}{\rho_s D} t}{\tau_d} = 3(1 - X_s)^{2/3} - 2(1 - X_s) \quad (27) \]

\[ 1 - \frac{t}{\tau_d} = 3(1 - X_s)^{2/3} - 2(1 - X_s) \quad (28) \]
\[ 1 - X_S = \left( \frac{1}{2} + \cos \left( \frac{\psi + 4\pi}{3} \right) \right)^3 \quad \text{where} \quad \psi = \cos^{-1} \left[ 1 - 2 \left( 1 - \frac{t}{\tau_d} \right) \right] \quad (29) \]

\( \tau_d \), the time required to completely leach a particle of size \( D \), contains the parabolic particle size relationship.

\[ \tau_d = \frac{\rho_S D^2}{24(S)D_R^e C^B_{R bulk}} \quad (30) \]

The effective diffusion through the product layer pores is \( D_R^e \) and the \( C^B_{R bulk} \) is the bulk concentration of the reagent. The relationship between the residence time and the particle size is parabolic; the leaching time is proportional to the particle size squared. Graphing the \( 3(1 - X_S)^{2/3} - 2(1 - X_S) \) term against time is a quick method to determine whether the leaching is parabolic; if a straight line is observed, the leaching is parabolic. The slope of this line is equivalent to \( 1/\tau_d \).

**Linear Leaching**

When the surface reaction on the core of the particle is rate controlling, the leaching is activation controlled. The concentration of the reagent will be the same through all layers of the particle, but will be zero across the core of the particle. The bulk concentration of the reagent will be equal to the available reagent to react on the surface of the core. The same steps are taken for the derivation of the equation to relate the residence time to the particle diameter and fraction unreacted. The result is a linear relationship between the residence time and the particle diameter, as seen in Equation (31).

\[ \tau_S = \frac{\rho_S D}{2(S)k_S * f(C^B_{R bulk})} \quad (31) \]

\[ 1 - X_S = \left( 1 - \frac{t}{\tau_S} \right)^3 \quad (32) \]

\( k_S \): rate constant for the activation controlled reaction
\( f(C_R^{Bulk}) \): a known function of the concentration of the reagent in the bulk for the reaction rate at the surface of the core

Similar to parabolic leaching, if \( 1 - (1 - X_S)^{1/3} \) is plotted against time and a straight line is the result, the leaching is linear. In linear leaching, the time required to leach the particle is directly proportional to the particle size.

**Mixed Control**

If the leaching reaction is under mixed control, each of the transport steps is a resistance to the overall leaching rate. An equation that quantifies the leaching rate with all of the resistances taken into account is seen in Equation (35).

\[
\tau_l \approx \tau_d \approx \tau_S
\]  (33)

\[
\tau = \tau_l + \tau_d + \tau_S
\]  (34)

\[
\tau - t = \tau_l (1 - X_S) + \tau_d \left[3(1 - X_S)^{2/3} - 2(1 - X_S)\right] + \tau_S (1 - X_S)^{1/3}
\]  (35)

The film layer and product layer mass transport are exemplified by the first and second terms respectively on the right hand side of the equation; hence, if the second term is the largest, the leaching rate is considered to be product-layer diffusion mixed controlled and if the third term is the largest, the leaching rate is considered to be film-layer diffusion mixed controlled. The shrinking rate of the particle due to the surface reaction is shown by the last term on the right hand side of the equation; if this term is the largest, then the leaching rate is considered to be surface reaction mixed controlled (Levenspiel, 1972).

**Shrinking Sphere**

When the reaction does not produce a porous product layer, the particle size decreases with time. This is the case for shrinking sphere micro models where there is only a film layer and the particle itself. As the reagent reacts with the particle surface, products are formed that are aqueous and dissolve into solution.
Film Layer Controlled Leaching

Diffusion controlled reactions are limited by the film layer as in the shrinking core micro model; however, the particle size decreases in the shrinking sphere micro model, meaning that the mass transport is decreasing as well. Therefore, a mass transfer coefficient must be derived that relates to the particle size. This is performed by assuming that the particles in the leaching tank are ground fine enough to be in free-fall within the solution, granted that the pulp densities are relatively low. Fluid flow equations such as the Reynolds number, Sherwood number, and the Schmidt number are utilized to solve for the mass transfer coefficient. The Reynolds number \( Re \) is a dimensionless ratio that determines whether a fluid follows turbulent or laminar flow, as it compares the inertial forces to the viscosity of the particular fluid (Levenspiel, 1972). The Schmidt number \( Sc \) is also a dimensionless ratio that compares the momentum to the mass diffusivity. Combining the Schmidt and Reynolds number in an equation gives the Sherwood number \( Sh \). The Sherwood number is simply an indicator of convective to diffusive mass transport, which is substituted in Equation (41) (Levenspiel, 1972). The terminal velocity at which particles fall in the leaching tanks is assumed to follow Stokes’s law, where the viscous forces dominate over the inertial forces. This is valid only if the Reynolds number is less than one, which must be verified in order to use Equation (36) for the terminal velocity.

\[
v_t = \frac{d^2 g (\rho_S - \rho)}{18 \mu}
\]  

(36)

\[
Re = \frac{dv \rho}{\mu}
\]  

(37)

\[
Sc = \frac{\mu}{\rho D_R}
\]  

(38)

\[
Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} = \frac{k_l d}{D_R}
\]  

(39)
Using the terminal velocity in the Reynolds number equation, it is possible to solve for the mass transfer coefficient.

\[
\frac{k_i d}{D_R} = 2 + 0.6\left[\frac{d^3 \rho g (\rho_S - \rho)}{18 \mu} \right]^{1/2} \left[\frac{\mu}{\rho D_R} \right]^{1/3}
\]  

(40)

\[
k_i = \frac{D_R}{D \delta} (2 + 0.6 Re_D^{1/2} Sc^{1/3} \delta^{3/2})
\]  

(41)

\(g\): gravitational acceleration (m/s\(^2\))
\(\rho\): density of the fluid (kg/m\(^3\))
\(\rho_S\): density of the solid (kg/m\(^3\))
\(\mu\): reagent or fluid viscosity (Pa·s)
\(D_R\): mass diffusivity of the reagent (m\(^2\)/s)
\(D\): original particle size (m)
\(d\): characteristic length (m)
\(\delta\): \(d/D\)

Once the mass transfer coefficient has been related with the particle size, this reaction can be modeled by substituting the variables into Equations (42) and (43) below and numerically integrating to solve for the fraction unreacted.

\[
\tau_d = \frac{\rho_S D}{6(S)k_i C_{R_{Bulk}}}
\]  

(42)

\[
\frac{d\chi_S}{dt} = \frac{1}{\tau_d}
\]  

(43)

For general leaching solutions that are ionic, the Schmidt number is equivalent to 1000. If the Reynolds number is assumed to be small enough that the Sherwood number is equivalent to 2, then the fraction unreacted can be simplified to Equation (44).
Some examples of irreversible leaching reactions that are diffusion controlled through the film layer using the shrinking sphere micro model do exist, such as the leaching of gold with cyanide.

\[
4Au + 8NaCN + O_2 + 2H_2O = 4Na[Au(CN)_2] + 4NaOH
\]  

(46)

However, all reversible leaching reactions that follow the shrinking sphere micro model are diffusion controlled. The leaching of zinc calcine is an example of a reversible diffusion controlled reaction shown in Equation (5).

**Linear Leaching**

Linear leaching is the same as in the shrinking core micro model; the product layer does not play a role in the leaching rate of the shrinking core micro model since diffusion is not the controlling process. Therefore, the same equations apply for both the shrinking core and the shrinking sphere micro models. Linear leaching is activation controlled by the surface reaction. In this case, the products of the reaction do not form a porous product layer; they are simply released into the solution (Levenspiel, 1972). The pressure leaching of zinc sulphide is a classic example of linear leaching with the shrinking sphere micro model, as seen in Equation (1). Other examples include the pressure oxidation of pyrite and arsenopyrite. Mixed-control leaching reactions are the same as described in the shrinking core micro model for leaching.

In hydrometallurgical pressure autoclaves, surfactants such as lignosulphonate and Quebracho are added to avoid the sulphur from coating the particles. This prevents the leaching reagents from having to diffuse through a sulphur product layer and increases
the leaching rates. For this reason, the majority of concentrates that are leached in pressure autoclaves follow the shrinking sphere micro model.

Continuous leaching reactors can be described by three types of fundamental models: the population balance model, the segregated flow model, and the multiple convolution integral model. All of these models utilize either the shrinking core or shrinking sphere micro model to describe the reduction in particle sizes as the reaction takes place.

**Population Balance Model**

The population balance model incorporates different size distributions, reactivities, and compositions of the particles, as leaching is a particulate process rather than a homogenous process. The importance of the size distribution is taken into account by defining a function for the number of particles in a given volume with size ranges. The equation given for the population balance is shown by Equation (47).

\[
\frac{d[R(l,L)n(l,L)]}{dl} = \frac{1}{\tau} [n_f(l,L) - n(l,L)]
\]  

(47)

\(n(l,L)\): function for the number of particles in a given volume (number/m\(^3\))

\(\tau\): mean residence time (min)

\(R(l,L)\): shrinkage rate (m/min)

The size function \(n(l,L)\) covers the size of the particles in the feed and the reactor. Therefore, both the initial size range in the feed and the current size range in the reactor are accounted for. The boundary condition for this equation is that as \(l\) approaches infinity, the numerator of the equation approaches zero. The \(R(l,L)\) function is the rate of shrinkage and is calculated by either the shrinking core or shrinking sphere micro model. This is equivalent to the \(\frac{dN_S}{dt}\) term expressed as the shrinkage rate for the micro models in Equations (6-16) except with different units for Equation (47).
The population balance model has proven to produce comparable performance results to leaching processes in hydrometallurgical plants. For example, Teck’s zinc pressure leaching plant in Trail, BC has been successfully modeled by the population balance approach (Baldwin et al., 1995). These models will be discussed further in detail throughout this thesis.

**Segregated Flow Model**

For homogenous reactors, the segregated flow model assumes that the entering solution is segregated into small quantities that remain intact for the duration of the leach in the reactor. These segregated fluids act as their own batch reactor. In the case of heterogeneous reactors where particulate leaching models are developed, each particle is represented as a batch reactor. This is shown by Equation (48) below.

\[
1 - X = \int_0^\infty \{1 - X(t, L, [B]_t)\} m_f(L)f(t)dLdt 
\]

\(X\): fraction reacted  
\(L\): initial size  
\(B\): reactant  
\(t\): time  
\(X(t, L, [B]_t)\): batch conversion equation derived from integrating the mixed control model  
\(m_f(L)\): particle-size density of the feed on a mass basis  
\(f(t)\): residence-time density

\[
[B]_t = [B]_f - F_f \eta X(t, L, [B]_t) 
\]

\([B]_t\): concentration of B at residence time t  
\([B]_f\): concentration of B in the feed  
\(F_f\): molar concentration of the mineral in the feed
\(\eta\): stoichiometric factor

The solution mass balance is shown by Equation (49). The major assumption with the segregated flow model is that the concentration of the reactant, \(B\), remains unchanged. The exit concentration of the reactant is taken to be constant throughout the reactor. This explains why the particles are acting as batch reactors since the concentration of the reactant does not decrease over time (Crundwell, 1995).

**Multiple Convolution Integral Model**

The multiple convolution integral (MCI) model was developed in 1996 by David G. Dixon. This model is derived from the segregated flow model, but allows for more accurate model prediction results because the convolution integral accounts for the varying reagent concentrations between compartments. Therefore, different reactor constants can be defined for each compartment. The MCI remains dependent on the particle leaching kinetics, the particle size distribution, and the residence time distribution, as does the segregated flow model. The shrinking core, shrinking sphere, or a mixed micro model can all be represented in the MCI particle leaching kinetics. An overall fraction reacted is calculated as the result for a set number of compartments under the assumption that each compartment is ideally mixed (Dixon, 1996).

