On the Operability of the
Sherritt-Gordon Ammonia Leach at the
Kwinana Nickel Refinery

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This thesis is presented for the degree of
Doctor of Philosophy of Murdoch University
2014
Declaration

I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

..........................................................
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Abstract

The objective of this thesis was a study of the operability of the leaching process at the Kwinana nickel refinery. The refinery makes use of the Sherritt-Gordon process for producing London Metal Exchange-grade nickel briquettes and other products. Like all industrial operations, the refinery embodies a considerable investment, demanding optimal performance in order to remain profitable. The 3-stage, 6-autoclave ammonia leach there is the most important process in the refining operation, yet it is also the most complex and least understood. A thorough understanding of the leach is critical in promoting optimal refinery operation, thus provoking the present work.

The operability study was conducted on the basis of mathematical modelling and computer simulation, focusing on steady-state operation. An examination of the chemistry of the Sherritt-Gordon ammonia leach was undertaken, leading to a chemical reaction system suitable for robust modelling. A mathematical model of the process was developed, which allowed for the construction of a computer program for the purpose of process simulation. The model was firstly used in a stand-alone fashion to examine the chemistry and operation of the leach. The model was secondly incorporated into an optimisation problem, augmenting the program as required, and used to investigate the impact of process disturbances and set-point changes on leach performance for a wide range of operating conditions.

On a fundamental basis, the following transpired from this work: (1) a new understanding of the Sherritt-Gordon ammonia leach chemistry, (2) a novel method for modelling generic leaching reactors, and (3) a modelling framework for the Sherritt-Gordon ammonia leach. On a practical basis, the operability study of the ammonia leach generated (1) significant insight into process behaviour, which may be directly used by refinery staff to support performance optimisation and process control, and (2) a series of recommendations for unlocking hidden capacity, which should form the basis of future efforts to optimise refinery operation.
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# Nomenclature

\( a \)  
- gas-liquid specific interfacial area, \( m^{-1} \)

\( A_i \)  
- atomic weight of species \( i \), \( kg \ mol^{-1} \)

\( A_{CS} \)  
- cross-sectional area, \( m^2 \)

\( \bar{B} \)  
- average birth rate of particles per unit volume, \( m^4 \ s^{-1} \)

\( C_i \)  
- molar concentration of species \( i \), \( mol \ m^{-3} \)

\( \bar{C}_i \)  
- mass concentration of species \( i \), \( kg \ m^{-3} \)

\( C'_{O_2} \)  
- solubility of oxygen, \( mol \ m^{-3} \)

\( C'_{p,i} \)  
- standard molar heat capacity of species \( i \), \( J \ mol^{-1} \ K^{-1} \)

\( C_v \)  
- coefficient of variation (ratio of standard deviation to mean)

\( D \)  
- particle diameter (or size), \( m \)

\( D_0 \)  
- initial particle diameter (or size), \( m \)

\( D_b \)  
- mean bubble diameter (or size), \( m \)

\( D^* \)  
- scale parameter of particle size distribution function, \( m \)

\( \dot{D} \)  
- rate of particle shrinkage, \( m \ s^{-1} \)

\( \dot{D}_i \)  
- diffusivity (or diffusion coefficient) of species \( i \), \( m^2 \ s^{-1} \)

\( \bar{D} \)  
- average death rate of particles per unit volume, \( m^4 \ s^{-1} \)

\( E \)  
- electrode potential, \( V \)

\( E_a \)  
- Arrhenius activation energy, \( J \ mol^{-1} \)

\( E_e \)  
- equilibrium potential of a redox couple, \( V \)
$E_i$  instantaneous enhancement factor

$E_m$  mixed potential, V

$E_{sys}$  energy within any given system (reactor), kJ

$E(t)$  residence time distribution function, s$^{-1}$

$E_{N}(t)$  residence time distribution function for $N$ reactors in series, s$^{-1}$

$f(C)$  function of concentration (reaction-specific units)

$f_m(D)$  mass-weighted particle size density function, m$^{-1}$

$f_n(D)$  number-weighted particle size density function, m$^{-1}$

$F$  Faraday’s constant, C mol$^{-1}$

$F_i$  molar flow rate of species $i$, mol s$^{-1}$

$F_i$  mass flow rate of species $i$, kg s$^{-1}$

$F_m(D)$  mass-weighted particle size cumulative distribution function

$F_{m,106}$  mass fraction of particles passing 106 micron

$g$  volumetric fraction of solids

$g^*$  acceleration due to gravity, m s$^{-2}$

$G_i$  rate of net generation of species $i$ via chemical reaction, mol s$^{-1}$

$\Delta G_i^*$  standard free energy change for species $i$, kJ mol$^{-1}$

$H$  volumetric gas holdup or volumetric fraction of gas

$\Delta H_i^*$  standard molar enthalpy change for species $i$, kJ mol$^{-1}$

$i$  net current density, A m$^{-2}$

$i_0$  exchange current density, A m$^{-2}$

$I$  electric current, A
\( k(T) \) intrinsic rate constant for overall reaction (reaction-specific units)

\( k_0 \) Arrhenius function pre-exponential factor (units equivalent to \( k(T) \))

\( k_i \) liquid-side mass transfer coefficient, \( \text{m s}^{-1} \)

\( \rightarrow k(T) \) intrinsic rate constant for the forward direction of a half-cell reaction

\( \leftarrow k(T) \) intrinsic rate constant for the reverse direction of a half-cell reaction

\( k_{i,a} \) volumetric mass transfer coefficient, \( \text{s}^{-1} \)

\( K_n \) stepwise stability constant for \( n \)th complexation reaction

\( \bar{m} \) mass of particles per unit volume, \( \text{kg m}^{-3} \)

\( M_i \) molecular weight of species \( i \), \( \text{kg mol}^{-1} \)

\( \bar{n} \) number of particles per unit volume, \( \text{m}^{-3} \)

\( N_{\text{H}} \) Hatta number

\( N_{\text{Ra}} \) Rayleigh number

\( N_{\text{Sh}} \) Sherwood number

\( N_i \) number of moles of species \( i \) in a reactor, \( \text{mol} \)

\( P_i \) partial pressure of species \( i \), Pa

\( P^*_g \) gassed power, W

\( Q \) volumetric flow rate, \( \text{m}^3 \text{s}^{-1} \)

\( Q \) rate of heat flow to the surroundings, kW

\( r_k \) rate of reaction \( k \), \( \text{mol m}^{-2} \text{s}^{-1}, \text{mol m}^{-3} \text{s}^{-1} \)

\( R_{\text{Cu}}, R_{\text{Cu}}^* \) hypothetical and actual ratio of copper(II) to total copper in solution

\( R \) ideal gas constant, \( \text{J mol}^{-1} \text{K}^{-1} \)
\( S_i \) surface area of solids species \( i \), \( \text{m}^2 \)

\( S'_i \) standard molar entropy of species \( i \), \( \text{J mol}^{-1} \text{K}^{-1} \)

\( t \) time, \( \text{s} \)

\( \bar{t} \) mean residence time, \( \text{s} \)

\( T \) temperature, \( \text{K} \)

\( V \) slurry volume, \( \text{m}^3 \)

\( W_s \) rate of shaft work done on the surroundings, \( \text{kW} \)

\( x \) charge transfer valency

\( x_j \) fraction of material in \( j \)th stream

\( x_{\text{NH}_3} \) mole fraction of ammonia in aqueous ammonia solution

\( \bar{x}_d \) mass fraction of aqueous solutes

\( \bar{x}_{\text{NH}_3} \) mass fraction of ammonia in aqueous ammonia solution

\( 1 - X^* \) fraction unreacted in a batch reactor

\( X^* \) conversion in a batch reactor

\( 1 - X \) fraction unreacted in a continuous reactor

\( X \) conversion in a continuous reactor

\( X_{\Sigma}^{\frac{N}{N}} \) cumulative conversion for \( N \) continuous reactors in series

**Greek Letters**

\( \alpha \) charge transfer coefficient

\( \beta_i \) overall stability constant for \( i \)th complexation reaction, \( \text{kg}^i \text{mol}^{-i} \)

\( \hat{\alpha}, \hat{\beta} \) density correlation coefficients
$\bar{\alpha}, \bar{\beta}$ partial pressure correlation coefficients

$\gamma_i$ mass composition of solids species $i$ in a mineral assembly

$\delta$ effective thickness of the Nernst diffusion layer, m

$\varepsilon_k$ rate of extent of reaction $k$, mol s$^{-1}$

$\varepsilon_{ik}$ rate of extent of reaction of species $i$ in reaction $k$, mol s$^{-1}$

$\eta$ electrical overpotential, V

$\kappa$ ratio of reactor mean residence time to the time it takes to completely leach a single particle of initial size $D^*$

$\mu$ viscosity, Pa s

$\mu_m, \mu_i$ mean of mass-weighted particle size density function for species $i$, m

$\mu_m^{(i)}$ $i$th moment of $f_m(D)$, m$^i$

$\mu_p^{(i)}$ $i$th moment of $\psi(D)$, m$^{i+3}$

$\nu_{ik}$ stoichiometric coefficient of species $i$ in reaction $k$

$\nu_s$ superficial gas velocity, m s$^{-1}$

$\nu_t$ bubble terminal velocity, m s$^{-1}$

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

$\sigma$ surface tension, N m$^{-1}$

$\sigma_m^2, \sigma_i^2$ variance of mass-weighted particle size density function for species $i$, m$^2$

$\tau$ reaction timescale, s

$\phi$ shape parameter of particle size distribution function

$\varphi_i$ fraction of water available to dissolve oxygen if species $i$ is present

$\psi(D)$ population density function, m$^{-4}$
\( \omega \)  pulp density, kg kg\(^{-1}\)

**Subscripts**

a  anodic

c  cathodic

d  dissolution

eff  effective

f  formation

g  gaseous

i(a)  aqueous species

i(g)  gaseous species

i(s)  solids species

i(s\(^*\))  mineral (solids) species

in  inlet (or feed) conditions

l  liquor or liquid

L  limiting

n  normal

o  overflow

r  reaction

r  room

R  reference

s  solids

T  temperature

T  total
Acronyms and Abbreviations

1SL  
first stage leach

2SL  
second stage leach

3SL  
third stage leach

AmSul  
collective term for ammonium sulphate, ammonium sulphamate, ammonium thiosulphate and ammonium polythionate

BV  
bromate value; see Chapter 3

(1 g L\(^{-1}\) S\(_2\)O\(_3\)\(^{2-}\) = 41 BV-units, 1 g L\(^{-1}\) S\(_3\)O\(_6\)\(^{2-}\) = 26 BV-units)

BV:[Cu]  
BV-to-total copper concentration ratio

CBF  
copper boil feed

CSTR  
continuous stirred tank reactor

DTO  
dosed thickener overflow

ETU  
effluent thickener overflow

FTO  
final thickener overflow

MFL  
metal free liquor

NH\(_3\):TM  
aqueous free ammonia-to-total metals molar ratio

PSD  
particle size distribution

RTD  
residence time distribution

tpa, tpd  
tonnes per annum/day

WTO  
wash thickener overflow
Acknowledgements

First and foremost, I would like to express the utmost gratitude to my supervisor, Professor Parisa A. Bahri (Murdoch University), for her guidance, insight and, above all, patience throughout the course of this work. Dr Bahri’s broad knowledge of the process engineering discipline was a welcomed resource for both establishing and refining the approach taken to pursue this research.

I would like to recognise the contribution of Professor David G. Dixon (University of British Columbia). Dr Dixon invited me to spend a semester at UBC to study two of his units that were aligned with this research topic. During this time, the foundation work underpinning the chemistry identification and model development was completed. Dr Dixon’s input (both inside and outside of the classroom) was instrumental in the success of these two phases of work.

My appreciation is given to the process staff at the Kwinana nickel refinery, for inviting me on site and always providing assistance. Particular thanks are given to Dr Tony Chamberlain, Michael Lee, Edmond Kim and Lorna Petchell. Thank you also goes to the other staff members who made my time at the refinery a pleasant and memorable one.

The time spent carrying out this research would not have been as enjoyable had it not been for the friendly temperament of the Murdoch University staff and students, particularly those in the Engineering Department. A special thank you goes out to you all.

I gratefully acknowledge the Australian Research Council and the Kwinana nickel refinery for providing financial support to carry out the research.

I would like to thank BHP Billiton Ltd for permission to publish the thesis.

Last, but certainly not least, I thank my family and friends. Words here cannot do justice to the contribution they made. They know.
Chapter 1

Introduction

The Kwinana nickel refinery of BHP Billiton Limited (formerly of Western Mining Corporation Limited), located 30 kilometres south of Perth, Western Australia, is a hydrometallurgical refinery that employs the Sherritt-Gordon ammoniacal pressure leaching process for the recovery of nickel, copper and cobalt from a nickel matte [1]. The site has been in operation since 1970, and has a current production capacity of 65,000 tonnes per annum (tpa) of nickel metal in the form of London Metal Exchange-grade briquettes and powder. Other products include copper sulphide, nickel-cobalt mixed sulphide and fertiliser-grade ammonium sulphate.

The refinery represents a significant investment. There is thus a need for perpetual improvement in process operation management in order to optimise performance and maximise shareholder return. This exists predominantly in the form of enhancing product quality, increasing plant availability, promoting higher process throughputs via de-bottlenecking and expansion, ensuring feasible operation and supporting greater process stability via improved control, all whilst minimising operating costs and adhering to safety and environmental regulations. The objectives outlined here are not easily attainable, demanding a detailed understanding of process operability.

The leaching process at the refinery is the most important step in the hydrometallurgical flowsheet. It is charged with both the dissolution of value metals in the refinery feed material and preparation of the pregnant liquor for favourable
downstream processing. Conditions established there greatly affect the efficiency of the entire refining operation, and thus its performance has a significant impact on the economics of metal production. Therefore, optimal operation of the leaching process should be the preliminary goal in seeking optimal operation of the refinery.

There are notable difficulties associated with normal operation of the leach. The process is comprised of an intricate arrangement of unit operations and streams. The chemistry is complex and not fully appreciated. There is only a partial understanding as to how natural deviations and manual alterations in operating conditions influence process behaviour. Operation is inherently subject to variability, limitations and other uncertainties. What is more, set-points for the leach are variable, and dictated by conditions established downstream. Managing these intrinsic factors is central to ensuring that operation remains optimal with respect to performance, and thus to profit.

Knowledge of process operability may be greatly enhanced with the development and application of robust mathematical models which feature a comprehensive specification of process chemistry (i.e. reaction stoichiometry and kinetics). Models may be utilised stand-alone or as part of an optimisation problem, each by way of the construction of computer programs capable of process simulation. This tool may be used to generate a great deal of insight into process performance that cannot be obtained through other means. Process investigations can range from an inspection of the micro- to the macro-scale, from an examination of chemistry to vessel interactions, or from those that show what is present to those that show what is absent, all for operating conditions that range from the familiar to the foreign. Simulation can ultimately lead to a fundamental understanding of the process, which may then be used to support performance optimisation and process control.

Present (and future) objectives for refinery operation represent considerable technical challenges. A thorough comprehension of the leaching process in terms of its operating characteristics, limitations and means for attaining optimal performance is required. The desired resolution of this problem has motivated the present work. The objective of this body of work is a study of the operability of the Sherritt-Gordon
ammonia leach at the Kwinana nickel refinery via mathematical modelling and computer simulation. The key performance issues associated with the leach principally concern long-term or sustained variations in operating conditions. The investigation of such problems is best reserved for a steady-state analysis.

A study such as this has not been performed on any industrial hydrometallurgical leaching operation, and so through this work there is opportunity to generate both specific and general knowledge in areas of interest to the fields of metallurgy and metallurgical engineering. Furthermore, given that the aspirations for and performance issues associated with normal operation of the leaching process under examination in this work is characteristic of many processes of the like, the modelling, simulation and analysis methodology applied here may be considered for other industrial operations.

The work carried out in this thesis is organised as follows. In Chapter 2, a literature review is presented. The main topics relevant to the objectives of this study include (1) the Sherritt-Gordon leach process chemistry, (2) the mathematical modelling of leaching processes and (3) the optimisation of leaching processes. In Chapter 3, the leaching process at the Kwinana nickel refinery is given attention. The leach feed material, process flowsheet and basic operating philosophy represent the main topics of discussion.

In Chapter 4, a detailed chemical reaction system suitable for robust mathematical modelling is presented. While the essential chemistry of the leach is well-established in the literature, the detail of the interactions amongst principal species – especially with respect to kinetics – remains uncharted. This work represents the first instance in which a complete reaction system comprised of stoichiometry and kinetics incorporating all major species is composed for the Sherritt-Gordon ammonia leach.

In Chapter 5, a new method for modelling continuous leaching reactor kinetics at steady-state is developed. This procedure is based on the mathematical derivation of analytical expressions for applicable process variables. The method is extended to describe particle mixing, which forms the basis for modelling complex reactor systems. This approach may be used to model a broad range of leaching processes.
In Chapter 6, a modular strategy for large-scale, multiple autoclave, leach flowsheet model development is proposed on the basis of describing mathematically the essential stream and unit operation types of the process, which are united via common stream properties that account for the transfer of mass, energy and particle size distribution. The scheme allows for the appropriate arrangement of the flowsheet of interest, or any variation of it that employs the same essential constituents. This strategy is then applied to the leaching process at the Kwinana nickel refinery, in which mathematical equations are developed to describe three stream types and nine unit operation types. The chemical reaction system (Chapter 4) and new method for describing leaching reactors and particle mixing (Chapter 5) are fundamental components in the industrial process model. Both the leach flowsheet modelling strategy and Sherritt-Gordon ammonia leach model represent novel contributions to the literature.

In Chapter 7, the assembly of essential streams and unit operation models (Chapter 6) to describe the leaching process of interest in this work is demonstrated via the construction of a computer program capable of process simulation. The industrial process model is validated by comparing the program output and plant data for a variety of operating situations. A very good correlation is established. The model is used in a stand-alone fashion to examine the chemistry and operation of the leaching process, the present knowledge of which does not exist in great detail. The analysis thus leads to a comprehensive understanding of the Sherritt-Gordon ammonia leach.

In Chapter 8, an optimisation problem is formulated for the leaching process, in which the model (Chapter 6) represents the primary component. The computer program (Chapter 7) is modified accordingly to allow the solution of the problem and thus the simulation of optimal process performance. The latter is pursued to identify optimal operating points that exist for a variety of conditions which are established in response to process disturbances and set-point changes. This analysis demonstrates improved performance, and may be used to close the gap that exists between current operating practices and optimal operation, while generating insight into process control matters. The outcome of the investigation is a series of recommendations for unlocking hidden
capacity in the leach. Finally, in Chapter 9, conclusions on the body of work are drawn and recommendations for future work are outlined.

Throughout the course of this study, the author spent a significant amount of time on site at the Kwinana nickel refinery. Discussions throughout this thesis that pertain directly to process knowledge were acquired by the author via personal experience or through discussions with refinery staff.
Chapter 2

Literature Review

2.1 Introduction

A review of literature pertinent to the work carried out in this thesis is presented in this chapter. The following subject areas are considered for hydrometallurgical leaching processes: (Sherritt-Gordon) process chemistry, mathematical modelling and optimisation.

2.2 Sherritt-Gordon Process Chemistry

The Sherritt-Gordon process was developed in the early 1950’s by Forward and Mackiw [2, 3]. The process is an ammoniacal pressure leaching operation that is employed to recover value metals from nickel-copper-cobalt-iron sulphide concentrates and mattes. In aqueous ammonia solution, nickel, copper, cobalt, ferrous iron, and other metals combine with ammonia to form metal ammine complexes of the form $M(NH_3)_n^{x+}$ [4]. The stability and solubility of each metal ammine is dependent upon the concentration of the metal ion and ammonia, as well as the concentration and type of anions in solution, such as sulphate ($SO_4^{2-}$). If ammonia is partially or completely removed from solution, the soluble ammines tend to decompose and the metals precipitate as basic salts. Forward and Mackiw [2, 3] used this chemical framework as a basis for developing a commercial process to recover nickel, copper and cobalt from Sherritt-Gordon sulphide concentrates.
Metal recovery from sulphides via the Sherritt-Gordon process has been put into practise at only two industrial sites: the Fort Saskatchewan refinery of Sherritt International Corporation (formerly Sherritt Gordon Mines Limited) and the Kwinana nickel refinery. The Fort Saskatchewan nickel refinery [5-9] is located in Fort Saskatchewan, Alberta, and was commissioned in 1954. This refinery initially processed a nickel concentrate mined at Lynn Lake, Manitoba, but presently refines a (predominant) nickel-cobalt mixed sulphide feed that is derived from processing a low-magnesium, limonitic laterite ore [6, 10]. The Fort Saskatchewan refinery was the basis of construction of the Kwinana refinery [11-16], which initially processed a nickel concentrate mined at Kambalda, Western Australia, before converting to matte. The changes in feed material have led to some modifications in the physical structure, chemistry and operation of the leaching processes at each refinery, relative to the foundation design of Forward and Mackiw [2, 3]. The industrial sites thus not only operate their processes in a manner differing that with which they were originally intended, but do so in a fashion unlike one another. In fact, given the degree of process modifications at the Fort Saskatchewan refinery, the Kwinana refinery is now probably the only one of the two that can be said to operate the “Sherritt-Gordon process”.

Four principal operations define the refining process: leaching, copper boil, oxydrolaxis and hydrogen reduction. The process flowsheet of the Kwinana nickel refinery is given in Figure 2.1, while a detailed discussion on the leaching process there is reserved for the next chapter. In the leaching process, the sulphide matrix is decomposed, resulting in the dissolution of nickel, copper, cobalt, iron and sulphur. The fundamental chemistry is the pressure oxidation of metal sulphide in the presence of ammonia. Upon oxidation, the metal ions combine with ammonia in aqueous solution to form metal ammine complexes, and sulphide sulphur is converted to sulphate:

$$4 \text{MS} + (x + 6) \text{O}_2 + 4(n - x + 2) \text{NH}_3 + 4(x - 2) \text{NH}_4^+ \rightarrow 4 \text{M(NH}_3)_n^{2+} + 4\text{SO}_4^{2-} + 2(x - 2) \text{H}_2\text{O} \quad (2.1)$$

where the effective coordination number, $n$, is dependent on the aqueous concentrations of the metal and free ammonia.
Dissolved iron is insoluble under the leaching conditions prevailing and precipitates from solution. Forward and Mackiw [3] measured the formation of hydrated ferric oxide at the surfaces of mineral particles as they leached, suggesting that nickel concentrates leach as shrinking cores. The iron ultimately reports to the leach residue, along with many of the impurities that enter with the feed material.

Although sulphur is usually depicted in the literature as being oxidised directly to sulphate, it is well-known that a whole host of sulphur oxyanions are capable of forming in aqueous solution. In ammoniacal solution, Forward and Mackiw [2, 3, 17] observed the formation of thiosulphate \((S_2O_3^{2-})\), polythionite \((S_4O_6^{2-})\) and sulphamate \((SO_3^2NH_2^-)\), in addition to sulphate. Thiosulphate and polythionite are unsaturated (incompletely oxidised) oxysulphur species that co-exist in solution as meta-stable intermediates, while sulphamate and sulphate represent the hexavalent sulphur products. The presence of these unsaturated oxysulphur species is important in the copper boil process.

Forward and Mackiw [3] proposed the following chemical reaction system to describe the leaching mechanism for nickel and iron sulphides (a similar mechanism may be assumed for copper and cobalt sulphides):

\[
NiS : FeS + 3FeS + 7O_2 + 10 NH_3 + 10 H_2O \\
\rightarrow Ni(NH_3)_6SO_4 + 2Fe_2O_3 \cdot H_2O + 2(NH_4)_2S_2O_3 \quad (2.2)
\]

\[
2(NH_4)_2S_2O_3 + 2O_2 \rightarrow (NH_4)_2S_3O_6 + (NH_4)_2SO_4 \quad (2.3)
\]

\[
(NH_4)_2S_3O_6 + 2O_2 + 4NH_3 + H_2O \rightarrow NH_4SO_3NH_2 + 2(NH_4)_2SO_4 \quad (2.4)
\]

Although the above reaction scheme represents an acceptable description of reaction stoichiometry for the leaching process, it was submitted by the authors mainly to account for the presence of the major species measured in the system and was not formulated on the basis of mechanistic information. Thus, the proposition of intermediate or alternate reactions with distinct kinetics is credible.
Figure 2.1: The Kwinana nickel refinery process flowsheet (after Wishaw [16])
The kinetics of oxidative sulphide leaching in the process is influenced predominantly by temperature, oxygen pressure, ammonia concentration, ammonium sulphate concentration, particle size and agitation [3]. While it was well-understood to Forward and Mackiw [2, 3] that widely varying process conditions can be established via manipulation of the preceding variables, no governing kinetic rate laws to describe mineral oxidation, sulphur oxidation or iron precipitation were developed by the authors.

Ultimately, Forward and Mackiw [3] described the following ideal chemical and physical conditions for leaching: (1) that sufficient oxygen be supplied to react with the sulphides, (2) that sufficient ammonia be supplied to neutralise the acid formed during sulphide oxidation, (3) that sufficient ammonia be additionally supplied to allow the formation of higher ammines, together with the amount of unbound ammonia necessary for equilibrium with the ammines, (4) that sufficient sulphate ions be present, (5) that the unbound ammonia be not so high as to reduce the solubility of the ammines, and (6) that the temperature be such that reactions progress at an acceptable rate, but not so high as to cause precipitation of basic salts or insoluble ammine complexes.

Solution purification is carried out sequentially in the copper boil and oxydrolysis processes. The leach discharge solution contains a higher concentration of ammonia than is ideal for hydrogen reduction of nickel. It also contains copper and unsaturated oxysulphur compounds, which would co-precipitate with the nickel and contaminate the final product. The solution purification processes are thus responsible for preparing the leach liquor for favourable nickel recovery.

The pregnant leach liquor reports to the copper boil process, where ammonia is partially removed from solution via boiling. The decrease in ammonia concentration and increase in temperature lowers the stability of the copper ammines, promoting reaction with the unsaturated oxysulphur species. The copper is recovered as both copper(I) and copper(II) sulphides, and the unsaturated oxysulphur species are oxidised to sulphate (and possibly sulphamate). Forward and Mackiw [3] proposed the following reaction system to describe the process:
The copper-free liquor is purified in the oxydrolysis process, in which simultaneous oxidation and hydrolysis reactions are invoked. The purpose of this process is to completely oxidise any unsaturated sulphur and completely hydrolyse any sulphamate remaining in the copper boil discharge solution. In each case, sulphate is the product, which is very stable under the conditions in hydrogen reduction. If not removed, however, thiosulphate, polythionate and sulphamate will decompose and contaminate the final nickel product with sulphur. Forward [2] proposed the following reaction system to describe the process:

\[
S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \\
S_3O_6^{2-} + 2O_2 + 2H_2O \rightarrow 3SO_4^{2-} + 4H^+
\]

Metal recovery is carried out in the hydrogen reduction process, in which nickel and cobalt react with hydrogen. Forward [2] proposed the following reaction system to describe the process:

\[
Ni(NH_3)_2SO_4 + H_2 \rightarrow Ni^0 + (NH_4)_2SO_4 \\
Co(NH_3)_2SO_4 + H_2 \rightarrow Co^0 + (NH_4)_2SO_4
\]
hydrogen under pressure in the same way as nickel, reaction with the latter metal proceeds under more moderate conditions and more readily than reaction with the former metal. It is thus possible to precipitate nickel and leave cobalt in solution. Although, a small, roughly equal concentration of nickel and cobalt must be left unprecipitated in order to ensure that a minimum amount of cobalt is precipitated with the nickel. Almost all the nickel is reduced with hydrogen gas, while the cobalt and residual nickel are later reduced with hydrogen sulphide gas. Ammonium sulphate, which is a by-product of the refining process, remains in solution and is recovered downstream. The reduction of nickel with hydrogen has been given attention in the literature more so than any other aspect of the Sherritt-Gordon process, which has included assessments on the thermodynamics and kinetics (e.g. [18-22]).

The Sherritt-Gordon process is a well-established hydrometallurgical operation that has been given extensive attention in the literature (e.g. [5-7, 12-14, 16, 23-28]). Discussions, however, have focused largely on the hydrometallurgical flowsheet and general operation of the refining process at either the Fort Saskatchewan or Kwinana refineries. Furthermore, with the exception of hydrogen reduction of nickel, almost all discussions on process chemistry have not ventured beyond the essential mechanisms put forward originally by Forward and Mackiw [2, 3]. Therefore, no detailed analysis of the leach chemistry has been carried out since the work of the foundation researchers and no detailed assessment of process operability has been carried out on either of the industrial operations that accommodate the ammoniacal pressure leach.

2.3 Mathematical Modelling of Leaching Processes

Industrial leaching processes are typically comprised of three essential process units: tanks, leaching reactors and thickeners. Tanks are employed to mix the reactor feed streams, leaching reactors are employed to dissolve the value metals and thickeners are employed to separate reactor discharge solids from the pregnant liquor. While each of these units plays an important role in the operation of the leaching process as a whole, it is the reactor that is most directly associated with process performance, and so modelling discussions in this section will be restricted to this unit only. Incidentally, the
fundamentals of reactor modelling are easily extended to tanks and thickeners, and many other unit operations.

Industrial leaching reactors generally exist as part of a large-scale atmospheric (low-temperature) or pressurised (high-temperature) multistage leaching system. The latter is most commonly constructed physically as a partitioned autoclave. Leaching autoclaves are typically continuous, horizontal, cylindrical, compartmentalised pressure vessels that accommodate complex three-phase (gas-liquid-solid) systems, that latter of which may comprise multiple series-parallel heterogeneous and homogeneous chemical reactions that release large amounts of heat due to their exothermic disposition. Each autoclave compartment is mechanically-agitated and may be considered to a first approximation to be well-mixed, such that conditions in the discharge are the same as those in the system. Each compartment can thus be viewed upon as a continuous stirred tank reactor (CSTR). An autoclave, then, can be seen as a series of CSTRs that operate under the same total pressure. If the mathematical description of an autoclave is considered on a compartment-by-compartment basis, whereby the discharge of one compartment becomes the feed to the next, then the modelling of an autoclave can be accomplished via the modelling of a single leaching reactor.

The objective of this section is to develop a fundamental understanding of mathematical modelling concepts as they pertain to leaching reactors and to discuss relevant studies. The descriptions of reactor and compartment are synonymous where the continuous autoclave is concerned, and each term will be used interchangeably throughout this thesis.

2.3.1 Fundamentals of Reactor Modelling

The essential premise in the mathematical modelling of a CSTR is a description of the mass and energy conservation laws. The general conservation equation is written as follows:

\[ \text{Accumulation} = \text{Input} - \text{Output} + \text{Net Generation} \]  \hspace{1cm} (2.17)

The conservation equation states that the rate of accumulation of some component in a
reactor is equal to the difference between its rate of input to and output from the reactor, plus its rate of net generation in the reactor. A mass balance for some species $i$ around a reactor at any time $t$ is given by [29]

$$\frac{dN_i}{dt} = F_{i,\text{in}} - F_i + G_i$$

(2.18)

where $N_i$ is the number of moles of species $i$ in the reactor at time $t$, $F_{i,\text{in}}$ is the molar feed rate of species $i$, $F_i$ is the molar discharge rate of species $i$, and $G_i$ is the rate of net generation of species $i$ as a result of chemical reaction. An energy balance around a reactor at any time $t$ is given by [29]

$$\frac{dE_{\text{sys}}}{dt} = \sum_i F_{i,\text{in}} H_{i,\text{in}} - \sum_i F_i H_i - \dot{Q} - \dot{W}_s$$

(2.19)

where $E_{\text{sys}}$ is the energy of the system (reactor) at time $t$, $H_{i,\text{in}}$ is the molar enthalpy of species $i$ in the reactor feed, $H_i$ is the molar enthalpy of species $i$ in the reactor discharge, $\dot{Q}$ is the rate of heat flow from the system to the surroundings and $\dot{W}_s$ is the rate of shaft work done by the system on the surroundings. For steady-state modelling applications, the accumulation terms in equations 2.18 and 2.19 take on values of zero.