**Particle Leaching Kinetics**

Normally, the shrinking core or the shrinking sphere micro model describes the particle leaching kinetics (Levenspiel, 1972). If neither of these models accurately represents the leaching data, a mixed micro model can be derived where a combination of these two models is the solution. Most sulphide leaching systems are optimized by using dispersants to ensure that the leaching kinetics follow the shrinking sphere micro model; the prevention of viscous sulphur coating the ore particles reduces the overall resistance to the leaching reaction and is clearly beneficial (Safari, 2009). The atmospheric leaching of sphalerite follows the shrinking core micro model with a sulphur product layer being formed. It is only when the conditions of the leach are above the melting point of solid sulphur at 115 °C that dispersants can benefit the kinetics (Peters, 1992).
**Particle Size Distribution**

The Rosin-Rammler particle size density distribution (PSD) function has been widely used to accurately represent the size distribution of ore particles in mineral processing and metal extraction (Gonzalez et al., 2008). A PSD for the specific ore sample being leached is required for an accurate model in most cases, as the leaching rates typically depend on the particle size. Two Rosin-Rammler parameters can be determined from the PSD: the critical particle size, $D^*$ (or the 63.2 % passing size), and $m$ (the Rosin-Rammler exponent). These two parameters can describe the entire size distribution and are included in the MCI calculation for the fraction reacted. The Rosin-Rammler equation is shown below as Equation (50) (Rosin & Rammler, 1933).

\[
f(\xi) = m\xi^{m-1}\exp(-\xi^m) \quad \text{where} \quad \xi = \frac{D}{D^*}
\]  

(50)

$m$: Rosin-Rammler exponent  
$D$: particle size (microns)  
$D^*$: critical particle size, the 63.2 % passing size (microns)

The Rosin-Rammler parameter $m$ can then be calculated by Equation (51) (Randolph & Larson, 1971; Rosin & Rammler, 1933).

\[
\phi = \left(\frac{r^{(m+2)}_m}{r^{(m+1)}_m}\right)^\mu - 1 \quad \text{where} \quad \phi = \frac{\sigma^2}{\mu^2}
\]  

(51)

$\sigma^2$: variance of the particle size distribution  
$\mu^2$: mean of the particle size distribution

The particle size distribution data enables the calculation of $\phi$, which is then substituted into Equation (51) and used iteratively to calculate the Rosin-Rammler parameter $m$. Two variables are required to solve for $\phi$, the mean and the variance of the PSD. Slightly different methods have been developed to determine these variables. The most common method to use is the trapezoidal integration rule. The smallest value and largest value are
averaged between each interval of particle size in the PSD and are essentially integrated to determine the mean. The variance can then be calculated using Equation (52) below, where \( a \) and \( b \) are the lower and upper bounds of each specific size interval in the PSD respectively. After all of the size intervals have a variance calculated, they are summed together for the total variance. Once the mean and variance are determined, \( \phi \) is calculated and \( m \) is solved for in Equation (51).

\[
\int_{a}^{b} f(x)dx \approx (b - a) \left[ \frac{f(a) + f(b)}{2} \right]
\]  

(52)

**Residence Time Distribution**

Residence time distributions (RTD) can be represented by Poisson distributions, which are specialized forms of Gamma distributions (Dixon & Dreisinger, 2002).

\[
\lim_{N \to \infty} \frac{N(N\theta)^{N-1}\exp(-N\theta)}{(N-1)!} = \delta(\theta - 1)
\]

(53)

For an ideal mixed flow reactor, the RTD function for any single tank connected in series with subsequent tanks can be represented by Equation (54) (MacMullin & Weber, 1935).

\[
E(\theta_i) = \frac{\theta_i^{N-1}\exp(-\theta_i)}{(N-1)!} \quad \text{where} \quad \theta_i = \frac{t}{t_i}
\]

(54)

\( N \): number of tanks

\( t \): residence time (min)

\( t_i \): mean residence time of one tank (min)

The mean residence time of one tank or compartment is required. If the tanks or compartments have varying residence times, they can also be represented; a valuable asset of the MCI model which will be demonstrated in the following sections.
The Overall MCI Model

Combining all components of the model results in the overall MCI model equation given below in Equation (55) (Dixon, 1996). The particle leaching kinetics, particle size distribution, and residence time distribution are all represented respectively.

\[ 1 - \bar{X}_N = \int_0^\infty \cdots \int_0^\infty \left[ \prod_{i=1}^N \left( 1 - \frac{\sum_{i=1}^N \theta_i \kappa_i}{\xi} \right)^3 m \xi^{m-1} \exp(-\xi^m) \, d\xi \right] \prod_{i=1}^N \exp(-\theta_i) \, d\theta_i \tag{55} \]

\[ \kappa_i = \frac{t_i}{\tau^*} \tag{56} \]

\( \kappa_i \): global reactor constant of tank \( i \)

\( t_i \): mean residence time of tank \( i \) (min)

\( \tau^* \): time required to completely leach a particle of size \( D^*(\text{min}) \)

The global reactor constant, \( \kappa \), is a critical component of the MCI model. The parameter is similar to \( \theta \) in Equation (54), where the residence time is compared with the mean residence time of one tank. However, the global reactor constant describes the fraction of the mean residence time in one tank compared to the total leaching time required. Different values of \( \kappa \) can be calculated for each tank.

The complex integral derived in Equation (55) can be evaluated with the Gauss-Laguerre quadrature after transforming the integral. If \( \omega = \xi^m \), some of the terms in the equation can be redefined, and \( d\omega = d\xi^m = m \xi^{m-1} d\xi \). Equation (57) expresses this transformed integral.

\[ 1 - \bar{X}_N = \int_0^\infty \cdots \int_0^\infty \left[ \prod_{i=1}^N \left( 1 - \frac{\sum_{i=1}^N \theta_i \kappa_i}{\omega^{1/m}} \right)^3 \exp(-\omega) \, d\omega \right] \prod_{i=1}^N \exp(-\theta_i) \, d\theta_i \tag{57} \]

The transformed integral allows the Gauss-Laguerre quadrature to be applied with ease. Gauss-Laguerre quadrature solves integrals in the form of Equation (58). The result after
simplification is given in Equations (59) and (60) (Dixon & Dreisinger, 2002). The process is also outlined in the original MCI publication (Dixon, 1996).

\[
\int_0^\infty f(z) \exp(-z) \, dz \cong \exp(-a) \sum_{i=0}^{n} w_i f(z_i + a) \quad (58)
\]

\[
1 - \frac{1}{N} \cong \sum_{j(1)=0}^{J(1)} \cdots \sum_{j(N)=0}^{J(N)} w_j(1) \cdots w_j(N) \exp\left(-S^m\right) \sum_{k=0}^{K} w_k \left(1 - \frac{S}{(z_k + \sum_{m} z^m)^{1/m}}\right)^3 \quad (59)
\]

\[
S = \sum_{i=1}^{N} \kappa_i z_{j(i)} \quad (60)
\]

\(w\): weights of the Gauss-Laguerre function

\(z\): roots of the Gauss-Laguerre function

Gauss-Laguerre weights and nodes are used to solve the integral. The more weights and nodes used, the more accurate the result. In general, six weights and nodes result in an accurate integration to the fourth decimal place. An example of the weights and roots for the 6-point or up to a 16-point Gauss-Laguerre function has been shown previously (Dixon, 1996). The constants are substituted for the weights and roots in Equations (59) and (60). If computation time is not a concern, a maximum of 16 points can be used. The integration approximation is nearly perfect in this case.

**Zinc Pressure Leaching**

The autoclave generally has four compartments with the first being the largest. The feed is entered as a slurry to the first compartment along with acid, composed of spent electrolyte or fresh plant acid. The autoclave has the ability to add acid to any of the first three compartments simultaneously, if necessary. The autoclave is maintained at a temperature of 150 °C within 5 °C throughout all of the compartments to provide sufficient reaction kinetics while minimizing the viscosity of the molten sulphur (Peters,
The industry operates the autoclave below 155 °C to avoid the higher viscosities that occur above this temperature. Surfactants such as lignosulphonate and Quebracho are added to avoid the molten sulphur from coating the particles at 150 °C. A diagram showing the different components of the autoclave is shown below:

![Diagram of Autoclave Components](image)

**Figure 3: Autoclave Components – each compartment is sparged with oxygen (Baldwin et al., 1995).**

Each of the compartments has the ability to be oxygen sparged and agitated. Most of the oxygen is generally sparged in the first few compartments to promote sulphide oxidation early in the autoclave. The remainder can be distributed into the following compartments if necessary. The major processes that occur in the autoclave can be summarized by the following (Baldwin et al., 1995):

1. Oxygen mass transfer from the gas phase into solution
2. Mineral sulphide dissolution
3. Ferrous to ferric oxidation
4. Iron Removal via precipitation

**Oxygen Mass Transfer**
The oxygen mass transfer rate is heavily dependent on the oxygen mass balance and the oxygen mass transfer coefficient. The interfacial area is incorporated in the mass transfer
coefficient. Equation (61) describes the oxygen mass transfer rate below (Baldwin et al., 1995).

\[
OMTR = \frac{k_L a}{H} \left( P_{O_2} - P_{O_2,aq} \right) V_s
\]  

(61)

\( OMTR \): oxygen mass transfer rate (mol/min)
\( k_L \): mass transfer coefficient (cm/min)
\( a \): interfacial area (cm\(^2\)/cm\(^3\) or 1/cm)
\( H \): Henry’s constant (atm\( \cdot \)L/mol)
\( P_{O_2} \): partial pressure of oxygen in the gas phase (atm)
\( P_{O_2,aq} \): partial pressure of oxygen in the aqueous phase (atm)
\( V_s \): liquid volume in stage s (L)

Henry’s constant is a method of relating the oxygen partial pressure and the oxygen concentration in solution. Empirical formulas were developed from experiments to determine Henry’s constant. This allowed for the oxygen concentration in solution to be calculated for varying sets of solution compositions. However, research has shown that this linear relationship is only valid for oxygen partial pressures under 10 atm (Baldwin et al., 1995).

\[
HC_{O_2} = P_{O_2,aq}
\]  

(62)

This is a relatively simple method of calculating the oxygen solubility. Other authors have calculated the oxygen solubility by using Tromans’s model (Tromans, 1998). Tromans’s model also accounts for the solution composition by calculating a salting-out parameter. Tables in literature outline the constants and variables in determining this value (Tromans, 1998). Tromans’s model provides an accurate oxygen solubility value, but basing the oxygen concentration in solution purely from the oxygen solubility alone is not sufficient to determine the oxygen concentration in solution. Tromans’s model must be combined with a calculated oxygen mass transfer coefficient to determine the
oxygen concentration. Otherwise, the sulphide oxidation could be severely over predicted. Additional methods have also been developed to determine the oxygen concentration in solution once the solubility has been determined through Tromans’s model. It is possible to calculate the oxygen concentration with knowledge of the autoclave and impeller components in addition to the solution conditions (Calderbank, 1967). The calculations are rigorous, but have been studied extensively for multiphase systems (Dixon, 2007; Gormely, 1992; Hughmark, 1980).

**Sulphide Mineral Dissolution**

Zinc can be contained in sphalerite, ZnS, or marmatite, (Zn,Fe)S, as sulphide minerals. Sphalerite can be easily described by leaching models as shown earlier in this thesis, but the dissolution of marmatite, or iron-containing sphalerite is harder to predict. Authors in literature found there was a direct proportional linear relationship between the dissolution rate and the concentration of iron in the marmatite (Crundwell, 1988; Piao & Tozawa, 1985). A study performed by Perez and Dutrizac further confirmed this theory by collecting marmatite concentrates for leaching with iron contents ranging from 0.04 to 14.7 wt.% (1991); a linear relationship also resulted from the experiment. Initially, activation energies were determined for iron containing sulphides and compared with those for iron free sulphides and no difference was found. However, through further research, increasing iron content in sulphides resulted in decreasing activation energies. The activation energies did not drop past 50 kJ/mol for iron contents above 2 wt.%. This is surprising because the leaching reaction is found to be charge transfer dominated, or reaction controlled. Authors of the studies suggested that systematical errors may have been present and disrupted the data (Perez & Dutrizac, 1991). Therefore, if the activation energy is assumed constant, an equation to describe the dissolution rate of iron containing sulphides in a ferric iron solution is shown in Equation (63) below (Baldwin et al., 1995; Perez & Dutrizac, 1991).

\[
- \frac{dL}{dt} = 4.0925 \times 10^6 [Fe^{3+}]^{1/2} (0.35 + 0.329 \times (% \text{ wt.} \text{ Fe}) \times \exp \left( - \frac{50,000}{RT} \right)
\] (63)

\[
\frac{dt}{dt}: \text{ the leaching rate (micron/min)}
\]
This equation has produced similar results with the same order of magnitude as observed in experiments mimicking actual zinc pressure leaching conditions (Baldwin et al., 1995).

**Ferrous to Ferric Oxidation**

The oxidation reaction of ferrous sulphate to ferric sulphate is dependent on the oxygen partial pressure fed to the autoclave. Cuprous also catalyzes the reaction and plays a role in the oxidation process. The reaction occurring for ferrous oxidation is shown by Equation (2). Experimental data taken in pressure leaching conditions is considered more accurate because ferrous speciation data suggests free ferrous is only present in small quantities (Filippou et al., 1993); Dreisinger and Peters developed an empirical equation for the ferrous oxidation shown by Equation (64) (1987).

\[
- \frac{d[Fe^{2+}]}{dt} = 4.0 \times 10^9 \times \exp\left(-\frac{80,300}{RT}\right) \times (1.0 + 5.0[Cu^{2+}])^{1/2}[Fe^{2+}]^2 \\
\times P_{O_2,aq} \times \left[(SO_4^{2-})'[H_2SO_4]^{-1/2}\right]
\]

\((SO_4^{2-})'\): The total sulphate subtracted by the sulphate associated with sulphuric acid

Alternatively, if plant data is available, the ferrous to ferric oxidation rate can be determined through an iron balance once the oxygen concentration in solution is known. In this case, the accuracy of the oxygen concentration in solution is significant and can drastically affect the results. However, this method of determining the ferrous oxidation rate has the potential to be more accurate in simulating an industrial autoclave. The oxidation rate would be based from plant data rather than empirical formulae developed in bench scale experiments, although the formulas developed have been proven effective in their corresponding solutions.

**Iron Removal**

Iron is precipitated during the leaching stages, which settles and requires filtration to remove in later operations. Three main types of iron compounds can form: jarosite,
goethite, and hematite. In the zinc pressure leaching process, the majority of the iron precipitates as jarosite, followed by goethite and finally hematite. The direct pressure leaching of zinc results in different precipitate compositions than in the atmospheric leaching conditions.

**Jarosite**

In atmospheric leaching, the leached zinc ferrite solution from the secondary leaching stage is neutralized with calcine to precipitate the jarosite out of solution. However, some zinc may be entrained in the precipitated jarosite. Hence, the zinc can then be recovered by an acid wash and sent back to the secondary leaching circuit. The remaining jarosite is then filtered to make a residue for usage or disposal. In the autoclave for the direct leaching of zinc, jarosite is also the most common iron precipitate formed because of the low concentration of acid discharged. The iron concentrations in the discharge are typically just above 2 g/L. An example reaction of jarosite precipitation in the case of ammonium jarosite is shown by Equation (65) below (Sinclair, 2005).

\[
3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12H_2O = (NH_4)_2Fe_6(OH)_{12}(SO_4)_4 + 6H_2SO_4 \quad (65)
\]

The ammonium can also be replaced with potassium or sodium. Since jarosite is not a marketable iron precipitate, some processes have been developed to dispose of the precipitates in an environmentally responsible way. One of the industrial processes employed is the Jarofix process, which incorporates jarosite residues into cement. Other methods include filling quarries from existing mines. Another process that has been examined is the transformation of jarosite to hematite using the hematite process. However, the process is difficult to justify economically and depends on the market for hematite.