Determining the rate of net generation of species $i$ is the crucial step in solving the mass and energy balance equations. This is achieved through a mathematical description of chemical reaction kinetics. For any system of $j$ simultaneous chemical reactions the following stoichiometric equation can be written [30]:

$$\sum_i \nu_{ik} A_i = 0 \quad \text{for } k = 1, 2, \ldots, j$$

(2.20)

where $i$ and $k$ refer to species and reactions, respectively. $A_i$ represents the $i$th species and $\nu_{ik}$ is the stoichiometric coefficient of species $i$ in reaction $k$; the latter takes on a negative value if species $i$ is a reactant, a positive value if species $i$ is a product and a value of zero if species $i$ does not participate. The extent to which some chemical reaction takes place is normally derived from the extent to which one of the species involved in the reaction is consumed or produced. The overall extent is then realised
through appropriate consideration of stoichiometry. The relationship between the overall rate of extent of reaction \( k \), \( \varepsilon_k \), and that of an individual species \( i \) involved in the reaction, \( \varepsilon_{ik} \), is given by

\[
\varepsilon_{ik} = V_{ik} \varepsilon_k
\]  

(2.21)

Thus, the rate of net generation of species \( i \) can be realised as follows:

\[
G_i = \sum_k \varepsilon_{ik} = \sum_k V_{ik} \varepsilon_k
\]  

(2.22)

Rate of extent of reaction is related to rate of reaction. Reaction rate laws typically take on the following mathematical form:

\[
r_k \propto k(T) f(C)
\]  

(2.23)

where \( r_k \) is the rate of reaction \( k \) (which has dimensions of mole time\(^{-1}\) area\(^{-1}\) for heterogeneous reactions and mole time\(^{-1}\) volume\(^{-1}\) for homogeneous reactions), \( k(T) \) is the intrinsic rate constant and \( f(C) \) is some function of concentration. One of the main objectives of a kinetic study is to determine the form of the latter two constituents. The intrinsic rate constant is typically temperature-dependent and can almost always be described via the well-known Arrhenius function:

\[
k(T) = k_0 \exp \left( -\frac{E_a}{RT} \right) \quad \text{or} \quad k(T) = k(T_R) \exp \left( -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_R} \right) \right)
\]  

(2.24)

where \( k_0 \) is the pre-exponential factor, \( E_a \) is the Arrhenius activation energy, \( R \) is the ideal gas constant, \( T \) is the reactor temperature and \( T_R \) is some reference temperature. The concentration function is highly-dependent on the type of chemical system under consideration and so further discussion here is futile. The topic of rate law concentration dependence is given suitable priority in Chapter 4.

For heterogeneous and homogeneous reactions, rate of extent of reaction is determined through multiplication of the reaction rate with reaction surface area, \( S \), and reactor liquor volume, \( V (1 - g - h) \), respectively, where \( V \) is the reactor slurry volume.
$g$ is the volumetric fraction of solids and $h$ is the volumetric gas holdup (i.e. the volumetric fraction of gas). That is to say, $\varepsilon_k = r_k S$ for heterogeneous reactions and $\varepsilon_k = r_k V (1 - g - h)$ for homogenous reactions. Reactor slurry volume is either a given or is determined via a total mass balance, while the fractions of solids and gas in the slurry may be solved for directly as a function of system variables, thus satisfying the requirements for homogeneous reaction kinetics. Reaction surface area is a much more complex quantity to establish, and is a task that is dependent on the type of heterogeneous reaction in question.

For mineral oxidation, reaction surface area refers to mineral surface area. The kinetics of mineral oxidation is thus not only affected by temperature and concentration, but also fundamentally influenced by the size, shape and disposition of the solid particles. Also, unlike for homogeneous reactions, the kinetics may be subject to mass transport limitations. Furthermore, there is significant distinction between batch reactor and continuous reactor kinetics.

The task of determining continuous leaching kinetics is carried out in two parts. Firstly, batch kinetic rate laws for single particles are developed for a given rate-limiting scenario. Secondly, models that allow the scale-up of batch particle kinetics are considered.

### 2.3.2 Batch Leaching Kinetics

Minerals encountered in most leaching processes are dense and non-porous, while the particles of any one mineral type in an assembly are expected to be of varying size, shape and composition. The inclusion of all such particulars in batch and continuous reactor models is highly restricted by the many assumptions that have to be made, and so it is generally not justified. Particles are thus customarily assumed to be of fixed shape and uniform mineralogical composition, and are almost always considered to be spherical in shape. Size is usually the only particle property of interest.

Two particle types are customarily considered when assessing batch leaching kinetics: shrinking cores and shrinking spheres. Particles that leach as shrinking cores
form a product layer at their surface, so while the particle core become smaller in size the total size of the particle remains relatively constant due to the accumulating layer. Particles that leach as shrinking spheres are taken completely into solution.

A number of mass transfer and chemical reaction steps take place in leaching systems. All operations exhibit at least some of the following processes [31]:

- Absorption of a gaseous reactant into solution
- Reaction between a dissolved gas and a redox catalyst
- Diffusion of reactants to the mineral surface
- Adsorption/reaction/desorption at the mineral surface
- Diffusion of products away from the mineral surface
- Reaction between a redox catalyst and product solutes
- Desorption of product solutes into the gas phase
- Reaction in the gas phase

For a given leaching system, while all mass transfer and chemical reaction steps contribute to the total time required to leach a particle, one step will generally occur at a comparatively slower rate and thus offer the greatest resistance to metal dissolution. This is the rate-limiting step.

Consider the following liquid-solid reaction involving an aqueous reactant and a mineral species:

\[ A(a) + b B(s) \rightarrow \text{products} \]  
(2.25)

For a single spherical particle, the batch fraction unreacted of mineral B is defined as follows:

\[ 1 - X_B^* = \left( \frac{D}{D_0} \right)^3 \]  
(2.26)

where \( X_B^* \) is the batch conversion of mineral B, \( D \) is particle core diameter and \( D_0 \) is initial particle diameter. For shrinking cores, initial particle diameter and total particle
diameter are equivalent, while for shrinking spheres, core particle diameter and total particle diameter are one and the same. Henceforth, where the spherical particle is concerned, the terms diameter and size shall be used synonymously.

Originally described for gas-solid reactions, but equally applicable to liquid-solid reactions, several first-order models are discussed in the literature [32-34] to describe batch fraction unreacted for single particles for different rate-limiting regimes. These shrinking core and shrinking sphere (or particle) models consider regimes of the following nature: mass transport control, in which diffusion of reactants from the bulk solution to the mineral surface is rate-controlling; product layer diffusion control (a situation commonly referred to as parabolic leaching), in which diffusion of reactants through the product layer at the surface of a shrinking core is rate-controlling; and chemical reaction control (a situation commonly referred to as linear leaching), in which chemical (or electrochemical) reaction at the mineral surface is rate-controlling.

Linear leaching kinetics is the most commonly observed situation in leaching systems. If the rate of reaction 2.25 is governed by the intrinsic rate of heterogeneous reaction, then the batch fraction unreacted of mineral B is described as follows [32]:

$$1 - X_B^* = \left(1 - \frac{t}{\tau}\right)^3$$

(2.27)

where $\tau$ is the reaction timescale (i.e., the theoretical time required to completely leach a single particle of initial size $D_0$). The description of timescale is distinct for a particular rate-limiting regime, and for linear leaching kinetics is given by [32]

$$\tau = \frac{\rho_B D_0}{2 b M_B k_B(T) f(C)}$$

(2.28)

where $\rho_B$ and $M_B$ are the mass density and molecular weight of mineral B, respectively; the term $k_B(T) f(C)$ has the dimensions of mole time$^{-1}$ area$^{-1}$. Given that this rate-limiting scheme assumes that no step preceding or following the heterogeneous leaching reaction occurs at a comparatively slower rate, equation 2.27 is equally applicable in describing the batch leaching kinetics for both shrinking cores and
shrinking spheres; this is the only case in which the kinetics depicting the leaching rate for each particle type is equivalent. Linear leaching kinetics may also be considered as a first approximation for systems with more complex kinetics. Incidentally, if reaction 2.25 proceeds under linear leaching kinetics, its rate is described by equation 2.23:

\[
\frac{d}{dt}\frac{1}{b}S_b = k_b(T)f(C)
\]  

(2.29)

It should be mentioned that diffusion-controlled kinetics is pertinent only for shrinking cores. Furthermore, while mass transport-controlled kinetics for shrinking cores can be described in theory, it does not represent a practical situation (except initially in batch reactors), since the diffusion of a reactant through the porous product layer of a leaching particle will almost always be a slower process than the mass transport of a reactant from the bulk solution to the particle surface. (In the latter case, it is nonetheless instructive to consider such scenarios during attempts to better-understand the various steps that take place in leaching systems.)

In some instances, more than one step may contribute to the overall rate of reaction, in which case mixed-control models may be derived [32]. In other instances, none of the standard models will suffice and a custom model may be required. Batch leaching models for those particles with shapes other than spheres, such as cylinders or flat plates, can also be described [32].

All shrinking core and shrinking sphere models customarily aim to describe batch fraction unreacted as a function of time. Therefore, substitution of equation 2.26 into any model allows one to describe particle core size as a function of time. Upon definition of the latter, describing (spherical) particle core surface area as a function of time is straightforward.

### 2.3.3 Continuous Leaching Kinetics

The central challenge in scaling up batch, single-particle kinetics to continuous, multiparticle kinetics is in considering the polydispersity and variable reactivity of the particles. The nature of particle polydispersity in continuous reactors certifies that particles that enter the reactor at the same time will most likely experience different
lengths of stay. The variable reactivity of the particles is due mainly to the variability in particle size. Shrinking core and shrinking sphere models alone will not suffice in describing such circumstances.

Two different approaches for particle kinetics scale-up are discussed in the literature: the segregated flow model (although three applications of this model are addressed) and the population balance model. Each of the four selections differs in nature, complexity and application.

**Segregated Flow Model**

The segregated flow model is based on the concept of residence time distribution (RTD). The RTD model was pioneered by Danckwerts [35, 36] and Zwietering [37] in an effort to describe the effects of incomplete mixing of fluid in homogeneous, continuous flow systems. The model considers that, upon entering a system, fluid is broken up into discrete volume elements that are small compared to the total system volume. Elements that enter the system at the same time do not experience the same length of stay, and so each can be classified according to its time of residence. Given an appropriate assumption on the extent of micromixing, the degree of mixing for the entire process is then defined according to the RTD of the system.

The segregated flow model [37] represents one of two limiting cases concerning the extent of micromixing in a homogeneous reactor with a given RTD [36]. This scenario suggests that the elements of fluid remain completely intact for their duration in the reactor. Molecules that reside in each element in the feed stream remain there indefinitely, and so each element can be thought of as a small batch reactor. Since extent of reaction is based on the length of stay of material in the continuous reactor, fluid elements that leave the reactor at the same time are identifiable as having residence time $t$, based on examination of the unreacted material contained within.

In heterogeneous leaching reactors, the particulate phase constitutes a disperse phase, and so the model of segregated flow may be extended to leaching particles. Now, each particle is a small batch reactor. The continuous phase is considered to be completely mixed, in the sense that fluid entering the reactor is dispersed completely on
the molecular scale. Molecules are permitted to flow freely between elements of fluid
such that the entire mixture is chemically uniform. This scenario represents the other
limiting case, called the maximum mixedness model [37].

If the solids RTD function for a continuous reactor, $E(t)$, is a probability density
function such that

$$\int_{0}^{\infty} E(t) \, dt = 1$$ (2.30)

then $E(t) \, dt$ is the fraction of reactor discharge solids that took residence in the reactor
between $t$ and $t + dt$. RTDs for continuous reactors can be determined experimentally
by injecting tracer material into the feed stream and measuring its concentration in the
discharge [32]. The RTD function for $N$ equally-sized ideal CSTRs in series, $\bar{E}_N(t)$, is
given as follows [32]:

$$\bar{E}_N(t) = \frac{(t/\bar{t})^{N-1} \exp (-t/\bar{t})}{\bar{t} (N-1)!}$$ (2.31)

where $\bar{t} = V/Q$ is the mean residence time of a single reactor and $Q$ is the volumetric
flow rate of the slurry in the reactor discharge. Solids RTDs can take on a number of
forms, and can even be functions of particle size (i.e. $E = E(D,t)$). RTDs not of the
form of equation 2.31 are sometimes referred to as pathological RTDs [38].

The segregated flow model can be combined with a particle size distribution
(PSD) function to account for the distribution of reactivity due to particle size. If the
PSD function, $f_m(D)$, is a mass-weighted probability density function such that

$$\int_{D_{\text{min}}}^{D_{\text{max}}} f_m(D) \, dD = 1$$ (2.32)

where $\{D_{\text{min}}, D_{\text{max}}\}$ is the range of particle sizes in the sample, then $f_m(D) \, dD$ is the
mass fraction of particles that have a diameter between $D$ and $D + dD$. Definition of the
particle size range is dependent solely on the probability distribution chosen to represent
the PSD. A number of suitable mathematical distribution functions are discussed in the
literature, such as the Gaudin-Meloy [39], Gates-Gaudin-Schuhmann [40], Rosin-Rammler [41] (also known as the Weibull distribution [42]), log-normal and gamma distributions. A modified normal distribution [43] has also seen specific application in leaching reactor modelling (see [44-47]). Typical ranges for $D$ include $\{0, D_{\text{max}}\}$ and $\{0, \infty\}$, where $D_{\text{max}}$ is a constant.

If the batch fraction unreacted for a single particle of mineral B is integrated over the entire range of feed particle sizes and solids residence times, then the cumulative fraction unreacted of mineral B in the $N$th continuous leaching reactor in a series can be calculated as follows [30, 32]:

$$1 - X_{B,N}^\Sigma = \int_0^{t_{\text{max}}} \int_{D_{0,\text{max}}}^{D_{0,\text{min}}} (1 - X_B^\ast) f_{m,\text{in}}(D_0) \, dD_0 \, E_N(t) \, dt \quad (2.33)$$

where $X_{B,N}^\Sigma$ is the cumulative conversion of mineral B in the $N$th reactor, $D_0$ is the initial/feed particle size, $D_{0,\text{max}}$ and $D_{0,\text{min}}$ are the maximum and minimum feed particle sizes, respectively, $f_{m,\text{in}}(D_0)$ is the feed particle size density function, $t_{\text{max}}$ is the maximum particle residence time and $E_N(t)$ is the solids RTD for $N$ reactors in series.

The batch fraction unreacted, $1 - X_B^\ast$, must be appropriately defined such that its value remains positive for all feed sizes and residence times. Note also that the RTD function in the above equation does not necessarily reflect that given by equation 2.31, but nonetheless remains a sole function of time.

The application of equation 2.33 has been considered for two scenarios: the cases in which $N = 1$ and $N > 1$. If $N = 1$, the equation is solved on a reactor-by-reactor basis. The PSD in the equation is that for the reactor feed, and it is a requirement that the PSD for partially-reacted solids in the reactor discharge be reconstructed such that mineral conversion in the subsequent reactor can be evaluated. When equations 2.27 and 2.31 are used in equation 2.33 (i.e. when chemical reaction-controlled kinetics and the well-mixed assumption apply), the following expression may be used for PSD reconstruction [48]:

$$\text{\ldots}$$
\[ f_n(D) = \frac{\int_0^{D_{b,n}} D^3 D_0^{-3} f_{m,in}(D_0) \exp \left( \frac{D_0 - D}{D\bar{t}} \right) dD_0}{\int_0^{D_{b,n}} D^3 D_0^{-3} f_{m,in}(D_0) \exp \left( \frac{D_0 - D}{D\bar{t}} \right) dD_0 dD} \]  \hspace{1cm} (2.34)

where \( \bar{D} \) is given by equation 2.41. The cumulative conversion of mineral B in the \( N \)th reactor no longer has any relevance, only conversion, \( X_B \); that is, \( X_B = X_{b,1}^\Sigma \). This procedure is only feasible if the leaching rate is a unique function of particle size.

If \( N > 1 \), the reactor series is considered as a whole. It is assumed that the temperature, solution composition and mean residence time of each reactor are the same. What is more, inter-stage feeding and recycling of material cannot be accommodated. This practice describes only a gross approximation of leach system behaviour and is limited in its application to industrial process modelling. This application of the segregated flow model has been referred to as the doubly-integrated micromodel (DIM) [49-51].

Each form of the segregated flow model offers distinct advantages. For the case of \( N = 1 \), there is the ability to consider the leaching conditions in each reactor and accommodate inter-stage feeding, while for the case of \( N > 1 \), there is the capacity to solve for fraction unreacted without PSD reconstruction. The third application of the segregated flow model, called the multiple convolution integral (MCI) [49-51], is a method that incorporates each of these capabilities. The defining equation is a \( N+1 \) multiple integral equation that is customarily given in dimensionless form, which must be solved for each reactor in the series. For the special case in which \( N = 1 \), the MCI equation and equation 2.33 are indistinguishable. While it is advantageous mathematically, the main disadvantage of the MCI is that it is not easily programmable when the simulation software demands a stage-by-stage approach, which is often the case. The model is not employed in the present work for this reason, and so for further discussion on the topic the reader is referred to the primary paper [50].
Figure 2.2: Conceptual application of the segregated flow model in reactor modelling

The term “segregated flow model” has also been used to describe a situation in particulate reactors that is more analogous to that with which it was originally defined for homogeneous systems [52-54]. This situation considers that, upon entering a particulate system, material is broken up into small volume elements comprised of both particles and fluid, and it is these elements of slurry that remain intact and behave as small batch reactors (not the particles). This particular model was utilised mainly to study the effects of micromixing in particulate reactors [52] and does not reflect the way in which the RTD model is normally applied in leaching reactor modelling. (This can be a source of confusion to the unfamiliar reader.)

The segregated flow model is limited to steady-state applications. Individual mineral conversion can be determined from cumulative mineral conversion, and mineral surface area is directly related to the former. Considering reaction 2.25, the following equation relates rate of reaction extent, mineral conversion and mineral surface area:

$$
\varepsilon_{2.25} = \frac{F_{B,in} X_B}{b} = r_{2.25} S_B
$$

(2.35)

where mineral B is the limiting reactant and $r_{2.25}$ is only given by equation 2.29 if chemical reaction-controlled kinetics prevail. The above equation satisfies equation 2.21, and thus equation 2.22, when the segregated flow model is used to determine mineral leaching kinetics. The use of the segregated flow model for a single leaching reactor is conceptualised in Figure 2.2.
Population Balance Model

The population balance model is based on the concept of conservation of number. This approach was developed independently by Hulburt and Katz [55] and Randolph and Larson [56, 57] as a means for describing particle populations in particulate processes. The model considers that the disperse phase of a particulate process is comprised of countable entities that enjoy a suite of properties (e.g. size, age, colour). By defining a number-based density function that represents the distribution of particle properties as a function of time, the authors conceived an equation that describes the continuity of particle number, called the population balance equation.

The equation is developed from the general conservation relation (i.e. equation 2.17). The input and output terms represent changes in the number of particles in the specified property intervals as a result of particle flow, while the net generation term accounts for particles entering and leaving the specified property intervals as a result of individual particle kinetics. Two types of population balance equations exist: a microscopic equation that describes changes in a particle population within an infinitesimal volume at any geometrical position, and a macroscopic equation that accounts for volume-averaged changes in a particle population within an entire process vessel [56]. The latter form of the equation is suitable for process vessels that are well-mixed, such as the CSTR. Thus, the macroscopic model may be used to describe particle populations in leaching reactors.

In most particulate systems, particle size is the only property of interest. The number-based density function, then, which is referred to as the population density function [57], $\psi = \psi(D,t)$, is defined such that, at any given time, $\psi(D)dD$ represents the number of particles per unit (slurry) volume that have a size between $D$ and $D + dD$. So, the population balance equation, as defined for most well-mixed particulate systems, is written to describe the conservation of particle number in a given size interval (i.e. between $D$ and $D + dD$). In a continuous leaching reactor, the accumulation of particles of mineral B in the specified size interval is given by the time derivative of particle number:
Accumulation = \frac{\partial (V \psi_B)}{\partial t} dD \tag{2.36}

where \( \psi_B \) is the particle population density in the reactor (and reactor discharge). The input and output of particles of mineral B to and from the reactor in the specified size interval, respectively, is given by

\begin{align*}
\text{Input} &= Q_{in} \psi_{B,in} dD \tag{2.37} \\
\text{Output} &= Q \psi_B dD \tag{2.38}
\end{align*}

where \( \psi_{B,in} \) is the particle population density in the reactor feed, and \( Q_{in} \) and \( Q \) are the volumetric flow rate of slurry in the reactor feed and discharge, respectively. The net generation of particles of mineral B in the specified size interval is given by

\begin{equation}
\text{Net Generation} = V \left[ (\bar{B}_B - \bar{D}_B) - \frac{\partial}{\partial D} (\dot{D} \psi_B) \right] dD \tag{2.39}
\end{equation}

where \( \bar{B}_B dD \) and \( \bar{D}_B dD \) are the average birth and death rate of particles of mineral B per unit (slurry) volume in the specified size interval, respectively. The first term, \( V (\bar{B}_B - \bar{D}_B) dD \), is the discrete generation of particles due to a so-called catastrophic event (such as particle breakage or agglomeration), while the second term, \( -V \frac{\partial (\dot{D} \psi_B)}{\partial D} dD \), is the continuous generation of particles due to chemical reaction.

Substitution of equations 2.36 – 2.39 into equation 2.17, and cancelling the differential \( dD \), describes the macroscopic population balance equation for any well-mixed particulate system in which particle size is the only property of interest. In leaching processes, discrete changes in particle size are not important, and so the birth and death terms can be ignored (i.e. \( \bar{B}_B = \bar{D}_B = 0 \)). The population balance equation for particulate leaching reactors is thus given as follows [58]:

\begin{equation}
\frac{\partial}{\partial t} (V \psi_B) = Q_{in} \psi_{B,in} - Q \psi_B - V \frac{\partial}{\partial D} (\dot{D} \psi_B) \tag{2.40}
\end{equation}

Given that particle size in the feed is limited by its maximum diameter, the boundary
condition for the above equation stipulates that the population density function approaches zero at \( D = D_{\text{max}} \).

For leaching processes, the rate of change of particle size is derived from the shrinking core and shrinking sphere models. If mineral B leaches under chemical reaction-controlled kinetics, the rate of particle core shrinkage is given by [32]

\[
\dot{D} = -\frac{2b M_B k_B(T) f(C)}{\rho_B} \tag{2.41}
\]

The rate of shrinkage for linear leaching kinetics is independent of particle size and is related to reaction timescale (see equation 2.28): \( \dot{D} = -D_0 / \tau \). If initial particle size also has relevance, such as for parabolic or mixed-controlled leaching kinetics, the population density function must be re-defined as \( \psi = \psi(D, D_0, t) \).

The population balance model is capable of both steady-state and unsteady-state applications. The unsteady-state equation can be solved for \( \psi(D, t) \) numerically using appropriate initial and boundary conditions. The steady-state equation is suitably solved for \( \psi(D) \) using the method of integrating factors [58]:

\[
\psi_B(D) = -\frac{Q_{in}}{V} \int_D^{D_{\text{max}}} \psi_B(D_0) \frac{D}{D_0} \exp \left( \frac{Q}{V} \int_D^{D_0} \frac{dD'}{D'} \right) dD_0 \tag{2.42}
\]

Mineral surface area can be calculated directly from the population density function according to the following expression (which is derived from the equation for calculating the surface area of a sphere):

\[
S_B = \pi V \int_0^{D_{\text{max}}} D^2 \psi_B dD \tag{2.43}
\]

Considering reaction 2.25, equation 2.35 is equally applicable here in relating rate of reaction extent, mineral conversion and mineral surface area. Thus, equation 2.35 satisfies equations 2.21 and 2.22 when the population balance model is used to determine mineral leaching kinetics. The use of the population balance model for a single leaching reactor is conceptualised in Figure 2.3.
2.3.4 Studies on Continuous Leaching Reactor Modelling

A number of modelling and simulation studies have been presented in the literature that concern continuous leaching systems. However, some do not include provisions for describing the polydispersity and variable reactivity (due to particle size) of the leaching particles. Such studies are limited and do not reflect the standpoint with which mathematical modelling and simulation is carried out in this thesis. Works of this nature will not be included in discussions here.

The first to consider the use of kinetic models in describing continuous leaching systems were Bartlett [59, 60] and Herbst [58, 61]. At a time when little application of reaction kinetics had been applied to hydrometallurgical process plant design and performance optimisation, the authors realised the importance of considering in such activities the particle size distribution in the feed and the residence time distribution of the solids in the reactor. Bartlett [59, 60] took advantage of the segregated flow model to develop design equations for both single-stage \( N = 1 \) and multistage \( N > 1 \) continuous leaching systems. The mathematical developments, however, were more constrained with respect to performance optimisation than they were design. This is true given the type of PSD function employed, the consideration of only a single liquid-solid reaction, and the lack of mass and energy balances. Furthermore, it has already been discussed that the case of \( N > 1 \) is limiting where the segregated flow model is concerned.
Around the same time, Herbst [58, 61] utilised the population balance model to develop steady-state equations for a single isothermal leaching reactor that are more suitable for performance optimisation. The consideration of an arbitrary PSD function, a combination of rate-limiting steps and a reactant mass balance allowed for a more meaningful description of reactor behaviour. The author modelled two, single-reaction liquid-solid systems: oxygen-acid leaching of chalcopyrite and acid leaching of chrysocolla. This modelling approach was later extended by Sepulveda and Herbst [62] to accommodate a generalised multistage leaching system. The authors expressed their equations in dimensionless form to reduce computational effort and render the numerical solution independent of the actual system being considered. The single-reaction acid ferric sulphate leaching of finely ground chalcopyrite was considered in the verification of the single-stage model. Herbst and Asihene [63] would later apply the models of Herbst [58, 61] and Sepulveda and Herbst [62] to several hydrometallurgical processes, as well as discuss the moment transformation of the population density function as an avenue for solving the system of equations.

Ruether [64] also considered the segregated flow model ($N > 1$) to describe a cascade of isothermal leaching reactors for design purposes. Model equations were developed specifically for treating systems for the removal of sulphur from coal by selective oxidation (chemical coal cleaning). Particles in this process react as shrinking cores under parabolic leaching kinetics. The limitations of this model are consistent with those of Bartlett’s [59, 60] developments. Papangelakis and Luus [65] would later propose a more comprehensive approach to autoclave design using the segregated flow model ($N > 1$), however said authors only assumed monosized feed particles.

Another detailed autoclave design procedure was developed by Henein and Biegler [66]. However, the generalised models proposed were highly restrictive. The authors used the maximum mixedness model to scale up single-particle rate equations described by shrinking core models and assumed monosized particles in the feed and discharge of the isothermal reactors. This modelling approach was later extended by Pritzker [67].
Dreisinger and Peters [68] developed a three-phase model of the Sherritt-Gordon zinc pressure leaching process at the Cominico zinc leach plant at Trail, British Columbia. The authors utilised the segregated flow model \((N = 1)\) and considered the following simultaneous reactions to describe the four-compartment autoclave: (1) the dissolution of oxygen, (2) the oxidation of ferrous to ferric iron, and (3) the ferric oxidation of sphalerite. Although an energy balance wasn’t developed, the authors realised the importance of modelling continuous leaching kinetics on a reactor-by-reactor basis and numerically reconstructed the PSD in the discharge of each compartment. A simplified model of the same process was later presented by one of the authors (Peters [69]).

Seven different leaching process types were characterised by Peters [70] to illustrate the application of a fresh approach to continuous leach modelling. The method supposes that leaching processes may be described by two kinds of models: a micromodel that deals with changes to solid particles as they undergo leaching and a macromodel that deals with system changes [38]. The micromodel is established by integrating a single-particle rate equation over all initial particle sizes and residence times in order to calculate an interfacial surface area with the solution. The macromodel is defined through mass and energy balance equations that utilise the surface area integrals. Conceptually, this generalised procedure is analogous to the RTD approach already discussed.

Papangelakis and Demopoulos [44, 45, 48, 71, 72], in a sequence of papers, have offered perhaps the most comprehensive analysis of continuous leaching reactor performance. Papangelakis et al. [71] developed batch and continuous single-stage models for the three-phase, three-reaction arsenopyrite pressure oxidation process for chemical reaction-controlled kinetics. This work saw first application of the energy balance to leaching reactor modelling. The authors made use of the segregated flow model to calculate mineral conversion, although a discrete feed PSD was considered.

Expanding on this work, Papangelakis and Demopoulos [44, 48, 72] presented and applied detailed equations suitable for generic multistage reactor modelling. For a
multiple mineral feed described by a continuous PSD, the authors developed methods for calculating mineral conversion and reconstructing mass-weighted PSDs for particles leaching under both chemical reaction-controlled kinetics [48] and gas-liquid mass transfer-controlled kinetics [72]. In the latter case, consideration of the population balance model was required in part. Following [44], for each type of rate-limiting step, the segregated flow model and PSD reconstruction equations, coupled with appropriate mass and energy balance equations, were applied to the three-phase, three-reaction pyrite-arsenopyrite pressure oxidation process to describe the autothermal behaviour of a five-compartment, pilot-scale autoclave. Subsequent analysis of the process was also considered by the authors [45], whereby simulation capabilities were channelled towards determining conditions ideal for autogenous autoclave operation when simultaneous chemical reaction and gas-liquid mass transfer controlled kinetics are rate-controlling. These works would later be used in the construction of an industrial process simulation package, called REACTSIM [73, 74], which was used to simulate operation of American Barrick’s Goldstrike #1 autoclave and Placer Dome’s Campbell Mine autoclave.

Crundwell and Bryson [75], soon after, employed the population balance model to extend the work of Derisinger and Peters [68] and describe in more detail the steady-state, non-isothermal autoclave behaviour of the Cominico zinc leach plant. Later on, using the population balance framework also, Baldwin et al. [73, 76] developed a more thorough steady-state model of the same process. This model was later used to simulate a hypothetical zinc pressure leach [77]. McInnes and Stange [78] also modelled an industrial leaching operation using the steady-state population balance approach, namely the Rossing uranium extraction circuit.

Until this point in time, treatment of the numerical solution of segregated flow model and steady-state population balance model equations had been given very little attention by researchers. Numerical solution techniques were either only briefly discussed qualitatively (which typically involved Newton-Cotes closed formulae, such as the trapezoidal rule and Simpson’s rule) or not mentioned at all. Dixon [49, 50], however, discussed in detail Gaussian quadrature as a means for solving such equations.
Specifically, with respect to the doubly-integrated micromodel (i.e. segregated flow model \( N > 1 \)) [49] and the multiple convolution integral [49, 50], the author presented a procedure for substituting an ideal RTD function and the Rosin-Rammler PSD function into each model equation, non-dimensionalising and simplifying the resulting expressions, and then solving the ensuing equations using Gauss-Laguerre quadrature. This approach demands semi-infinite limits of integration. If this is not the case, as required for some PSD functions, then Gauss-Legendre quadrature may be considered for finite limits of integration. Six-point Gaussian quadrature was previously used by Ruether [64], but no detail beyond this assertion was expressed.