**Goethite**

Goethite is an iron compound that can only be formed if the ferric concentrations in solution are less than 2 g/L. The leach solution from the RLE processing circuit contains around 30 g/L of ferric, thus the ferric iron must be reduced to ferrous to ensure that crystalline goethite is precipitated. Zinc sulphide concentrates are utilized to convert
ferric to ferrous and calcine is added to precipitate the goethite. Air sparging is used at low levels to maintain the ferric concentration to less than 2 g/L in a series of precipitation tanks. This is known as the Goethite process with the reaction shown in Equation (66) below.

$$2FeSO_4 + \frac{1}{2}O_2 + 3H_2O = 2FeO \cdot OH + 2H_2SO_4$$ (66)

Goethite precipitation can occur in one tank in order to adjust the ferric levels from over 30 g/L to below 2 g/L if a slow feed rate of the leach solution is maintained. This is known as the para-goethite process, where the iron reduction stage is eliminated by simply only allowing small amounts of the leaching solution and hence small amounts of ferric (under 2 g/L) to precipitate. It is harder to control the ferric concentration in this process and results in the precipitation of hydrated basic sulphate as well as goethite. The precipitate is less pure and contains higher levels of entrained zinc. The para-goethite reaction is similar to the goethite process reaction except more sulphuric acid is produced, which requires more calcine to neutralize as seen in Equation (67).

$$Fe_2(SO_4)_3 + 4H_2O = 2FeO \cdot OH + 3H_2SO_4$$ (67)

The losses of zinc are higher with the increased quantities of iron residue in this process.

**Hematite**

The hematite process reduces ferric to ferrous, as is performed in the goethite process, with zinc sulphides. An autoclave operates between 180 and 220 °C with the addition of oxygen to maintain the ferric concentrations at a low level. Pure hematite is produced this way, but if either the ferric or acid concentrations are too high, basic ferric sulphate is produced instead (Tozawa & Sasaki, 1986). Basic ferric sulphate is not very stable at atmospheric conditions and cannot be disposed of safely; hematite is more thermodynamically stable. The reaction for hematite precipitation is shown in Equation (68) below.
Prior to hematite removal, some plants using the RLE zinc process treat the primary leach residue by processing it in an autoclave at 100-105 °C with sulphur dioxide to break up the zinc ferrites and dissolve most of the solids. Hydrogen sulphide is then used to precipitate copper, gold, and silver out of the solution. The remaining solution is treated with calcine to neutralize the acid and produce pure gypsum while removing impurities such as gallium, germanium, arsenic, and antimony as precipitates. Hematite precipitation can now occur with the pH raised high enough to carry out the process. One issue with hematite precipitation is that the precipitate tends to attach to the walls of the autoclaves and vessels. This reduces the efficiency and requires cleaning, resulting in interruptions of the operating times unless multiple units are in use. If this precipitation process is to be continuous, a higher capital cost is required to purchase more than one unit.

Table 1: Comparison of iron removal methods based on 100 tonnes of zinc concentrate feed – hematite is observed to be the best process, but economics can make the other processes more attractive (Sinclair, 2005).

<table>
<thead>
<tr>
<th>Process</th>
<th>Jarosite</th>
<th>Paragoethite</th>
<th>Goethite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Residue Fe content (%)</td>
<td>29.0</td>
<td>34.0</td>
<td>40.0</td>
<td>57.0</td>
</tr>
<tr>
<td>Zn content (%)</td>
<td>3.5</td>
<td>13.0</td>
<td>8.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Pb content (%)</td>
<td>1.9</td>
<td>2.2</td>
<td>1.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Quantity of Fe residue (tonnes)</td>
<td>22.5</td>
<td>19.2</td>
<td>16.2</td>
<td>11.2</td>
</tr>
<tr>
<td>Zinc loss in Fe residue (%)</td>
<td>1.51</td>
<td>4.79</td>
<td>2.65</td>
<td>0.21</td>
</tr>
<tr>
<td>Quantity of secondary leach residue (tonnes)</td>
<td>6.0</td>
<td>6.0</td>
<td>6.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Zinc loss in secondary leach residue (%)</td>
<td>0.58</td>
<td>0.58</td>
<td>0.63</td>
<td>0.77</td>
</tr>
<tr>
<td>Overall zinc recovery (%)</td>
<td>97.9</td>
<td>94.6</td>
<td>96.7</td>
<td>99.0</td>
</tr>
<tr>
<td>Capital cost</td>
<td>Low</td>
<td>Medium</td>
<td>Higher</td>
<td>Highest</td>
</tr>
</tbody>
</table>

All of these processes have comparative advantages and disadvantages. The hematite process appears to be the best option for iron precipitation according to Table 1.
However, one important factor is the cost for each of the processes. The hematite process requires a high capital cost in return for a high zinc recovery and pure precipitate residue, whereas the jarosite process is the least expensive method of iron removal. Jarosite is also easily filterable and minimizes the loss of zinc associated with the precipitation of iron. Most zinc metallurgical plants form plumbojarosite in the industry, which is a lead jarosite combination that allows for the removal of lead and iron together (Sinclair, 2005).

Looking at the Teck Cominco plant in Trail, BC, the iron removal solids residue is composed of lead sulphate and lead jarosites. Galena contained in the feed is readily dissolved in the autoclave and forms a solid precipitate of lead sulphate. Lead sulphate can then transform rapidly to plumbojarosite, Pb$_{0.5}$Fe$_3$(SO$_4$)$_2$(OH)$_6$. The slope of the equilibrium line of jarosite formation is [Fe$^{3+}$/H$_2$SO$_4$] = 0.2193. This $k_E$ value is often used for modeling jarosite precipitation in pressure leaching (Baldwin et al., 1995). On the contrary, Hudbay’s plant in Flin Flon, Manitoba produces hydronium jarosite and plumbojarosite. The lower acid and iron concentrations in the discharge form more iron oxides. Galena is present in the HudBay autoclave, but in lower amounts relative to the Teck Cominco feed, making lead sulphate a less dominant precipitate.

**Population Balance Model Preparation**

The sulphide dissolution reaction extents are determined through using a population balance model, and the extent of precipitation is determined through a mass balance since the ferric and sulphuric acid concentrations are restricted due to the $k_E$ value for iron precipitation. An outline of Baldwin et al.’s model follows (1995):

**Reactions**

Oxygen transfer:

$$O_{2g} = O_{2aq}$$  (69)
Ferrous to ferric oxidation:

\[ 2FeSO_4 + H_2SO_4 + \frac{1}{2}O_2 = Fe_2(SO_4)_3 + H_2O \]  
(70)

Sulphide mineral dissolutions:

(Marmatite) \[ Zn_{1-x}Fe_xS + Fe_2(SO_4)_3 = (2 + x)FeSO_4 + (1 - x)ZnSO_4 + S^o_2(l) \]  
(71)

(Pyrrhotite) \[ FeS + H_2SO_4 + \frac{1}{2}O_2 = FeSO_4 + H_2O + S^o_2(l) \]  
(72)

(Pyrite) \[ FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4 \]  
(73)

(Marcasite) \[ FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4 \]  
(74)

(Galena) \[ PbS + H_2SO_4 + \frac{1}{2}O_2 = PbSO_4 + H_2O + S^o_2(l) \]  
(75)

Lead jarosite precipitation in the form of plumbojarosite:

\[ PbSO_4 + 12H_2O + 3Fe_2(SO_4)_3 = PbFe_6(SO_4)_4(OH)_{12} + 6H_2SO_4 \]  
(76)

The model developed in this thesis incorporated these reactions as well in addition to Equation (3).

**Gas Phase Mass Balance**

The balance assumes that any inert gases and the carbon dioxide produced in the vessel leaves through the vent. Equation (77) allows for the oxygen feed rate to be fixed, and the remaining oxygen partial pressures, \( P_{O_2} \) and \( P_{O_{2,aq}} \), can be solved with the mass balance as long as the oxygen utilization is fixed (Baldwin et al., 1995). Alternatively, the stoichiometric oxygen required can be calculated incorporating the additional oxygen
required to satisfy the utilization targeted and the oxygen feed rate can be determined as long as the desired $P_{O_2}, P_{O_2,aq}$, and the oxygen mass transfer rate are known.

$$F_{O_2}x_{O_2} = \frac{k_La}{H}(P_{O_2} - P_{O_2,aq})V_s + \frac{P_{O_2}(F_{CO_2} + F_{O_2}(1 - x_{O_2}))}{(P_T - P_{H_2O} - P_{O_2})}$$ (77)

$F_{O_2}$: oxygen feed flow rate (mol/min)

$x_{O_2}$: oxygen purity (fraction)

$\frac{k_La}{H}(P_{O_2} - P_{O_2,aq})V_s$: oxygen mass transfer rate (OMTR) defined in Equation (61)

$F_{CO_2}$: carbon dioxide flow rate (mol/min) produced from the dissolution of carbonates

$P_T$: total pressure (atm)

$P_{H_2O}$: partial pressure of water vapour (atm)

$V_s$: liquid volume in stage s (L)

Oxygen consumption has been proven the largest energy cost for the autoclave (Mason, 1990); therefore, there is an incentive to optimize the oxygen usage. High partial pressures of oxygen are the driving force to convert the oxygen from the gaseous phase into the aqueous phase for sulphide oxidation reactions. However, higher partial pressures of oxygen require more significant costs. Therefore, there is potential to optimize the oxygen added depending on the sulphide dissolution reaction rates and the oxygen utilizations desired.

**Population Balance Model Utilization**

The population balance equations developed are observed in Baldwin et al.’s publication (1995). It is important to note that the shrinkage rate $k_j$ for each mineral is dependent on the particle leaching kinetics determined through the micro models. Therefore, the population balance equations depend on the simultaneous calculation of the linear leaching equations. Baldwin et al.’s model uses an initial guess for the solution composition in order to solve the population balance models (1995). Substituting the resultant extents of dissolution into the aqueous mass balances gives residuals from the existing solution composition. These residuals are minimized by iterating for new guesses.
of the solution composition until a certain tolerance has been calculated, which in turn, allows for the optimization of the solution composition. Crundwell and Bryson’s model uses a shrinkage rate based on the same principles, but assumes a diffusion layer is present on the surface of the ore particles in addition to the surface reaction. The addition of this extra resistance to the dissolution kinetics increases the leaching time slightly and is heavily dependent on the diffusion coefficient used for the diffusion through the porous product layer (Crundwell & Bryson, 1992). Crundwell and Bryson’s model is more sophisticated in this aspect, but through more modern research, the reaction kinetics for zinc sulphide pressure leaching have been proven to be surface reaction controlled or activation controlled rather than diffusion controlled. Therefore, the incorporation of a diffusion dominant mechanism for the sulphide dissolution could be detrimental to the model results.

**Aqueous Mass Balance**
Mass balances for the aqueous solutions are performed under the assumption of steady state in Baldwin et al.’s model (1995). Equation (78) below describes the mass balance for a particular component i.

\[
Q_{s-1}C_{i,s-1} + \sum_{j=1}^{NR} v_{j,i} \epsilon_{j,s} = Q_s C_{i,s}
\]  

(78)

\(C_{i,s}\): concentration of component i in compartment s (mol/L)
\(C_{i,s-1}\): concentration in the feed of component i to compartment s (mol/L)
\(\sum_{j=1}^{NR} v_{j,i} \epsilon_{j,s}\): net rate of production/consumption of component i
\(v_{j,i}\): stoichiometric coefficient for the i\(^{th}\) component in the j\(^{th}\) reaction
\(\epsilon_{j,s}\): extent of the j\(^{th}\) reaction in compartment s (mol/min)

If the sum term is positive, then the component i is being produced. On the other hand, if the sum term is negative, component i is being consumed. The total sulphate concentration is determined through a charge balance by Equation (79).
\[ 2[SO_4^{2-}] = \sum_{i=1}^{NR} CN_iC_i \]  

(79)

\( CN_i \): charge number  
\( C_i \): total concentration of the positive ion species \( i \) (mol/L)

**Iron Precipitation**

The mass balance for the precipitate is dependent on the extent of precipitation, which can be positive for precipitation, or negative for dissolution.

\[ Q_{s-1}C_{p,s-1} + \varepsilon_{p,s} = Q_sC_{p,s} \]  

(80)

The extent of precipitation can be solved using the \( k_E \) equation and the mass balance equation for sulphuric acid.

\[ \frac{[Fe^{3+}]}{[H_2SO_4]} = k_E \]  

(81)

Therefore, the concentrations of each species is solved simultaneously along with the extent of precipitation through the use of the population balance equations, the gas balance, the energy balance, and the total mass balance. To have iron precipitation occur, the ratio of ferric to sulphuric acid must exceed the \( k_E \) value of 0.2193 for jarosite precipitation. The extent of precipitation will be zero if this threshold value is not reached. It is possible for the feed to contain some precipitates of iron that dissolve within the solution. In this case, if \( \varepsilon_p \) is less than \(-Q_{s-1}C_{p,s-1}\), then \( \varepsilon_p \) is set to equal the value of \(-Q_{s-1}C_{p,s-1}\) and the mass balances are calculated without the precipitation taken into effect.