Rubisov and Papangelakis [46, 47, 79, 80] are the only researchers to have pursued unsteady-state modelling of continuous leaching processes. To begin with, the authors [79] developed a generic framework for modelling a single isothermal CSTR for two simultaneous, hypothetical leaching and precipitation reactions, utilising the population balance model. The system of equations was solved by combining the moment transformation of the population balance equation with the numerical method of lines. This framework was then employed to model the two-reaction pyrite pressure oxidation process for chemical reaction controlled kinetics [47]; the five-compartment, pilot-scale example autoclave considered was previously the focus of attention by one of the authors (Papangelakis and Demopoulos [44]). The latter model was subsequently extended to allow the description of non-isothermal operation [46]. Rubisov and Papangelakis [80] also presented a study dedicated solely to the development of analytical and numerical methods for solving systems of equations that describe the unsteady-state behaviour of simultaneous leaching-precipitation reaction systems in batch and continuous heterogeneous reactors. The use of the population balance framework to describe particle populations in such systems was advocated.

Stange et al. [81] also used the population balance equation to model Carbon-in-Pulp (CIP) and Carbon-in-Leach (CIL) processes, which are inherently unsteady-state operations. However, the authors did not present in any detail the analytical development and numerical solution of the system of equations, while the model itself was intended for steady-state simulation.
Mathematical modelling methods for continuous (and batch) leaching reactors are well-established. Over four decades, a number of influential mass- and number-based methods were developed for coupling kinetic rate equations with mass and energy balance equations to describe single-stage and multistage, multiphase continuous leaching systems. The chief problem associated with said methods is their complexity. The solutions of segregated flow and population balance model equations have only ever been performed numerically. This is a rather intimidating task, and is probably the reason why little or no kinetic modelling is employed for design or analysis in the hydrometallurgical industry outside of the academic circle. The development of analytical solutions of said equations would certainly help improve this situation. No analytical solutions have ever been developed for equations 2.33 or 2.40 (the latter at steady-state only). (The numerical solution of equation 2.40 for unsteady-state applications is unavoidable for effectively all situations of interest; see [80].)

Concerning the application of the segregated flow and population balance models, the vast majority of work has focused on hypothetical, laboratory-scale or pilot-scale processes. Only a small number of studies (of varying detail) have considered industrial leaching processes, and none have considered the Sherritt-Gordon ammonia leach. Furthermore, no models have comprised the integration of one or more tanks, thickeners and autoclaves into a unified process flowsheet model. Particular attention for the latter is drawn to a method for accommodating the mixing and separating of slurry streams containing unreacted or partially-reacted solids, or both, where particle kinetics in continuous leaching reactors is concerned. Such a method is integral to modelling leach flowsheets and no such method has been proposed in the literature.

2.4 Optimisation of Leaching Processes

Process optimisation is the logical step following the development of a steady-state mathematical model. The model can be used stand-alone or as part of an optimisation problem. The latter involves defining an objective function or performance index (such as profit, cost or yield) and utilising the model to determine the set of process conditions that renders it optimal, subject to appropriate (equality and inequality) constraints. The
problem can be solved manually or automatically, the latter through use of an optimisation algorithm. These methods can be used to support both optimal design and operation, and leach modellers have considered each case.

For continuous multistage leach system design, interest is typically placed with determining the optimal number of stages and the optimal size of each stage. Generally, the procedure has been to manually generate design curves that relate cumulative solids conversion with some function of mean residence time for $N$ CSTRs in series. Based on the consideration of solids conversion at a given throughput, the design curves are used to select the best combination of reactor number and size to optimise the performance index. The performance index in this case is the ratio of solids conversion to said function of mean residence time. Several authors cited in the last section considered their models in such design activities.

Pritzker [67], Ruether [64], Bartlett [59, 60] and Dixon [49] developed distinct procedures for manually constructing the design curves. Another method was later presented by Crundwell [54], but that approach is conceptually similar to Dixon’s [49]. The design process was automated by Papangelakis and Luus [65] through coupling their non-isothermal model with an optimisation algorithm. Henein and Biegler [66] presented a different method to that discussed thus far by considering two types of optimal design scenarios: minimum-volume and minimum-cost.

For continuous multistage leach system operation, interest is typically placed with determining optimal stream flow rates, stream concentrations, reactor gas pressures and reactor temperatures. The procedure for carrying out such an analysis has normally revolved around conducting manual process simulations, whereby one manipulated variable at a time is allowed to vary in order to assess its impact on the performance index. Several authors referenced in the last section considered their models in such performance optimisation activities. A summary of studies is given in Table 2.1.

The most commonly observed performance index in leaching reactor optimisation studies is mineral conversion. The variables evaluated against conversion include reactor mean residence time (or feed flow rate), temperature and oxygen pressure, as
Table 2.1: Summary of Performance Optimisation Studies for Continuous Leaching Systems via Stand-Alone Model Application

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactor Configuration</th>
<th>Performance Index</th>
<th>Manipulated Variable</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen-acid leaching of chalcopyrite</td>
<td>Single-stage</td>
<td>Mineral conversion</td>
<td>Mean residence time, Feed PSD, O₂ pressure</td>
<td>Herbst [58]</td>
</tr>
<tr>
<td>Acid leaching of chrysocolla</td>
<td>Single-stage</td>
<td>Mineral conversion</td>
<td>Mean residence time, Feed wt. % solids, Feed pH</td>
<td>Herbst [58]</td>
</tr>
<tr>
<td>Acid ferric sulphate leaching of chalcopyrite</td>
<td>Single-stage</td>
<td>Mineral conversion</td>
<td>Mean residence time</td>
<td>Sepulveda and Herbst [62]</td>
</tr>
<tr>
<td>Pressure oxidation of arsenopyrite</td>
<td>Single-stage</td>
<td>Mineral conversion, rate of heat removal/generation</td>
<td>Mean residence time, Temperature, Feed temperature</td>
<td>Papangelak</td>
</tr>
</tbody>
</table>
Table 2.1: Summary of Performance Optimisation Studies for Continuous Leaching Systems via Stand-Alone Model Application (continued)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactor Configuration</th>
<th>Performance Index</th>
<th>Manipulated Variable</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure oxidation of</td>
<td>Multistage</td>
<td>Sulphur conversion in 1&lt;sup&gt;st&lt;/sup&gt; reactor</td>
<td>Feed temperature</td>
<td>Papangelakis and Demopoulos [44]</td>
</tr>
<tr>
<td>pyrite-arsenopyrite</td>
<td></td>
<td>Mineral conversion in 1&lt;sup&gt;st&lt;/sup&gt; reactor</td>
<td>Size of 1&lt;sup&gt;st&lt;/sup&gt; reactor/no. of reactors</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulphur conversion</td>
<td>Temperature in 1&lt;sup&gt;st&lt;/sup&gt; reactor</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed flow rate</td>
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<td></td>
<td></td>
<td></td>
<td>Water addition ratio</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Size of 1&lt;sup&gt;st&lt;/sup&gt; reactor/no. of reactors</td>
<td></td>
</tr>
<tr>
<td>Pressure oxidation of</td>
<td>Multistage</td>
<td>Recycle ratio, feed wt. % solids Sulphur conversion, mean residence time Sulphur conversion, feed temperature</td>
<td>Feed wt. % sulphur Feed flow rate Feed wt. % sulphur Feed flow rate Size of 1&lt;sup&gt;st&lt;/sup&gt; reactor/no. of reactors</td>
<td>Papangelakis and Demopoulos [45]</td>
</tr>
<tr>
<td>pyrite-arsenopyrite</td>
<td></td>
<td></td>
<td>Feed wt. % sulphur Feed flow rate Feed wt. % sulphur Feed flow rate</td>
<td></td>
</tr>
<tr>
<td>Sherritt-Gordon zinc</td>
<td>Multistage</td>
<td>Mineral conversion</td>
<td>Feed flow rate</td>
<td>Crundwell and Bryson [75]</td>
</tr>
<tr>
<td>pressure leach</td>
<td></td>
<td></td>
<td>Mean residence time</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.1: Summary of Performance Optimisation Studies for Continuous Leaching Systems via Stand-Alone Model Application (concluded)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactor Configuration</th>
<th>Performance Index</th>
<th>Manipulated Variable</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure oxidation of pyrite-marcasite</td>
<td>Multistage</td>
<td>Feed temperature, O₂ utilisation</td>
<td>Feed wt. % sulphur, Feed wt. % carbonates, O₂ supply purity, O₂ partial pressure</td>
<td>Baldwin et al. [74]</td>
</tr>
<tr>
<td>Pressure oxidation of pyrite-arsenopyrite-pyrrhotite</td>
<td>Multistage</td>
<td>Sulphur conversion</td>
<td>Mean residence time, Temperature</td>
<td>Baldwin et al. [74]</td>
</tr>
</tbody>
</table>
well as the PSD and weight percent solids in the feed. For leaching processes that operate autogenously (such as the pressure oxidation of refractory gold minerals [44, 45, 74]), particular attention is also given to conditions in the autoclave feed and the first compartment, given the latter’s capability for autothermal initialisation of the entire autoclave. Performance indexes include sulphur conversion, temperature and the rate of heat generation and removal in the first compartment, while the most important manipulated variables considered are temperature in the first compartment (this variable is an important indicator in both respects), feed flow rate and temperature, water addition ratio and temperature, weight percent sulphur in the feed, and the size of the first compartment relative to the rest. The latter consideration (by Papangelakis and Demopoulos [44, 45]) is notably a design feature.

There are two main limitations with the manual approach. Firstly, some process constraints are difficult to incorporate, particularly inequalities, and if omitted there is the possibility of constraint violation. Secondly, a large number of simulations need to be pursued and a considerable amount of data examined in order to determine a globally optimal performance index. So, if not carried out systematically and in sufficient capacity, the manual exercise can bring about a suboptimal outcome. The use of an optimisation algorithm can greatly assist in circumventing such a result.

An optimisation algorithm is a mathematical procedure for solving the optimisation problem. The only authors to have attempted such an approach were Papangelakis and Luus [65], as mentioned before. However, the kinetic model developed – the segregated flow model $(N > 1)$ – was intended mainly for design purposes and is not suitable for performance optimisation, a sentiment that has been expressed by this author on more than one occasion.

A limited number of performance optimisation studies have been carried out where the leaching reactor or autoclave is concerned. Of these, only the study conducted by Papangelakis and co-workers [44, 45, 71] was pursued with sufficient scope to certify the attainment of optimum autoclave operation. All remaining authors considered their analysis mainly as a means for demonstrating model simulation
capabilities. No authors considered the use of an optimisation algorithm. Few studies considered industrial leaching operations; but once again, each analysis was limited largely to model demonstration. No optimisation studies have been carried out for industrial leaching processes that comprise one or more tanks, thickeners and autoclaves. No optimisation studies have considered the Sherritt-Gordon ammonia leach.

2.5 Summary

A study of the operability of a large-scale, industrial leaching process via mathematical modelling and computer simulation has not been carried out previously. In this thesis, said study is performed for the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery. The following topics represent the foundation knowledge for such a study: (Sherritt-Gordon) leach process chemistry, leach process modelling and leach process optimisation. A survey of the literature for each topic was presented. Existing knowledge that will be drawn upon and new knowledge that will be generated (in the form of literature gaps) by way of the objectives of this body of work formed the basis of discussions.

Before the first topic is given relevance in this thesis, an inspection of the leaching process at the Kwinana nickel refinery is warranted. The following chapter is dedicated to this.
Chapter 3

The Leaching Process

3.1 Introduction

A preliminary discussion on the Sherritt-Gordon ammonia leach has already been given on the topic of process chemistry (Chapter 2). This subject matter is given continuous attention throughout the thesis. The objective of this chapter is to develop an overall appreciation of the leaching process at the Kwinana nickel refinery via communication of the feed material, flowsheet and basic operating philosophy.

3.2 Feed Material

In Western Australia, BHP Billiton mines and processes nickel sulphide ores at its operations in Mt Keith, Leinster, Cliffs and Kambalda [1]. The Mt Keith and Leinster sites each operate a mine and concentrator plant, which also process ore from the Cliffs mining operation, while the concentrator at Kambalda processes third party ores. At each concentrator plant, the ore is finely ground and the sulphide and non-sulphide particles are separated by froth flotation. The effective sulphide mixture is a nickel concentrate (15 wt.% nickel) that has the following principal mineralogy: pentlandite ((Ni,Fe)$_9$S$_8$), violarite (FeNi$_2$S$_4$), chalcopyrite (CuFeS$_2$), pyrrhotite (FeS), pyrite (FeS$_2$), gersdorffite (NiAsS) and niccolite (NiAs); cobalt, and traces of lead, palladium and selenium also exist in the sulphide concentrate.
The nickel concentrates are transported to the Kalgoorlie nickel smelter where they are combined and smelted into a nickel matte [82]. Smelting is a pyrometallurgical process that is commissioned to purify a concentrate of unwanted material. When heat is applied to a nickel concentrate in a flash furnace, chemical and physical changes are invoked and two layers are formed in the settling zone: slag (upper oxide layer) and matte (lower sulphide layer). The slag typically contains iron oxide, gangue and silica (\(\text{SiO}_2\)), while the matte contains nickel, copper, cobalt, sulphur, and some iron. The process is carried out in two stages at the site: firstly, the concentrate is smelted in an integrated flash furnace, and secondly, the low grade matte product is converted to a high grade matte by means of Pierce-Smith converters. The converter matte is granulated by dispersing the molten material in water. Two grades of matte are produced: an export matte containing about 72 wt.% nickel and a high-iron matte containing about 66 wt.% nickel. The export matte is dried, bagged and railed to the Western Australian coast for shipping, while the high-iron matte is railed in bulk wagons to the Kwinana nickel refinery for further processing.

The elemental components of the high-iron matte are predominantly nickel, copper, cobalt, iron and sulphur. The balance is mainly inert components such as silica, however, some deleterious elements such as arsenic and selenium also exist. Given the nature of the smelting and cooling processes, the matte mineralogy is not well defined. It is expected to have the following principal components: awaruite (nominally \(\text{Ni}_3\text{Fe}\)), heazlewoodite (\(\text{Ni}_3\text{S}_2\)), chalcocite (\(\text{Cu}_2\text{S}\)), sycoporite (\(\text{CoS}\)), pyrrhotite, and the balance impurities. The majority of minerals considered here are consistent with the known mineralogies of other nickel mattes (e.g. see [83]).

On a point of historical interest, when the refinery processed nickel concentrate, it did so via a two-stage, counter-current leach (i.e. foundation Sherritt-Gordon process design [2, 3]), and for a time received all or part of its feed material directly from the Kambalda mine (now decommissioned) and concentrator operation. Matte was gradually introduced into the refinery feed following the commissioning of the nickel smelter at Kalgoorlie in 1972. Between 1973 and 1985, the refinery processed a blend
of concentrate and matte, and has since treated only the latter. For a period (1985-1989), a mixture of flash furnace and converter matte was administered, but only the latter is presently managed. In response to the transition from a concentrate to a matte feed, as well as to equipment and configuration changes in the leach and elsewhere, the refinery’s nickel production rate has increased from its design capacity of 15,000 tpa to its present amount (i.e. 65,000 tpa).

3.3 Flowsheet

Upon entering the refinery, nickel matte is first processed in the ball mill grinding circuit. Water is mixed with the unground matte and the slurry is pumped through two ball mills where the matte is ground to suitable leaching size. The fraction of mass passing 106 μm is typically around 90 percent, which is rather coarse relative to industry standards. The ground solids are de-watered and sent to the leaching process.

The leaching process is a three-stage, counter-current continuous leach. A flowsheet of the process is given in Figure 3.1. In addition to several tanks, thickeners and trim coolers, a total of six horizontal, cylindrical, compartmentalised, stainless steel clad pressure leaching autoclaves are employed. All autoclaves take on the same physical dimensions, each being comprised of four mechanically-agitated, equally-sized compartments with cooling coils and four vertical wall baffles, all of which are separated by weir gates. Each autoclave has a total volume capacity of 220 m$^3$, of which 160 m$^3$ may be occupied by slurry. The first three compartments operate at full slurry capacity, while the final compartment normally operates at half of this in order to promote phase disengagement. Temperature set-points for the first three compartments are the same for any given autoclave, while the final compartment operates at lower temperatures. The autoclave discharge slurry is further cooled by trim coolers to both promote flocculation in the thickeners (which are also supplied with a flocculant) and minimise the vaporisation of ammonia.

The agitators in Compartments 1 to 3 of Autoclaves 1A and 1B employ radial 6-blade Ekato Phasejet impellers for gas-liquid dispersion and axial 4-blade Ekato Viscoprop impellers for solids suspension. All other autoclave compartment agitators in
Figure 3.1: The Kwinana nickel refinery leaching process
the leach make use of radial 6-blade, disk flat-blade impellers (i.e. Rushton turbines) for gas-liquid dispersion and axial 4-blade, pitched-blade impellers for solids suspension. The radial flow impellers are situated below the axial flow impellers in all cases. The Phasejet impellers employ a connected rotating gas sparger that makes use of a gas feed-pipe, while for each of the Rushton turbines a separate ring sparger is situated below the radial flow impeller.

In the first and second stages, the first three autoclave compartment agitators draw around 60 kW, while the fourth compartment agitators draw around 44 kW. In the third stage, all autoclave compartment agitators draw around 44 kW. Oxygen is sparged into all autoclave compartments in the form of fresh or partially-spent air. The first three compartments of each autoclave receive roughly 30 percent of the total autoclave air, while the remaining 10 percent is supplied to the final compartment. Fresh air is supplied to the second and third stages (and is distributed evenly), while the combined vent gas of each is fed to the first stage. Autoclave vent gas is removed through a vent valve that ensures a constant total gas pressure. Ammonia is usually supplied to the first two compartments. A standard autoclave is illustrated in Figure 3.2.

The first stage is comprised of the following operations in series: a feed tank, two parallel autoclaves and a thickener. Fresh matte slurry is fed to the first stage feed tank (Tank 1) where it is pulped with a variety of liquors, including (1) metal free liquor

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Figure 3.2: Four-compartment horizontal autoclave used at the Kwinana nickel refinery
(MFL) (aqueous ammonium sulphate solution), (2) dosed thickener overflow (DTO), which is the third stage thickener overflow (aqueous nickel-copper-cobalt-ammonia-ammonium oxysulphur salts solution) dosed with ammonium sulphate, and (3) wash thickener overflow (WTO) (aqueous nickel-copper-cobalt-ammonia-ammonium oxysulphur salts solution). (Ammonium oxysulphur salts collectively represents ammonium sulphate, ammonium sulphamate, ammonium thiosulphate, and ammonium polythionate; ammonium sulphate is always present in greatest quantity. This assembly of salts will henceforth be referred to by its colloquial term, “AmSul”.) The discharge slurry reports to the first stage autoclaves (Autoclave 1A and Autoclave 1B), in roughly equal proportion. Under certain conditions (typically related to throughput), fresh matte is allowed to bypass the first stage leach in order to reduce the loading on said leaching stage.

Autoclave 1A receives partially-spent air directly from the second and third stage combined vent stream. Vent gas from Autoclave 1A is then supplied to Autoclave 1B, the off-gas of which is sent to the tail-gas scrubber. Anhydrous ammonia is injected into the first two compartments of each autoclave. Autoclave 1A operates under a total pressure of 850 kPa, while Autoclave 1B operates at 750 kPa. The first three compartments of each autoclave operate at temperatures of 85-95 ºC, while the final compartment operates at 65-75 ºC. Combined first stage discharge slurry is sent to the first stage thickener (Thickener 1). The overflow of this thickener is fed to the second stage thickener (Thickener 2) and the underflow is sent to the second stage.

The second stage is comprised of the following operations in series: a feed tank, three parallel autoclaves and two thickeners. Thickener 1 underflow slurry is fed to the second stage feed tank (Tank 2) where it is re-pulped with DTO (and periodically with the effluent thickener underflow (ETU)). The discharge slurry reports to the second stage autoclaves (Autoclave 2A, Autoclave 2B and Autoclave 3B) in equal proportion.

Anhydrous ammonia is injected into the first two compartments of Autoclave 2B and Autoclave 3B. Autoclave 2A receives recycled ammonia from the Ammonia Still in the form of overhead gas, which is sparged directly into the first compartment only.
Each autoclave operates under a total pressure of 1000 kPa. The first three compartments of each autoclave operate at temperatures of around 95 ºC, while the final compartment operates at 60-70 ºC. Combined second stage discharge slurry is sent to Thickener 2.

The overflow of Thickener 2 is the leach discharge liquor, which, following mixing with a portion of the third stage (or “final”) thickener overflow (FTO), reports to the copper boil feed (CBF) tank. The underflow is sent to the second stage wash thickener (Thickener 2W), where the solids are washed with DTO or MFL. The overflow of this thickener (i.e. WTO) is recycled to Tank 1 and the underflow is sent to the third stage.

The third stage is comprised of the following operations in series: a feed tank, an autoclave and a thickener. Thickener 2W underflow slurry is fed to the third stage feed tank (Tank 3), which also periodically receives MFL and medium aqua (MA) (aqueous ammonia solution). The discharge slurry reports to the third stage autoclave (Autoclave 3A).

The Ammonia Still distillate (aqueous ammonia solution) is combined with the autoclave feed stream and delivered directly to the first compartment. The total operating pressure is 950 kPa. The first three compartments operate at temperatures of around 85 ºC, while the final compartment operates at 60-70 ºC. The discharge slurry is sent to the third stage thickener, which also receives a number of intermittent, miscellaneous flows. A small portion of the overflow is directed to the copper boil feed tank (as discussed previously), while the majority of overflow is dosed with ammonium sulphate to produce what has been discussed as DTO. The underflow reports to the residue filters for solution recovery.

Ammonia is lost from the process via several sources. It is vented from tanks and thickeners, however, only Thickeners 1 and 2 are expected to exhibit any appreciable evaporation. The residual ammonia lost from the leach is in the form of Autoclave 1B vent gas, which is recovered via the tail-gas scrubber. Furthermore, ammonia is lost from the copper boil process as a vapour, the reasons for which were given in the
previous chapter. All streams of lost ammonia are directed to the Ammonia Still for recovery. Product streams for the still include an overhead gas and a distillate, which recycle ammonia to Autoclaves 2A and 3A, respectively (as discussed earlier in the section).

3.4 Basic Operating Philosophy

The leaching process normally operates with a nickel matte solids feed rate of 320 tonnes per day (tpd). This results in a refinery nickel production rate of roughly 210 tpd, which corresponds with the annual production rate at around 85 percent process availability. Operation may be carried out at lower and higher throughputs, which depend on conditions established in the leach and elsewhere. This may involve activating the matte-bypass stream.

The principal controlled variables in the process are the concentrations of nickel, ammonia, AmSul and total unsaturated oxysulphur species in the CBF liquor, as well as nickel extraction in the first stage leach. Of these, nickel concentration is the most significant. All other process conditions are based on the set-point for this variable, which can take on a limited range of values that depend on conditions downstream in the copper boil and oxyhydrolysis processes.

Although the presence of copper is known to be important in the process, it is only a requirement that its concentration be maintained at some minimum; this notion is discussed in greater detail in the next chapter. This condition is automatically attainable under normal operation, given the typical composition of copper in the matte. The concentration of cobalt is only ever small, given its usual composition in the matte, and its effect on leach chemistry is inconsequential. However, since cobalt is the least reactive metal, a fall in its concentration or extraction rate is generally an indication that conditions in the leach are tending towards the unfavourable; so, its measurement serves as an important indicator. Copper and cobalt concentrations are free variables under normal operating conditions. While agitation is also important, it is not a manipulated variable. Maximum agitation is maintained at all times to support gas-liquid mixing and solids suspension requirements.
Mineral conversion is controlled with total leach air supply rate, although the latter variable is manipulated to suit the matte solids feed rate. The air supply rate will typically only be altered otherwise if metal extraction in Autoclave 1B is retarding, given that it receives the most-spent air. Nickel concentration in the first and second stages is controlled by manipulating the pulp density in their respective feed tanks. Ammonia concentration in the first and second stages is controlled by manipulating the total ammonia flow rate to each autoclave, although the former variable is always controlled to maintain a target ammonia-to-total metals molar ratio in such a way as to promote the stability of metal ammine complexes. AmSul concentration in the second stage is controlled by manipulating the ammonium sulphate concentration in the DTO stream, while in the first stage it is controlled by manipulating the ratio of MFL-to-DTO feeding Tank 1. The concentration of AmSul is significant in terms of its ammonium sulphate component. Appropriate concentrations of the latter species are important from two standpoints: (1) to provide sufficient sulphate ions to balance the metal ions in solution, given that the matte is sulphur-deficient, and (2) to provide sufficient ammonium ions to buffer the system at a suitable pH, in order to prevent metal hydrolysis and the subsequent precipitation of metal hydroxide.

The concentrations of unsaturated oxysulphur species are controlled relative to the concentration of copper. The former concentrations are measured collectively on-site and expressed in units of “bromate value” or BV. A BV-unit represents a unit of oxidisable material, according to certain experimental conditions established in the on-site laboratory. In the leach, the substances oxidisable by bromate are thiosulphate and polythionate. The BV values of thiosulphate and trithionate (S₃O₆²⁻) (which is the dominant thionate species) are found by direct determination to be 41 BV-units per 1 g L⁻¹ S₂O₃²⁻ and 26 BV-units per 1 g L⁻¹ S₃O₆²⁻, respectively. In the first stage leach, the ratio of BV-to-copper concentration is controlled by manipulating temperature, which in turn is controlled by manipulating cooling water flow rate. In the second stage leach, it is the intention that unsaturated oxysulphur species are completely oxidised, although very small quantities are usually observed in the discharge liquor. Temperatures in this
stage are operated close to their maximum limit, which is dictated by metal ammine stability. The preservation of unsaturated oxysulphur species in the first stage leach is the basis behind the lower operating temperatures there, and for this reason it is often referred to as the “adjustment leach” (i.e. signifying the adjustment of the ratio of unsaturated sulphur to copper).

Little control is carried out in the third stage. The only objective is that the nickel concentration in the feed is limited to some maximum, which is a control for minimising the amount of dissolved nickel that reports to the residue filters. This is enforced by manipulating the rate of DTO or MFL that feeds Thickener 2W, and so the displaced nickel reports to Tank 1. The rate of Ammonia Still distillate being fed to the third stage is a function of the still operation, and only becomes an issue if the third stage ammonia concentration falls below some minimum, which is usually not the case. The rate of MFL and MA that report to Tank 3 can be used for feed control if need be, but are usually manipulated to alleviate process disturbances at their source.

3.5 Summary

An overview of the leaching process at the Kwinana nickel refinery has been presented. The feed material, flowsheet and basic operating philosophy were given attention. This information represents the basis of understanding for all subsequent work, and will be referenced appropriately throughout the thesis.

In the next chapter, contribution is made to the chemistry of the Sherritt-Gordon ammonia leach. This culminates in the development of a chemical reaction system suitable for robust mathematical modelling of the process discussed in the present chapter.
Chapter 4

Process Chemistry

4.1 Introduction

In the development of mathematical models for the purpose of examining industrial process operability, a thorough understanding of process chemistry cannot be undervalued. Particularly, the modeller requires a chemical reaction system specification that accommodates the most influential reaction stoichiometry and kinetics. As revealed in Chapter 2, efforts at the academic and industry levels to define a detailed reaction system for the Sherritt-Gordon ammonia leach that is suitable for rigorous mathematical modelling of the leaching process at the Kwinana nickel refinery have been inadequate. The objective of this chapter is to rectify that shortcoming.

4.2 Fundamental Leaching Mechanism in the Sherritt-Gordon Process

The general leach chemistry of the Sherritt-Gordon process has already been established (Chapter 2). Despite the understanding, at this point, that the specification of leach process chemistry is incomplete from the standpoint of reaction kinetics, there is additional evidence in the literature suggesting that the leaching mechanism proposed by Forward and Mackiw [2, 3] represents only an overall depiction of the actual reaction system, and that a more complex fundamental mechanism for leaching is transpiring. This section is devoted to expounding that notion.
Oxygen is almost always the primary oxidant in hydrometallurgical leaching systems. The fate of oxygen is thus the most essential indicator in establishing a fundamental mechanism for leaching. In some processes, oxygen is reduced directly on the mineral surface. Based on this scheme, oxygen gas is physically absorbed into solution at the gas-liquid interface and dissolved oxygen is carried by mass transport processes to the bulk solution. From the bulk solution, dissolved oxygen diffuses to the liquid-solid interface where it is reduced via mineral oxidation. Seemingly, all literature discussions on the Sherritt-Gordon leach chemistry have effectively supported this view. This mechanism is depicted in Figure 4.1, which includes the oxidation of sulphur and ferrous iron.

In many processes, oxygen reacts in solution with an aqueous reducing agent, the latter usually being a product of mineral oxidation. Under this scheme, oxygen gas is absorbed into solution at the gas-liquid interface, beyond which dissolved oxygen will either react at or near the interface (if the reaction is fast) or diffuse to the bulk solution and react (if the reaction is slow). In each case, the reaction product is a surrogate oxidant, which is then witnessed to carry out the oxidative work in favour of the oxygen. Several studies support the view that the latter oxidation mechanism is favourable in certain ammoniacal leaching systems.

Appropriate leaching systems support one of two commonly observed redox catalysts: iron (in acidic solutions) and copper (in alkaline solutions). In such systems, the more reduced form of the redox catalyst (the reducing agent, i.e. iron(II) or copper(I)) is oxidised by oxygen to its more oxidised form (the surrogate oxidant, i.e. iron(III) or copper(II)), which then proceeds to oxidise the minerals and potentially other oxidisable material in the system. By means of mineral oxidation (or other redox reactions), the more oxidised form of the redox catalyst is reduced, preserving the redox cycle. Redox catalysts are thus responsible for transporting electrons from the minerals to the oxygen.
Figure 4.1: The oxidation mechanism of the Sherritt-Gordon ammonia leach if dissolved oxygen was the oxidant at the mineral surface

Peters [84, 85] proposed that copper is most likely a redox catalyst in the Anaconda-Arbiter process. The process [86] (which is no longer in operation) is an aqueous oxygen-ammonia leach (60-90 °C, 35 kPa oxygen pressure) for copper concentrates, the general leach chemistry of which shares similarity with that of the Sherritt-Gordon process. Two motivating factors were used to support the claim: (1) the leach liquor was expected to contain fairly significant concentrations of cuprous ammine, and (2) the very low oxygen pressure of the process was unlikely to sustain the oxygen gas-liquid mass transfer requirement at the mineral surface.

On the first point, it was known at the time that copper(I) reacts very rapidly with oxygen in ammoniacal solution, even at room temperature [85]. Thus, the presence of relatively large concentrations of cuprous ammine suggests that most, if not all, of the oxygen should be consumed by reaction with the highly reactive reducing agent at or near the gas-liquid interface. On the second point, the Anaconda-Arbiter process obtains one of the most rapid oxygen absorption rates in hydrometallurgy [85]. Given the very low solubility of oxygen under the low pressure conditions, it is not likely that the
commercially-viable leaching rates observed in the process are supported by a simple mechanism of physical absorption of oxygen gas. If the absorption of oxygen gas is accompanied by chemical reaction in the vicinity of the gas-liquid interface, in any given chemical system, it is expected that the kinetics of gas-liquid mass transfer will be enhanced \[87, 88\]. Subsequent to this, in any given leaching system, it is expected that the kinetics of leaching will be improved as a result of the enhanced gas-liquid mass transfer. The leaching rates observed in the Anaconda-Arbitier process may thus be explained by the reduction of dissolved oxygen by cuprous ammine. So, based on the above logic, Peters [85] argued that cupric ammine is probably acting as a surrogate oxidant at the mineral surface.