**Heat Balance**

Assuming steady state, a heat balance can be performed where the flow rates multiplied by the change in enthalpy in each compartment, and with the addition of the heat lost through the reactor, must match the sum of the enthalpies of each reaction multiplied by
the extents. The heat balance equation is shown in Equation (82) below (Baldwin et al., 1995).

\[
\sum_{k=1}^{NI} N_k (H_k - H_s) + HT = \sum_{j=1}^{NR} \Delta H_{rxn_j} \varepsilon_j
\]  

(82)

\(N_k\): molar flow rate of stream \(k\)

\(H_k\): enthalpy of feed stream \(k\) at the input temperature

\(H_s\): enthalpy of feed stream \(k\) at the reactor temperature

\(HT\): heat loss through the vessel

\(\Delta H_{rxn_j}\): heat of reaction for reaction \(j\) (J/mol)

The heat balance is set up by the fact that the heat generated is equal to the heat lost or removed. The input is split into six separate streams:

1. Aqueous feed entering the autoclave
2. Aqueous feed from the previous compartment
3. Water from feed
4. Sulphide minerals, precipitates, and other solids
5. Sulphur
6. Vapour phase

The first two stream enthalpies are calculated by functions dependent on temperature and solution compositions as described in this broader Population Balance Model Preparation section. The third stream is calculated by using the heat capacity for water alone. The enthalpies for the sulphide minerals, precipitates, and other solids were calculated individually using temperature dependent heat capacity data. The heat capacity data for marcasite was taken to be the same as pyrite, regardless of the iron content (Baldwin et al., 1995). The vapour phase enthalpy is calculated as the heat loss by water evaporation. The heat of vaporization was taken into account for the enthalpy calculation in this case. For jarosite, the heat of formation was taken from literature resulting in an enthalpy of -2.917x10^3 J/mol (Dutrizac, 1980).
Overall Mass Balance

The exit liquid flow rate and the liquid volume taken up by the solution within the compartment are determined by the parameter \( Q_s \) in Baldwin et al.'s model (1995). An overall mass balance is required to solve for this variable.

\[
Q_{s-1}(\rho_{l,s-1} + \sum_{j=1}^{NS} M_{j,s-1} + C_{S,s-1}MW_S) = Q_s(\rho_{l,s} + \sum_{j=1}^{NS} M_{j,s} + C_{S,s}MW_S) \quad (83)
\]

\( Q_s \): exit liquid flow rate
\( \rho_{l,s-1} \): density of the liquid at the feed temperature (g/L)
\( M_{j,s-1} \): slurry density for each solid species (g/L)
\( C_{S,s-1} \): liquid sulphur concentration in the feed (mol/L)
\( MW_S \): molecular weight of sulphur (g/mol)

The exit stream, any parameter with the subscript \( s \), is on the right hand side of the equation. The exit density is a function of solution composition, and the other parameters incorporate the population balance and energy balances to solve for \( Q_s \). The liquid volume taken up by the solution within the compartment can be determined through Equation (84) below.

\[
V_s = \frac{V_{T,s}}{(1 + \sum_{j=1}^{NS} \frac{M_{j,s}}{\rho_j} + C_{S,s} \frac{MW_S}{\rho_s})} \quad (84)
\]

\( V_s \): liquid volume in compartment \( s \) (L)
\( V_{T,s} \): total working volume of compartment \( s \) (L)

This volume is crucial because it plays a role in the aqueous and solid mass balances. It also determines the fill level in the compartments and indicates if the impeller speeds are sufficient to provide enough mixing to keep the slurry suspended and enough shear for oxygen solubility.
**Model Solution**

The model does not respond well to real size distribution data in some cases since the distribution may not be smooth. In this case, Baldwin et al. utilize the trapezium rule to help smoothen out the distribution (1995). Crundwell and Bryson, on the other hand, attempt to fit the data to a Rosin-Rammler distribution (1992). Both methods are successful, but are dependent on the initial size distribution data whether one method is more accurate than the other. Steady state temperatures are determined by graphically observing the intersection point where the heat generated and heat removed curves cross. Overall, the model is solving 10 algebraic equations along with an $NS$ amount of ODEs. The model was performed for the Cominco plant autoclave in Trail, BC.

The addition of aqueous solution occurred in the first two compartments after the solution was preheated to 60 °C to help facilitate and expedite the autoclave operation. The solutions were identical in composition, containing 50 g/L of zinc and 161 g/L of sulphuric acid. The oxygen feed purity to the autoclave was taken to be 98.5 % volume, according to the Cominco plant, and the total pressure of the autoclave was given to be 12.5 atm. The oxygen partial pressures in each compartment were calculated by using the known amount of oxygen in the vent gas, 93 % volume on a dry basis, and the equation $P_{O_2} = 0.93(P_T - P_{H_2O})$ based on an oxygen balance.

The model makes some underlying assumptions to calculate the sulphuric acid balance over the first compartment to determine the aqueous feed rate. It uses the fact that there is negligible pyrite conversion and minimal jarosite precipitation to assume that the only acid production comes from marcasite dissolution. This model could be more accurate if the pyrite and jarosite cases were taken into account, but the effect is small. The general assumption that 75 % of each sulphide mineral is dissolved is also not optimal, even though it is only preliminary used to calculate the sulphuric acid balance. A shrinking particle model could estimate more precisely the conversion of each sulphide mineral and enhance the model overall. However, the computation time would increase from these additions and could hinder the model performance.
The results from the model present an exit sulphuric acid concentration of 24 g/L compared to the 161 g/L in the feed, with an acid consumption of 1890.0 mol/min. The slurry flow rate in the feed was calculated to be 115 L/min, making the aqueous feed rate to the first compartment 1380.0 L/min. Model verification could be improved by further plant sampling for data.

Plant specific variables including the mass transfer coefficient and the specific interfacial area for oxygen phase transfers are more difficult to determine accurately compared to sulphide mineral dissolution, ferrous to ferric oxidation, and iron precipitation. Experimental results can verify the latter parameters, but a sensitivity analysis is required to observe the effects of changing $k_La$. In Figure 4 below, the $k_La$ value, measured in 1/min, is varied from 17.5 to 35. Above 20 1/min, the sulphide mineral dissolutions undergo little improvement whereas below 20 1/min, the ferrous to ferric conversion rate drops dramatically, resulting in lower sulphide dissolution rates as shown in Figure 4. Therefore, the optimal value of $k_La$ for the model is 20 1/min to best fit the experimental data. However, the total iron in solution is slightly under predicted by the model at 9 g/L instead of the actual concentration of 10 g/L. This is a result of the sulphide dissolution extent being lower in the model for iron dominant minerals than in the experimental data, particularly for pyrrhotite dissolution.
Baldwin et al.’s results predicted by the model correspond closely to the experimental data at the Cominco plant. The final solution composition is 0.67 g/L ferrous iron, 4.08 g/L ferric iron, 32.7 g/L sulphuric acid, and 107.3 g/L zinc and the final solution temperature calculated by the energy balance is 140 °C (1995). Crundwell and Bryson’s model resulted in the same final temperature, but had a slightly different solution composition. Crundwell and Bryson focused more on the solution flow rates in each compartment rather than the composition. Although the flow rates compare well, there is no mention of the exact composition Crundwell and Bryson’s model produced (1992). Baldwin et al. display the model results more precisely indicating the composition comparison between the model and the plant data is more accurate. However, Baldwin et al.’s model slightly over predicts the acid concentration because the jarosite precipitation equilibrium value, $k_E$, taken at 0.2913 is actually higher than what was discovered at the Cominco autoclave, 0.217. The model predicts a higher conversion of ferrous to ferric, which increases the ferric concentration in solution. As a result, the acid concentration also increases because it is constrained by $k_E$ due to Equation (81). However, the results are very promising and compare well to the autoclave at Cominco.
Summary

Zinc pressure leaching is proven to be modeled accurately with the population balance approach (Baldwin et al., 1995; Crundwell & Bryson, 1992). Further plant data is required for an improvement in the model, but overall the model results are promising when simulating the autoclave at Cominco. The main disadvantage of their model approaches is that the methodology and equations are complex. Therefore, the model interpretation is also complicated and the methodology creates difficulties for having user-controlled values. Another disadvantage stems from the population balance ideology for the particle size distribution. There are two main types of weighted distributions: population-weighted and mass-weighted. The population balance model, being developed originally for crystallization systems, uses population-weighted particle size distributions. These distribution equations are more effective at describing a distribution of fine particles that are nucleating and growing in size. If particles are disappearing, as is the case for leaching, these equations tend to approach infinity. Mathematically, this creates instabilities within the mass balance and affects the convergence of the model when variable flow rates are present. Therefore, population-weighted distributions may not be optimal for describing leaching systems. However, mass-weighted particle size distributions are more effective at describing a distribution of coarse particles. Since coarser particles are more limiting to the overall leaching rate, mass-weighted distributions are the better choice. An additional benefit of the MCI model is the ability to account for non-ideal flow if necessary. The derivation of the population balance model requires ideal flow implicitly, whereas in the MCI, sections of non-ideal flow can be solved by further integration or by treating sections of likewise conditions as separate compartments. Finally, the most significant advantage of utilizing the MCI is the ease of application while maintaining accurate results (Dixon, 1996). The workability of the model is crucial for universal applications; the user should be able to define a set of input parameters that can account for different plant conditions and various types of leaching phenomena while the model predicts the leach extents. It is for this purpose that the MCI model is chosen over the population balance model.

The MCI has yet to be applied in literature for any zinc leaching system, although it has been applied for pyrite pressure oxidation as a pretreatment for refractory gold ores
(Dixon & Dreisinger, 2002). One of the primary objectives of this thesis is to investigate the accuracy of the MCI model when simulating the zinc pressure leaching system.
Chapter 3: Model Methodology and Development

MCI Model Inputs
The first and foremost input to the MCI model is the particle leaching kinetics. Since the targeted leaching process involves using dispersants in this study, the shrinking sphere micro model was applied within the broader MCI model. The linear leaching shrinking sphere micro model equation is shown below in Equation (82) (Levenspiel, 1972).

\[
\left(1 - \frac{t}{\tau_l}\right)^3 = 1 - X_S \tag{82}
\]

\[
\tau_l = \frac{D_0}{k(T)f(C)} \tag{83}
\]

\[
k(T) = k(T_0)\exp\left[\frac{-E}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{84}
\]

\[
f(C) = \left(\frac{C_{Fe(III)}}{K + C_{Fe(II)}}\right)^n \tag{85}
\]

- \( t \): time step (min)
- \( \tau_l \): time required to completely leach a particle of size \( D_0 \) (min)
- \( X_S \): fraction reacted
- \( D_0 \): initial diameter of the particle (m)
- \( k(T) \): rate constant function
- \( k(T_0) \): rate constant function at a reference temperature \( T_0 \)
- \( E \): activation energy for the reaction (J/mol)
- \( f(C) \): concentration function (Dixon & Dreisinger, 2002)
- \( C_{Fe(III)} \): concentration of ferric
- \( C_{Fe(II)} \): concentration of ferrous
- \( K \): hybrid model constant (set to zero)
- \( n \): concentration function exponent (set to 0.5)
The combination of Equations (82-85) allows for the calculation of the fraction unreacted at specific time steps $t$ in comparison to the time required to completely leach a particle of size $D_0$. It is worth mentioning that the only equation that changes in the shrinking sphere micro model is the concentration function $f(C)$, which depends on the dominant leaching type. For sphalerite, the leaching reaction is limited by slow anodic decomposition (Crundwell, 1988; Perez & Dutrizac, 1991). In other words, the mineral itself is slow to release electrons and the reaction is chemically controlled at the surface. Therefore, the overall leaching reaction rate is dependent on the ferric and ferrous concentrations in solution; this is also known as type II leaching (Verbaan & Crundwell, 1986). The hybrid model constant and exponential term can be adjusted to achieve a better fit to experimental data. Hence, the MCI model developed in this thesis calculates the concentration function based on the ferric and ferrous concentrations in solution, which is dependent on the leach extents of iron minerals present in the concentrate and any additions of soluble iron. The oxidation of ferrous to ferric is then determined through analyzing the plant data and conducting an iron balance. The total measured soluble iron and iron precipitates were recorded in the industrial autoclave periodically at the first and fourth compartments. The soluble ferrous ions in solution can be predicted from the leach extents of the iron containing minerals. With the knowledge of these two iron concentrations and the quantity of iron precipitated, the resultant soluble ferric ions can then be solved through a simple iron mass balance where the concentration of ferric is equal to the difference between the total iron and the soluble ferrous iron. The oxidation rate of ferrous to ferric iron is determined through Equation (2) once the oxygen concentration in solution is calculated. The following sections will describe how the soluble oxygen concentration was determined. In the case where different leaching mechanisms are present, the concentration function will change. Other concentration function equations have been detailed in the original MCI derivation (Dixon, 1996).

**Plant-Specific Parameters**

In addition to the particle leaching kinetics, the particle size distribution is another critical input to the model. The feed concentrate to the low acid leach autoclave in the plant is ground in a ball mill down to 99 % passing 45 microns. The PSD result reveals the $D^*$ (or the 63.2 % passing size), which was determined by the Malvern Mastersizer 2000 Laser
Diffraction Particle Size Analyzer to be 19.4 microns for this particular study. The resultant Rosin-Rammler \( m \) value for this industrial plant is calculated by Equation (51) to be 0.991. A randomly selected subsample of ground concentrate from the plant was used to obtain these values.

The residence time distribution is the last term in the overall MCI equation and must be determined from the compartment residence times (min). Knowing the volume of the compartments and the approximate fill levels, it is possible to calculate the measured mean residence time for each compartment. The plant measures the volumetric flows entering and exiting the autoclave. The residence times (min) for the four compartments respectively are 31.2, 7.9, 7.5, and 8.4.

The additional inputs entered for the MCI model are shown in Table 2. Values were chosen based on the industrial data given and samples reported by the plant unless otherwise referenced. It is important to note that the exponents listed in Table 2 are taken from literature studies. These values assist in calculating the actual \( k_La \) value and the effects of sparging on the leaching reaction. The detailed calculations can be found in Van’t Reit’s publication (1979). The reactor heat loss is assumed to be zero. A heat balance has been developed for the plant to achieve a constant autoclave temperature. Steam is utilized to maintain the temperature at 150 °C within 5 °C. Any heat that would be lost through the reactor walls would be replaced by inserting steam. In the case where an operator desires to account for heat loss, the software will incorporate the percentage value into the internal heat balance. The CADSIM simulation software has the capability to simultaneously solve the energy balances based on the inputs to the model while calculating the leach extents, as is necessary.
Table 2: MCI Model Inputs – parameter values used for the MCI model. Values were chosen from plant data and literature. These parameters are crucial for an accurate model representation of the leaching reactor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Volume (m$^3$)</td>
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<td>Plant data</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>150</td>
<td>Plant data</td>
</tr>
<tr>
<td>Leaching Type</td>
<td>2</td>
<td>(Verbaan &amp; Crundwell, 1986)</td>
</tr>
<tr>
<td>Impeller Power (Hp)</td>
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<td>Plant data</td>
</tr>
<tr>
<td>Tank Diameter (m)</td>
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</tr>
<tr>
<td>Impeller Diameter (m)</td>
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</tr>
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<td>Rotational Speed (Hz)</td>
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<td>Plant data</td>
</tr>
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<td>Total Pressure (psi)</td>
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<td>Plant data</td>
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<tr>
<td>Impeller Power Exponent</td>
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<td>(Van’t Reit, 1979)</td>
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<tr>
<td>Superficial Velocity Exponent</td>
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<td>(Van’t Reit, 1979)</td>
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<tr>
<td>Slurry Viscosity (μPa·s)</td>
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</tr>
<tr>
<td>Slurry Density (kg/m$^3$)</td>
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<td>(Dixon, 2007)</td>
</tr>
<tr>
<td>Hybrid Model Constant</td>
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<td></td>
</tr>
<tr>
<td>Heat Loss (%)</td>
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<td>(Kontopoulos, 1994)</td>
</tr>
</tbody>
</table>

**Slurry and Gas Parameters**

A number of gas parameters need to be solved to calculate the final oxygen concentration in solution. Among these parameters is the oxygen solubility, which is calculated using Tromans’s model (Tromans, 1998).

\[
K_{O_2} = \psi \exp\left[\frac{686.23 - 1430.47 - 0.046T^2 + 203.357\ln(T)}{RT}\right]
\]

(86)

\[
\psi = \left[\frac{1}{1 + 2.01628[H_2SO_4]^{1.253475}}\right]^{0.168954}
\]

(87)

\[K_{O_2}: \text{oxygen solubility (mol/kg/atm)}\]

\[\psi: \text{salting-out parameter}\]
$T$: elevated temperature (K)

$[H_2SO_4]$: concentration of sulphuric acid (mol/kg)

The salting-out parameter ranges between zero and one, for a pure salt solution (or electrolyte) and pure water respectively. Most leaching solutions follow closely to the value of one because the electrolyte concentrations are dilute. Equations developed by Filippou et al. (2000) are used to determine the salting-out effect for electrolyte solutions below 1 mol/L. Compared to pyrite oxidation, the oxygen solubility is much lower because the temperature is lower in zinc pressure leaching and because oxygen is not catalyzed efficiently on the mineral surface, as is the case with pyrite (Lowson, 1982).

The purpose of sparging oxygen is to convert ferrous iron to ferric iron, which enables ferric to act as a surrogate oxidant and reduce on the mineral surface leaching the zinc ore. However, in pyrite oxidation, the oxygen concentration is limiting the leaching reaction itself. Hence, the solubility of oxygen is of paramount importance and is maximized further than in zinc pressure leaching (Bailey & Peters, 1976; Lowson, 1982).

The oxygen diffusivity is estimated at the elevated leaching temperature by the Stokes-Einstein law. The diffusivity of oxygen at room temperature and the viscosity of water are used in comparison to the elevated temperature and the viscosity of the solution, as observed in Equation (88) (Krynicki et al., 1978).

$$D_{O_2-H_2O} = D_{0,O_2-H_2O} \frac{\mu_w T}{\mu_{s_l} T_0}$$ (88)

$D_{O_2-H_2O}$: diffusivity of oxygen in water at temperature (mm$^2$/s)

$D_{0,O_2-H_2O}$: diffusivity of oxygen in water at the reference temperature (mm$^2$/s)

$\mu_w$: viscosity of water at temperature (Pa·s)

$\mu_{s_l}$: viscosity of the slurry at temperature (Pa·s)

$T$: elevated temperature (K)

$T_0$: reference temperature (K)
The power ratio estimates the actual power draw of the impeller in comparison to the power draw calculated. It is a method of quantifying the impeller power loss due to an increase in the gassing rate (Hughmark, 1980).

\[
\frac{P_g}{P_0} = 0.10 \left[ \frac{NV}{Q_g} \right]^{1/4} \left[ \frac{gWV^{2/3}}{N^2D^4} \right]^{1/5}
\]  

(89)

\(\frac{P_g}{P_0}\): gassed power ratio

\(N\): impeller rotational speed (Hz)

\(V\): working volume (m\(^3\))

\(Q_g\): gassing rate (m\(^3\)/s)

\(g\): gravitational acceleration (m/s\(^2\))

\(W\): impeller blade width (m)

\(D\): impeller diameter (m)

The power ratio is critical to calculate other gas parameters, such as the bubble diameter. Typically, the value of the ratio is around 60 % in hydrometallurgical applications (Gormely, 1992). Higher power ratios exemplify that the system is more efficient with a larger margin for error; this suggests that any viscosity fluctuations or other process upsets will not overload the impeller, assuming a reasonable feed rate has been calculated to enter the reactor.

Gas density is approximated using ideal gas law according to the gas composition; this calculation is shown in Equation (90) below.

\[
\rho_g = \frac{p_{O_2}M_{O_2} + p_{H_2O}M_{H_2O}}{RT}
\]  

(90)

\(\rho_g\): gas density (kg/m\(^3\))

\(p_{O_2}\): partial pressure of O\(_2\) (Pa)

\(p_{H_2O}\): partial pressure of H\(_2\)O (Pa)
$M_{O_2}$: molecular weight of $O_2$ (g/mol)

$M_{H_2O}$: molecular weight of $H_2O$ (g/mol)

$T$: elevated temperature (K)

The gas density is a useful tool for plant operators to identify potential process upsets. Along with the density of the gas, the gas holdup also provides an additional method to monitor the performance. Equations (91-93) below describe how this parameter is calculated. The gas density is critical for estimating the volume fraction of gas within the autoclave (Calderbank, 1967; Gormely, 1992). The superficial velocity is based on the gassing rate and the cross-sectional area as observed in Equation (93).

\[
\varphi = \frac{v_s}{v_t} \quad (91)
\]

\[
v_t = \frac{d_b^2 g (\rho_{sl} - \rho_g)}{18 \mu_{sl}} \quad (92)
\]

\[
v_s = \frac{Q_g}{S} \quad (93)
\]

$\varphi$: gas holdup fraction

$v_s$: superficial gas velocity (m/s)

$v_t$: terminal rise velocity of the bubbles (m/s)

$d_b$: bubble diameter (m)

$g$: gravitational acceleration (m/s$^2$)

$\rho_{sl}$: slurry density (kg/m$^3$)

$\rho_g$: gas density (kg/m$^3$)

$\mu_{sl}$: slurry viscosity (Pa·s)

$v_s$: superficial velocity of gas flow in the tank (m/s)

$Q_g$: gassing rate (m$^3$/s)

$S$: cross-sectional area of the tank (m$^2$)
The gas holdup values are difficult to measure at operating temperatures within autoclaves. Studies involving hydrometallurgical stirred reactor tanks report values from 0.0054 to 0.0289 (Gormley, 1992). Other stirred reactor tanks can have gas holdups of up to 0.10 (Poncin et al., 2002). The results generated by this model agree with these literature values.

It is also possible to estimate the bubble diameter based on the properties of the slurry and gas phases within the autoclave. The bubble diameter is typically between 2-4 mm in non-electrolytic solutions (Dixon, 2007). However, in electrolytic solutions, the bubble diameter decreases because of surface charges that prohibit bubbles from coalescing easily. Calderbank’s calculation requires the gas viscosity to be solved for in Equation (95) before calculating the bubble diameter in Equation (94) (1967). Values were found to be between 0.22 to 0.56 mm for similar hydrometallurgical applications (Dixon, 2007; Gormley, 1992). The bubble diameter predicted by this model was also confirmed to be within the literature range.

$$d_b = 2.25 \left[ \left( \frac{V}{P_G} \right)^{0.4} \frac{\sigma^{0.6}}{\rho_{sl}^{0.2}} \phi^{0.4} \frac{\mu_g}{\mu_{sl}} \right]$$  \hspace{1cm} (94)

$$\mu_g = \frac{P_{O_2} \mu_{O_2} + P_{H_2O} \mu_{H_2O}}{P_T}$$  \hspace{1cm} (95)

$\mu_g$: gas viscosity (Pa·s)

$P_{O_2}$: partial pressure of oxygen (Pa)

$P_{H_2O}$: partial pressure of water (Pa)

$\mu_{O_2}$: viscosity of oxygen (Pa·s)

$\mu_{H_2O}$: viscosity of water (Pa·s)

$P_T$: total pressure (Pa)

$V$: volume ($m^3$)

$P_G$: gassed impeller power (W)

$\sigma$: surface tension (N/m)
The \( k_La \) value expresses a mass transfer coefficient for oxygen, where \( k_L \) is the gas-liquid mass transfer term, and \( a \) is the specific interfacial area of the reactor. Most models iteratively match the model results to plant data by altering the \( k_La \) value; however, the Equations (96-98) outline how the mass transfer coefficient for oxygen can be determined with knowledge of the autoclave and impeller components (Calderbank, 1967). Equation (97) can change if the impeller diameter and rotational speeds are significantly lower. Modifications to this equation can be observed in literature (Treybal, 1980).

\[
k_L = \left( 2 + 0.31 \left[ \frac{d_b^3 g (\rho_{sl} - \rho_g)}{\mu_{sl} D_{O_2-H_2O}} \right]^{1/3} \right) \left( \frac{D_{O_2-H_2O}}{d_b} \right) \times 60
\]  

\[
a = \left[ 8.33 \times 10^{-5} \left( \frac{D^2 N \rho_{sl}}{\mu_{sl}} \right)^{0.7} \left( \frac{DN}{v_s} \right)^{0.3} - 1.5 \right] (a_0)
\]  

\[
a_0 = \frac{S}{V}
\]

\( k_L \): gas-liquid mass transfer term (m/min)  
\( a \): interfacial area (m\(^2\)/m\(^3\))  
\( a_0 \): initial interfacial area (m\(^2\)/m\(^3\))

Multiplying the interfacial area by the gas-liquid mass transfer term gives the overall \( k_La \) value. The final effective oxygen concentration in solution can be determined through an oxygen balance of the leaching system. Equation (99) shows the resulting equation to predict the soluble oxygen concentration in mol/L using the oxygen solubility predicted in mol/kg/atm by Tromans’s model (Dixon, 2007; Tromans, 1998).

\[
[O_2]_{aq} = \frac{(O_{2in} - O_{2consumed})}{k_La_v} + K_{O_2}P_i \sqrt{\frac{P_{O_2in} \times P_{O_2out}}{P_{O_2}}}
\]  

\([O_2]_{aq}\): final oxygen concentration in solution (mol/L)
\(O_{2\text{in}}\): oxygen flow rate entering in with the slurry (mol/hr)

\(O_{2\text{consumed}}\): oxygen flow rate consumed by the slurry (mol/hr)

\(k_{L,a}\): volumetric overall mass transfer coefficient for oxygen (L/hr)

\(\rho_l\): density of the solution (kg/L)

\(P_{O_2\text{in}}\): oxygen partial pressure of the slurry entering in (atm)

\(P_{O_2\text{out}}\): oxygen partial pressure of the slurry exiting out (atm)

With all of the input variables calculated, the overall MCI model can now be solved using Equations (59) and (60). The model derived for this study includes 16 points for all integrals solved by the Gauss-Laguerre.
Chapter 4: Model Results and Discussion

MCI Model Outputs
The global reactor constant values calculated in Equation (56) by the model for each compartment cannot adequately be compared with literature because of the strong dependence on compartment residence times. The methods outlined by Dixon and Dreisinger (2002) have been followed to achieve the results for the global reactor constant. The ability to calculate different reactor constant values for each compartment allows for versatility in the model results, including the fraction converted for each compartment. The reactor constant values are calculated by the model for each compartment by utilizing Equation (56). These values were found to be 0.0352, 0.0772, 0.0517, and 0.0546 respectively. The remainders of the MCI model outputs are shown in Table 3.
Table 3: MCI Model Outputs – the summarized results of the model are given as the output parameters described above. The fraction converted in each compartment follows closely to plant data.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction Reacted ZnS</td>
<td>0.840</td>
</tr>
<tr>
<td>Compartment 1 Conversion</td>
<td>0.620</td>
</tr>
<tr>
<td>Compartment 2 Conversion</td>
<td>0.724</td>
</tr>
<tr>
<td>Compartment 3 Conversion</td>
<td>0.782</td>
</tr>
<tr>
<td>Compartment 4 Conversion</td>
<td>0.840</td>
</tr>
<tr>
<td>Gassing Rate (m$^3$/s)</td>
<td>0.0733</td>
</tr>
<tr>
<td>Oxygen Solubility (mol/kg/atm)</td>
<td>0.000781</td>
</tr>
<tr>
<td>Salting-out Parameter</td>
<td>0.830</td>
</tr>
<tr>
<td>Oxygen Diffusivity (mm$^2$/s)</td>
<td>0.00871</td>
</tr>
<tr>
<td>Power Ratio</td>
<td>0.648</td>
</tr>
<tr>
<td>Gas Density (kg/m$^3$)</td>
<td>8.12</td>
</tr>
<tr>
<td>Gas Holdup</td>
<td>0.00879</td>
</tr>
<tr>
<td>Superficial Velocity (m/s)</td>
<td>0.00555</td>
</tr>
<tr>
<td>Bubble Diameter (mm)</td>
<td>0.477</td>
</tr>
<tr>
<td>Gas Viscosity ($\mu$Pa·s)</td>
<td>93.6</td>
</tr>
<tr>
<td>$k_L a$ (1/min)</td>
<td>37.5</td>
</tr>
<tr>
<td>Oxygen Concentration (mol/L)</td>
<td>0.00390</td>
</tr>
</tbody>
</table>

Compartment one has the largest increase in the fraction reacted because the concentration gradients are maximized at the beginning of the leaching process (Baldwin et al., 1995; Crundwell, 1995; Crundwell & Bryson, 1992; Dreisinger & Peters, 1987). As the leaching reactions occur, the driving force for sphalerite conversion decreases, making the final compartment have the smallest increase in the fraction reacted in comparison to the previous compartments.