Through similar argument, it is possible to extend this affirmation to the Sherritt-Gordon process. The following can be said about the leaching process at the Kwinana nickel refinery: (1) cuprous ammine is present in the leach liquor, and (2) a high oxygen gas-liquid mass transfer requirement is seen in the first stage (i.e. adjustment) leach, where the majority of mineral oxidation takes place under an atmosphere of low oxygen pressure resulting from the counter-current air flow arrangement. Based on these two factors alone, one can support the claim that the copper(II)/copper(I) redox couple is most likely driving mineral oxidation in the Sherritt-Gordon ammonia leach in a manner analogous to that considered for the Anaconda-Arbitier leach. A final mitigating factor is that copper is well-known by process staff at the refinery to have a catalytic influence on metal extraction. This has been observed in both the on-site laboratory and the plant. No mechanism has been established thus far to explain this effect.

In the laboratory, batch leach studies on nickel concentrates have shown that initial leaching rates are greater if initial concentrations of cupric ammine is present. Moreover, the results demonstrated that the leaching rates increased with increase in initial cupric ammine concentrations up to some maximum amount, beyond which no further improvements were observed. Copper catalysis can explain each of these findings. Of course, it is expected that some limiting value of initial concentration should exist. Yet, the maximum quantity seems to be a function of degree of agitation. Under less severe agitation the presence of initial concentrations of cupric ammine was
significant, while under more severe agitation it was not. Thus, an inverse relationship exists between degree of agitation and the effect that initial concentrations of cupric ammine have on leaching rates. Two explanations may be offered.

Firstly, if the degree of agitation is low enough, and thus the oxidation potential becomes sufficiently low, the stability of copper in solution declines and the metal precipitates from solution as a sulphide. Under such conditions, improved initial leaching rates have a significant dependence on initial concentrations of cupric ammine. Secondly, if the degree of agitation is such that no copper precipitation is invoked, the inverse relationship can be justified in terms of the rate at which copper in the concentrate is permitted to dissolve. Under more and less severe agitation conditions, concentrate copper will dissolve at faster and slower rates as a consequence of the larger and smaller gas-liquid interfacial areas, all respectively. Thus, dissolving copper may displace dissolved copper (that is present initially) in the establishment of appropriate concentrations of cupric ammine at any given time, and so the faster the rate of dissolution the smaller the requirement is for initial concentrations, and vice versa.

In the plant, a minimum concentration of dissolved copper is required in each of the leaching stages to support viable leaching rates, below which results in lower extractions for all three value metals. Low copper concentration has two main sources: low copper composition in the feed matte and low autoclave compartment oxidation potential. The copper composition in the matte is normally sufficient to establish adequate concentrations of dissolved copper. However, if the composition is low, copper sulphides recovered in the copper boil process may be added directly to the leach to circumvent this situation. Low oxidation potential is a more likely source of low copper concentration, and can arise from inadequate agitation, or from increased pulp density or throughput relative to oxygen supply rate (i.e. overfeeding). Under the conditions that prevail, copper sulphides precipitate. Following the onset of this situation, retardation of mineral decomposition is observed and restoration of normal operation is difficult.

Concerning the problems associated with reinstating normal operating conditions,
it is likely that both matte copper and precipitated copper must be allowed time to
dissolve and re-dissolve, respectively. If the copper concentration falls to zero, the metal
dissolution process would be facilitated, initially, almost certainly through oxidation of
minerals directly by dissolved oxygen. Following sufficient dissolution, the steady-state
concentration of copper would return to a level that can maintain the enhancement of
oxygen gas-liquid mass transfer that is necessary for feasible leaching rates. The return
to normal operation would also be complicated by the fact that slurry in continuous
reactors is subject to a residence time distribution. Thus, even if the oxidation potential
can be increased swiftly to restore the stability of dissolved copper, only a portion of the
precipitated copper will re-dissolve in the same compartment.

The precipitation of copper under low oxidation potential conditions in the on-site
laboratory and plant has historically been attributed to copper cementation, although the
reasoning behind this deduction is uncertain. Evidence for an alternate explanation may
be found in the literature. The precipitation of copper sulphides has been reported to
take place at low oxidation potentials during the oxidative dissolution of gold in copper-
ammonia-thiosulphate systems [89, 90]. Since sulphur is present only as an oxyanion
(i.e. those observed by Forward and Mackiw [2, 3, 17]), this suggests that it is
thiosulphate or polythionate, or both, that is reacting with copper (since they are the
incompletely oxidised compounds). Furthermore, even under oxidising conditions, it
has been suggested [91] that the reaction between cupric copper and thiosulphate in
aqueous solution is accompanied by a slower side reaction between cuprous copper and
thiosulphate, which results in the precipitation of copper(I) sulphide. (The oxidation of
thiosulphate by copper(II) in ammoniacal solution is a well-documented reaction, as
will be discussed in greater detail later in the chapter.) It has also been reported [92]
that, during gold oxidation in ammoniacal solution, cupric ammine may react with
thiosulphate to form copper(II) sulphide (equation 2.7), in addition to the expected
soluble products. Therefore, it is more likely the case that copper is precipitating as
copper sulphides by way of reaction with the unsaturated oxysulphur species, than by
cementation, and probably does so in a manner comparable to that observed in the
Sherritt-Gordon copper boil process. (Although the decomposition of polythionate by
way of reaction with copper(I) or copper(II) does not seem to have been reported (or even alluded to) in the literature, it is not unreasonable to accept that such reactions may also be taking place alongside those for thiosulphate, as documented by Forward and Mackiw [3] (i.e. equations 2.6 and 2.9).

Aside from the evidence presented above for the Anaconda-Arbitr and Sherritt-Gordon processes, copper catalysis in ammoniacal leaching systems is supported by other studies. Researchers have demonstrated that the leaching rates of chalcopyrite [93-96], sphalerite (ZnS) [97, 98], gold (e.g. [92, 99-104]), as well as pyrite, pyrrhotite and arsenopyrite (FeAsS) [96] are enhanced by the presence of copper(II) in ammoniacal solution. Filmer [105] and Ghosh et al. [98] have suggested that the copper(II)/copper(I) couple is specifically responsible for the oxidation of covellite and sphalerite in copper-ammonia systems, respectively, and a whole host of authors (e.g. Wan [90], Ritchie et al. [106], Aylmore and Muir [89], Jeffrey et al. [107], Breuer and Jeffrey [108]) have given the same assessment concerning the oxidation of gold in copper-ammonia-thiosulphate systems.

Based on discussions in this section, a clear association between the presence of copper and improved mineral oxidation kinetics in ammoniacal leaching systems can be established. Where this has not already been recognised, it is most likely the case that copper is a redox catalyst in such systems. Although an experimental analysis is required to demonstrate this unequivocally, it will be the position henceforth that the copper(II)/copper(I) couple is responsible for mineral oxidation in the Sherritt-Gordon ammonia leach. Based on this mechanism, the overall leach chemistry (reaction 2.1) can be considered to take place in two steps. Firstly, oxygen is reduced by cuprous ammine:

$$\text{O}_2 + 4 \text{Cu(NH}_3)_2^+ + 4 \text{NH}_4^+ + 4 \text{NH}_3 \rightarrow 4 \text{Cu(NH}_3)_4^{2+} + 2 \text{H}_2\text{O}$$

(4.1)

Secondly, metal sulphide is oxidised by cupric ammine:

$$\text{MS}^+ (x + 6) \text{Cu(NH}_3)_4^{2+} + (n - 2x - 4) \text{NH}_3 + 4 \text{H}_2\text{O}$$

$$\rightarrow \text{M(NH}_3)_n^{x+} + \text{SO}_4^{2-} + (x + 6) \text{Cu(NH}_3)_2^+ + 8 \text{NH}_4^+$$

(4.2)

Under this scheme, cupric ammine would also be the surrogate oxidant for the
homogeneous oxidation of ferrous iron and intermediate valence states of sulphur.

4.3 Sherritt-Gordon Ammonia Leach Chemistry for Nickel Matte

For any given chemical system, a detailed description of reaction stoichiometry and kinetics is customarily submitted following a comprehensive bench- or pilot-scale experimental campaign. Such an investigation is beyond the scope of this work. Rather, a chemical reaction system is developed via literature scrutiny and plant observation.

As discussed in Chapter 2, the majority of what is presently understood about the chemistry was established in the foundation work of Forward and Mackiw [2, 3]. However, since that time a significant amount of independent work on various aspects of the ammonia leach chemistry has been carried out. This body of work – in conjunction with information concerning industrial process operation – is sufficient to allow the development of an appropriate chemical reaction system, precluding the need for laboratory analysis. The examination of suitable literature works and application of findings is given in this section.

The Sherritt-Gordon ammonia leach chemistry may be classified with the following essential reaction groups:

- Ammonia and water evaporation
- Oxygen gas-liquid mass transfer and reduction
- Mineral oxidation
- Sulphur oxidation
- Iron precipitation and associated adsorption
- Metal ammine formation

4.3.1 Ammonia and Water Evaporation

Gaseous ammonia and water represent the vapour phase. The reaction stoichiometry depicting ammonia and water evaporation may be described as follows:
\[ \text{NH}_3(a) \rightarrow \text{NH}_3(g) \] \hspace{1cm} (4.3)

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \] \hspace{1cm} (4.4)

The net rate of evaporation of a condensable gas in a reactor is best determined as a function of its vapour pressure. The relationship between partial pressure and number of moles in the gas phase may be approximated by the ideal gas equation of state. This equation also stipulates that for a mixture of ideal gases the ratio of moles to partial pressure is a constant for each gas. Substitution of the latter relation into a mass balance on ammonia and water vapour permits one to calculate their rates of evaporation, and thus the rates of extent of reactions 4.3 and 4.4, respectively, as a function of partial pressure. Vapour pressure data for aqueous ammonia solutions are widely available in the literature (e.g. Perry’s Chemical Engineers’ Handbook), and may be utilised to develop appropriate equations for use in said mass balances. Quantitative descriptions of the rates of extent of reactions 4.3 and 4.4 are given attention in Chapter 6 (see Section 6.5.1).

4.3.2 Oxygen Gas-Liquid Mass Transfer and Reduction

Oxygen dissolves into solution from air bubbles saturated with ammonia and water; nitrogen gas is inert. Oxygen gas is carried by mass transport processes through the gas film at the gas-liquid interface, through the interface, and then through the liquid film at the interface. Although it is expected that there is some gas-side mass transfer resistance, it is unlikely that it is significant. This is because the solubility of oxygen in the leaching system would be so low that resistance to mass transfer in the gas phase is negligible compared to that in the liquid phase. It is thus assumed that only the liquid-side mass transfer resistance is important.

Peters [85] established a basic mechanism for oxygen gas-liquid mass transfer in copper-catalysed ammoniacal leaching systems. In the presence of sufficient concentrations of cuprous ammine, oxygen will dissolve and be reduced at the gas-liquid interface, while in the absence of such concentrations, oxygen will dissolve and diffuse to the bulk solution. The former and latter situations embody oxygen gas-liquid
mass transfer with and without chemical reaction, respectively [87, 88]. There is no work reported in the literature that specifically concerns the fate of oxygen in the Sherritt-Gordon ammonia leach. However, the outcome of a recent study on the oxidation of copper(I) in ammoniacal sulphate solution [109], in conjunction with Peters’ [85] mechanism, provides a sound basis with which to describe oxygen gas-liquid mixing in the present process.

Kimweri [109] studied the oxidation of copper(I) in ammoniacal solution under conditions used for ammonia leaching of copper sulphides to appraise the influence that the former component has on oxygen gas-liquid mass transfer kinetics. For the case in which sufficient concentrations of cuprous ammine is present, the author was able to demonstrate that the characteristics of the reaction between dissolved oxygen and cuprous ammine follows that of an instantaneous reaction regime, which substantiates Peters’ [85] proposal. The instantaneous reaction model (Case A as defined by Levenspiel [32], or \( N_{Ha} > 10 E_i \) as defined by Charpentier [110], where \( N_{Ha} \) is the Hatta number and \( E_i \) is the instantaneous enhancement factor) stipulates that the chemical reaction between dissolved oxygen and cuprous ammine is so fast that it is virtually immeasurable. The reaction itself takes place within the stagnant film that surrounds the gas bubbles and so no dissolved oxygen exists in solution. In the presence of acceptable concentrations of cuprous ammine, it can therefore be said that oxygen is reduced heterogeneously. The gas-liquid mass transfer and reduction of oxygen is thus realised in a single step:

\[
O_2(g) + 4 \text{Cu(NH}_3)_2^+ + 4 \text{NH}_4^+ + 4 \text{NH}_3(aq) \rightarrow 4 \text{Cu(NH}_3)_4^{2+} + 2 \text{H}_2\text{O(l)}
\] (4.5)

The instantaneous reaction model also specifies a governing kinetic rate law. The rate of reaction 4.5 is thus given by

\[
r_{4.5} = E_i k_i a C_o^{*}
\] (4.6)

where \( k_i a \) is the so-called volumetric mass transfer coefficient and \( C_o^{*} \) is the solubility of oxygen. The instantaneous enhancement factor is given by
\[ E_i = 1 + \frac{\dot{D}_{\text{Cu}(I)}}{4 \dot{D}_{O_2}} \frac{C_{\text{Cu}(I)}}{C^*_O} \]  

(4.7)

where \( C_{\text{Cu}(I)} \) is the concentration of copper(I), and \( \dot{D}_{\text{Cu}(I)} \) and \( \dot{D}_{O_2} \) are the diffusivities of cuprous ammine and dissolved oxygen, respectively.

The reaction between oxygen and cuprous ammine enhances gas-liquid mass transfer (relative to pure physical absorption) in two ways. Firstly, the reaction modifies the concentration profile of oxygen in the vicinity of the gas-liquid interface. The concentration of oxygen in solution is effectively zero and so a greater driving force for gas-liquid mass transfer is established. Secondly, the liquid-side mass transfer coefficient is increased in magnitude by an amount equal to the instantaneous enhancement factor. If the film model is assumed, this has the effect of reducing the effective thickness of liquid film by the same scale. No effect on interfacial surface area would be observed.

If there are insufficient concentrations of cuprous ammine at the gas bubble surface capable of instantaneous reaction with oxygen, the oxygen will dissolve. In this situation, the oxygen reduction chemistry may be more complicated. While cuprous ammine is still capable of reducing dissolved oxygen, the latter component may also act as an oxidant alongside cupric ammine, and so could therefore be reduced via mineral, iron(II) and sulphur oxidation. However, it is unlikely that oxygen would be reduced in any appreciable amount by the latter means, given that (1) cupric ammine would be present in solution in much greater concentration than dissolved oxygen, and (2) the reduction of dissolved oxygen on mineral surfaces is probably not as fast as the reduction of cupric ammine. Therefore, the reduction of dissolved oxygen would most likely take place, primarily, via reaction with cuprous ammine at either the mineral surface or in the bulk solution. The gas-liquid mass transfer and reduction of oxygen is realised in two steps, respectively:

\[ O_2(g) \rightarrow O_2(a) \]  

(4.8)

\[ O_2(a) + 4 \text{Cu(NH}_3)_2^+ + 4 \text{NH}_4^+ + 4 \text{NH}_3(a) \rightarrow 4 \text{Cu(NH}_3)_4^{2+} + 2 \text{H}_2\text{O(l)} \]  

(4.9)
The rate of oxygen dissolution would not be chemically enhanced, and so the rate of reaction 4.8 may be expressed by

\[ r_{4,8} = k_{a} a (C_{O_2} - C_{O_2(a)}) \]  

(4.10)

where \( C_{O_2(a)} \) is the concentration of dissolved oxygen. The above equation is the rate expression for pure physical absorption of oxygen gas, as given by the well-known two-film theory.

Given that the reaction between dissolved oxygen and cuprous ammine would still proceed at an analytically unobservable rate, cuprous ammine is not permitted to accumulate in solution when a steady-state concentration of dissolved oxygen is present. Thus, the rate of reaction 4.9 is limited kinetically by the availability of cuprous ammine (i.e. by the rate of production of copper(I) through reduction of copper(II)). The rate law can be expressed mathematically by a mass balance on copper(I), where \( C_{Cu(I)} = 0 \).

The nature of gas-liquid mass transfer in the Sherritt-Gordon ammonia leach is dictated by the concentrations of cuprous ammine relative to the solubility of oxygen. The models presented above exemplify a simple inference: in copper-catalysed ammoniacal leaching systems, under steady-state conditions, copper(I) and dissolved oxygen cannot mutually exist. Thus, the two states of leaching may be described qualitatively as that in the presence of copper(I) or dissolved oxygen. In the presence of copper(I), the chemical reaction network is driven by oxygen gas-liquid mass transfer; that is, oxygen dissolution is the rate-determining process. In the presence of dissolved oxygen, the chemical reaction network is driven by reaction at the mineral surface; that is, mineral oxidation is the rate-determining process.

The oxidation mechanism for the Sherritt-Gordon ammonia leach as exposed in this subsection is shown in Figures 4.2 and 4.3 for the cases in which leaching takes place in the presence of copper(I) and dissolved oxygen, respectively. These figures may be compared with Figure 4.1 to illustrate the impact that the copper(II)/copper(I) redox couple has on the leaching mechanism.
Figure 4.2: The oxidation mechanism of the Sherritt-Gordon ammonia leach when copper(II) is the oxidant at the mineral surface (copper(I) present in solution)

Figure 4.3: The oxidation mechanism of the Sherritt-Gordon ammonia leach when copper(II) is the oxidant at the mineral surface (oxygen present in solution)
4.3.3 Mineral Oxidation

Stoichiometry

Elemental sulphur is probably the initial sulphur product of metal sulphide oxidation in ammoniacal leaching systems. This is the case, under certain conditions, for the oxidation of copper sulphides [111-116]. Moreover, the elemental sulphur most likely forms as a result of a solid state reaction, rather than by a solution reaction of sulphide ion [113]. Thus, it is expected that sulphide mineral oxidation in the Sherritt-Gordon leach can be described with the following general stoichiometry:

\[
\text{MS} + x \text{Cu(NH}_3\text{)}_2^{2+} + (n - 2x) \text{NH}_3(a) \rightarrow \text{M(NH}_3\text{)}_n^{x+} + x \text{Cu(NH}_3\text{)}_2^{+} + S^0 \quad (4.11)
\]

The nickel matte mineralogy was introduced in the last chapter. Awaruite is a ferronickel solid solution, and so the nickel and iron composition is variable. For modelling purposes, awaruite is thus best represented as metallic nickel and metallic iron, separately. And given that the latter two components likely react at around the same rate, as is discussed later in the section, the mathematical description of particle kinetics for awaruite oxidation is not influenced. The stoichiometry of awaruite oxidation may therefore be described as follows:

\[
\text{Ni}^{0} + 2 \text{Cu(NH}_3\text{)}_2^{2+} + (n - 4) \text{NH}_3(a) \rightarrow \text{Ni(NH}_3\text{)}_n^{2+} + 2 \text{Cu(NH}_3\text{)}_2^{+} \quad (4.12)
\]

\[
\text{Fe}^{0} + 2 \text{Cu(NH}_3\text{)}_2^{2+} \rightarrow \text{Fe}^{2+} + 2 \text{Cu(NH}_3\text{)}_2^{+} + 4 \text{NH}_3(a) \quad (4.13)
\]

It is possible that an iron oxide layer may form at the surface of awaruite as it leaches, in a mode not unlike that of other iron-bearing sulphide minerals in ammoniacal solution (such as those in nickel concentrates). However, the high extraction of nickel in the leaching process at the refinery suggests that no form of impedance on nickel dissolution takes place, which is in contrast to what would be expected from such a product layer. Although, it may be the case that agitation is preventing the formation of such a layer on the awaruite surface, given that iron is the minor component of the mineral [3, 86]. Nonetheless, it is the assumption that awaruite leaches as a shrinking sphere.
In sulphate [117-119] and chloride [120] media, heazlewoodite leaches via a two-part mechanism. In the first part it leaches as if it was a metal and in the second part it leaches as if it was a sulphide; millerite (NiS) is an intermediate oxidation product. In ammoniacal solution, heazlewoodite probably leaches in a similar manner. The stoichiometry of heazlewoodite oxidation is thus considered as follows:

$$\text{Ni}_3\text{S}_2 + 2\text{Cu(NH}_3\text{)}^2_4 + (n - 4) \text{NH}_3(a) \rightarrow \text{Ni(NH}_3\text{)}^2_n + 2\text{Cu(NH}_3\text{)}^+_2 + 2\text{NiS}$$

(4.14)

$$\text{NiS} + 2\text{Cu(NH}_3\text{)}^2_4 + (n - 4) \text{NH}_3(a) \rightarrow \text{Ni(NH}_3\text{)}^2_n + 2\text{Cu(NH}_3\text{)}^+_2 + \text{S}^0$$

(4.15)

Chalcocite also leaches via a two-part mechanism, where covellite (CuS) is an intermediate oxidation product. This has been observed in ammoniacal solution [111-113, 121], as well as other media (e.g. acid ferric sulphate [122]). The stoichiometry of chalcocite oxidation is given as follows:

$$\text{Cu}_2\text{S} + \text{Cu(NH}_3\text{)}^2_4 \rightarrow \text{CuS} + 2\text{Cu(NH}_3\text{)}^+_2$$

(4.16)

$$\text{CuS} + \text{Cu(NH}_3\text{)}^2_4 \rightarrow 2\text{Cu(NH}_3\text{)}^+_2 + \text{S}^0$$

(4.17)

The complete mechanism is more complex than that outlined above, and is likely to follow that given by Filmer et al. [111-113]. Only a cursory explanation is given here. The first part leach of chalcocite is expected to proceed via the formation of several intermediate copper sulphide phases, including digenite (Cu$_{1.8}$S) and blaubleibender (“blue-remaining”) covellite (Cu$_{1.1}$S), where the composition of the mineral becomes progressively more copper-deficient until reaching a composition approximating covellite. This leaching behaviour is characteristically similar to the way in which chalcocite leaches in acid ferric sulphate solution [122], where the intermediate product is blaubleibender covellite (Cu$_{1.2}$S). The mechanism in ammoniacal solution follows that of a diffusion-controlled shrinking core (specifically, copper(I) diffusion away from the core), in which the copper sulphide intermediates form a layer on the chalcocite surface. The mechanism for covellite leaching practically follows that of a chemical reaction-controlled shrinking sphere. The oxidation of chalcocite is significantly faster.
than that of covellite [112]. The leaching of heazlewoodite may take place in a similar manner, where millerite forms at the surface of a shrinking core of heazlewoodite.

The oxidation of sycoporite results in the dissolution of cobalt as cobalt(II). Although cobaltous ions can complex with ammonia in aqueous solution [4], appropriate Eh-pH (or Pourbaix) diagrams for the Co-NH$_3$-H$_2$O system [123-125] suggest that it is cobaltic ammine that is stable under the leaching conditions in the Sherritt-Gordon process, not cobaltous ammine. Cobalt(III) ammine complexes have been reported to exist in the leaching process at Sherritt’s Fort Saskatchewan refinery [6]. It is expected that cobalt(II) is promptly oxidised to cobalt(III), and so the sycoporite oxidation reaction stoichiometry may be expressed as follows:

$$\text{CoS} + 3\text{Cu(NH}_3\text{)}_4^{2+} \rightarrow \text{Co(NH}_3\text{)}_6^{3+} + 3\text{Cu(NH}_3\text{)}_2^+ + S^0$$ (4.18)

The oxidation of pyrrhotite results in the dissolution of ferrous iron. The reaction stoichiometry is given as follows:

$$\text{FeS} + 2\text{Cu(NH}_3\text{)}_4^{2+} \rightarrow \text{Fe}^{2+} + 2\text{Cu(NH}_3\text{)}_2^+ + 4\text{NH}_3(\text{a}) + S^0$$ (4.19)

An iron oxide layer probably forms at the surface of pyrrhotite. Forward and Mackiw [2, 3] observed this during leach tests on nickel concentrates. Thus, pyrrhotite is likely the only nickel matte mineral that leaches as a shrinking core.

**Kinetics**

The leaching of nickel matte in ammoniacal solution is probably electrochemical in nature. Minerals are generally good electrical conductors, or at least semi-conductors, and so electron exchange tends to take place between minerals and redox species in solution much more readily than between molecules or ions. An electrochemical reaction is distinct from a chemical redox reaction in the sense that charge transfer does not occur at the same physical location, but rather the anodic (oxidation) and cathodic (reduction) half-cell reactions are separated by some finite distance. What this signifies for the leaching of a mineral particle is that the half-cell reactions occur simultaneously on separate anodic and cathodic sites on the particle surface, while the particle itself acts as a conduit for electrons. A leaching process may thus be considered as a corrosion
process (i.e. a short-circuited electrochemical process), and so the same concepts that
describe the kinetics of the latter (i.e. electrode kinetics) can be used to describe the
kinetics of the former, a topic that has been given extensive treatment in the
hydrometallurgical literature (e.g. [126-139]).

Consider that the essential leaching reaction in the Sherritt-Gordon process
(equation 4.11) may be expressed in terms of the following coupled anodic and cathodic
half-cell reactions:

\[
\begin{align*}
MS + n \text{NH}_3(a) & \rightleftharpoons M(\text{NH}_3)^{x+}_n + S^0 + xe^- \\
x \text{Cu}(\text{NH}_3)_2^{2+} + xe^- & \rightleftharpoons x \text{Cu}(\text{NH}_3)^+_2 + 2x \text{NH}_3(a)
\end{align*}
\]  

When a sulphide mineral is placed in contact with a solution containing cupric ammine,
in the absence of an applied potential, a corrosion cell will result in the anodic oxidation
of the mineral and the cathodic reduction of copper(II). A steady-state potential is
established and the cell attains dynamic equilibrium, where the total anodic and
cathodic electron currents are equal and opposite, and the net current flow is zero. That
is, at equilibrium, \( I = I_a + I_c = 0 \), where \( I \) is the total net current, \( I_a \) is the total anodic
current and \( I_c \) is the total cathodic current.

The principal relation of phenomenological electrode kinetics is the Butler-
Volmer equation, which relates the current density (or electrochemical reaction rate), \( i \),
at a solution-electrode interface to the established overpotential. The net (anodic)
current density of a \( z \)-electron transfer process is expressed as follows [140-142]:

\[
i = i_0 \left[ \exp \left( \frac{\alpha z F \eta}{RT} \right) - \exp \left( - \frac{(1-\alpha) z F \eta}{RT} \right) \right]
\]  

where \( i_0 \) is the exchange current density (i.e. the current density at the equilibrium (or
reverse) potential of the redox couple, \( E_r \), which is a function of the concentrations of
the redox species involved in the reaction, \( \eta = E - E_c \) is the overpotential, \( E \) is the
potential with respect to some reference electrode, \( \alpha \) is the transfer coefficient, \( z \) is the
number of electrons transferred (or, equally, the number of single-electron transfer
steps) in the overall reaction, \( F \) is Faraday’s constant, \( R \) is the ideal gas constant and \( T \) is temperature. The first and second right-hand-side terms in the above equation are the partial current densities for the anodic and cathodic processes, respectively.

If \( \eta \) is sufficiently positive (anodic) or sufficiently negative (cathodic), then the Butler-Volmer equation may be reduced, respectively, to the following high-field approximations:

\[
i = i_0 \exp \left( \frac{\alpha \, z \, F}{R \, T} \eta \right) \quad (4.23)
\]

\[
i = -i_0 \exp \left( -\frac{(1 - \alpha) \, z \, F}{R \, T} \eta \right) \quad (4.24)
\]

Through appropriate manipulation, the above equations can be shown to take on semi-logarithmic expressions of the form \( \eta = a + b \log |i| \), which are known to as Tafel equations. When represented graphically on an Evans diagram as plots of \( E \) vs. \( \log i \), known as Tafel plots, the polarisation curves are straight lines (Tafel lines) and the gradient of each (i.e. \( b \)) is known as a Tafel slope.

What the Butler-Volmer and Tafel relations signify for a given mineral leaching reaction is that its rate is dependent not only on the concentrations (at the mineral surface) of the species participating in the rate-limiting step, but on the mineral (i.e. electrode) potential. The steady-state potential at which the rate of the anodic reaction is balanced by that of the cathodic reaction is the potential at which leaching takes place. This is referred to as the mixed potential, \( E_m \) [143].

Nicol [130] proposed four models to describe the rate-limiting kinetics of an electrochemical leaching reaction, each of which is based on the relative rates of the anodic and cathodic processes. Of the leaching situations described, the first three are valid only when the anodic oxidation of the mineral takes place irreversibly, which is almost always the case. The models are best demonstrated by example. For the system described by equations 4.20 and 4.21, a Type I situation exists if the partial anodic current due to the anodic oxidation of copper(I) is negligible compared to that due to the
anodic oxidation of MS. That is, only the anodic characteristics of the mineral and the cathodic characteristics of the oxidant are significant in the region of the mixed potential, and so it may be said that the anodic and cathodic partial currents fall within their respective high-field (or Tafel) regions. A Type II situation exists if the partial anodic currents due to the anodic oxidation of MS and copper(I) are of comparable magnitude in the region of the mixed potential. This occurs when the equilibrium potentials for each half-cell reaction are in close proximity. A Type III situation exists if the partial anodic current due to the anodic oxidation of MS is negligible compared to that due to the anodic oxidation of copper(I). That is, only the electrochemical characteristics of the oxidant are significant in the region of the mixed potential, which, in this case, may be taken as the equilibrium potential of the copper(II)/copper(I) couple. Finally, a Type IV situation exists if the rates of the anodic and cathodic half-cell reactions (i.e. the rate of charge transfer across the solution-mineral interface) are fast relative to the rate of mass transport of cupric ammines from the bulk solution to the surface of MS. The rate-limiting step is thus the mass transport process. So, while the reaction taking place at the mineral surface is still electrochemical in nature, the kinetics of leaching is not limited by an electrochemical process and so the Butler-Volmer equation is not relevant in describing this circumstance.

The overall rate (molar flux per unit time) of a leaching reaction is directly proportional to the net current density (charge flux per unit time) of the anodic or cathodic half-cell reaction at the mixed potential, which is the dissolution current density, \(i_d\). Regardless of the rate-limiting step, the intrinsic rate of reaction 4.11 may be expressed in general terms as follows:

\[
r_{411} = -\frac{1}{S_{MS}} \frac{dN_{MS}}{dt} = \frac{i_d}{x F} = k_{MS}(T) f(C)
\]

where \(S_{MS}\) is the effective surface area of MS, \(N_{MS}\) is the number of moles of MS, \(x\) is the charge transfer valency in the anodic reaction, and \(f(C)\) is some function of redox species concentration. \(k_{MS}(T)\) is the intrinsic rate constant, which may be described by the Arrhenius function:

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\[ k_{\text{MS}}(T) = k_{0,\text{MS}} \exp \left( -\frac{E_{a,\text{MS}}}{RT} \right) \] (4.26)

where \( k_{0,\text{MS}} \) is the pre-exponential factor and \( E_{a,\text{MS}} \) is the Arrhenius activation energy.