Geometric parameters and solution chemistry leads to the prediction of 37.5 1/min for the $k_L a$ value—a reasonable number for a leaching reactor. Baldwin et al. (1995) found the $k_L a$ value to be between the ranges of 17.5 to 35 1/min for similar zinc pressure leaching.
conditions. However, the value was found by using the $k_La$ as a fitting parameter without accounting for impeller geometry. Mehta and Sharma (1971) studied the sensitivity of the $k_La$ parameter and reported values between 1 and 20 l/min for mechanically agitated gas-liquid reactors at atmospheric pressure for various electrolytic solution conditions. Dixon and Dreisinger (2002) developed a model for pyrite autoclaving where the maximum $k_La$ value was found to be 51.6 l/min. The higher $k_La$ value in pyrite autoclaving makes sense because of the increased pressure and temperature. Oxygen is a direct oxidant in the pyrite leaching system, and therefore, its solubility is more important than the ferric concentration in pressure oxidation. However, the calculated $k_La$ value is still large for zinc pressure leaching.

The gas parameters and oxygen values are significant in any leaching system if the leaching is dependent on the oxygen concentration in solution, whether oxygen is a direct oxidant or a surrogate oxidant is involved. The resultant oxygen concentration calculated for this zinc pressure leaching system compares closely with literature values; Filippou et al. (2000) calculated a value of 0.004 mol/L for zinc pressure leaching conditions. It is interesting to compare the oxygen concentration values when Tromans’ model alone is utilized. Without the incorporation of the oxygen related parameters, such as the $k_La$ value, the oxygen concentration in solution would be equivalent to the oxygen solubility multiplied by the partial pressure of oxygen (Tromans, 1998). This value is calculated to be 0.00478 mol/L for the same zinc pressure leaching conditions. This difference signifies the importance of incorporating the $k_La$ value and other oxygen related parameters. It is not appropriate to assume that the oxygen solubility multiplied by the partial pressure of oxygen gives a realistic and accurate oxygen concentration in solution for sulphide pressure leaching systems at elevated temperatures.

**Comparison of the MCI Model to Plant Data**

The overall model results accurately represent the plant data following the targeted extraction rates within 1.5 %, which are comparable accuracies to other zinc pressure leach kinetic models in literature (Baldwin et al., 1995; Crundwell & Bryson, 1992). The data values used are a result of the average extractions from the low acid leach autoclave
over a one-week period from the plant. Samples are only taken from the first and last compartment in this particular industrial autoclave. However, the model predicts the values for all of the compartments. A graphical representation is shown below in Figure 5.

Figure 5: MCI Model Accuracy – the plant can only sample from compartments one and four. The fraction reacted from these compartments were the average values over a one-week period. Samples were taken via a release valve port in the industrial plant. The model generated values that closely relate to the plant data.

The MCI model developed has the capability for the user to account for different rate-controlling mechanisms during leaching. For example, if the user decides the ferric concentration in the compartment is rate limiting, the model will calculate the concentration function accordingly. Also, the application of hybrid models where more than one concentration can be limiting for the same reaction is available at the user’s discretion. Other user-controlled inputs include the temperature, pressure, oxygen flow rate, slurry flow rates, and volumes of each compartment. This ensures that a correct global reactor constant or κ value can be tabulated for each compartment.
MCI Model Fitting Parameters

The rate constant is an Arrhenius expression related to the activation energy of the sphalerite reaction. The model predicts this activation energy and rate constant to best fit the plant data. Studies in literature show that the activation energy of sphalerite leaching can vary between 40 kJ/mol and 70 kJ/mol (Perez & Dutrizac, 1991; Verbaan & Crundwell, 1986; Xie, 2007). It is evident from the moderately high activation energy that the process is not diffusion-controlled (Jin et al., 1984). The optimization results for the reference rate constant (1/min) and the activation energy (kJ/mol) are respectively 0.00224 and 42.8. An iterative process is used to determine these values to achieve the model’s best fit. In addition, bench scale pressure leaching experiments were performed at the University of British Columbia with the same concentrate received from the industrial plant. The goal of these experiments was to validate the true activation energy by analyzing the effect of temperature on the leaching kinetics and to validate that the particle kinetics follows the shrinking sphere micro model.

Reference Rate Constant and Activation Energy

The model sensitivity to variations in the reference rate constant and the activation energy is substantial. The overall fraction reacted can be greatly affected by the activation energy. A range of activation energy values taken from literature is inserted into the MCI model to compare the overall fraction reacted results. The model’s predicted result of 42.8 kJ/mol matches closely with the experimental result determined to be 40.8 kJ/mol in this thesis. In addition, the reference rate constant is also an effective optimization parameter; iterative adjustments can increase model accuracy. Contrary to the activation energy, the reference rate constant is more abstract. Some authors define the rate constant in different units; hence, the value will be significantly different. Verbaan and Crundwell (1986) describe the rate constant in units of mol/m^2s in comparison to 1/min.

Ferric to Ferrous Ratio

Process upsets can alter the fraction reacted from the model. Reagent concentrations can vary throughout the continuous operation of a zinc plant, especially if modifications to further downstream processes are required. The gypsum and iron precipitation circuits are
sensitive to the reagent concentrations exiting the leaching reactor, and reagent concentrations can be altered to minimize issues associated with the removal of these species. The flow sheet in Figure 1 shows the order of these operations and how they interact. Relationships between the ferric/ferrous concentrations versus the overall fraction reacted in the leaching circuit are useful to monitor and predict the resulting operation of the iron precipitation circuit. In addition, this ratio can also significantly affect the leaching rate of sphalerite. Figure 6 below describes the dependence of the overall fraction reacted upon these concentrations.

![Figure 6: Sensitivity Analysis on the Fraction Reacted – the relationship between the ferric to ferrous ratio in the LAL autoclave and the overall fraction reacted is predicted by the MCI model results.](image)

The ferric to ferrous ratio is optimized between 2 and 3 in the industrial LAL autoclave to maximize the leaching rates while not causing further upsets downstream. The lower acid levels in the LAL autoclave encourages iron to precipitate as jarosite and thus reduces the ferric concentrations in solution, explaining why the ratios in Figure 6 are quite low. Figure 1 shows how the filtrate eventually gets processed in the gypsum and iron.
precipitation circuits. Therefore, the benefit of sustaining low acidities in the LAL autoclave becomes clear. Less lime or limestone is needed to neutralize the solution and less iron is present in solution. However, the HAL autoclave operates at much higher acidity levels and therefore dissolves most, if not all, of the iron present. The ferric concentrations are increased in the HAL as a result and ferric to ferrous ratios of up to 25 are observed in plant conditions. This makes it possible to still achieve high extractions during leaching while minimizing the acid leaving the process circuit. The limiting quantities of ferric in solution to still see leach extraction improvements has been briefly studied in literature. Chang et al. (1994) discovered that increasing ferric concentrations up to 1 mol/L enhanced the leaching rate, but the experiments were performed under atmospheric leaching conditions. Hence, a suspected increased sulphur product layer coated the ore particles retarding the leaching rate. Ferric concentrations can be higher in pressure leaching systems, but iron precipitation control can become a dominant issue in downstream processes. The results from this sensitivity analysis signify that industrial plants may be able to allow a larger operating range for their ferric to ferrous ratio, as the fraction reacted is not as heavily dependent as expected. If the ratio decreases to 1, the fraction reacted remains close to 80%. However, the ferric to ferrous ratio is confirmed to play a role in the zinc extraction rates.

**Particle Size**
The feed particle size is also a process variable that fluctuates throughout a continuous process. It is interesting to examine the effect of particle size on the fraction reacted in these conditions with the MCI model. The expected trend would be an increase in the fraction reacted as the particle size decreased, as predicted by the MCI model in Figure 7 shown below.
Particle sizes affect the leaching rates of sphalerite quite significantly according to the model. Experiments performed by Yan et al. (2010) confirm the particle size dependence of sphalerite leaching; a similar trend is observed with the same conclusion that the particle size has a strong effect on the leaching rate. Plant data is monitored tightly for both the particle size and the ferric to ferrous ratio. Experiments within a lab setting are required to verify the trends predicted by the model at a wider range of parameter values. These experiments will enable the parameter effects to be analyzed individually while holding other factors constant; hence, the model verification will be more useful.

$K_L a$ Value

The predicted oxygen concentration in solution can be determined from the $k_L a$ and compared to other models in literature. One zinc pressure leaching model found a similar relationship between the $k_L a$ and the reagent concentrations (Baldwin et al., 1995); there was a sudden increase in ferric concentration as the $k_L a$ initially increased through model
simulation, but the saturation point occurred rapidly. Ferric concentration increases can be directly related to the increases in oxygen concentration because of the ferric and ferrous-coupled reaction. The oxidation of ferrous depends heavily on the oxygen concentration in solution, since ferric is a surrogate oxidant for the zinc pressure leaching system. Therefore, it is possible to compare their model results and confirm the trends predicted by the MCI model developed in Figure 8. On the contrary, the marmatite leaching rate was affected by this increased oxygen solubility and released more iron into solution, since marmatite is an iron-containing zinc mineral. This iron would then be oxidized to ferric because of the enhanced oxidizing conditions from purging oxygen, and therefore, would reduce on the zinc mineral surfaces as the true oxidant of sphalerite leaching (Baldwin et al., 1995; Dixon, 2007; Peters, 1992). The mechanism is similar with the sphalerite concentrate used in this study, except the source of iron comes from different iron-containing minerals rather than marmatite. This explains why the $k_La$ value indirectly affects the zinc extraction rate and is considered in the MCI model developed.

![Figure 8: Sensitivity of the Oxygen Concentration in Solution](image)

*Figure 8: Sensitivity of the Oxygen Concentration in Solution – the oxygen concentration is expressed as a function of the $k_La$ value. A similar trend is observed in Baldwin et al.’s publication (1995). It is interesting to note the saturation point of the oxygen concentration.*
**MCI Model Validation**

The measured extraction percentages relate to a set of operating conditions from the industrial plant. It was possible to utilize the same set of operating conditions as inputs to the model and compare the result. Each data point in Figure 9 represents this comparison. The closer the proximity to the ideal line, the more accurate the model prediction. The most significant input parameters were entered, but not every single input parameter could be taken into account. After examining the results, it was determined that the model is over sensitive to the ferric to ferrous ratio and insensitive to the acid concentration for the overall fraction reacted. Outliers in the ratio values were found to be the cause for the model under or over predicting the result. Deviations from the ideal line could be due to the assumption that the measured concentrations from the plant in the first compartment of the autoclave are taken to be the initial concentrations for the model. Ideally, the concentrations should be measured prior to entering the autoclave in one solution. However, different solutions enter the autoclave and mix in the first compartment. Therefore, the closest to the initial concentrations would be the first compartment concentrations in the plant. The larger fluctuations in the ferric to ferrous ratio could come from this assumption. Any measured concentrations could also have errors due to non-ideal mixing or human error. Another reason for the increased model sensitivity to the ferric to ferrous ratio could be from the exponential value in Equation (85) being slightly too high. Additional optimizations to this value could be made with more plant data fluctuations.
Figure 9: Model Validation – comparison of the predicted model overall fraction reacted and the measured overall fraction reacted for multiple sets of operating conditions. Discrepancies in the results were attributed the model being over sensitive to the ferric to ferrous ratio.

To summarize, the following information was determined from the model. A slightly larger operating range for the ferric to ferrous ratio would be sufficient to achieve satisfactory overall zinc extractions. The ratio is maintained from 2 to 3 in the LAL autoclave, but it is observed from the model that if this ratio decreases to 1, the overall zinc extraction remains just above 80%. The robustness of the leaching process to low iron content in the feed is greater than expected. The particle size is confirmed to have a strong effect on the zinc leaching rates. The ball mill discharge must be regulated tightly to achieve adequate extractions consistently. The model predicts that if the $D^*$ particle size is 2 microns larger than optimum, the overall extraction drops below 80%. The oxygen solubility and $k_La$ values compare well with literature, and it is observed that the $k_La$ is fairly optimal for the geometric parameters of the industrial autoclave. Any further
increases in the $k_l a$ value results in marginal increases in the oxygen concentration. The model discoveries are also validated and confirmed with Figure 9 above, which provides more confidence in the trends predicted.

Improvements can be made to the MCI model to increase the accuracy. As an example, precipitation kinetics can be studied further and incorporated into the model rather than replicating plant data extents. In addition, the phases of iron precipitates are crucial for downstream processing; hence, the predicted knowledge of precipitation kinetics can be beneficial. A revolutionary improvement in kinetic modeling would be the application of dynamic models that could account for fluctuations in feed rates and start up/shut down operations for plant maintenance. Having the ability to dynamically track the reagent concentrations and particle sizes between compartments would enhance the operators’ control over the system. Optimization can be performed without delay, further enhancing the efficiency of the plant. The CADSIM software offers the potential for dynamic simulation, in which this model would be the benchmark for validation purposes.
Chapter 5: Experimental Validation of Model Results

Materials Feed
Concentrate samples were randomly selected by the method of riffling and splitting from the Hudbay bulk sample received. The combined subsamples were ground in a batch rod mill with 60 wt.% solids until a target P99 of 45 microns was achieved. The Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer was utilized for particle size measurements, where slurry samples were taken from the ball mill in three different locations periodically. Figure 10 shows the PSD curve. The concentrate was then dried according to the E877 ASTM standard at 105 °C until a constant mass was achieved. It was immediately sealed after drying to avoid moisture absorption.