By describing each of the charge transfer-controlled (or activation-controlled) scenarios (i.e. Type I, II and III leaching situations) mathematically using the Butler-Volmer equation, and through appropriate use of mixed potential theory [143], it can be shown that for each scenario the differences in the leaching rate law resides in the form of the concentration-dependent term, \( f(C) \). Moreover, it can also be shown that even for the case of reactant mass transport-controlled kinetics (i.e. the Type IV leaching situation) the difference may be found in the same term. The details of the theoretical derivation of said terms for each of the four leaching situations are given in Appendix A. Only the final results are offered here.

If the rate-limiting step is charge transfer at the solution-mineral interface, then the case for Type I, Type II or Type III leaching may be made in terms of the significance of the concentration of copper(I), since it is the latter quantity that determines the degree of reversibility of the cathodic half-cell reaction. If the concentration of copper(I) is insignificant, then leaching would proceed according to a Type I situation and the concentration-dependent term takes on the following form:

\[ f(C) = C_{\text{Cu(II)}}^{1/2} C_{\text{NH}_3(T)}^{1/2} \] (4.27)

where \( C_{\text{Cu(II)}} \) and \( C_{\text{NH}_3(T)} \) are the concentrations of copper(II) and total aqueous ammonia, respectively. If the concentration of copper(I) is significant, then leaching would proceed according to a Type II or Type III situation. The concentration-dependent term for the latter is given by

\[ f(C) = \left( \frac{C_{\text{Cu(II)}}}{C_{\text{Cu(I)}}} \right)^{1/2} C_{\text{NH}_3(T)}^{1/2} \] (4.28)

If the rate-limiting step is the mass transport of cupric ammine from the bulk solution to the mineral surface, then the significance of copper(I) concentration is immaterial and
the concentration-dependent term is given as follows:

\[ f(C) = C_{\text{Cu(II)}} \]  

(4.29)

It is important to recognise that the concentrations of the redox species participating in the leaching reactions, as required in equations 4.27 and 4.28 (but not equation 4.29), refer to those at the mineral surface, since that is where the mixed potential is established. However, since reaction at the mineral surface is rate-controlling and slurry in continuous reactors is well-mixed, concentrations at the mineral surface are comparable to those in the bulk solution. Conversely, this supposition may not always be valid in the laboratory [144].

If the concentration of copper(I) is such that a Type III situation prevails, then as the concentration is allowed to approach zero the kinetics of leaching will gradually shift from Type III to Type II to Type I. A measure for the significance of copper(I) concentration is thus required. This is a classification that can only be determined indisputably in the laboratory, and so in this work an assumption must be made. It is assumed that the concentration of copper(I) is significant if copper(I) is present in solution. For the cases of Type II and Type III leaching, one further level of distinction is required concerning this significance in order to segregate each situation. But, once again, this is an outcome that can only be achieved experimentally under controlled conditions. Of the two situations, Type II leaching kinetics is the most difficult to ascertain in the absence of laboratory data (see Appendix A), and so this situation is approximated in this work with a Type III model. Therefore, if \( C_{\text{Cu(I)}} = 0 \) (i.e. leaching in the presence of dissolved oxygen) then \( f(C) \) is given by equation 4.27, and if \( C_{\text{Cu(I)}} > 0 \) (i.e. leaching in the presence of copper(I)) then \( f(C) \) is given by equation 4.28.

The fractional-order dependence of the leaching rate on the oxidant is indicative of an electrochemical reaction-controlled mechanism. If the rate of anodic dissolution of the mineral is found to be limited by a single-electron transfer process (which is typically the case for sulphide minerals since it is favoured energetically [127]), then the
significance of the one-half-order dependence can be related directly to the value of the transfer coefficient (as defined in the Butler-Volmer equation) for each half-cell reaction. The transfer coefficient represents a measure of the symmetry of the activation energy barrier for a given charge transfer reaction. If the energy barrier is taken as being symmetrical, then the transfer coefficient is given by \( \alpha = 0.5 \). According to Bockris and Reddy [141], electrode experiments usually reveal that the value of the transfer coefficient is close to 0.5. The fractional reaction order is also related to the relative values of the Tafel slopes for relevant anodic and cathodic processes. If the absolute values of the Tafel slopes are equal, then the leaching reaction has a one-half-order dependence on the oxidant.

The expected transfer coefficient value is supported by numerous studies on mineral leaching that is driven by electrochemical reaction. Nicol [130] presented a robust summary of published data that underscores the effects that the concentrations of various oxidants have on the rates of selected dissolution systems. The compilation of studies represents a host of sulphide minerals, such as pyrite, sphalerite, chalcopyrite and heazlewoodite, with oxidants that include oxygen (in sulphate, alkali, cyanide and hydroxide media), iron(III) (in sulphate and chloride media) and copper(II) (in a chloride medium). All of the rate laws display fractional-order dependence on the concentration of the oxidant, while nearly all exhibit either one-half- or near-one-half-order dependence in the same respect. As declared by said author, this compilation represented only a fraction of the available studies that support the same reasoning. In the near-two decades that have passed between then and now, the literature has only increased in breadth where studies of this nature are concerned, as demonstrated by a recent review [145] on the topic. Consequently, the assumption of symmetrical energy barriers for charge transfer reactions that take place during the oxidative leaching of sulphide minerals is justified.

Several literature studies may be highlighted as being particularly constructive in supporting leaching rate law development for leaching situations in this work. Ghosh et al. [98] and Zhang [104] demonstrated experimentally that the leaching reactions for sphalerite and (colloidal) gold, respectively, in copper-catalysed ammoniacal solution
are fractional-order with respect to both copper(II) and ammonia. Filmer [105] and Reilly and Scott [146] established experimentally that the reaction for covellite leaching in the same system is fractional-order with respect to oxygen (in terms of pressure) and ammonia. Since the concentration of copper(II) is a function of oxidation potential and thus of oxygen pressure (as established via equations 4.5 or 4.9), the preceding authors would probably have discovered that the covellite leaching rate has a fractional-order dependence on copper(II). Thus, in this sense, the rate law proposed by each group of authors for covellite is consistent with those for sphalerite and (colloidal) gold, which cater for the sole case of Type I leaching kinetics.

Some other studies that considered the oxidation of metallic nickel [147, 148] and cobalt [149] in oxygenated ammoniacal solution are also of relevance. Although copper was not present in solution, and thus the experimental results are limited in terms of their affiliation with this work, the authors determined that the reactions between each metal and dissolved oxygen were electrochemical in nature. Moreover, in the case of cobalt oxidation, Vu and Han [149] demonstrated that the rate law is fractional-order with respect to oxygen and ammonia.

The above studies demonstrate that oxidant concentration (or pressure, where appropriate) and ammonia concentration are common terms of dependence when describing rates of oxidation of metals and metal sulphides in ammoniacal systems. Since it is reasonable to expect that the oxidation rates of different sulphide minerals (and even metals) that leach in any given system under the same rate-limiting mechanism are dependent upon the same variables, the evidence outlined in the preceding paragraphs implies that assumptions made during the theoretical development of the leaching rate laws in this work (i.e. those employed in the derivations of Appendix A) are valid.

The leaching of nickel matte may be evaluated for two mineral types: metallic and sulphide. Metallic mineral leaching is considered for awaruite and the first-part leaching of heazlewoodite and chalcocite, while sulphide mineral leaching is considered for millerite (second-part leaching of heazlewoodite), covellite (second-part leaching of
chalcocite), sycporite and pyrrhotite. At the refinery, the metallic minerals are observed to disappear entirely within the first stage leach (i.e. awaruite is completely consumed and heazlewoodite and chalcocite are completely converted to millerite and covellite, respectively), while the sulphides are present in the third stage leach discharge. What this signifies is that the leaching kinetics of the former minerals is much faster than that of the latter. This is unsurprising, given that the dissolution of metals is generally characterised by a much higher electrochemical reversibility (or exchange current density) compared to metallic compounds [130].

Of all the nickel matte minerals, only the leaching behaviour of chalcocite and covellite has been studied in copper-catalysed ammoniacal solution; an account of these mineral oxidation mechanisms was given previously. Filmer et al. [112] estimated the apparent activation energies of the first- and second-part reactions for chalcocite leaching to be 27 kJ mol$^{-1}$ and 60 kJ mol$^{-1}$, respectively, which may be used to establish the rate-limiting steps for each reaction. It is widely-accepted that leaching kinetics are controlled by mass transport processes if the activation energy is less than 20 kJ mol$^{-1}$, by reaction at the mineral surface if the activation energy is greater than 40 kJ mol$^{-1}$, and by a combination of the two steps (i.e. mixed control) if the activation energy falls in between. The quantities determined by Filmer et al. [112] advocate that the rate of chalcocite oxidation (i.e. first-part leach) is fast, and controlled by a combination of mass transport and reaction at the mineral core surface, while the rate of covellite oxidation is slow, and governed solely by reaction at the mineral surface.

Given the distinction between each mineral type in the matte and the rates by which they collectively leach at the refinery, it is reasonable to assume that the apparent activation energies and corresponding rate-limiting steps for chalcocite and covellite oxidation could well-represent those generally for the oxidation of metals and sulphides, respectively. That is, it may be considered that the activation energies for awaruite and heazlewoodite oxidation are close to 27 kJ mol$^{-1}$, while those for millerite, sycporite and pyrrhotite oxidation are in the vicinity of 60 kJ mol$^{-1}$. Although no comparable studies exist for the metallic minerals, a study on sphalerite oxidation in copper-catalysed ammoniacal solution [98] revealed the apparent activation energy to be 48.3
kJ mol$^{-1}$ and the rate-limiting step to be reaction at the mineral surface, which is consistent with that determined for covellite. Thus, it is with confidence that the preceding assumptions for apparent activation energy are made.

With respect to metallic mineral oxidation, the governing rate law could probably take on the form of equation 4.25, where the Arrhenius activation energy is 27 kJ mol$^{-1}$ and $f(C)$ is given by equation 4.29. The unknown parameters are thus the pre-exponential factors for each metallic mineral, which require some form of estimation. With respect to sulphide mineral oxidation, the governing rate law is given by equation 4.25, where the Arrhenius activation energy is 60 kJ mol$^{-1}$ and $f(C)$ is given by equations 4.27 or 4.28, the latter depending, respectively, on whether dissolved oxygen or copper(I) is present in solution. The unknown parameters are therefore the pre-exponential factors for each sulphide mineral in the presence of copper(I) or dissolved oxygen (i.e. eight pre-exponential factors). The estimation of said parameters is addressed in Chapter 7.

4.3.4 Sulphur Oxidation

The chemical behaviour of sulphur-oxygen compounds in many aqueous environments has received considerable attention in the literature and is well-understood to be very complex. In ammoniacal leaching systems, the mechanism by which sulphide sulphur is oxidised to sulphate and sulphamate remains a topic of discussion. Specifically, it is the nature of formation and subsequent decomposition of the unsaturated oxysulphur species that is incompletely understood. The emergence of such intermediates in ammoniacal solution, including thiosulpate and polythionate, was first observed by Forward and Mackiw [2, 3, 17], who suggested a simple reaction mechanism on the basis of progressive oxidation of sulphur from lower to higher valence states (equations 2.3 and 2.4). Since that work, a number of published studies have demonstrated that the chemistry of unsaturated oxysulphur intermediates in aqueous solution, in both the presence and absence of an oxidant, is considerably more complex. Such studies may assist in formulating a more complete understanding of sulphur chemistry in the Sherritt-Gordon ammonia leach.
Although elemental sulphur is most likely the initial sulphur product of the oxidative leaching of sulphide minerals in ammoniacal solution, it is thermodynamically unstable at high pH under oxidising conditions [150]. Filmer et al. [111-113], Reilly and Scott [115, 116], and Muir et al. [114] were able to promote its formation during the oxidative ammoniacal leaching of copper sulphides by manipulating experimental conditions to promote kinetic stability. Although several factors may influence the formation of elemental sulphur, such as pH and free ammonia concentration, the most significant factor seems to be temperature. It appears to be the case that the kinetics of elemental sulphur decomposition is sufficiently slow at lower temperatures (i.e. less than 50 ºC) such that its presence may be observed. At the temperatures and solution conditions seen in the Sherritt-Gordon ammonia leach, the decomposition of elemental sulphur probably takes places at a rate comparable with its formation, which explains why Forward and Mackiw [2, 3, 17] did not measure any during the oxidative leaching of nickel sulphide concentrates.

In ammoniacal solution, elemental sulphur disproportionates to polysulphide and thiosulphate, and thus dissolves by a non-oxidative reaction [105, 151]. Furthermore, in the presence of dissolved oxygen, polysulphides are promptly oxidised to thiosulphate [105, 151, 152], which would probably also be the situation if cupric ammine was the oxidant. Given that the dissolution of elemental sulphur and subsequent oxidation of polysulphides in ammoniacal solution is fast, it can be supposed that thiosulphate is the effective product of sulphide sulphur oxidation. Thus, if cupric ammine is the oxidant, then the oxidation of elemental sulphur may be described with the following stoichiometry:

\[
2S^0 + 4\text{Cu(NH}_3\text{)}^2_2^+ + 3\text{H}_2\text{O(l)} \rightarrow \text{S}_2\text{O}_3^{2-} + 4\text{Cu(NH}_3\text{)}^2_2^+ + 6\text{NH}_4^+ + 2\text{NH}_3(a) 
\]

(4.30)

The rate of reaction 4.30 is limited kinetically by the availability of elemental sulphur (i.e. by the rate of production of elemental sulphur through sulphide mineral oxidation). The rate law can be determined mathematically via a mass balance on elemental sulphur, where its concentration is taken as zero.
Thiosulphate is predominantly oxidised in the presence of an oxidant in ammoniacal solution [151, 153-157]. Whether the oxidant is dissolved oxygen or cupric ammine, tetrathionate is the reaction product. In the presence of the latter oxidant, the stoichiometry is given as follows:

$$2S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \rightarrow S_4O_6^{2-} + 2Cu(NH_3)^{+} + 4NH_3(a)$$

(4.31)

Byerley et al. [153] are the only researchers to have proposed a rate law for the above reaction, which describes thiosulphate oxidation in copper-catalysed ammoniacal solution in the presence of copper(I):

$$r_{4.31} = k_{0,s,0^{+}} \exp \left(-\frac{102508}{RT}\right) \frac{C_{Cu(II)}C_{S,0^{+}}}{C_{NH_3(T)}}$$

(4.32)

where $k_{0,s,0^{+}} = 4.0 \times 10^{-4} \exp(102508/303.15/R)$ is the pre-exponential factor and $C_{S,0^{+}}$ is the concentration of thiosulphate. It has been suggested [158-160] that thiosulphate oxidation is also hindered by the presence of sulphate, however, no rate law has been proposed that accommodates the sulphate concentration term.

In the presence of dissolved oxygen, the stoichiometry expressed in equation 4.31 may still be considered for purposes relevant to this work, however, the actual mechanism by which thiosulphate is oxidised is more complicated. Although the details of the reaction mechanism are beyond the scope of discussions pertinent here, what is significant is that dissolved oxygen assists in electron transfer between thiosulphate and copper(II) [154, 155]. The presence of dissolved oxygen considerably enhances the rate of oxidation, which is expected to be more than an order of magnitude higher than that in its absence [154, 155, 161]. Thus, thiosulphate oxidation under these conditions is fast, and is probably limited kinetically by the availability of thiosulphate (i.e. by the rate of production of thiosulphate through elemental sulphur oxidation). While no rate law has been proposed in the literature, if the latter assumption is considered then an approximate rate law may be determined mathematically via a mass balance on thiosulphate, where $C_{S,0^{+}} = 0$. 

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In both the presence and absence of an oxidant, the formation of tetrathionate spawns a highly convoluted system of reactions in aqueous solution, which, depending on the solution conditions (such as pH and temperature), may promote the formation of some or all of the following sulphur oxyanions: thiosulphate (i.e. it is regenerated), trithionate, pentathionate, sulphite, polysulphide, sulphamate (in aqueous ammonia only) and sulphate. In the presence of an oxidant in ammoniacal solution, the central argument put forward by researchers – such as Naito and co-workers [151, 152, 156, 157], and Byerley and colleagues [153-155] – is that tetrathionate and the unsaturated oxysulphur intermediates that subsequently form (with the exception of thiosulphate, which oxidises) undergo hydrolytic or ammonolytic decomposition until all sulphur exists as sulphamate and sulphate. Under this scheme, tetrathionate is hydrolysed principally to trithionate and thiosulphate [153, 156, 162, 163]. However, under certain conditions, pentathionate (and possibly other thionates), sulphite and polysulphide are intermediate reaction products [153, 155, 156, 163-165]. While trithionate degrades via hydrolysis to thiosulphate and sulphate in aqueous solution [162, 166-168], in the presence of ammonia the species in question also decomposes via ammonolysis to thiosulphate and sulphamate in a competing reaction [156, 168]. Under the prevailing conditions, sulphamate and sulphate are immune from further reaction.

There is additional evidence in the literature, however, suggesting that the preceding reaction system may be incomplete. Recently, it has been demonstrated that, under certain conditions, tetrathionate and trithionate can be oxidised by copper(II) in ammoniacal solution [158]. Although the conditions under which this occurs is uncertain, it is in direct opposition to the preceding position. Therefore, it seems that polythionate may hydrolyse/ammonolyse or oxidise, or both, in the presence of an oxidant. Of course, the oxidant in question may be significant.

Forward and Mackiw [3] observed the presence of copper(II) to influence the conversion of thiosulphate to polythionates, sulphamate and sulphate, and suggested that cupric ammine is acting as an oxidation catalyst. Naito and associates [151, 152, 156, 157] carried out their experiments using compressed oxygen as the oxidant. In fact, the prime evidence put forward by the latter authors for hydrolysis of polythionate was
that thiosulphate was a reaction product when an initial batch of tetrathionate was oxidised with dissolved oxygen [156]. Although Naito and co-workers [151, 152, 156, 157] were aware of Forward and Mackiw’s [3] findings, and even confirmed it experimentally [151, 157], it was not appreciated that cupric ammine may directly oxidise the unsaturated oxysulphur species. Thus, the oxidation of the latter species with the former was not investigated. The authors did, however, study the effects that copper(II) has on the oxidation of elemental sulphur [151] and thiosulphate [157], in the form of appraising rates of formation and yield of hexavalent sulphur compounds. In the presence of cupric ammine, it was observed not only that the rates were faster – which is to be expected from Forward and Mackiw’s [3] conclusions – but that the yield of sulphamate and sulphate were greater and smaller, respectively. Given that sulphamate may only form via the decomposition of trithionate [151, 156, 168], and although it remains uncertain as to the degree to which copper(II) benefits the formation of sulphamate, it seems that copper(II) not only catalyses the overall oxidation of sulphur but directly influences the kinetics of trithionate decomposition. If trithionate is oxidised by cupric ammine, then the preceding experimental results would be expected.

Byerley and colleagues [153-155], on the other hand, carried out a series of experiments in which (1) only copper(II) was present in ammoniacal solution [153], and (2) both copper(II) and dissolved oxygen were present [154, 155]. The authors acknowledged a similar mechanism for polythionate decomposition as that proposed by Naito and associates [151, 152, 156, 157], even though they were aware that cupric ammine could oxidise thiosulphate. The central evidence in support of this scheme was that, in the presence of copper(II) only, a stoichiometrically-higher-than-expected concentration of thiosulphate was present in solution following the completion of oxidation reactions in an experiment in which copper(II) and thiosulphate were present initially [153]. If copper(II) may only be reduced by thiosulphate (equation 4.31), then stoichiometricaly-higher concentrations of the latter component relative to the former suggest that thiosulphate is regenerated, most probably via hydrolytic decomposition of tetrathionate, and perhaps also via hydrolytic or ammonolytic decomposition of trithionate. However, if it is accepted that copper(II) can also be reduced by
tetraphionate and trithionate, and it is furthermore assumed that thiosulphate is not
regenerated via such reactions, then this mechanism may also be verified by the same
experimental results.

Although there is still a great deal of uncertainty concerning polythionate
decomposition, the following appears to be true. In oxygenated ammoniacal solution, it
seems to be the case that polythionate is predominantly hydrolysed or ammonolysed.
That is, in the absence of copper(II), the literature evidence supports this reaction
scheme, and there does not seem to be any evidence suggesting that any other
mechanism prevails. However, in copper(II)-catalysed ammoniacal solution, there is
convincing evidence to suggest that polythionate is oxidised by cupric ammine.
(However, the possibility of a series-parallel reaction network that features both
hydrolysis/ammonolysis (albeit at a slower rate) and oxidation cannot be ignored.) An
explanation as to why polythionate can be oxidised by cupric copper and, seemingly,
not by oxygen (when both oxidants are present), or the precise conditions under which
the former situation take place, remains unknown. It may simply be the case that the
kinetics of oxygen gas-liquid mass transfer and subsequent reduction by polythionate
cannot compete with the kinetics of polythionate hydrolysis/ammonolysis, whereas the
kinetics of copper(II) reduction by polythionate can. Of course, the explanation may be
more intricate.

If tetrathionate is hydrolysed in ammoniacal solution, it does so according to the
following reaction [153, 156, 162, 163]:

$$4S_4O_6^{2-} + 6NH_3(a) + 3H_2O(l) \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 6NH_4^+$$ \hspace{1cm} (4.33)

Although no rate law has been developed, it is known that the kinetics of tetrathionate
decomposition is fast. In the Sherritt-Gordon ammonia leach, trithionate is the dominant
(i.e. most stable) thionate species [2, 3, 17]. Moreover, tetrathionate has been shown to
decompose rapidly relative to trithionate in ammoniacal solution [156]. If it is assumed
that trithionate is the sole thionate species, then the kinetics of tetrathionate hydrolysis
may be considered to take place instantaneously.
If trithionate is not oxidised in ammoniacal solution, it will undergo hydrolytic and ammonolytic decomposition in parallel reactions to produce sulphate and sulphamate, respectively [168]:

$$S_3O_6^{2-} + 2 NH_3(a) + H_2O(l) \rightarrow SO_4^{2-} + S_2O_3^{2-} + 2 NH_4^+ \quad (4.34)$$

$$S_3O_6^{2-} + 2 NH_3(a) \rightarrow SO_3NH_2 + S_2O_3^{2-} + NH_4^+ \quad (4.35)$$

Naito et al. [168] are the only researchers to have proposed rate laws for the above reactions, which are given respectively as follows:

$$r_{4.34} = \left[ k_{0,w} \exp\left( -\frac{84517}{RT} \right)C_{H_2O} + k_{0,a} \exp\left( -\frac{50208}{RT} \right)C_{S,O_6^{2-}} \right] C_{S,O_6^{2-}} \quad (4.36)$$

$$r_{4.35} = \left[ k_{0,a} \exp\left( -\frac{80751}{RT} \right)C_{NH_3(T)} + k_{0,t} \exp\left( -\frac{50208}{RT} \right)C_{S,O_6^{2-}} \right] C_{S,O_6^{2-}} \quad (4.37)$$

where $C_{S,O_6^{2-}}$ and $C_{H_2O}$ are the concentrations of trithionate and water, respectively. The pre-exponential factors were calculated as averaged-values from original data presented by the authors (Table 3 in [168]), and are given as follows:

$$k_{0,w} = 2.167 \times 10^{-11} \exp(84517/303.15/R), \quad k_{0,a} = 3.489 \times 10^{-10} \exp(80751/303.15/R)$$

and

$$k_{0,t} = 5.090 \times 10^{-8} \exp(50208/303.15/R).$$

As has been discussed, it is unlikely that polythionate decomposes solely by hydrolytic or ammonolytic means when copper(II) is present in ammoniacal solution. In Chapter 7, it is demonstrated that this chemistry is unlikely to be occurring in the ammonia leach at the Kwinana nickel refinery. That is, either most or all of the polythionate is oxidised. It is furthermore demonstrated that thiosulphate is probably not regenerated in reactions of the latter type. Forward and Mackiw [2, 3, 17] are the only researchers to have proposed a mechanism for polythionate oxidation in ammoniacal solution, and the stoichiometry developments to follow reflect the basis of that submission.

If tetrathionate is oxidised, it is likely that trithionate is the reaction product [158, 169]. Based on this assumption, and supposing furthermore that thiosulphate is not
regenerated, the reaction stoichiometry may take on the following form:

\[
3S_4O_6^{2-} + 10 \text{Cu(NH}_3)_2^{2+} + 6 \text{H}_2\text{O(l)} \rightarrow 4S_3O_4^{2-} + 10 \text{Cu(NH}_3)_2^{+} + 12 \text{NH}_4^+ + 8 \text{NH}_3(a)
\]

(4.38)

Based on the evidence presented above for tetrathionate hydrolysis, the kinetics of tetrathionate oxidation is probably fast, and by the same logic may also be considered to take place instantaneously. If tetrathionate is only oxidised, then in the presence of copper(I) or dissolved oxygen the rate of the above reaction is limited kinetically by the availability of tetrathionate (i.e. by the rate of production of tetrathionate through thiosulphate oxidation). The rate law can be determined mathematically via a mass balance on tetrathionate, where its concentration is taken as zero. If tetrathionate reacts according to both equations 4.33 and 4.38, then an additional equation is required to determine what fraction is hydrolysed or oxidised.

If trithionate is oxidised, it may also do so to produce sulphate and sulpha-mate in parallel reactions. If it is furthermore assumed that thiosulphate is not regenerated, then the reaction stoichiometry may take on the following form:

\[
S_3O_6^{2-} + 8 \text{Cu(NH}_3)_2^{2+} + 6 \text{H}_2\text{O(l)} \rightarrow 3 \text{SO}_4^{2-} + 8 \text{Cu(NH}_3)_2^{+} + 12 \text{NH}_4^+ + 4 \text{NH}_3(a)
\]

(4.39)

\[
S_3O_6^{2-} + 8 \text{Cu(NH}_3)_2^{2+} + 3 \text{H}_2\text{O(l)} \rightarrow 3 \text{SO}_3\text{NH}_2^+ + 8 \text{Cu(NH}_3)_2^{+} + 9 \text{NH}_4^+ + 4 \text{NH}_3(a)
\]

(4.40)

Rate laws for the above reactions are proposed below on the basis that the kinetics is probably first-order with respect to each reactant. Thus, in the presence of copper(I), the rate equations are assumed to take on the following forms:

\[
r_{4.39} = k_{0,SO_4^{2-}} \exp \left( -\frac{E_{a,SO_4^{2-}}}{RT} \right) C_{\text{Cu(II)}} C_{S_3O_6^{2-}}
\]

(4.41)

\[
r_{4.40} = k_{0,SO_3\text{NH}_2^+} \exp \left( -\frac{E_{a,SO_3\text{NH}_2^+}}{RT} \right) C_{\text{Cu(II)}} C_{S_3O_6^{2-}} C_{\text{NH}_3(T)}
\]

(4.42)
Figure 4.4: The decomposition mechanism of sulphur in the Sherritt-Gordon ammonia leach (Solids lines: oxidation; dashed lines: hydrolysis/ammonolysis.)

where $k_{0,SO_4^{2-}}$ and $k_{0,SO_3NH_2}$ are the pre-exponential factors for the above rate laws, while $E_{a,SO_4^{2-}}$ and $E_{a,SO_3NH_2}$ are the Arrhenius activation energies. Each of the preceding parameters is unknown. The estimation of said parameters is addressed in Chapter 6 (for the latter two) and Chapter 7 (for the former two).

In the presence of dissolved oxygen, the actual mechanism by which polythionate is oxidised may, like thiosulphate, be more complicated. If it is assumed that the kinetics of polythionate oxidation is influenced in a manner similar to that of thiosulphate, then it may be taken that reactions 4.38, 4.39 and 4.40 are fast, and limited kinetically by the availability of each thionate. In the case of tetrathionate, as already mentioned, oxidation kinetics in the presence of dissolved oxygen is the same as in the presence of copper(I). In the case of trithionate, if it is assumed simply that the ratio of the rates of production of sulphate and sulphamate in the presence of copper(I) (equations 4.41 and 4.42, respectively) remains unchanged, then rate laws for reactions 4.39 and 4.40 can be determined mathematically via a mass balance on trithionate, where $C_{s,SO_3^{2-}} = 0$.

The mechanism of sulphur decomposition via oxidation and hydrolysis/ammonolysis in the Sherritt-Gordon ammonia leach as exposed in this subsection is illustrated in Figure 4.4.
4.3.5 Iron Precipitation and Associated Adsorption

The oxidation of awaruite and pyrrhotite (equations 4.13 and 4.19, respectively) results in the dissolution of iron as ferrous. The thermodynamic instability of dissolved iron in the Sherritt-Gordon ammonia leach has already been disclosed (Chapter 2). This observation is supported by Eh-pH diagrams for the Fe-NH₃-H₂O system under oxidising conditions [170], where iron is stable in the solids phase as iron(III) oxide. Refinery leach liquor assays reveal that the concentration of iron in solution is virtually zero at all times. This suggests that, upon dissolution, iron(II) is rapidly oxidised to iron(III), the latter of which is then promptly hydrolysed, resulting in precipitation of the metal as an oxide. It is for this reason that references to iron(II) thus far have been to ferrous ion, and not ferrous ammine.

Forward and Mackiw [2, 3] proposed the precipitation of hydrated iron oxide, taken as Fe₂O₃·H₂O. However, in ammonia-ammonium sulphate solutions under oxidising conditions, a host of iron(III) oxides are known to form, including ferric hydroxide (Fe(OH)₃), hematite (Fe₂O₃), goethite (FeOOH), ferrihydrite (Fe₂O₃·xH₂O) and magnetite (Fe₃O₄) [171]. The precipitated iron in the refinery leach probably exists in a number of forms that reflects the preceding list, however, the final leach residue is only expected to contain ferrihydrite and some magnetite. Given that this aspect of the chemistry is relatively insignificant in terms of the objectives in this work, the definition of a single species will suffice in representing iron(III) compounds. Here, the form considered by Forward and Mackiw [2, 3] is used. The stoichiometry of iron precipitation is thus given as follows:

\[
2 \text{Fe}^{2+} + 2 \text{Cu(NH}_3)_2^{2+} + 2 \text{NH}_3(a) + 4 \text{H}_2\text{O(l)} \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2 \text{Cu(NH}_3)_2^{+} + 6 \text{NH}_4^+
\]

(4.43)

Since no dissolved iron exists in solution, the above reaction may be considered to take place instantaneously. The rate of the above reaction is thus limited kinetically by the availability of iron(II) (i.e. by the rate of production of iron(II) via reactions 4.13 and 4.19). The rate law can be determined mathematically via a mass balance on iron(II),
where its concentration is taken as zero.

An important consequence of iron precipitation in the Sherritt-Gordon process is the associated adsorption effect. Iron oxide is a strong adsorbent, and tends to scavenge from solution the potentially harmful components that enter with the refinery feed material and dissolve. Most notable are compounds of arsenic and selenium [172]. Such elements would contaminate the final nickel product if not removed. Consequently, the ratio of iron-to-deleterious-elements in the leach must be maintained at an appropriate level in order to ensure sufficient removal [173]. Under normal conditions in the leaching process at the refinery, there is typically adequate iron present in the matte to adsorb virtually all arsenic and selenium. It is thus assumed in this work that all impurities that enter with the refinery feed material report to the leach tailings, along with all of the iron.

An adverse effect of iron precipitation is that value metals may co-precipitate with the iron via adsorption [174-178]. In the refinery, this phenomenon seems to affect cobalt more so than nickel and copper, however, even the latter metals may experience uptake in some respect. Although little is understood about this aspect of the chemistry, the prospect of re-dissolution of value metals cannot be ignored. Given that value metal precipitation in the leach does not represent a performance issue at the refinery, this aspect of the chemistry will not be given attention in this work.

4.3.6 Metal Ammine Formation

Thus far, dissolved metals have been considered in terms of the complex ions that they form in aqueous ammonia solution; that is, metal ammines. However, no discussion on their formation has been given. It is well-understood that metals dissolve in aqueous solution by complexing with water; that is, they form aquo ions. Metal ammines are formed subsequently by successive substitution of aquo ligands with ammonia. The ammine complexes are formed in a stepwise fashion, where the number of steps – and thus the number of ammines formed – is dictated by the thermodynamic characteristics of the metal in question. If aquo ligands are ignored, then the complexing of a metal M of valency \(x\) with ammonia in aqueous solution may be described as follows:

\[
\text{M}^{(x+)} + \text{NH}_3 \rightarrow \text{M}
\text{NH}_2
\]

\[
\text{M}
\text{NH}_2 + \text{NH}_3 \rightarrow \text{M}
\text{NH}_3
\]

\[
\vdots
\]

\[
\text{M}
\text{NH}_{2x-}\text{NH}_3\rightarrow \text{M}
\text{NH}_{2x}
\]

As the number of steps increases, the formation constants for each successive ammine decrease. This is because the stability of the ammine complexes decreases as the number of ammine ligands increases. The overall stability of the ammine complex is thus determined by the stability of the first ammine ligand, which is typically the most stable.
\[
\begin{align*}
\text{M}^{x+} + \text{NH}_3(a) & \rightleftharpoons \text{MNH}_3^{x+} \quad K_1 = \frac{[\text{MNH}_3^{x+}]}{[\text{M}^{x+}][\text{NH}_3]} \\
\text{MNH}_3^{x+} + \text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_2^{x+} \quad K_2 = \frac{[\text{M(NH}_3)_2^{x+}]}{[\text{MNH}_3^{x+}][\text{NH}_3]} \\
\vdots & \quad \vdots \\
\text{M(NH}_3)_{n-1}^{x+} + \text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_n^{x+} \quad K_n = \frac{[\text{M(NH}_3)_n^{x+}]}{[\text{M(NH}_3)_{n-1}^{x+}][\text{NH}_3]} \\
\text{M(NH}_3)_N^{x+} + \text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_N^{x+} \quad K_N = \frac{[\text{M(NH}_3)_N^{x+}]}{[\text{M(NH}_3)_{N-1}^{x+}][\text{NH}_3]}
\end{align*}
\]

where \( N \) is the maximum coordination number of the metal ion and \( K_n \) \((1 \leq n \leq N)\) is the stepwise stability constant for the \( n \)th complexation reaction. The above system of reactions may also be represented in an overall manner as follows:

\[
\begin{align*}
\text{M}^{x+} + \text{NH}_3(a) & \rightleftharpoons \text{MNH}_3^{x+} \quad \beta_1 = \frac{[\text{MNH}_3^{x+}]}{[\text{M}^{x+}][\text{NH}_3]} = K_1 \\
\text{M}^{x+} + 2\text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_2^{x+} \quad \beta_2 = \frac{[\text{M(NH}_3)_2^{x+}]}{[\text{M}^{x+}][\text{NH}_3]^2} = K_1K_2 \\
\vdots & \quad \vdots \\
\text{M}^{x+} + n\text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_n^{x+} \quad \beta_n = \frac{[\text{M(NH}_3)_n^{x+}]}{[\text{M}^{x+}][\text{NH}_3]^n} = \prod_{i=1}^{n} K_i \\
\text{M}^{x+} + N\text{NH}_3(a) & \rightleftharpoons \text{M(NH}_3)_N^{x+} \quad \beta_N = \frac{[\text{M(NH}_3)_N^{x+}]}{[\text{M}^{x+}][\text{NH}_3]^N} = \prod_{i=1}^{N} K_i
\end{align*}
\]

where \( \beta_n \) is the overall stability constant for the \( n \)th complexation reaction. The stepwise and overall stability constants may be determined experimentally or
thermodynamically, the latter as a function of Gibbs free energy of reaction.

The concentrations of metal ammine, metal ion and uncomplexed aqueous ammonia are all influenced collectively by the values of the equilibrium constants, total metal concentration and total aqueous ammonia concentration. If the latter two concentrations are known, then simultaneous solution of mass balances on the metal and ammonia allow for the calculation of metal ion and uncomplexed aqueous ammonia concentrations, respectively:

\[
[M]_T = [M^{i+}] \left(1 + \sum_{i=1}^{N} \beta_i [NH_3]^i\right)
\]

\[
[NH_3]_T = [NH_3] + [M^{i+}] \sum_{i=1}^{N} i \beta_i [NH_3]^i
\]

where the subscript ‘T’ refers to total concentration. Upon calculation of the latter terms, the concentrations of metal ammines may be determined via their equilibrium relationships:

\[
[M(NH_3)^{n+}] = K_n [M(NH_3)^{n+}] [NH_3]^n = \beta_n [M^{n+}] [NH_3]^n
\]

In the Sherritt-Gordon process, each value metal forms ammine complexes. The maximum coordination numbers for nickel(II), copper(II), copper(I) and cobalt(III) ammines are six, five, two and six, respectively [4]. With the exception of nickel(II), each value metal ion has been discussed thus far in this chapter to form only a single metal ammine. According to appropriate Eh-pH diagrams for the Cu-NH_3-H_2O and Co-NH_3-H_2O systems [123-125], tetraamminecopper(II) \((n = 4)\), diamminecopper(I) \((n = N = 2)\) and hexaamminecobalt(III) \((n = N = 6)\) are the most stable ammines under conditions in the Sherritt-Gordon ammonia leach, and are thus the dominant species for each metal ion. According to appropriate Eh-pH diagrams for the Ni-NH_3-H_2O system [123-125], however, nickel(II) is capable of forming several stable ammine complexes, the speciation of which depends on the relative concentrations of nickel and free ammonia. Therefore, only the stepwise formation of nickel(II) ammines requires consideration in this work in determining the concentrations of said species. The
concentrations of tetraamminecopper(II), diamminecopper(I) and hexaamminecobalt(III) may be taken as the concentrations of copper(II), copper(I) and cobalt(III), respectively, since the concentrations of cupric ion, cuprous ion and cobaltic ion are all negligibly small.

The total concentrations of nickel and ammonia in a continuous reactor may be determined via mass balances, through appropriate use of the stoichiometry and kinetics put forward in this chapter. Thus, in a manner similar to that outlined above generically, the concentrations of all six nickel ammine complexes may be calculated. Alternatively, the rate of net generation of the ammine complexes may also be described mathematically via suitable mass balances on each. In the latter case, the notion of metal ammine formation kinetics is not to be confused with equilibrium kinetics, which is assumed here as being instantaneous.

4.4 Summary

A chemical reaction system that is suitable for robust mathematical modelling of the leaching process at the Kwinana nickel refinery has been proposed. It was established that the chemistry of the Sherritt-Gordon ammonia leach is considerably more complicated than both that put forward by the foundation researchers and that assumed to be taking place by other researchers and practitioners. It was demonstrated that the long-held view that dissolved oxygen is directly responsible for mineral oxidation in the process is probably not the case. The more likely scenario is that copper is acting as a redox catalyst, whereby copper(II) is a surrogate oxidant. This latter mechanism, involving the copper(II)/copper(I) redox couple, formed the basis for all subsequent submissions of process chemistry.

Six chemical reaction groups were identified for the Sherritt-Gordon ammonia leach. For each group, reaction stoichiometry and kinetics that represent all principal species in the system were composed via the survey of literature studies and observation of plant behaviour. A host of reaction rate law parameters remain unknown, and thus some form of estimation is required before the applicable chemistry may be utilised in a process model.
Three developments are worthy of specific mention: (1) the establishment of two distinct kinetic frameworks in the system – leaching in the presence of copper(I) or dissolved oxygen – was exposed, which influences almost every aspect of the system kinetics; (2) metal dissolution rate laws for mineral leaching in copper-catalysed ammoniacal systems were developed theoretically on the basis of an electrochemical mechanism using mixed potential theory, the forms of which are supported via relevant literature studies; and (3) the conversion of sulphide sulphur to sulphate and sulphanate was shown to take place in a considerably more convoluted manner compared to that thought originally, in which the actual oxidant in ammoniacal systems may play a vital role in determining the mechanism and decomposition pathway of intermediately-oxidised sulphur oxyanions.

In Chapter 6, the reaction stoichiometry and kinetics described in this chapter is used as a basis for the development of a mathematical model of the Sherritt-Gordon ammonia leach. In the next chapter, however, a new method for modelling continuous leaching reactors at steady-state is presented, which also sees application in the work presented in Chapter 6.
Chapter 5


5.1 Introduction

This chapter digresses from the main theme of the thesis. However, its content is linked intimately with the development of the process model of the leaching process at the Kwinana nickel refinery, to be discussed in the next chapter.

The mathematical modelling of continuous leaching reactors was given attention in Chapter 2. At present, the process is a rather daunting task. Specifically, it is the mathematics of describing leaching kinetics in both single-stage and multistage systems that represents the source of the challenge. In this chapter, a new approach is discussed. This method offers considerable simplicity over the existing method of best practice and may be used without sacrificing any accuracy. Furthermore, the method may be extended to describe particle mixing, which is the basis for modelling generic reactor networks. These novel developments have the potential to alter industry practises on the use of kinetics in leaching process design and analysis.
5.2 A New Method for Calculating Leaching Reactor Mineral Conversion

5.2.1 Background and Motivation

As discussed in Chapter 2, leaching kinetics in continuous reactors is established via the calculation of either mineral conversion or mineral surface area. The calculation of either variable in a steady-state CSTR may be carried out using the segregated flow model or the (steady-state) population balance model. The former and latter models are customarily solved for conversion and surface area, respectively, while said variables may be related via equation 2.35. For the typical case in which the well-mixed assumption applies (i.e. the solids residence time distribution (RTD) is taken to be that for an ideal CSTR), the two models are mathematically indistinguishable. (There does not seem to be a proof for this in the literature, and so one is given in Appendix B.) The ideal RTD is employed in seemingly all relevant leach modelling studies discussed in the literature (see Chapter 2), and its application is emulated in this work. As such, either of the preceding models may be used with equal effect in determining reaction kinetics for mineral leaching reactions.

The segregated flow model for a single reactor allows for the scale-up of batch, single-particle kinetics to continuous, multiparticle kinetics as a function of the solids RTD in the reactor, \( E(t) \), and the mass-weighted particle size distribution (PSD) in the reactor feed, \( f_{m,in}(D_0) \), both of which are probability density functions. The central equation (equation 2.33) permits the calculation of mineral fraction unreacted [30, 32]:

\[
1 - X = \int_0^{t_{max}} \int_{D_0(X^* = 1)}^{D_{0,max}} (1 - X^*) f_{m,in}(D_0) \, dD_0 \, E(t) \, dt
\]

(5.1)

where \( D_0 \) is the initial/feed particle size, \( t \) is the particle residence time, \( D_{0,max} \) is the maximum particle size and \( D_0(X^* = 1) \) represents the vanishing feed particle size (i.e. the feed size of those particles that react completely after taking up residence in the reactor for time \( t \)). The use of the latter variable accounts explicitly for the fact that
$1 - X^*$ must remain greater than or equal to zero for all feed sizes and residence times. $X^* = X^*(D_0, t)$ is the single-particle conversion in a batch reactor, the form of which is related to the corresponding mineral oxidation rate law (i.e. the rate-limiting mechanism).

Chemical reaction-controlled (linear leaching) kinetics represents the most commonly observed rate-limiting step. Less common regimes include more complicated mechanisms, such as mass transport- or product layer diffusion-controlled (parabolic leaching) kinetics, the single-particle kinetics of which are dependent on particle size. A mixed-controlled mechanism may also be established if two or more of the preceding three processes take place at comparable rates. It is typically the case, however, that the complexity of modelling the more complicated leaching situations outweighs its usefulness, given the assumptions that have to be made. It is generally accepted that the chemical reaction-controlled model may be used as a good first approximation for describing the more complicated kinetics, and thus it has wide applicability.

For the chemical reaction-controlled model, particle fraction unreacted in a batch reactor is given by (equation 2.27) [32]

$$1 - X^* = \left(1 + \frac{\dot{D}}{D_0} t\right)^3 \tag{5.2}$$

where $\dot{D} = dD/dt$ is the particle shrinkage rate (equation 2.41; where $r = k(T) f(C)$)

$$-\dot{D} = \frac{D_0}{\tau} = \frac{2bM}{\rho} r \tag{5.3}$$

and $\tau = \tau(D_0)$ (equation 2.28) is the time required to completely leach a particle of original size $D_0$, such that when $t = \tau$, $X^* = 1$. $b$ is the stoichiometric coefficient of the mineral (e.g. see reaction 2.25), $M$ and $\rho$ are the molecular weight and mass density of the mineral, respectively, while $r$ is the rate of reaction. Given that leaching particles are assumed to be spherical in shape (according to the shrinking core model), it follows that $1 - X^* = D^3/D_0^3$ (equation 2.26), where $D$ is the particle size at time $t$. A
linear relationship between $D$, $D_0$ and $t$ may thus be established by combining equations 2.26 and 5.2: $D = D_0 + \dot{D} t$, and thus $dD = \dot{D} \, dt$.

$1 - X^*$ is only permitted to take on values between zero and one (inclusive). It follows therefore that $-\dot{D} t \leq D_0 \leq D_{0,\text{max}}$ and $0 \leq t \leq -D_{0,\text{max}} / \dot{D}$. The lower limit for $D_0$ represents the vanishing feed particle size, i.e. $D_0(X^* = 1) = -\dot{D} t$, while the upper limit for $t$ represents the maximum residence time, i.e. $t_{\text{max}} = -D_{0,\text{max}} / \dot{D}$. $D_{0,\text{max}}$ is dictated by the type of mathematical function employed to represent $f_{m,\text{in}}(D_0)$.

The solids RTD function is invariably given by that for an ideal CSTR [30, 32]:

$$E(t) = \frac{1}{\bar{t}} \exp \left( -\frac{t}{\bar{t}} \right)$$  \hspace{1cm} (5.4)

where $\bar{t} = V / Q$ is the reactor mean residence time. The use of the above equation may be justified by the fact that the agitation in leaching reactors (like in most slurry reactors) is sufficiently vigorous to maintain a uniform suspension, and so the flow of particles would closely approximate those in an ideal reactor. The above equation is equivalent to equation 2.31 for the special case in which $N = 1$.

The feed PSD can be described with a number of mathematical distribution functions. In Appendix D, an analysis of size distribution data for the Kwinana nickel refinery leach feed is given. The main purpose of the appendix is to support discussions in Chapter 6, however, attention here is drawn to Table D.2, which exhibits a host of commonly employed distribution functions. In said appendix, the Gaudin-Meloy, Gates-Gaudin-Schuhmann, Rosin-Rammler, log-normal and gamma distributions (all of which are commonly cited in the leach modelling literature) are fitted to discrete size data. The Gaudin-Meloy, Rosin-Rammler and gamma distributions all demonstrate a very good fit.

The Rosin-Rammler distribution (also referred to as the Weibull distribution) is typically the best for describing the size distribution of particles produced from grinding, milling and crushing operations (i.e. those of interest to leaching systems),
given its tendency to better-represent highly-skewed distributions [179]. This has been demonstrated both empirically (by Rosin and Rammler [41] and many others) and theoretically (based on physical principles [180]). That said, the gamma distribution is equally as adept. The analysis in Appendix D demonstrates that the Rosin-Rammler and gamma distributions offer almost identical fits to the discrete size data (see Figure D.1). Moreover, it is shown in Figure 5.1 (using the equations listed in Table D.2) that the two distributions exhibit analogous behaviour for a wide range of mean ($\mu$) and variance ($\sigma^2$) values, facilitated with the coefficient of variation ($C_v = \sigma / \mu$). The validity of this exercise may be extended to practically any mean and variance combination. This correspondence is due to their mathematical resemblance, which follows from the fact that each is a special case of the well-known generalised gamma distribution; when $C_v = 1$, the two distributions take on the same mathematical form, namely that of the exponential distribution. Ultimately, the similarities between the Rosin-Rammler and gamma distributions are sufficient to certify that the application of either in leaching reactor modelling will generate comparable results.

The use of the gamma distribution to describe the mass-weighted PSD in the reactor feed may be done with the following expression:

$$f_{m,in}(D_0) = \left(\frac{D^*}{\Gamma(\varphi)}\right)^{\varphi} D_0^{-\varphi} \exp\left(-\frac{D_0}{D^*}\right)$$  \hspace{1cm} \text{(5.5)}

where $\varphi = \mu_{m,in}^2 / \sigma_{m,in}^2$ is the shape parameter, $D^* = \sigma_{m,in}^2 / \mu_{m,in}$ is the scale parameter (and index of dispersion of the feed PSD), $\mu_{m,in}$ and $\sigma_{m,in}^2$ are the mean and variance of the feed mass-weighted PSD, respectively, and $\Gamma(\varphi)$ is the gamma function:

$$\Gamma(\varphi) = \int_0^\infty x^{\varphi-1} e^{-x} \, dx$$  \hspace{1cm} \text{(5.6)}

Given the application of equation 5.5, it follows that $D_{0,\text{max}} \to \infty$ and $t_{\text{max}} (=-D_{0,\text{max}} / \dot{D}) \to \infty$ in equation 5.1.
Figure 5.1: A comparison of the Rosin-Rammler and gamma distributions for various combinations of mean (\( \mu \)) and variance (\( \sigma^2 = (C_v \mu)^2 \)) (1: mean = 25 \( \mu m \); 2: mean = 50 \( \mu m \); 3: mean = 75 \( \mu m \); 4: mean = 100 \( \mu m \))
According to the literature, the segregated flow model and (steady-state) population balance model have only ever been solved numerically for leaching reactors. For the modelling studies discussed in Chapter 2 (Section 2.3.4), methods for solving the integral equations have included Newton-Cotes closed formulae (such as the trapezoidal rule and Simpson’s rule) and Gaussian quadrature (specifically, Gauss-Laguerre quadrature). The solution method also has an impact on the way in which the PSD in the reactor discharge, \( f_m(D) \), is reconstructed. Accordingly, an appropriate numerical reconstruction is necessary, given that it becomes the feed PSD for the next reactor in the series. Seemingly, no attention in the literature has been given as to why the two models required a numerical solution. One is given here.

Assuming that \( E(t) \) is given by equation 5.4, the attempted analytical solution of equation 5.1 will ultimately require the modeller to solve a gamma function of the form \( \Gamma(\varphi + n) \), where \( \varphi \) is the PSD shape factor and \( n \) is some integer. This eventuality is irrespective of the mathematical function chosen to represent \( f_{m,in}(D_0) \); this is true for all of the distributions considered in Appendix D, and is thus most likely the general case. As is well-known, the gamma function has no analytical solution, only a numerical one. So, for all mathematical distribution functions except one, quadrature is unavoidable, and thus in those situations it is less problematic to solve equation 5.1 in its given form. The exception is the gamma distribution.

The gamma distribution contains in its denominator the gamma function. Concerning the latter, it may be shown that \( \Gamma(\varphi + n) \propto \Gamma(\varphi) \), where the coefficient of proportionality is some function of \( \varphi \). Therefore, when attempting to solve a modified version of equation 5.1 analytically using the gamma distribution, substitution of the preceding expression for all \( \Gamma(\varphi + n) \) in the numerator will cancel out \( \Gamma(\varphi) \) in the denominator. The result is an algebraic expression for \( X \).

The fact that equation 5.1 has an analytical solution has major implications for how continuous leaching reactors are modelled. This application may be extended to the manner in which particle size distribution in the reactor discharge is reconstructed, and
to how particle mixing can be managed in order to describe generic reactor networks. The central motivation for this new direction for leach process modelling is simplicity without sacrificing accuracy. This will become evident as the chapter proceeds.

The means to solve the segregated flow model and (steady-state) population balance model analytically has been at hand throughout the complete history of leaching reactor modelling. The ability of the gamma distribution to facilitate such an opportunity has seemingly gone unnoticed.

In the next subsection, the algebraic expression for $X$ is derived via the analytical solution of the segregated flow model. It is more straightforward to use said model than the (steady-state) population balance model for this purpose, although either would generate the same result.

### 5.2.2 Derivation of Reactor Mineral Conversion

Mineral conversion, $X$, in a steady-state continuous leaching reactor may be calculated via the segregated flow model (equation 5.1):

$$1 - X = \frac{t_{\text{exp}}}{\tau_{\text{exp}}} \int_{0}^{D_{0} \min} \int_{D_{0}(1 - X^{*})}^{D_{0}} (1 - X^{*}) f_{m,\text{in}}(D_{0}) \ dD_{0} \ E(t) \ dt \quad (5.7)$$

where $1 - X^{*}$, $E(t)$ and $f_{m,\text{in}}(D_{0})$ are given by equations 5.2, 5.4 and 5.5, respectively:

$$1 - X^{*} = \left(1 + \frac{D}{D_{0}} \cdot t \right)^{3} \quad (5.8)$$

$$E(t) = \frac{1}{t} \exp \left( - \frac{t}{\tau} \right) \quad (5.9)$$

$$f_{m,\text{in}}(D_{0}) = \frac{(D_{0}^{*})^{-\varphi}}{\Gamma(\varphi)} D_{0}^{\varphi-1} \exp \left( - \frac{D_{0}}{D_{0}^{*}} \right) \quad (5.10)$$

The substitution of each of the above expressions into equation 5.7 is performed in a step-by-step fashion.

The substitution of equation 5.8 yields the following:
\[ 1 - X = \int_0^{D_{i,\text{max}} / D} \int_{-\dot{D}t}^{D_{i,\text{max}}} D_0^{-3} (D_0 + \dot{D}t)^3 f_{m,in}(D_0) \, dD_0 \, E(t) \, dt \]  

(5.11)

In its present form, the above equation cannot be solved analytically. An interchange of the order of integration must first be carried out:

\[ 1 - X = \int_0^{D_{i,\text{max}} / D} \int_0^{D_{i,\text{max}}} D_0^{-3} (D_0 + \dot{D}t)^3 E(t) \, dt \, f_{m,in}(D_0) \, dD_0 \]  

(5.12)

While the above equation may now be solved analytically, it is less tedious to do so by integrating over \( D \) rather than \( t \) in the inner integral. A change of variables is thus required. The relationship between \( D, D_0 \) and \( t \) is given by \( D = D_0 + \dot{D}t \) and \( dD = \dot{D} \, dt \) (as discussed in the previous subsection). Substitution of the latter expressions into the above equation gives

\[ 1 - X = -\frac{1}{D} \int_0^{D_{i,\text{max}}} \int_0^{D_{i,\text{max}}} D_0^{-3} D^3 E \left( \frac{D - D_0}{D} \right) \, dD \, f_{m,in}(D_0) \, dD_0 \]  

(5.13)

The substitution of equation 5.9 into the above expression yields the following:

\[ 1 - X = -\frac{1}{\dot{D}t} \int_0^{D_{i,\text{max}}} \int_0^{D_{i,\text{max}}} D_0^{-3} D^3 \exp \left( \frac{D_0 - D}{\dot{D}t} \right) \, dD \, f_{m,in}(D_0) \, dD_0 \]

\[ = -\frac{1}{\dot{D}t} \int_0^{D_{i,\text{max}}} D_0^{-3} \exp \left( \frac{D_0}{\dot{D}t} \right) \int_0^{D_{i,\text{max}}} D^3 \exp \left( -\frac{D}{\dot{D}t} \right) \, dD \, f_{m,in}(D_0) \, dD_0 \]  

(5.14)

The inner integral can now be solved. Using integration by parts, it may be shown that

\[ \int_0^{D_{i}} D^n \exp \left( -\frac{D}{\dot{D}t} \right) \, dD = -\dot{D}t \left[ D^n \exp \left( -\frac{D}{\dot{D}t} \right) \right]_0^{D_{i}} - n \int_0^{D_{i}} D^{n-1} \exp \left( -\frac{D}{\dot{D}t} \right) \, dD \]  

(5.15)

By writing the above equation for \( n = 1, 2 \) and \( 3 \), and combining the expressions appropriately, the inner integral in equation 5.14 can be evaluated:
\[
\int_0^{D_0} D^3 \exp \left( -\frac{D}{\hat{D} t} \right) dD = \\
\quad -\hat{D} t \left[ D_0^3 + 3 (\hat{D} t) D_0^2 + 6 (\hat{D} t)^2 D_0 + 6 (\hat{D} t)^3 \right] \exp \left( -\frac{D_0}{\hat{D} t} \right) - 6 (\hat{D} t)^3 \right] 
\]

(5.16)

Equation 5.14 may now be recast as

\[
1 - X = \\
\int_0^{D_{0\text{max}}} \left[ 1 + 3 (\hat{D} t) D_0^{-1} + 6 (\hat{D} t)^2 D_0^{-2} + 6 (\hat{D} t)^3 D_0^{-3} - 6 (\hat{D} t)^3 D_0^{-3} \exp \left( \frac{D_0}{\hat{D} t} \right) \right] \\
\times f_{m,m}(D_0) dD_0 
\]

(5.17)

Incidentally, the above equation can be solved numerically with any mathematical distribution function, the task of which now only involves a single integral equation.

The substitution of equation 5.10 into the above statement yields the following:

\[
1 - X = \\
\frac{(D^*)^{-\varphi}}{\Gamma(\varphi)} \left[ \int_0^{\infty} \left( D_0^{\varphi-1} + 3 (\hat{D} t) D_0^{\varphi-2} + 6 (\hat{D} t)^2 D_0^{\varphi-3} + 6 (\hat{D} t)^3 D_0^{\varphi-4} \right) \exp \left( -\frac{D_0}{D^*} \right) \\
- 6 (\hat{D} t)^3 D_0^{\varphi-4} \exp \left( -\frac{D_0}{D^*} \left( 1 - \frac{D^*}{\hat{D} t} \right) \right) dD_0 \right] 
\]

(5.18)

Four steps are required to transform the above equation into its analytical form. In the first step, algebraic expansion is carried out on the expression inside the square brackets, describing the sum of five integral terms:

\[
1 - X = \\
\frac{(D^*)^{-\varphi}}{\Gamma(\varphi)} \left[ \int_0^{\infty} D_0^{\varphi-1} \exp \left( -\frac{D_0}{D^*} \right) dD_0 + 3 (\hat{D} t) \int_0^{\infty} D_0^{\varphi-2} \exp \left( -\frac{D_0}{D^*} \right) dD_0 \\
+ 6 (\hat{D} t)^2 \int_0^{\infty} D_0^{\varphi-3} \exp \left( -\frac{D_0}{D^*} \right) dD_0 + 6 (\hat{D} t)^3 \int_0^{\infty} D_0^{\varphi-4} \exp \left( -\frac{D_0}{D^*} \right) dD_0 \\
- 6 (\hat{D} t)^3 \int_0^{\infty} D_0^{\varphi-4} \exp \left( -\frac{D_0}{D^*} \left( 1 - \frac{D^*}{\hat{D} t} \right) \right) dD_0 \right] 
\]

(5.19)

In the second step, a change of variables is performed, initially letting \( \xi_0 = D_0 / D^* \) for
all terms and subsequently letting \( \bar{\xi}_0 = (1 - D^t (\dot{\bar{D}}t)) \xi_0 \) only for the last term:

\[
1 - X = \frac{1}{\Gamma(\phi)} \left[ \int_0^\infty \xi_0^{\phi-1} \exp \left( -\xi_0 \right) d\xi_0 + 3 \left( \frac{\dot{D}t}{D^t} \right) \int_0^\infty \xi_0^{\phi-2} \exp \left( -\xi_0 \right) d\xi_0 \right.
\]
\[
+ 6 \left( \frac{\dot{D}t}{D^t} \right)^2 \int_0^\infty \xi_0^{\phi-3} \exp \left( -\xi_0 \right) d\xi_0 + 6 \left( \frac{\dot{D}t}{D^t} \right)^3 \int_0^\infty \xi_0^{\phi-4} \exp \left( -\xi_0 \right) d\xi_0
\]
\[
- 6 \left( \frac{\dot{D}t}{D^t} \right)^3 \left( 1 - \frac{D^*}{\dot{D}t} \right)^{3-\phi} \int_0^\infty \xi_0^{\phi-4} \exp \left( -\xi_0 \right) d\xi_0 \right]
\]

(5.20)

It is apparent that each integral component is a gamma function (equation 5.6) of the form \( \Gamma(\phi+n) \), where \( n \) is some integer. In the third step, each term is evaluated as such, the resultant expression is expanded algebraically, and subsequent factorisation is suitably carried out:

\[
1 - X = 1 + 3 \left( \frac{\dot{D}t}{D^t} \right) \Gamma(\phi-1) + 6 \left( \frac{\dot{D}t}{D^t} \right)^2 \frac{\Gamma(\phi-2)}{\Gamma(\phi)} + 6 \left( \frac{\dot{D}t}{D^t} \right)^3 \left[ 1 - \left( 1 - \frac{D^*}{\dot{D}t} \right)^{3-\phi} \right] \frac{\Gamma(\phi-3)}{\Gamma(\phi)}
\]

(5.21)

The following well-known association may be written concerning the gamma function:

\[
\Gamma(\phi+1) = \phi \Gamma(\phi) .
\]

By extending the latter for the general case, it may be shown that

\[
\frac{\Gamma(\phi+n)}{\Gamma(\phi)} = \begin{cases} 
\prod_{i=1}^{n} (\phi + i - 1), & n > 0 \\
\prod_{i=1}^{-n} (\phi - i)^{-1}, & \phi \neq i, \quad n < 0
\end{cases}
\]

(5.22)

In the fourth and final step, the above equation is written for \( n = -1, -2 \) and \( -3 \), and the expressions are substituted into equation 5.21, thus eliminating all gamma function terms:

\[
1 - X = 1 + 3 \left( \frac{\dot{D}t}{D^t} \right) (\phi-1)^{-1} + 6 \left( \frac{\dot{D}t}{D^t} \right)^2 (\phi-1)^{-1} (\phi-2)^{-1}
\]
\[
+ 6 \left( \frac{\dot{D}t}{D^t} \right)^3 \left[ 1 - \left( 1 - \frac{D^*}{\dot{D}t} \right)^{3-\phi} \right] (\phi-1)^{-1} (\phi-2)^{-1} (\phi-3)^{-1}, \quad \phi \notin \{1, 2, 3\}
\]

(5.23)
The above equation may be tidied up by factorising all \((\varphi + n)^{-1}\), introducing dimensionless variable \(\kappa\) and rearranging to solve for \(X\), thus allowing the explicit calculation of mineral conversion:

\[
X = 3\kappa (\varphi - 1)^{-1} (1 - 2\kappa (\varphi - 2)^{-1} (1 - \kappa (\varphi - 3)^{-1} (1 - (1 - \kappa^{-1})^{3+\phi})))) \quad \varphi \notin \{1, 2, 3\}
\]  

where \(\kappa = \frac{-\bar{D}t}{D^*}\) is the ratio of reactor mean residence time to the time it takes to completely leach a single particle of initial size \(D^*\) under the prevailing conditions.

Equation 5.24 is the analytical solution of equation 5.1 and is a novel mathematical expression, communicated here for the first time. It specifically describes conversion for minerals that leach under chemical reaction-controlled kinetics, and so is directly applicable in the vast majority of leaching situations. Furthermore, given that the chemical reaction-controlled model may be used as a good first approximation for describing the more complicated kinetics (as discussed previously), equation 5.24 has wide-reaching applications beyond those pertinent to the constraints of this derivation.