A subsample from the dried concentrate was randomly selected by riffling and splitting for a mineralogy analysis using the Bruker D8 Advance Bragg-Brentano diffractometer. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6 degrees. The results of the analysis can be observed in Table 4. Zinc is present as sphalerite, iron is present as pyrite and pyrrhotite, copper is present as chalcopyrite, lead is present as galena, and other minor elements exist as sulphides. Inductively coupled plasma (ICP) was also performed by Hudbay at the Flin Flon plant with the identical feed material. Multi-acid digestion was used to dissolve any amorphous phases present. These phases contributed significantly to the analysis results, as the sphalerite content changed from 90.1 % by QXRPD to 51.2 % by ICP. The results of the ICP can be observed in Table 5 below.
Figure 10: Feed Mineralogy – PSD curve of the feed concentrate for the experimental work.

Table 4: Feed Mineralogy – QXRPD analysis of the feed concentrate for the experimental leach tests.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>90.1</td>
</tr>
<tr>
<td>Fe₉S₁₀</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe₇S₈</td>
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<tr>
<td>FeS₂</td>
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<tr>
<td>CuFeS₂</td>
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<tr>
<td>CaSO₄·2H₂O</td>
<td>0.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.6</td>
</tr>
<tr>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.5</td>
</tr>
<tr>
<td>(Zn,Fe²⁺)(Fe³⁺)₂O₄</td>
<td>0.3</td>
</tr>
<tr>
<td>PbS</td>
<td>trace</td>
</tr>
</tbody>
</table>
Figure 11: Feed Mineralogy – QXRPD Rietveld refinement plot of the feed concentrate. (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below - difference between observed and calculated intensities; vertical bars - positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
Table 5: Feed Mineralogy – ICP analysis by Hudbay of the feed concentrate for the experimental leach tests.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.92</td>
</tr>
<tr>
<td>Au</td>
<td>0.06</td>
</tr>
<tr>
<td>F</td>
<td>0.02</td>
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<tr>
<td>As</td>
<td>0.02</td>
</tr>
<tr>
<td>Cd</td>
<td>0.12</td>
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<tr>
<td>Cu</td>
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</tr>
<tr>
<td>Fe</td>
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<tr>
<td>MgO</td>
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<tr>
<td>Ni</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.56</td>
</tr>
<tr>
<td>Zn</td>
<td>51.20</td>
</tr>
<tr>
<td>S</td>
<td>34.80</td>
</tr>
</tbody>
</table>

**Equipment Setup and Procedure**

75 g samples were randomly selected by coning and quartering from the dried concentrate for each experiment. Leach tests were performed in a 600 mL 316L stainless steel Parr vessel with a 4545 Parr controller. To avoid vessel oxidation, hydrogen sulphide gas formation, and premature leaching, 5 or 20 mL boro-silicate glass ampules were sealed with concentrated sulphuric acid for each experiment and inserted into the vessel prior to increasing the temperature. The experiment was designed to have the impellers strike the glass ampule once the elevated operating temperature was reached and in order to commence the test. The solution conditions chosen replicated plant conditions for the slurry entering into the LAL autoclave. The standard conditions were 180 g/L (1.8 mol/L) sulphuric acid, 1 g/L (0.018 mol/L) ferric added as ferric sulphate pentahydrate, 0.3 g/L lignosulphonate, 0.1 g/L quebracho, 90 psi oxygen overpressure, and 30 wt.% solids with a P99 particle size of 45 microns. Analytical grade chemicals and gases along with deionized water were used for all experiments.
Figure 12: Autoclave Setup – ports include an oxygen inlet, a sampling port, an exhaust port, a cooling line port, and a pressure relief port.
The autoclave head and fittings were designed to have an oxygen inlet port, a sampling port that coupled with the oxygen inlet stream, a thermocouple port, a cooling coil port, a pressure relief valve port, a pressure gauge port, an exhaust outlet port for the vapour phase, and an impeller port. A schematic can be observed in Figure 12. The experiments began by making the leaching solution in a 200 mL volumetric flask along with a 100 mL volumetric solution of distilled water. These flasks were combined and mixed with a magnetic stirrer prior to being poured into the vessel. After mixing for 15 minutes, the solution was poured into the vessel along with the ore concentrate. The glass ampules had to be carefully placed in the autoclave to ensure the dual pitched four-blade impellers would strike at sufficient angles to release the acid. After all of the components had been added to the vessel, the autoclave was sealed and the temperature controller was set. Cooling tap water ran through the internal cooling coil for temperature regulation within 1 °C. Once a stable temperature of 150 °C was reached, oxygen gas was injected into the autoclave at an overpressure of 90 psi through a dip tube making the total vessel pressure 150 psi. 1 minute was given for the oxygen to stabilize within the vessel prior to starting the impellers, which would also ensure the autoclave contained an oxidizing environment prior to releasing the acid to avoid hydrogen sulphide gas formation through Equation (4). The leaching experiment was initiated once the impellers had broken the ampule and were flowing continuously at 800 rpm. In cases where the ampule failed to collapse and prevented the continuous motion of the impellers, the operator would manually turn the top of impeller motor protruding from the top of the autoclave with the intent of breaking the ampule.

Kinetic samples were then taken through the oxygen dip tube at 2, 5, 10, 15, 20, 30, 45, and 60 minutes. Oxygen sparging was interrupted through the dip tube valve to allow for sampling. There was an additional valve controlling the flow of the slurry from the vessel into the sampling bomb, which was cooled externally by cooling coils to help flash any steam released along with the solution. The samples were cooled, filtered using a Whatman 0.02-micron syringe filter and a 5 mL syringe, and measured for their volume within a few minutes. The residue samples were dried for 24 hours at 60 °C, then measured for their weights and stored. The filtrate samples were measured for their volumes and stored. In some cases the sampling valve would become plugged from small
glass shards of the broken ampule. The test would continue regardless of whether the glass pieces dislodged from the mixture of the solution. Kinetic samples were taken if the sampling valve remained unplugged, but no additional kinetic samples were taken if glass was obstructing the valve pathway. This explains the absence of any kinetic data points in the results. Oxygen dip tube plugging was also encountered. Attempts were made to vent small portions of the gas with the oxygen valve shut to decrease the pressure in the vessel. The oxygen valve was then opened again with the hopes of the positive pressure unplugging the dip tube. Some attempts were successful while others were not. Experiments were repeated if dip tube plugging affected the sustained vessel pressure for more than 5 minutes.

The total leaching time was 90 minutes for the final extraction to gain a clear understanding of the leaching kinetics. When the experiment was completed, the gas was purged out of the vessel and the internal cooling coil was fully activated. The resultant slurry was vacuum filtered with two 11-micron Whatman filter papers within 10 minutes. Residues and filtrates were kept for analysis in the final extracts as well. Again, the filtrates were measured for their volumes and the residues were dried for 24 hours at 60 °C before recording the weights. The vessel would be rinsed with acid after each experiment using a 5 % volume hydrochloric acid solution at 80 °C for 30 minutes to clean the iron precipitates and avoid contamination.

Substantial dilutions were required to analyze the filtrates via the Varian Atomic Absorption Instrument because of the high sensitivity to zinc. Standard dilutions of 0, 0.2, 0.5, 1, 2, 5 mg/L zinc sulphate in 1 % volume nitric acid solution were made accurately to produce a calibration curve on the atomic absorption (AA) instrument. Filtrates were then heavily diluted in 1 % volume nitric acid to ensure the zinc sulphate concentration remained below 5 mg/L. Measurements were repeated to ensure the accuracy of the instrument was sufficient. The results can be observed in Tables 6 and 7.
**Varying Conditions**

To examine the individual effects of the operating parameters on the leach extractions, different conditions were employed while keeping all other variables constant. Ferric concentrations were varied from 0.1-10 g/L to analyze the effect of the iron concentration in solution on the leaching rate. An increase in the ferric concentration is expected to have quite a significant effect on the overall zinc leach extractions, since ferric iron is the surrogate oxidant leaching the zinc mineral (Baldwin et al., 1995; Crundwell, 1988; Perez & Dutrizac, 1991). As oxygen plays an important role in ferrous oxidation, oxygen overpressures were also varied between 70-110 psi. Higher oxygen overpressures were expected to increase the rate of the ferrous to ferric oxidation reaction, thus increasing the ferric concentration in solution as seen in Equation (2). Therefore, the overall zinc extractions should increase from the enhanced production rate of ferric iron. The temperature effects on the leaching rate were also investigated to determine the activation energy: experiments were performed at 125, 130, 140, 150, and 170 °C. Temperature increases generally have a strong positive impact on leaching rates, so it was expected that the overall zinc extractions would increase significantly as the temperature increased (Verbaan & Crundwell, 1986; Xie et al., 2007). Activation energies are a good measure of how sensitive the leaching system is to temperature changes. Higher activation energies generally suggest the leaching system is chemically controlled, meaning temperature changes will have a strong effect on the leaching rate in comparison to diffusion controlled leaching systems. Activation energies below 20 kJ/mol are generally considered to be diffusion controlled (Souza et al., 2007). From other values in literature, zinc pressure leaching tends to be chemically controlled with an activation energy value between 40-70 kJ/mol (Perez & Dutrizac, 1991; Verbaan & Crundwell, 1986; Xie, 2007). Therefore, increases in temperature should still affect the leaching rate, but not too drastically. However, any temperatures above the viscous phase change of liquid sulphur might result in a decrease in the overall extraction. This temperature is around 160 °C, and therefore, any temperatures above this point risk a significant decrease in the leaching rate from the ore particles being covered by molten sulphur (Peters, 1992). Depending on the dynamics of the autoclave and the utilization of dispersants, it is possible that the molten sulphur issue can be avoided. It would be interesting to observe this phenomena in this particular leaching system and determine if the leaching rate
increases at a temperature above 160 °C. The acid concentration in solution also has an effect on the leaching rate, as more iron will be soluble at increased acidities. Pyrite oxidation increases and the solubility of iron precipitates also increases at higher acidities (Long & Dixon, 2004). The difference in acid concentration is what characterizes the two-stage pressure leaching systems installed in the industrial process at Flin Flon. Thus, acid concentrations of 140, 160, 180, and 200 g/L were used in the experiments to verify the effect of acid on the overall leach extractions. The particle size distribution of the ore is another parameter that deserves attention. Since finer particles will leach faster, smaller particle sizes should improve the leach extractions. The sensitivity of the leaching rate to a decrease in particle size is critical as plants can determine whether the excess energy to grind the ore to a finer particle size is worth the extraction benefits. The effect of particle size was examined by choosing P99 grind sizes of 35, 45, and 55 microns.

**Experimental Results**

The results of the bench scale leach tests successfully show the investigated effects of critical parameter changes. A number of leach tests were repeated throughout the work of this thesis. The experimental procedure was optimized over time and the conditions had to be altered to achieve similar values to those obtained at the plant. Dilutions of the filtrates had to be extremely precise since the AA instrument was very sensitive to zinc concentrations. Micropipettes were used after ensuring they were calibrated correctly. Some filtrate samples were diluted a second or third time if the initial dilution was not accurate or not strong enough.

**Table 6: Leach Data – the resultant leach extractions for each test performed.**

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<th>Undiluted Zn (g/L)</th>
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<th>Zn Mass out (g)</th>
<th>Extraction (%)</th>
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The shrinking sphere micro model was utilized to fit the data. Equation (32) was used to determine the required leaching time to achieve a complete fraction reacted. The test of
plotting \(1 - (1 - X)^{1/3}\) against time was performed to validate the linear leaching kinetics. A straight line is the result, verifying that the shrinking sphere micro model fits the result well. An example is shown in Figure 13 for three of the temperatures from the kinetic experiments.

![Figure 13: Linear Leaching Validation](image)

Figure 13: Linear Leaching Validation – three kinetic experiments are shown as examples of testing linear leaching. All of the experimental data fit well to the shrinking sphere micro model with the exception of the highest temperature test. This is explained in more detail following the kinetic data for the experiments at different temperatures.
Table 7: Calculated Model Values – the shrinking sphere micro model predicted values.

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**Effect of Fe(III)**

The first set of experiments analyzed the effects of the iron concentration on the leaching extraction. The initial ferric concentrations used in increasing order are 0.1, 1, 5, and 10 g/L. Soluble iron has a substantial effect on the sphalerite leach rate, as observed in literature (Jan et al., 1976; Verbaan & Crundwell, 1986). The dependence of the predicted overall leach extraction on the ferric concentration can be observed by the substitution of Equations (82-85) into Equations (55) and (56). Although the experimental data verifies this relationship through Figure 14, one must evaluate the effect of increasing the initial ferric concentration carefully. Having increased amounts of ferric initially can increase the leaching rate of the sulphide minerals, some of which contain iron. This would release more ferrous iron into solution buffering the effect of adding ferric to increase the ferric to ferrous ratio. The oxygen kinetics would then be the determining factor of the ferrous to ferric conversion through Equation (2). In the case where the oxygen reduction kinetics is slow, there is a possibility that the ferrous to ferric ratio would decrease from adding small amounts of ferric initially. However, this situation is unlikely. There would have to be large amounts of iron-containing minerals present in the feed, which is not the case. Some literature studies added ferrous iron as
opposed to ferric iron and concluded similar results (Dutrizac, 2006; Xie et al., 2007). There must have been enough oxygen present in solution that the ferrous to ferric conversion was not kinetically limiting. All of the reactors were bench scale vessels in these tests, making it feasible to achieve a sufficient oxygen concentration in solution early. Other authors investigated the effect of having more iron content in the feed. The results were interesting, as there seemed to be an inconclusive effect. Perez and Dutrizac plotted the iron weight percentage present in the feed ore as a function of the overall zinc extraction rate and concluded there was generally a linear relationship between the two parameters (1991). However, other authors concluded that there was an exponential relationship, as the case in this particular study, when iron was added to the solution (Dutrizac, 2006; Jan et al., 1976; Souza et al., 2007). The effect of iron was different depending on where the iron originated. The complexity of the iron chemistry and the oxygen kinetics could explain the differences found. Iron contained in the feed could have galvanic effects on the leaching of pyrite in comparison to directly affecting the oxidation rate by increasing the ferric ions (Estrada-de los Santos, 2016). The ferric to ferrous ratio is dependent on many factors as explained previously. The shrinking sphere micro model fits the data well, confirming the original hypothesis that the surfactants and dispersants successfully prevent the viscous sulphur from coating the ore particles. Each solid curved line in the kinetic data figures represents the shrinking sphere micro model.
Figure 14: Fe(III) – the effect of initial ferric additions verify the MCI’s model dependence on ferric ions. Kinetic sampling enabled the fraction reacted for zinc to be calculated at different times.
Figure 15: Fe(III) – the effect of initial ferric additions on the $\tau$ value. The relationship is exponential between the parameters (Dutrizac, 2006; Jan et al., 1976; Souza et al., 2007).

**Effect of O$_2$ Overpressure**

Oxygen overpressure changes did not affect the leach extractions significantly. Small increases were observed, if any, in the leaching rates. One possible explanation for this could be that the oxygen concentration in solution increases faster in the small 600 mL autoclave reactor compared to the industrial autoclave vessels due to the smaller volume. Therefore, the industrial autoclaves would be more sensitive to oxygen overpressures. The experimental data displayed a slightly larger increase in extractions from the 70 to 90 psi oxygen overpressures compared to the increase from 90 to 110 psi, but overall they are very similar. This suggests there is enough oxygen present in all cases that only marginal increases in the ferric production rate are observed, if any. It was expected that a larger increase in the leaching rate would result from a higher ferric concentration, and that the 110 psi oxygen overpressure experiment would have a larger increase from the 90 psi overpressure experiment.
Figure 16: O₂ Overpressure – the effect of varying the oxygen overpressure is negligible above 70 psi.

**Effect of Temperature**

The Arrhenius plot in Figure 17 shows the effect of temperature on the leaching rate for this particular system. The slope of the linear trendline multiplied by $R$, the gas constant, indicates the activation energy in kJ/mol. The kinetic leach data in Figure 18 was analyzed to verify the micro model leaching mechanism. The only exception of when the shrinking sphere micro model did not fit the data well is the experiment where the temperature was 170 °C. The temperature in this case was higher than the viscous sulphur phase change temperature at around 160 °C, resulting in the solids being coated by sulphur that is difficult to displace. It is for this reason that the 170 °C experiment is excluded from the activation energy calculation. The calculated result is 40.8 kJ/mol when all of the other temperature tests are included. This result is consistent with literature and further confirms that charge transfer limits the leaching and thus the reaction is electrochemically controlled (Crundwell, 1988; Perez & Dutrizac, 1991; Verbaan & Crundwell, 1986). Although the activation energy is in the lower range of the reported values, it agrees with the trend predicted by Perez and Dutrizac (1991). Sphalerite concentrates containing higher solid iron contents were found to have a
decreasing activation energy. The iron content of 11.24 wt.% for the concentrate used in this study is relatively high, and therefore can be attributed to the activation energy result.

Figure 17: Arrhenius Plot – the effect of temperature on the leaching rate is shown above. The slope of the data points multiplied by $R$, the gas constant, gives the activation energy in kJ/mol.
Figure 18: The Temperature Dependence – the viscous phase change of sulphur is evident at the 170 °C test, which explains the obvious dramatic decrease in the leach extractions.

**Effect of Acidity**

Acid sensitivity was also tested with significantly higher extractions for the highest acid concentrations. As expected, the lowest acid concentration resulted in low extraction rates. Low acidities result in more iron being precipitated, and hence, less soluble ferric is available to leach the sphalerite. Higher acid concentrations enhance the leaching rates as more iron becomes soluble and can oxidize the sulphide minerals. However, acid concentrations that are too high (levels above twice the stoichiometric amount) can result in hydrogen sulphide gas being formed. Not only is this gas extremely dangerous, it slows the leaching kinetics as it reacts with ferric iron to produce more ferrous iron. This lowers the ferric to ferrous ratio and therefore decreases the sphalerite leaching rate (Harvey et al., 1993; Jan et al., 1976; Torma, 1985). Low acid concentrations resulted in final extractions that did not reach 100 %. This agrees with the industrial data and further confirms the elegance and significance of the two-stage pressure leaching process. Higher acidities enhance the leaching rate while recirculating the pregnant leach solution to the
low acid autoclave to avoid having to neutralize excess acid in the discharge solution downstream.

![Graph showing the effect of acid on extraction](image)

**Figure 19:** The Effect of Acid – increased acidities resulted in higher extractions with a strong sensitivity.

**Effect of Particle Size**

The leaching curves were all fitted according to the P99 size of the feed PSD seen in Figure 12, even though finer particles were present in small fractions. This explains why the kinetic leach data is higher than the predicted extraction curves earlier in the leach for all of the experiments. However, distinguishing the particle sizes by their P99 size is suitable because the coarser particles affect the overall leaching rate the most. Using the P80 size in leaching experiments is not as effective since it does not describe the coarser particle sizes. The minor 10-micron changes in the P99 size result in relatively large extraction differences, indicating the strong dependence of the leaching rate on the particle size. These results provide insight into whether the additional energy required to grind the particles further is worth the increased extraction benefits. It is an economic decision that has to be evaluated by every hydrometallurgical plant. Other studies have been performed to examine the effect of particle size on the leaching rate in zinc pressure
leaching systems. Yan et al. also found a trend determining that the particle size had a serious effect on the leaching rate, although not as large as observed in Figure 20 (2010). This could be due to the ore compositional differences, as their sphalerite ore contained significantly less iron. Further studies are required to determine if the individual parameter effects of particle size and iron content in the feed interact with each other.

![Graph showing particle size dependence](image)

**Figure 20: Particle Size Dependence – a small change in the particle size resulted in noticeable extraction differences.**

**Repeatability**

Finally, an additional leach test was performed on a freshly ground ore sample containing the same particle size distribution to compare the standard test results. The standard conditions were identically used for each test. The extractions are comparable and confirm the accuracy of the experiments.
Comparison of the Experimental and Plant Model Results

The results of the industrial data model are successfully verified by the experimental data. The activation energy predicted by the model was 42.8 kJ/mol. Experiments needed to be performed at different temperatures in a laboratory setting under the same chemical conditions as the plant to confirm this value. The experiments resulted in an activation energy of 40.8 kJ/mol, confirming that the industrial model values were accurate. Expanded ranges of the ferric to ferrous ratio, the oxygen overpressure, the acidity, and the particle sizes were tested and the trends predicted by the industrial plant model are also confirmed. The residence time for the ore particles in the industrial autoclave is 50 minutes. Comparing the extractions for the laboratory experiments at this residence time, the industrial autoclave achieves slightly higher extractions. This is expected as a continuous autoclave constantly has fresh feed going into the vessel, hence there is a greater opportunity for concentration gradients to be maximized between the reagents in

Figure 2: Sample Comparison – two separate subsamples of ore with the same particle size distribution were leached under the same standard conditions.
solution and the ore particles. A fresh ore particle has potential to be leached faster than an existing partially leached ore particle in the autoclave of the same size.

The expanded ranges of parameter values were tested to verify the trends predicted by the industrial model. Figures 14 to 21 show the experimental data points comparatively with the micro model used for the overall plant model. The model slightly over predicted the leach extractions as the ferric to ferrous ratio increased. At very low ratios, the model predictions become closer to the experimental data. One reason for this could be the exponential value chosen of 0.5 is slightly higher than the optimum exponential value in Equation (85), increasing the predicted overall fraction reacted. Another reason could be that as the ferric to ferrous ratio decreases, the denominator becomes larger and the numerator becomes smaller in Equation (85). Therefore, the concentration function becomes smaller and is less significant in the overall MCI equation shown by Equation (55). Overall, the observed experimental trend agrees with the industrial model. The activation energy generated by the model compares well with the experimental data. This offers further industrial applications for predicting the extractions when shifts in the activation energies occur due to solution chemistry differences or ore composition changes. The experiments for different particle sizes compare well with the trend predicted by the plant model. Again, the model slightly over predicts the extractions, but the data points follow closely to the model trend line.
Chapter 6: Conclusion and Recommendations

Summary
The MCI model was utilized for predicting the plant data of zinc pressure leaching. The current MCI model was developed according to the industrial low acid zinc pressure leaching conditions. Bench scale autoclave experiments in addition to plant data confirmed the model results. Increased parameter changes were tested to investigate the sensitivity of the leach extractions in comparison to the model results. The model developed in this thesis stood out significantly from other leaching models in the following ways:

i) More detailed relationships between parameters such as the reagent concentrations and the overall fraction reacted were discovered through the development of this model.

ii) A further advantage is the versatility of the model, meaning different leaching reactions can be accounted for in varying plant conditions in the industry.

iii) The shrinking sphere or shrinking core micro model can be represented with the MCI.

On the other hand, the major limitation of this model is that the MCI is based on a steady state system. This limitation applies to all other leaching models to date; although, one more significant advantage of the MCI is that it can account for non-ideal flow throughout a reactor whereas population balance models cannot.

Overall, kinetic modeling is a useful tool that can enhance the confidence of engineers for the scale-up of pilot testing to a full size plant in addition to predicting process changes within an operating plant. The MCI model results shown in this thesis are promising when simulating an industrial autoclave, and also this model has the potential to be accurate with various other plants.

Future Work
Further experimental work can be continued to examine the effects of other parameters such as the pulp density, surfactant dosage, and the analysis of other metal ions in solution. Testing concentrates with different amounts of iron would also be beneficial to verify the linear relationship that it has on the extraction rates as observed in literature
(Crundwell, 1988; Perez & Dutrizac, 1991; Piao & Tozawa, 1985). The results could provide insight for the reason iron in the concentrate has a different effect than adding iron as ferric sulphate. This would improve the model accuracy for varying feed conditions. As for the modeling work, the development of a dynamic model for the zinc pressure leach would account for start up and shut down operations and help mitigate the economic losses associated with these necessary procedures. Dynamic simulation would also increase the accuracy of the sulphate balance throughout the plant, avoiding the need to purchase or bleed acid out of the system for process upsets.

The universal applications of this model should aid the industrial uptake of simulation. Leaching processes are a major plant operation; the benefits of simulation in this area could drastically improve the process control. The industry and researchers must take advantage of the advances in technological development; the author hopes that this model also encourages the development of models in other hydrometallurgical processes, such as purification. Accurately modeling an entire plant will eminently benefit the industry.
References


Appendix

The computer code was developed in the CADSIM software, which uses a C++ compiler called Embarcadero. The critical section of the MCI code is attached below for reference. This code calculates the overall fraction reacted for the reaction specified by the user.

```c++
/////Multiple Convolution Integral Section/////  
for( c = 0; c < NumTanks; c++ ) {
    Loop[c] = 1;
}
for( I = 0; I < NumTanks; I++ ) {
    n2[I] = 6;
}
NCON = 0;
while( NCON < NumTanks ) {
    A[3] = 0;
    for( NN3 = 0; NN3 < Loop[3]; NN3++ ) {
        J[3] = NN3;
        A[2] = 0;
        for( NN2 = 0; NN2 < Loop[2]; NN2++ ) {
            J[2] = NN2;
            A[1] = 0;
            for( NN1 = 0; NN1 < Loop[1]; NN1++ ) {
                J[1] = NN1;
                A[0] = 0;
                for( i2 = 0; i2 < n2[0]; i2++ ) {
                    J[0] = i2;
                    double S = 0;
                    for( kappacount = 0; kappacount <= NCON; kappacount++ ) {
                        kappa[ kappacount ] = Kappa[kappacount];
                        S += kappa[ kappacount ];
                    }
                }
            }
        }
    }
}
```


* roots6point[ J[kappacount] ];

}

double sum1 = 0;
for( i1 = 0; i1 < n1; i1++ ) {
    sum1 += weights15point[ i1 ]
    * pow( 1 - S / pow(roots15point[ i1 ] + pow
        (S, RRParameter), inverse_RRParameter), 3.0 );
}
A[0] += sum1 * weights6point[ J[0] ]
    * exp( -pow(S, RRParameter) );
if( NCON == 0 ) {
    if( ReactionCount == 0 )
        lDerivedStuff.Compartment1ConversionZnS = 1 - A[ NCON ];
    else if( ReactionCount == 1 )
        lDerivedStuff.Cprtment1ConversionCuFeS2 = 1 - A[ NCON ];
}
else if( NCON == 1 ) {
    if( ReactionCount == 0 )
        lDerivedStuff.Compartment2ConversionZnS = 1 - A[ NCON ];
    else if( ReactionCount == 1 )
        lDerivedStuff.Cprtment2ConversionCuFeS2 = 1 - A[ NCON ];
}
else if( NCON == 2 ) {
    if( ReactionCount == 0 )
        lDerivedStuff.Compartment3ConversionZnS = 1 - A[ NCON ];
    else if( ReactionCount == 1 )
        lDerivedStuff.Compartment3ConversionCuFeS2 = 1 - A[ NCON ];
}
if( ReactionCount == 1 )
IDerivedStuff.Cprtmnt3ConversionCuFeS2 = 1 - A[ NCON ];
}
else if( NCON == 3 ) {
if( ReactionCount == 0 )
IDerivedStuff.Compartment4ConversionZnS = 1 - A[ NCON ];
else if( ReactionCount == 1 )
IDerivedStuff.Cprtmnt4ConversionCuFeS2 = 1 - A[ NCON ];
}
NCON += 1;
Loop[NCON] = n2[NCON];
}
fractionreacted = (1 - A[NCON - 1]);\* pow((t / taoStar), 0.33);
double overallRate;
overallRate = fractionreacted * GetInputVariable(kFirstPort,
local->solFlowIndex); // * convFacts.fVolumeFlowName;

if( ReactionCount == 0 ) {
IDerivedStuff.FractionReactedZnS = fractionreacted;
IDerivedStuff.GlobalReactorConstantZnS = Kappa[i];
}
else if( ReactionCount == 1 ) {
IDerivedStuff.FractionReactedCuFeS2 = fractionreacted;
IDerivedStuff.GlobalReactorConstantCuFeS2 = Kappa[i];
}
return fractionreacted;