5.3 A New Method for Reconstructing Leaching Reactor Discharge Particle Size Distribution

5.3.1 Background and Motivation

The calculation of mineral conversion or surface area by way of the segregated flow model or (steady-state) population balance model makes use of the size distribution of particles in the reactor feed. The nature of the distribution is a reflection of the way in which the latter models are solved. Prior to this work, distributions were numerical in nature. If a complete discrete distribution is available for the leach process feed, an appropriate continuous distribution function would be fitted to it (as discussed in Appendix D), and would subsequently be re-discretised in a manner consistent with the numerical method used to solve the segregated flow model or (steady-state) population balance model so that it may be used to describe the first reactor in the process. The numerical reconstruction of the PSD for partially-reacted solids in the reactor discharge...
would then be necessary for use in the subsequent reactor in series, and so on; equation 2.34 may be used for this purpose when chemical reaction-controlled kinetics prevails.

In the present work, numerical distributions are unnecessary. It is apparent from equation 5.24 (via the variables used in equation 5.5) that only the mean and variance of the mass-weighted PSD in the reactor feed is necessary to calculate mineral conversion. In other words, the complete description of particle size distribution is no longer necessary, only its mean and variance. The former and latter variables are already available for the leach process feed. However, a method is required for determining the mean and variance of the reactor discharge PSD.

In the next subsection, algebraic expressions for the mean and variance of the reactor discharge particle size distribution are derived using the (steady-state) population balance model. Unlike the case for deriving mineral conversion (Section 5.2.2), it is more straightforward to use the population balance model than the segregated flow model for this purpose. But, like before, either model would produce the same result.

### 5.3.2 Derivation of Reactor Discharge PSD Mean and Variance

The population balance model (equation 2.40) describes the continuity of particle number, and its steady-state macroscopic form is given as follows to describe leaching in a continuous reactor [58]:

\[
0 = Q_{\text{in}} \psi_{\text{in}} - Q \psi - V \frac{\partial}{\partial D} (D \dot{\psi}) , \quad \psi|_{D=D_{\text{max}}} = 0 \tag{5.25}
\]

where \( \psi = \psi(D) \) is the population density function and \( D_{\text{max}} = D_{0,\text{max}} \) (since it is possible for the largest particle in the feed to short-circuit the reactor). The \( i \)th moment of \( \psi \) is defined as

\[
\mu_p^{(i)} = \int_0^{D_{\text{max}}} D^i \psi(D) \, dD \tag{5.26}
\]

By multiplying each term in equation 5.25 by \( D^i \, dD \) and integrating from zero to \( D_{\text{max}} \), one obtains
\[ 0 = Q_{in} \int_0^{D_{max}} D' \psi_{in} \, dD - Q \int_0^{D_{max}} D' \psi \, dD - V \int_0^{D_{max}} \frac{\partial}{\partial D} (\dot{D} \psi) \, dD \tag{5.27} \]

The first and second right-hand side integrals may be evaluated directly via equation 5.26:

\[ \mu_p^{(i)} = \int_0^{D_{max}} D' \psi_{in} \, dD \tag{5.28} \]

\[ \mu_p^{(i)} = \int_0^{D_{max}} D' \psi \, dD \tag{5.29} \]

The third right-hand side integral may be determined via integration by parts:

\[ \int_0^{D_{max}} D' \frac{\partial}{\partial D} (\dot{D} \psi) \, dD = D' \dot{D} \psi \bigg|_0^{D_{max}} - i \int_0^{D_{max}} D^{i+1} \dot{D} \psi \, dD \tag{5.30a} \]

\[ = D' \dot{D} \psi \bigg|_0^{D_{max}} - i \dot{D} \mu_p^{(i-1)} \tag{5.30b} \]

where the second right-hand side term in equation 5.30b can be written as such given that \( \dot{D} \) is not a function of particle size when chemical reaction-controlled kinetics prevail.

Substitution of equations 5.28, 5.29 and 5.30b into equation 5.27 gives the \( i \)th moment equation of the population density function when chemical reaction-controlled kinetics prevail:

\[ 0 = Q_{in} \mu_p^{(i)} - Q \mu_p^{(i)} - V D' \dot{D} \psi \bigg|_0^{D_{max}} + V i \dot{D} \mu_p^{(i-1)}, \quad i \geq 0 \tag{5.31} \]

The moments of the population density function are related to the moments of the corresponding mass-weighted PSD. The mean and variance of a mass-weighted PSD are related to its first and second raw moments. The task here is thus to transform the above equation into one that describes the \( i \)th moment of the mass-weighted PSD, so that the mean and variance may be evaluated.

A new particle size distribution function requires definition. In a manner analogous to \( f_m(D) \) (see discussion in Chapter 2; Section 2.3.3), let \( f_n(D) \) represent
the number-weighted probability density function for a particle assembly such that

\[ \int_{D_{\text{min}}}^{D_{\text{max}}} f_n(D) \, dD = 1 \quad (5.32) \]

where \([D_{\text{min}}, D_{\text{max}}]\) is the range of particle sizes and \(f_n(D) \, dD\) is the number fraction of particles that have a size between \(D\) and \(D + dD\). The population density function has a direct relationship with the number-weighted PSD:

\[ \psi(D) \, dD = \bar{n} f_n(D) \, dD \quad (5.33) \]

where \(\bar{n}\) is the total number of particles per unit volume:

\[ \bar{n} = \int_{0}^{D_{\text{max}}} \psi(D) \, dD \quad (5.34) \]

Each side of equation 5.33 thus describes the total number of particles per unit volume with a size between \(D\) and \(D + dD\).

The mass-weighted PSD is also directly related to the number-weighted PSD:

\[ \bar{m} f_m(D) \, dD = \frac{\rho \pi}{6} D^3 \bar{n} f_n(D) \, dD \quad (5.35) \]

where \(\rho \pi D^3 / 6\) is the mass of a single spherical particle of size \(D\) and \(\bar{m}\) is the total mass of particles per unit volume, which via integration of the above equation is given by

\[ \bar{m} = \frac{D \pi}{6} \bar{n} \int_{0}^{D_{\text{max}}} D^3 f_m(D) \, dD \quad (5.36) \]

Each side of equation 5.35 thus describes the total mass of particles per unit volume with a size between \(D\) and \(D + dD\). Incidentally, through suitable integration of equation 5.35, \(\bar{n}\) also takes on the following form:

\[ \bar{n} = \frac{6}{\rho \pi} \bar{m} \int_{0}^{D_{\text{max}}} D^{-3} f_m(D) \, dD \quad (5.37) \]

The independent substitution of equations 5.36 and 5.37 into equation 5.35, and
cancellation of relevant differentials \( dD \), allows for the direct determination of \( f_m(D) \) from \( f_n(D) \), respectively:

\[
 f_m(D) = \frac{D^3 f_n(D)}{\pi \rho \sigma_m} \int_0^{D_{\text{max}}} D^3 f_n(D) dD \tag{5.38}
\]

\[
 f_n(D) = \frac{D^{-3} f_m(D)}{\pi \rho \sigma_n} \int_0^{D_{\text{max}}} D^{-3} f_m(D) dD \tag{5.39}
\]

The above two equations are not pertinent for deriving reactor discharge PSD mean and variance, but represent relationships that are fundamental to working with particle size distributions (e.g. see [58]), and have thus been included as a matter of completeness.

It may be observed that the term \( \overline{n} f_n(D) dD \) shares commonality with equations 5.33 and 5.35. By combining the latter appropriately and cancelling the differential \( dD \), a relationship between \( \psi(D) \) and \( f_m(D) \) may thus be written:

\[
 \psi(D) = \frac{6 \overline{m}}{\rho \pi} D^{-3} f_m(D) \tag{5.40}
\]

The above equation can also be derived by combining equations 5.34 and 5.37.

By multiplying each term in equation 5.40 by \( D^i dD \) and integrating from zero to \( D_{\text{max}} \) one obtains

\[
 \int_0^{D_{\text{max}}} D^i \psi(D) dD = \frac{6 \overline{m}}{\rho \pi} \int_0^{D_{\text{max}}} D^{i-3} f_m(D) dD \tag{5.41}
\]

Given that the \( i \)th moment of \( f_m(D) \) is defined as

\[
 \mu_m^{(i)} = \int_0^{D_{\text{max}}} D^i f_m(D) dD \tag{5.42}
\]

the substitution of equation 5.26 and the above equation into equation 5.41 yields a relationship between \( \mu_p^{(i)} \) and \( \mu_m^{(i)} \):
\[ \mu^{(i)}_m = \frac{6 \bar{m}}{\rho \pi} \mu^{(i-3)}_m \]  

(5.43)

By substituting the above equation into equation 5.31, one obtains the \( i \)th moment equation of the mass-weighted PSD when chemical reaction-controlled kinetics prevails:

\[ 0 = Q_{in} \bar{m}_m \mu^{(i)}_{m,in} - Q \bar{m} \mu^{(i)}_m - \frac{\rho \pi}{6} V D^{i+3} \psi \left[ \frac{D_{max}}{0} + V \bar{m} (i+3) \dot{D} \mu^{(i-1)}_m \right] \]  

(5.44)

The above equation may be tidied up by substituting \( \dot{D} = \frac{V}{Q} \), realising that \( Q \bar{m} = (1-X) Q_{in} \bar{m}_{in} \), and by recognising that

\[ -\frac{\rho \pi}{6} V D^{i+3} \psi \left[ \frac{D_{max}}{0} \right] = 0 \text{ for } i > -3 \]

Equation 5.44 may thus be recast as

\[ 0 = \mu^{(i)}_{m,in} (1-X)^{-1} - \mu^{(i)}_m + (i+3) \dot{D} \bar{D} \mu^{(i-1)}_m, \quad i > 0 \]  

(5.45)

where \( \mu^{(0)}_m = 1 \), \( X \) is given by equation 5.24 and \( \dot{D} \bar{D} \) is given by equation 5.3.

The mean and variance of \( f_m(D) \) are equivalent to its first raw moment (i.e. moment about zero) and second central moment (i.e. moment about the mean), respectively:

\[ \mu_{m} = \int_{0}^{D_{max}} D f_m(D) \, dD = \mu^{(1)}_m \]  

(5.46)

\[ \sigma_{m}^2 = \int_{0}^{D_{max}} (D - \mu_m)^2 f_m(D) \, dD = \mu^{(2)}_m - \mu_m^2 \]  

(5.47)

By writing equation 5.45 for \( i = 1 \) and 2 one obtains

\[ 0 = \mu^{(1)}_{m,in} (1-X)^{-1} - \mu^{(1)}_m + 4 \dot{D} \bar{D} \]  

(5.48)

\[ 0 = \mu^{(2)}_{m,in} (1-X)^{-1} - \mu^{(2)}_m + 5 \dot{D} \bar{D} \mu^{(1)}_m \]  

(5.49)

Therefore, by combining the above equations with equations 5.46 and 5.47, the reactor
discharge PSD mean and variance may be determined explicitly:

\[
\mu_m = \mu_{m,\text{in}} (1 - X)^{-1} + 4 \hat{D} \bar{t} \\
\sigma^2_m = (\sigma^2_{m,\text{in}} + \mu^2_{m,\text{in}}) (1 - X)^{-1} + (5 \hat{D} \bar{t} - \mu_m) \mu_m
\]

The above equations are novel mathematical expressions, communicated here for the first time. If needed, the cumulative distribution and probability density functions for particle size may be constructed from \( \mu_m \) and \( \sigma^2_m \) by using any mathematical distribution function of choice via the method discussed in Appendix D. The Rosin-Rammler or gamma distributions are the recommended options.

5.4 Applications for Modelling Complex Reactor Networks

According to the literature, no modelling studies have considered leaching processes in which the mixing of multiple slurry streams containing unreacted or partially-reacted solids, or both, is important in describing reactor performance. The modelling work being pursued as part of the broader aims of this thesis is seemingly the first to consider a multiple autoclave leaching process flowsheet. Consequently, a method for describing how particle size distribution is influenced by such particle mixing is required. This is best managed by modelling behaviour at the slurry mixing point itself. The use of mean and variance to represent particle size distribution lends itself aptly to the present cause.

Consider a slurry mixing point that has \( N \) feed streams and one discharge stream. A mass balance can be written for some particulate material:

\[
0 = \sum_{j=1}^{N} Q_{\text{in}(j)} \bar{m}_{\text{in}(j)} - Q \bar{m}
\]

Given that \( \bar{m} f_m(D) \, dD \) represents the total mass of particles per unit volume with a size between \( D \) and \( D + dD \), it follows that

\[
0 = \sum_{j=1}^{N} Q_{\text{in}(j)} \bar{m}_{\text{in}(j)} f_m(D) \, dD - Q \bar{m} f_m(D) \, dD
\]

Cancelling the differential \( dD \) and rearranging, the PSD in the mixing point discharge
may be expressed as a mass-weighted average of those in the feed:

\[ f_m(D) = \sum_{j=1}^{N} x_{m(j)} f_{m,in(j)}(D) \]  

where \( x_{m(j)} = (Q_{in(j)} \bar{m}_{in(j)})/(Q \bar{m}) \) is the mass fraction of total particles in the \( j \)th input stream. To accommodate the new modelling strategy, however, the mean and variance of the PSD is required.

The \( i \)th moment of \( f_m(D) \) is given by equation 5.42. Therefore, by multiplying each side of equation 5.54 by \( D^i \, dD \) and integrating from zero to \( D_{\text{max}} \), an expression for \( \mu_m^{(i)} \) results:

\[ \mu_m^{(i)} = \sum_{j=1}^{N} x_{m(j)} \mu_{m,in(j)}^{(i)} \]  

The mean and variance of \( f_m(D) \) are related to \( \mu_m^{(1)} \) and \( \mu_m^{(2)} \) via equations 5.46 and 5.47, and so the following relationships ensue:

\[ \mu_m = \sum_{j=1}^{N} x_{m(j)} \mu_{m,in(j)} \]  

\[ \sigma_m^2 = \sum_{j=1}^{N} x_{m(j)} (\sigma_{m,in(j)}^2 + \mu_{m,in(j)}^2) - \mu_m^2 \]

If needed, the cumulative distribution and probability density functions for particle size may be constructed from \( \mu_m \) and \( \sigma_m^2 \) in a manner just like that discussed for the leaching reactor.

So, the novel use of mean and variance to describe particle size distribution in leach process models (when chemical reaction-controlled kinetics prevails) extends beyond that employed for quantifying particle kinetics in a series of reactors (i.e. the repetitive use equations 5.24, 5.50 and 5.51). Through the appropriate use of slurry mixing points as described here, one is able to model any series or parallel combination of leaching reactor, or any other unit operation of relevance.
5.5 Summary

A new method was developed for quantifying mineral oxidation kinetics in continuous leaching reactors at steady-state. This approach combines the use of an algebraic expression for calculating mineral conversion with the representation of particle size distribution via its mean and variance. The former is accomplished through the analytical solution of the segregated flow model when (1) chemical reaction-controlled kinetics prevails, (2) the well-mixed assumption is valid and (3) the feed (mass) PSD is described with the gamma distribution. The latter is realised through moment transformation of the steady-state population balance equation, followed by the equivalence of moments of the population density function and mass-weighted PSD. The use of mean and variance to represent size distribution was also utilised to describe particle mixing, which allows for the construction of any complex reactor network.

The collective use of equations 5.24, 5.50, 5.51, 5.56 and 5.57 represents a novel approach for quantifying mineral dissolution kinetics in steady-state continuous leaching processes, offering significant advantages over existing techniques. It is evident that evaluating equation 5.24 for $X$ is much simpler than solving equation 5.1 numerically. Likewise, equations 5.50 and 5.51 are much simpler to solve than equation 2.34 (or equation B.5 written for $\dot{D}$=constant) (i.e. the equation normally used to numerically reconstruct the mass-weighted PSD under comparable circumstances), which has numerical solution complexities comparable to those of equation 5.1. The numerical solutions require knowledge of multivariable calculus, numerical integration and computer programming. If values for $\phi$, $D^*$, $\dot{D}$ and $\bar{t}$ are available for determining reactor conversion and reconstructing reactor discharge particle size distribution, what formerly required programming can now be accomplished with a handheld calculator! And while no prior method for modelling multiple autoclave systems existed, equations 5.56 and 5.57 offer the most straightforward response. Beyond the simplicity of the new equations, the mathematical framework’s capacity to describe a wide range of leaching systems – given that it also serves as a good first approximation to systems with more obscure kinetics – virtually eliminates the need to
consult the literature pertaining to leaching reactor theory (i.e. that presented in Chapter 2), which is extensive, convoluted and largely inapplicable to the majority of situations.

The use of the new method for a single leaching reactor is conceptualised in Figure 5.2, which may be compared with Figures 2.2 and 2.3 for the existing methods. A comparison of the equations used in the existing and new approaches to leaching reactor modelling is shown in Table 5.1.

The use of kinetics in process design and analysis is something that – unlike in the chemical process industry – is rarely adopted by engineers in the hydrometallurgical industry. For the leaching reactor, the cause of this deficiency is most likely due to the complexities of solving equations 5.1 and 2.34 (for the segregated flow model) or equations 2.40 and 2.43 (for the population balance model), as well as the need to consider the associated theory. The new modelling approach discussed in this chapter is considerably easier to apply than the existing method of best practice, may be done without sacrificing any accuracy, and does not require the use of any further information. The development of equations 5.24, 5.50, 5.51, 5.56 and 5.57 is thus significant enough to alter industry practices related to design and analysis.

In the next chapter, the new methods for calculating reactor mineral conversion, reconstructing reactor discharge particle size distribution and describing particle mixing are demonstrated for the multiple autoclave leaching process at the Kwinana nickel refinery.
Table 5.1: A Comparison of the Existing and New Approaches to Continuous Leaching Reactor Modelling at Steady-State

<table>
<thead>
<tr>
<th>Variable</th>
<th>Existing Methods</th>
<th>New Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Feed</td>
<td>$f_{m,in}(D_0)$ or $\psi_{in}(D_0)$, each described via suitable mathematical</td>
<td>$\mu_{m,in}$ and $\sigma^2_{m,in}$</td>
</tr>
<tr>
<td></td>
<td>distribution functions using $\mu_{m,in}$ and $\sigma^2_{m,in}$</td>
<td></td>
</tr>
<tr>
<td>Reactor Information</td>
<td>$\bar{m}<em>{in}$, $Q</em>{in}$, $Q$, $V$ and $\dot{D}$</td>
<td>$\bar{m}<em>{in}$, $Q</em>{in}$, $Q$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V$ and $\dot{D}$</td>
</tr>
<tr>
<td>Conversion</td>
<td>$1 - X = \int_{0}^{t_{\text{max}}} \int_{D_0(X^<em>=1)}^{D_{0,m}} (1 - X^</em>) f_{m,in}(D_0) dD_0 E(t) dt$</td>
<td></td>
</tr>
<tr>
<td>or</td>
<td>or</td>
<td></td>
</tr>
<tr>
<td>Surface Area</td>
<td>$S = \pi V \int_{0}^{D_{0,m}} D^2 \psi dD$, where $0 = Q_{in} \psi_{in} - Q \psi - V \frac{\partial}{\partial D} (\dot{D} \psi)$, each solved via suitable numerical integration methods, where $1 - X^*$ and $E(t)$ are functions of $\dot{D}$ and $\tilde{r} = V/Q$</td>
<td></td>
</tr>
<tr>
<td>(Equation 2.43)</td>
<td>$X = 3 \kappa (\varphi - 1)^{-1} (1 - 2 \kappa (\varphi - 2)^{-1} (1 - \kappa (\varphi - 3)^{-1} (1 - (1 - \kappa^{-1})^{3-\varphi})))$, where $\kappa = -\dot{D} \tilde{r} / D^<em>$, $\varphi = \mu_{m,in}^2 / \sigma^2_{m,in}$, $D^</em> = \sigma^2_{m,in} / \mu_{m,in}$ and $\tilde{r} = V/Q$</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.1: A Comparison of the Existing and New Approaches to Continuous Leaching Reactor Modelling at Steady-State (concluded)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Existing Methods</th>
<th>New Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of Reaction Extent (Equation 2.35)</td>
<td>( \varepsilon = b^{-1} F_{in} X ) or ( \varepsilon = r S ), where ( F_{in} = M^{-1} Q_{in} \overline{m}_{in} )</td>
<td>( \varepsilon = b^{-1} F_{in} X ), where ( F_{in} = M^{-1} Q_{in} \overline{m}_{in} )</td>
</tr>
</tbody>
</table>

\[
f_{m}(D) = \frac{D^{3} \int_{D}^{D_{0,\text{max}}} D_{0}^{-3} f_{m,in}(D) \exp \left( \frac{D_{0} - D}{D_{i}} \right) dD_{0}}{\int_{0}^{D} D^{3} \int_{D}^{D_{0,\text{max}}} D_{0}^{-3} f_{m,in}(D) \exp \left( \frac{D_{0} - D}{D_{i}} \right) dD_{0} dD},
\]

solved via a suitable numerical integration method, and is only valid when \( 1 - X^{*} \) and \( E(t) \) are given by equations 5.8 and 5.9, respectively (Equation 2.34)

or

\[
\psi(D) = \frac{Q_{in}}{V} \int_{D}^{D_{0,\text{max}}} \frac{\psi_{m,in}(D) \exp \left( \frac{Q}{V} \int_{D}^{D} \frac{dD'}{D} \right) dD_{0}}{D},
\]

solved via a suitable numerical integration method, and is valid for any rate limiting kinetics (Equation 2.42)

\[
\mu_{m} = \mu_{m,in} \left( 1 - X \right)^{-1} + 4 \dot{D} \bar{t} \]

\[
\sigma_{m}^{2} = (\sigma_{m,in}^{2} + \mu_{m,in}^{2}) \left( 1 - X \right)^{-1} + (5 \dot{D} \bar{t} - \mu_{m}) \mu_{m}
\]
Chapter 6
Mathematical Modelling: Development

6.1 Introduction

The examination of steady-state process operability requires a comprehensive model that allows the simulation of process performance over a wide range of operating conditions. The discussion of such a model spans this chapter and the next.

In the present chapter, onus is placed with the development of model equations. A strategy for model development for multiple autoclave leaching processes is presented. The latter is then considered for the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery, on the basis of process operation discussed in Chapter 3, process chemistry discussed in Chapter 4 and the new method for modelling continuous leaching processes discussed in the previous chapter.

6.2 The Chemical Reaction System

A detailed description of the process chemistry was presented in Chapter 4. The following 28 reactions are considered to represent the chemical reaction system that is established in the leach:

\[ \text{NH}_3(l) \rightarrow \text{NH}_3(a) \] (6.1)
\[
\begin{align*}
\text{NH}_3(a) & \rightarrow \text{NH}_3(g) \quad (6.2) \\
\text{H}_2\text{O}(l) & \rightarrow \text{H}_2\text{O}(g) \quad (6.3) \\
\text{O}_2(g) & \rightarrow \text{O}_2(a) \quad (6.4) \\
\text{O}_2(a) + 4\text{Cu}^+ + 4\text{NH}_4^+ & \rightarrow 4\text{Cu}^{2+} + 4\text{NH}_3(a) + 2\text{H}_2\text{O}(l) \quad (6.5) \\
\text{Ni}^0 + 2\text{Cu}^{2+} & \rightarrow \text{Ni}^{2+} + 2\text{Cu}^+ \quad (6.6) \\
\text{Ni}_3\text{S}_2 + 2\text{Cu}^{2+} & \rightarrow \text{Ni}^{2+} + 2\text{Cu}^+ + 2\text{NiS} \quad (6.7) \\
\text{NiS} + 2\text{Cu}^{2+} & \rightarrow \text{Ni}^{2+} + 2\text{Cu}^+ + S^0 \quad (6.8) \\
\text{Cu}_2\text{S} + \text{Cu}^{2+} & \rightarrow \text{CuS} + 2\text{Cu}^+ \quad (6.9) \\
\text{CuS} + \text{Cu}^{2+} & \rightarrow 2\text{Cu}^+ + S^0 \quad (6.10) \\
\text{CoS} + 3\text{Cu}^{2+} & \rightarrow \text{Co}^{3+} + 3\text{Cu}^+ + S^0 \quad (6.11) \\
\text{Fe}^0 + 2\text{Cu}^{2+} & \rightarrow \text{Fe}^{2+} + 2\text{Cu}^+ \quad (6.12) \\
\text{FeS} + 2\text{Cu}^{2+} & \rightarrow \text{Fe}^{2+} + 2\text{Cu}^+ + S^0 \quad (6.13) \\
2S^0 + 4\text{Cu}^{2+} + 6\text{NH}_3(a) + 3\text{H}_2\text{O}(l) & \rightarrow \text{S}_2\text{O}_3^{2-} + 4\text{Cu}^+ + 6\text{NH}_4^+ \quad (6.14) \\
2\text{S}_2\text{O}_5^{2-} + 2\text{Cu}^{2+} & \rightarrow \text{S}_4\text{O}_6^{2+} + 2\text{Cu}^+ \quad (6.15) \\
3\text{S}_4\text{O}_6^{2+} + 10\text{Cu}^{2+} + 12\text{NH}_3(a) + 6\text{H}_2\text{O}(l) & \rightarrow 4\text{S}_3\text{O}_6^{2-} + 10\text{Cu}^+ + 12\text{NH}_4^+ \quad (6.16) \\
\text{S}_3\text{O}_6^{2-} + 8\text{Cu}^{2+} + 12\text{NH}_3(a) + 6\text{H}_2\text{O}(l) & \rightarrow 3\text{SO}_4^{2-} + 8\text{Cu}^+ + 12\text{NH}_4^+ \quad (6.17) \\
\text{S}_3\text{O}_6^{2-} + 8\text{Cu}^{2+} + 12\text{NH}_3(a) + 3\text{H}_2\text{O}(l) & \rightarrow 3\text{SO}_3\text{NH}_2^+ + 8\text{Cu}^+ + 9\text{NH}_4^+ \quad (6.18) \\
2\text{Fe}^{2+} + 2\text{Cu}^{2+} + 6\text{NH}_3(a) + 4\text{H}_2\text{O}(l) & \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{Cu}^+ + 6\text{NH}_4^+ \quad (6.19) \\
\text{Ni}^{2+} + \text{NH}_3(a) & \rightarrow \text{NiNH}_3^{2+} \quad (6.20) \\
\text{NiNH}_3^{2+} + \text{NH}_3(a) & \rightarrow \text{Ni(NH}_3)_2^{2+} \quad (6.21) \\
\text{Ni(NH}_3)_2^{2+} + \text{NH}_3(a) & \rightarrow \text{Ni(NH}_3)_3^{2+} \quad (6.22)
\end{align*}
\]
The above reactions may not correspond precisely with the stoichiometry discussed in Chapter 4. Such differences include the omission of ammine ligands (equations 6.5–6.19), the absence of polythionate hydrolysis/ammonolysis reactions, and the presence of the anhydrous ammonia dissolution reaction (equation 6.1). The former is adopted for modelling purposes, while the latter two are explained in due course.

Reactions 6.1–6.28 are all considered to take place in the autoclave compartments, while some are also considered to occur in other process units. The governing kinetic rate laws are described appropriately throughout the chapter.

### 6.3 Model Development Strategy

Large-scale, multiple autoclave leaching processes are complex systems, typically comprised of an intricate network of process vessels and streams. The development of flowsheet models for said processes can prove to be an involved task. The best approach to take is one of modularity.

The strategy for flowsheet model development for any given leaching operation should be one of identifying and describing mathematically the behaviour of the essential unit operation and stream types of the process. Once defined, the unit and stream models may be arranged appropriately to represent the process flowsheet. Moreover, given the nature of model development, the same unit and stream models may be used to describe any other (hypothetical) process of interest. With the exception
of those that pertain to anhydrous ammonia, all modular elements of the present process
to be discussed below are relevant to any industrial leaching process.

The objective in this work is the development of a model that may be used to simulate the process examined in Chapter 3 (see Figure 3.1). The process is comprised of the following vessels: autoclaves, tanks, thickeners and trim coolers. Nine essential unit operation types are identified as a basis for representing the process vessels: the leaching reactor (i.e. autoclave compartment), the mixing vessel, the solid-liquid separator, the trim cooler, the mixing point (slurry and gas) and the splitting point (slurry, gas and anhydrous ammonia). Three stream types are identified to unite the process vessels: slurry, gas and anhydrous ammonia. By means of stream models, the transport of mass and energy to and between the unit operations is facilitated. The variables that account for mass and energy flow are best defined in a manner consistent with that stipulated by the mathematics of unit operation modelling, a realisation that will become evident as the chapter proceeds.

The following variables are considered for slurry streams: volumetric flow rate ($Q$), slurry mass density ($\rho$), volumetric fraction of solids ($g$), molar concentration of some solids species $i(s)$ ($C_{i(s)}$), molar concentration of some aqueous species $i(a)$ ($C_{i(a)}$) and temperature ($T$). Two special variables are also required: the mean ($\mu_{i(s')}$) and variance ($\sigma^{2}_{i(s')}$) of the mass-weighted particle size distribution (PSD) for some (sulphide) mineral species $i(s'^{*})$. (Although the latter variables do not contribute directly to the mass accounting, they are necessary for quantifying mineral oxidation kinetics and particle mixing, as demonstrated via the new modelling method established in the previous chapter, which is to be used as a basis for process modelling in this chapter.) The following variables are considered for gas streams: the molar flow rate of some gaseous species $i(g)$ ($F_{i(g)}$) and temperature. Lastly, the following variables are considered for anhydrous ammonia streams: anhydrous ammonia molar flow rate ($F_{\text{NH}_3(l)}$) and temperature. The list of variables for each stream type will henceforth be referred to collectively as the “properties” of that stream, with references as appropriate.
A register of all species considered in this process, as well as pertinent physical and thermodynamic data, is given in Table 6.1. Reference to solids, aqueous and gaseous component species – in terms of number, name or data value – will be done so with respect to the lists in the aforementioned table. Silica (Component 10) is taken to collectively represent all impurities in the feed matte, Component 26 represents uncomplexed aqueous ammonia, while liquid water (Component 34) is treated as an aqueous species when generic references are made.

The following general assumptions are made concerning the development of stream and unit operation models:

- Refinery sensors (for flow, temperature and pressure) that pertain to the leach are calibrated.
- On-site sampling and laboratory analysis is carried out such that measurements (accounting for temperature difference) accurately reflect the state of the process.
- Each mineral in the leach feed has the same particle size distribution (PSD).
- Unit operations are well-mixed.
- Chemical reaction takes place only in unit operations (i.e. not in pipes).
- Heat lost by process units to their surroundings is negligible (unless stated otherwise).
- Shaft work done by process units on their surroundings is negligible.
- Scale formation on process unit walls or agitators is negligible.
- Any gland seal water that enters the process is negligible relative to the flow of water in principal streams.

The following specific assumptions are made concerning the development of the leaching reactor model:

- All solid particles are liberated and complete off-bottom suspension of solids is maintained, such that the entire surface area of particles is exposed to the aqueous solution.
Table 6.1: Physical and Thermodynamic Data for all Species

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>( \rho ) (kg m(^{-3}))</th>
<th>( \Delta G_{f,298} ) (kJ mol(^{-1}))</th>
<th>( S_{298}^\circ ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta H_{f,298}^\circ ) (kJ mol(^{-1}))</th>
<th>( C_p^\circ = A + B10^{-3}T + C10^{5}T^{-2} + D10^{-6}T^2 ) (J mol(^{-1}) K(^{-1}))</th>
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<tbody>
<tr>
<td>1</td>
<td>Ni(^0)</td>
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<td>-</td>
<td>-</td>
<td>0.000</td>
<td>16.270 36.758 0.167 -16.154</td>
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<td>-</td>
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<td>-</td>
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<td>4</td>
<td>Cu(_2)S</td>
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<td>-</td>
<td>-79.496</td>
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<td>5</td>
<td>CuS</td>
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<td>-</td>
<td>-</td>
<td>-56.000</td>
<td>43.671 20.136 -2.102 -0.005</td>
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<td>6</td>
<td>CoS</td>
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<td>-</td>
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<td>-</td>
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<td>11</td>
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<td>13</td>
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<td>14</td>
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<td>85.395</td>
<td>-246.438</td>
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<td>165.322</td>
<td>-334.427</td>
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<td>-194.4</td>
<td>242.003</td>
<td>-441.496</td>
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<td>17</td>
<td>Ni(NH(_3))(_2),(^{2+})</td>
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<td>306.193</td>
<td>-539.862</td>
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<td>18</td>
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<td>394.635</td>
<td>-630.194</td>
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<tr>
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<td>97.069</td>
<td>65.689</td>
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<td>273.634</td>
<td>-348.527</td>
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<tr>
<td>21</td>
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<td>40.585</td>
<td>71.680</td>
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<td>22</td>
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<td>-</td>
<td>-64.6</td>
<td>242.500(^a)</td>
<td>-151.144(^b)</td>
<td>0.000 190.393 0.000 0.000</td>
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<td>24</td>
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<td>146.022</td>
<td>-584.965</td>
<td>0.000 418.618 0.000 0.000</td>
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</table>
Table 6.1: Physical and Thermodynamic Data for all Species (concluded) *

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>$\Delta G_{f,298}^\circ$ (kJ mol$^{-1}$)</th>
<th>$S_{298}^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta H_{f,298}^\circ$ (kJ mol$^{-1}$)</th>
<th>$C_p^\circ = A + B 10^{-3} T + C 10^5 T^{-2} + D 10^{-6} T^2$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>25</td>
<td>Fe$^{2+}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-92.257</td>
<td>-1943.789 8530.467 293.747 -10684.993</td>
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<td>26</td>
<td>NH$_3$(a)</td>
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<td>-</td>
<td>-107.800</td>
<td>-80.291</td>
<td>1111.750 3781.319 -236.141 4035.335</td>
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<td>27</td>
<td>NH$_4^+$</td>
<td>-</td>
<td>-</td>
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<td>-909.602</td>
<td>-3610.891 16366.381 364.885 -21432.513</td>
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<td>-</td>
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<td>-3610.891 16366.381 364.885 -21432.513</td>
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<tr>
<td>29</td>
<td>SO$_3$NH$_2$</td>
<td>-</td>
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<td>-3028.302 13219.319 428.623 -16682.869</td>
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<td>-11.715</td>
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<td>34</td>
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<td>-</td>
<td>-65.800$^f$</td>
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<tr>
<td>39</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.000 0.000 0.000</td>
</tr>
</tbody>
</table>

* Standard Gibbs free energy of formation data is sourced from [181]. All other data, unless specified otherwise, is sourced from [182].

$^a$ Sourced from [123].

$^b$ Sourced from [183].

$^c$ Calculated via the entropy correspondence principle of Criss and Cobble [184, 185] (see Appendix C).

$^d$ All thermodynamic data for SO$_3$NH$_2$ is assumed equivalent to that of SO$_2$$^{2-}$.

$^e$ Standard heat capacity coefficients for NH$_3$(l) are assumed equivalent to those of NH$_3$(g).

$^f$ Standard enthalpy of formation of NH$_3$(l) is calculated from the enthalpy of vapourisation of NH$_3$ at 25 ºC, $\Delta H_{f,298}^\circ$(NH$_3$) = 19.86 kJ mol$^{-1}$ [186]:

$\Delta H_{f,298}^\circ$(NH$_3$(l)) = $\Delta H_{f,298}^\circ$(NH$_3$(g)) - $\Delta H_{f,298}^\circ$(NH$_2$) = -65.8 kJ mol$^{-1}$, where $\Delta H_{f,298}^\circ$(NH$_3$(g)) = -45.94 kJ mol$^{-1}$ is given in the above table.
The residence time distribution (RTD) of solid particles is independent of particle size.

- Slurry backwash between adjacent compartments is negligible.
- No surface aeration takes place.
- A volumetric gas holdup is maintained only within the reactor itself (i.e. a negligible volumetric fraction of gas reports to the reactor discharge).

## 6.4 Streams

A stream can originate from a unit operation either within or outside of the process flowsheet (Figure 3.1). The specification of all properties for those streams of the former case is managed by the unit operation models. For streams that satisfy the latter criteria, which will be referred to henceforth as ‘flowsheet input streams’, this is handled explicitly through the appropriate use of plant data. Streams of this nature include the following: fresh matte slurry, flocculant slurry, DTO, MFL, MA, FTO, ETU, Ammonia Still distillate, fresh air, Ammonia Still overhead gas, and anhydrous ammonia. With the exception of the latter three streams, which may be classified as gas, gas, and anhydrous ammonia stream types, respectively, all others fall under the category of stream type slurry. The calculations for determining flowsheet input stream properties are discussed in the following subsections. A list of available data for said streams is given in Table 7.1 in the following chapter (see Section 7.3.2).

### 6.4.1 Slurry

The following plant data is available (with the exception of the Ammonia Still distillate stream): volumetric flow rate, solids mass flow rate \( (\bar{F}_s) \) or mass fraction of solids in a slurry (i.e. the mass-weighted pulp density) \( (\omega) \), mineralogical composition by mass \( (\gamma^i (s)) \), the mass fraction of particles passing 106 micron \( (F_{m,106}) \) (for fresh matte slurry only), temperature, as well as the mass concentrations of total aqueous nickel \( (\bar{C}_{Ni(T)}) \), copper \( (\bar{C}_{Cu(T)}) \), cobalt \( (\bar{C}_{Co(T)}) \), ammonia \( (\bar{C}_{NH_3(T)}) \) and AmSul \( (\bar{C}_{AmSul}) \) (all measured at room temperature, \( T_r \), which is taken to be 25 °C).
$Q$ and $T$ are given and thus do not require any manipulation. The volumetric fraction of solids is evaluated as follows:

$$g = \omega \rho \sum_{i(x)} \frac{y_{i(x)}}{\rho_{i(x)}}$$

(6.29)

where $\rho_i$ is the density of some component $i$ (see Table 6.1 for solids densities). The slurry mass density may be calculated as a function of $\omega$, the solids mass density, $\rho_s$, and the liquor mass density, $\rho_l$:

$$\rho = \left( \frac{\omega}{\rho_s} + \frac{1-\omega}{\rho_l} \right)^{-1}$$

(6.30)

If the pulp density is not measured directly, then it may be calculated from $Q$ and $F$:

$$\omega = \left[ \left( \frac{Q}{F} - \frac{1}{\rho_s} \right) \rho_l + 1 \right]^{-1}$$

(6.31)

The solids density is given by

$$\rho_s = \left( \sum_{i(x)} \frac{y_{i(x)}}{\rho_{i(x)}} \right)^{-1}$$

(6.32)

while the liquor density takes on the following form:

$$\rho_l = (\hat{\alpha} \bar{x}_d^2 + \hat{\beta} \bar{x}_d + 1) \rho_{H,\text{ox}(l)}$$

(6.33)

where $\hat{\alpha}$ and $\hat{\beta}$ are empirical constants, and $\bar{x}_d$ is the mass fraction of aqueous solutes. A correlation for liquid water density was obtained from fitting a quadratic polynomial to available data [186] over the temperature range 0 – 100 °C at 100 kPa:

$$\rho_{H,\text{ox}(l)} = -3.564 \times 10^{-3} T^2 + 1.8775 T + 753.6$$

(6.34)

The mass fraction of solutes may be calculated as a function of measured concentrations:
\[ \bar{r}_{d} = \left[ \bar{C}_{\text{Ni}(T)} \left( 1 + \frac{M_{\text{SO}_{4}^{2-}}}{A_{\text{Ni}}} \right) + \bar{C}_{\text{Cu}(T)} \left( 1 + \frac{M_{\text{SO}_{4}^{2-}}}{A_{\text{Cu}}} \right) + \bar{C}_{\text{Co}(T)} \left( 1 + \frac{3}{2} \frac{M_{\text{SO}_{4}^{2-}}}{A_{\text{Co}}} \right) + \bar{C}_{\text{NH}_{3}(T)} + \bar{C}_{\text{AmSul}} \right] \rho_{i}(T_{r})^{-1} \]

(6.35)

where \( A_{i} \) and \( M_{i} \) are the atomic and molecular weights of component \( i \), respectively, and \( \rho_{i}(T_{r}) = \rho_{\text{H}_{2}\text{O}(i)}(T_{r}) (\rho_{i} / \rho_{\text{H}_{2}\text{O}(i)}) \) is the liquor density at room temperature. Since nickel(II), copper(II) and cobalt(III) are present in solution as metal ammine salts (taken to be sulphates), the above equation has facilitated the additional mass accordingly.

The values of the coefficients in equation 6.33 are dependent on the slurry stream in question: for fresh matte and flocculant slurries, \( \hat{\alpha} = \hat{\beta} = 0 \) (i.e. the liquor is taken as pure water); for MA, \( \hat{\alpha} = 0.2084 \) and \( \hat{\beta} = -0.4271 \), which were obtained from a fit of the known densities of aqueous ammonia solutions at 25 °C [187]; and, for DTO, MFL, FTO, and ETU, \( \hat{\alpha} = 0 \) and \( \hat{\beta} = 0.5887 \), which were obtained from a fit of the known densities of aqueous ammonium sulphate solutions over the temperature range 0 – 100 °C [187]. The use of the latter model may be justified by the fact that ammonium sulphate is always the major component in solution.

Solids species molar concentration is calculated as a function of mineralogical composition:

\[ C_{(s)} = \omega \rho \frac{\gamma_{i(s)}}{M_{i(s)}} \]

(6.36)

where only the concentration of Components 1, 2, 4, 6, 7, 8, and 10 take on nonzero values. Aqueous species molar concentration is determined only for select components as a function of measured concentrations. It is assumed that: (1) all aqueous nickel, copper and cobalt exists as nickel(II), copper(II) and cobalt(III) ion, respectively, (2) all aqueous ammonia exists as free ammonia, and (3) all AmSul exists as ammonium and sulphate ions. The following relationships may thus be established to calculate the concentrations of components 12, 19, 23, 26, 27, 28 and 34, respectively:

\[ C_{\text{Ni}^{2+}} = \frac{\bar{C}_{\text{Ni}(T)}}{A_{\text{Ni}}} \frac{\rho_{i}(T_{r})}{\rho_{i}(T_{r})} \]

(6.37)
\begin{align}
C_{\text{Cu}^{2+}} &= \frac{\overline{C}_{\text{Cu}(T)}}{A_{\text{Cu}}} \frac{\rho_l}{\rho_l(T_f)} \\
C_{\text{Co}^{3+}} &= \frac{\overline{C}_{\text{Co}(T)}}{A_{\text{Co}}} \frac{\rho_l}{\rho_l(T_f)} \\
C_{\text{NH}_4} &= \frac{\overline{C}_{\text{NH}_4(T)}}{M_{\text{NH}_4}} \frac{\rho_l}{\rho_l(T_f)} \\
C_{\text{SO}_4^{2-}} &= \left( \frac{\overline{C}_{\text{Ni}(T)}}{A_{\text{Ni}}} + \frac{\overline{C}_{\text{Cu}(T)}}{A_{\text{Cu}}} + \frac{3 \overline{C}_{\text{Co}(T)}}{2 A_{\text{Co}}} + \frac{\overline{C}_{\text{AmSul}}}{2 M_{\text{NH}_4} + M_{\text{SO}_4^{2-}}} \right) \frac{\rho_l}{\rho_l(T_f)} \\
C_{\text{H}_2\text{O}(l)} &= \frac{(1 - \bar{x}_d) \rho_l}{M_{\text{H}_2\text{O}}} 
\end{align}

The concentration of all other aqueous components (i.e. 13-18, 20-22, 24, 25, 29-33) is zero.

The only plant data available for calculating \( \mu_{(s')} \) and \( \sigma_{(s')}^2 \) in the fresh matte slurry is \( F_{m,106} \). The latter on its own is insufficient, and thus the mass fraction passing another sieve size is required. In Appendix D, a typical discrete PSD of the leach feed matte (sampled during a special data survey at the refinery) is used to perform several tasks: (1) to demonstrate how its mean and variance is calculated, (2) to determine an appropriate mathematical function to describe particle size distribution in this work, of which the Rosin-Rammler distribution demonstrates a very good correlation, and (3) to aid in the development of a method for estimating PSD mean and variance as a function of the mass fraction of particles passing two sieve sizes. The first two tasks are reserved mainly for discussions later on, however the third is pertinent here.

Upon fitting the Rosin-Rammler function to the discrete size distribution data (see Appendix D), the following equation ensues:
\[ F_m(D) = 1 - \exp \left[ -\frac{10^6 D}{50.15} \right]^{1.15} \] (6.44)

where \( F_m(D) \) is a mass-weighted cumulative distribution function. The above equation may be used to make an assumption about a second sieve size. It is apparent that the 99.99 percent mass passing size is around 350 µm. If it is assumed that this is always the case, then the mean and variance may be calculated solely from \( F_{m,106} \) according to the method discussed in Appendix D.

The mean and variance of the Rosin-Rammler distribution is determined by

\[ \mu = D^* \Gamma \left( \frac{\varphi + 1}{\varphi} \right) \] (6.45)

\[ \sigma^2 = (D^*)^2 \left[ \Gamma \left( \frac{\varphi + 2}{\varphi} \right) - \Gamma^2 \left( \frac{\varphi + 1}{\varphi} \right) \right] \] (6.46)

where the adjustable parameters are given by equations D.7 and D.8, respectively:

\[ \varphi = \frac{\ln(1-0.9999)}{\ln(1-F_{m,106})} \] (6.47)

\[ D^* = 10^{-6} \exp \left[ \frac{\ln(106) \ln[-\ln(1-0.9999)] - \ln(350) \ln[-\ln(1-F_{m,106})]}{\ln \frac{\ln(1-0.9999)}{\ln(1-F_{m,106})}} \right] \] (6.48)

Since it is the assumption that all mineral species in the leach feed have the same PSD, \( \mu_{i(s')} = \mu \) and \( \sigma^2_{i(s')} = \sigma^2 \). It is also pertinent to mention here that, even though they do not physically enter with the leach process feed matte, millerite and covellite effectively have the same PSD also, given the manner in which heazlewoodite and chalcocite leach, respectively (as discussed in Chapter 4; see Section 4.3.3). The mean and variance for solids species in slurry steams other than fresh matte slurry may be taken as zero.

A special case exists for the Ammonia Still distillate stream, in which the
following relevant plant data is available: Ammonia Still reflux drum temperature ($T_{\text{Reflux}}$) and pressure ($P_{T(\text{Reflux})}$). $T_{\text{Reflux}}$ is a given and thus does not require any manipulation. The volumetric flow rate ($Q_{\text{Dist.}}$) is unmeasured and requires calculation, a task that is discussed in the next chapter (see Section 7.3.3). The slurry density is equivalent to the liquor density, which is described according to the model for MA (see equation 6.33 and accompanying discussion):

$$\rho_{\text{Dist.}} = (\hat{\alpha} \bar{x}_{\text{NH}_3(\text{Dist.})}^2 + \hat{\beta} \bar{x}_{\text{NH}_3(\text{Dist.})} + 1) \rho_{\text{H}_2\text{O}(\text{Dist.})}$$

(6.49)

where $\hat{\alpha} = 0.2084$, $\hat{\beta} = -0.4271$, $\bar{x}_{\text{NH}_3(\text{Dist.})} = C_{\text{NH}_3(\text{Dist.})} M_{\text{NH}_3} / \rho_{\text{Dist.}}$ is the mass fraction of ammonia, while $C_{\text{NH}_3(\text{Dist.})}$ and $\rho_{\text{H}_2\text{O}(\text{Dist.})}$ are ammonia concentration and density of liquid water in the distillate, respectively. The volumetric fraction of solids, the concentrations of all solids and aqueous species (with the exception of liquid water and ammonia), and the mean and variance of the PSD for appropriate solids species are all equal to zero.

The concentration of liquid water in the distillate is calculated via equation 6.43:

$$C_{\text{H}_2\text{O}(\text{Dist.})} = \frac{(1 - \bar{x}_{\text{NH}_3(\text{Dist.})}) \rho_{\text{Dist.}}}{M_{\text{H}_2\text{O}}}$$

(6.50)

$C_{\text{NH}_3(\text{Dist.})}$ is calculated as a function of $P_{T(\text{Reflux})}$. Since the distillate is an aqueous ammonia solution, the total drum pressure is the sum of the partial pressures of ammonia ($P_{\text{NH}_3(\text{Reflux})}$) and water vapour ($P_{\text{H}_2\text{O}(\text{Reflux})}$):

$$P_{T(\text{Reflux})} = P_{\text{NH}_3(\text{Reflux})} + P_{\text{H}_2\text{O}(\text{Reflux})}$$

(6.51)

Ammonia and water vapour are condensable gases and thus their partial pressures may be determined directly. The pressures of each component is assumed to be the same as that over aqueous ammonia solutions, and in this work were correlated as functions of aqueous ammonia content and temperature. $P_{\text{NH}_3(\text{Reflux})}$ and $P_{\text{H}_2\text{O}(\text{Reflux})}$ may thus be shown to take on the following form:
\[ P_i = \alpha_{i,2} \exp \left( -\beta_{i,2} / T \right) x_{\text{NH}_3(\text{Dist.})}^2 + \alpha_{i,1} \exp \left( -\beta_{i,1} / T \right) x_{\text{NH}_3(\text{Dist.})} + \alpha_{i,0} \exp \left( -\beta_{i,0} / T \right) \]  

(6.52)

where \( P_i \) is the partial pressure of some gaseous component \( i = \{ \text{NH}_3(\text{Reflux}), \text{H}_2\text{O(Reflux)} \} \), \( \alpha_{i,j} \) and \( \beta_{i,j} \) for \( j = 0, 1, 2 \) are temperature-dependent, \( i \)-specific empirical constants and \( x_{\text{NH}_3(\text{Dist.})} \) is the mole fraction of ammonia in the distillate:

\[ x_{\text{NH}_3(\text{Dist.})} = \frac{C_{\text{NH}_3(\text{Dist.})}}{C_{\text{NH}_3(\text{Dist.})} + C_{\text{H}_2\text{O(Dist.)}}} \]  

(6.53)

According to available data [187] over the range \( 0.4 \leq x_{\text{NH}_3(\text{Dist.})} \leq 0.6 \), the pressures of ammonia and water vapour over aqueous ammonia solutions have linear (i.e. \( \alpha_{i,2} = \beta_{i,2} = 0 \)) and quadratic relationships with \( x_{\text{NH}_3(\text{Dist.})} \), respectively, at any given temperature over the range \( 0 \leq 121.11 \) °C (32 – 250 °F). Moreover, the linear and quadratic coefficients are related exponentially to \( T^{-1} \). The following models may thus be constructed from said data over said ranges:

\[ P_{\text{H}_2\text{O(Reflux)}} - P_{\text{v,H}_2\text{O(Reflux)}} = 1.1707 \times 10^9 \exp \left( -3981/T_{\text{Reflux}} \right) x_{\text{NH}_3(\text{Dist.})}^2 - 2.5492 \times 10^{10} \exp \left( -4576/T_{\text{Reflux}} \right) x_{\text{NH}_3(\text{Dist.})} \]  

(6.54)

\[ P_{\text{NH}_3(\text{Reflux})} = 7.4528 \times 10^9 \exp \left( -2537/T_{\text{Reflux}} \right) x_{\text{NH}_3(\text{Dist.})} - 6.5585 \times 10^8 \exp \left( -2176/T_{\text{Reflux}} \right) \]  

(6.55)

where \( P_{\text{v,H}_2\text{O(Reflux)}} = 1.0623 \times 10^{11} \exp \left( -5169/T_{\text{Reflux}} \right) \) is the vapour pressure of water in the reflux drum. Simultaneous solution of equations 6.51, 6.54 and 6.55 yields a result for \( x_{\text{NH}_3(\text{Dist.})} \), while the simultaneous solution of equations 6.49, 6.50 and 6.53 yields a result for \( C_{\text{NH}_3(\text{Dist.})} \).

### 6.4.2 Gas

The following plant data is available for fresh air: temperature \( T_{\text{Air}} \) and total leach volumetric flow rate \( Q_{\text{Air}} \) (in units of Nm\(^3\) h\(^{-1}\)). Temperature is a given and thus does
not require any manipulation. The molar flow rates of ammonia and water vapour are equal to zero. The molar flow rates of oxygen and nitrogen gas are calculated from $Q_{\text{Air}}$ by way of the ideal gas law, based on the assumption that the air is composed of 21 percent oxygen and 79 percent nitrogen by mole:

$$F_{O_2(g)} = 0.21 \frac{P_n}{R T_n} Q_{\text{Air}}$$  \hspace{1cm} (6.56)$$

$$F_{N_2} = 0.79 \frac{P_n}{R T_n} Q_{\text{Air}}$$  \hspace{1cm} (6.57)$$

where $T_n = 288.15$ K and $P_n = 101325$ Pa are the normal temperature and pressure, respectively (as measured at the Kwinana nickel refinery). The total leach air is distributed evenly to second and third stage autoclaves.

There is no additional plant data for the Ammonia Still that would allow the appropriate calculation of gas molar flow rates in the overhead gas. The temperature is taken as that of the reflux drum, i.e. $T_{\text{Reflux}}$. The molar flow rates of oxygen and nitrogen gas are equal to zero. The molar flow rate of ammonia vapour ($F_{\text{NH}_3(\text{Still})}$) requires estimation; a suitable discussion is given in the next chapter (see Section 7.3.3). The molar flow rate of water vapour ($F_{\text{H}_2\text{O(Still)}}$) is calculated from the ideal gas law:

$$F_{\text{H}_2\text{O(Still)}} = F_{\text{NH}_3(\text{Still})} \frac{P_{\text{H}_2\text{O(Reflux)}}}{P_{\text{NH}_3(\text{Reflux})}}$$  \hspace{1cm} (6.58)$$

6.4.3 Anhydrous Ammonia

For the anhydrous ammonia stream type, only the temperature and total leach feed mass flow rate is obtainable. Thus, the molar flow rate for each stream that feeds a leaching autoclave must be calculated. An appropriate discussion is given in the next chapter (see Section 7.3.3).

6.5 Leaching Reactor (Autoclave Compartment)

A leaching reactor is considered to have single slurry and gas feed streams, single slurry and gas discharge streams, and a single anhydrous ammonia feed stream (i.e. a total of
five streams). Although cooling water input and output streams exist in the physical process (see Figure 3.2), in the model the cooling effect is quantified with an overall cooling duty rather than a cooling water flow rate, and thus the explicit consideration of cooling water input and output streams is unnecessary.

All feed stream properties are given. The calculation of discharge stream properties is performed via mass and energy balances. However, before said calculations can be carried out, rates of reaction extent for equations 6.1 – 6.28 need to be quantified. The kinetic rate laws presented in Chapter 4 form a basis for such expressions. Rate of extent of reaction, $\varepsilon$, is related to rate of reaction, $r$, according to the following two equations: $\varepsilon = rV(1-g-h)$ (for homogenous and gas-liquid mass transfer reactions) and $\varepsilon = rS$ (for heterogeneous reactions), where $V$ is the slurry volume, $g$ is the volumetric fraction of solids, $h$ is the volumetric gas holdup (i.e. the volumetric fraction of gas) and $S$ is the reaction surface area. The compartment working volume, $V_w$, and cooling coil volume, $V_c$, are givens and are related to the slurry volume as follows: $V = V_w - V_c$.

### 6.5.1 Chemical Reaction Kinetics

Reaction 6.1 was not included in discussions in Chapter 4, and thus represents a special case for the leaching process at the refinery. Autoclaves are supplied with liquid anhydrous ammonia, which is combined with the air stream to each compartment that it services. Upon exposure to the lower pressure, the liquid ammonia flashes and is sparged into appropriate compartments along with the air. For modelling purposes, it is taken that the ammonia remains in liquid form until contacting the reactor slurry, at which point it is assumed to dissolve instantaneously in the aqueous solution. The rate of extent of reaction 6.1 is therefore limited kinetically by the availability of anhydrous ammonia (i.e. by the rate at which the species in question is fed to any given compartment). This may be expressed mathematically via a mass balance on anhydrous ammonia, where its concentration in the reactor is taken as zero:

$$\varepsilon_{6.1} = F_{\text{NH}_3,(l),\text{in}}$$ (6.59)
where \( F_{\text{NH}_3,\text{in}} \) is the molar flow rate of anhydrous ammonia in the feed and \( \varepsilon_{6,k} \) refers to the rate of extent of reaction 6.\( k \).

The rates of extent of reactions 6.2 and 6.3 may be expressed mathematically with the aid of the ideal gas law via mass balances on ammonia and water vapour, respectively:

\[
\varepsilon_{6.2} = -F_{\text{NH}_3(g),\text{in}} + (F_{\text{N}_2,\text{in}} + F_{\text{O}_2(g),\text{in}} - \varepsilon_{6.4}) \frac{P_{\text{NH}_3(g)}}{P_T - P_{\text{NH}_3(g)} - P_{\text{H}_2\text{O}(g)}} \tag{6.60}
\]

\[
\varepsilon_{6.3} = -F_{\text{H}_2\text{O}(g),\text{in}} + (F_{\text{N}_2,\text{in}} + F_{\text{O}_2(g),\text{in}} - \varepsilon_{6.4}) \frac{P_{\text{H}_2\text{O}(g)}}{P_T - P_{\text{NH}_3(g)} - P_{\text{H}_2\text{O}(g)}} \tag{6.61}
\]

where \( F_{i(g),\text{in}} \) refers to the molar flow rate of some gaseous species \( i(g) \) in the feed, \( P_{i(g)} \) is the partial pressure of some gaseous species \( i(g) \) and \( P_T = P_{\text{NH}_3(g)} + P_{\text{H}_2\text{O}(g)} + P_{\text{N}_2} + P_{\text{O}_2(g)} \) is the (constant) total pressure. \( F_{\text{NH}_3(g),\text{in}} \) and \( F_{\text{H}_2\text{O}(g),\text{in}} \) only take on nonzero values for first stage leach autoclave compartments.

Solving for \( P_{\text{N}_2} \) and \( P_{\text{O}_2(g)} \) is discussed in the next subsection.

\( P_{\text{NH}_3(g)} \) and \( P_{\text{H}_2\text{O}(g)} \) take on forms analogous to equation 6.52:

\[
P_i = \tilde{\alpha}_{i,2} \exp(-\tilde{\beta}_{i,2}/T) x_{\text{NH}_3}^2 + \tilde{\alpha}_{i,1} \exp(-\tilde{\beta}_{i,1}/T) x_{\text{NH}_3} + \tilde{\alpha}_{i,0} \exp(-\tilde{\beta}_{i,0}/T) \tag{6.62}
\]

where \( P_i \) is the partial pressure of some gaseous component \( i = \{\text{NH}_3(g), \text{H}_2\text{O}(g)\} \), \( \tilde{\alpha}_{i,j} \) and \( \tilde{\beta}_{i,j} \) for \( j = 0, 1, 2 \) are temperature-dependent, \( i \)-specific empirical constants, and \( x_{\text{NH}_3} \) is the mole fraction of ammonia in aqueous ammonia solutions:

\[
x_{\text{NH}_3} = \frac{C_{\text{NH}_3(a)}}{C_{\text{NH}_3(a)} + C_{\text{H}_2\text{O}(i)}} \tag{6.63}
\]

According to available data [187] over the range \( 0 \leq x_{\text{NH}_3} \leq 0.1 \), the pressures of ammonia and water vapour over aqueous ammonia solutions have quadratic and linear (i.e. \( \tilde{\alpha}_{i,2} = \tilde{\beta}_{i,2} = 0 \)) relationships with \( x_{\text{NH}_3} \), respectively, at any given temperature over the range \( 0 – 121.11 \, ^\circ\text{C} (32 – 250 \, ^\circ\text{F}) \). Moreover, the quadratic and linear coefficients
are related exponentially to $T^{-1}$. The following models may thus be constructed from said data over said ranges:

$$P_{H_2O(g)} - P_{v, H_2O} = -2.6858 \times 10^{10} \exp (-4711/T) x_{NH_3}$$  \hspace{1cm} (6.64)

$$P_{NH_3(g)} = 5.8961 \times 10^9 \exp (-2841/T) x_{NH_3}^2 + 2.1146 \times 10^{11} \exp (-4441/T) x_{NH_3}$$  \hspace{1cm} (6.65)

where $P_{v, H_2O} = 1.0623 \times 10^{11} \exp (-5169/T)$ is the vapour pressure of water. Solving for $C_{i(a)}$ and managing $T$ is discussed in the next subsection.

The form of the rate law for reaction 6.4 is dependent, effectively, on whether cuprous ammine or dissolved oxygen is present in solution, as suggested by equations 4.6 and 4.10, respectively. Since neither component can exist in solution at the same time, the rate laws for each case may be combined to represent the general case, and thus the following expression for rate of reaction extent may be formulated:

$$\epsilon_{6.4} = E_i k_i a (C_{O_2}^* - C_{O_2(a)}) V (1 - g - h)$$  \hspace{1cm} (6.66)

The instantaneous enhancement factor was given in Chapter 4 (equation 4.7):

$$E_i = 1 + \frac{\hat{D}_{Cu(NH_3)_2}}{4 \hat{D}_{O_2}} \frac{C_{Cu(NH_3)_2}}{C_{O_2}}$$  \hspace{1cm} (6.67)

It seems that neither of the diffusivities of relevance to the above equation is specified in the literature. Although the diffusivity of dissolved oxygen, $\hat{D}_{O_2}$, can be estimated (e.g. via the Stokes-Einstein equation; see equation 6.77), the same cannot be said about the diffusivity of cuprous ammine, $\hat{D}_{Cu(NH_3)_2}$, given the lack of data in the literature. The ratio of diffusivities of dissolved gases to aqueous solutes with which they react upon dissolution is found to be between 0.25 and 4 for most practical cases [188]. The majority of researchers tend to use the ratio 1 [88], which is the intermediate value for the practical range for the diffusivity ratio, and in this work the same consideration has been made. That is to say, $\hat{D}_{Cu(NH_3)_2}/\hat{D}_{O_2} = 1$. 

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may be estimated using Tromans’ [189] model for oxygen solubility in ammoniacal-ammonium sulphate leaching solutions for sulphide concentrates. The model follows Henry’s law, and supposes that the solubility of oxygen in aqueous ammonia solutions containing inorganic solutes may be considered as some fraction of that in pure water. The equation describing oxygen solubility in the present leaching system is thus given as follows:

\[
C_{O_2}^* = \varphi_f \cdot C_{O_2, H_2O}^*
\]  

(6.68)

where \( C_{O_2, H_2O}^* \) is the solubility of oxygen in pure water [189, 190]:

\[
C_{O_2, H_2O}^* = P_o \cdot C_{H_2O(l)} \cdot M_{H_2O} / 101325 \\
\times \exp \left( \frac{0.046 T^2 + 203.35 T \ln (T / 298) - (299.378 + 0.092 T) (T - 298) - 20591}{8.3144 T} \right)
\]

(6.69)

Several aqueous components in the refinery leach liquor influence the capacity of the solution to dissolve oxygen. The fraction of water available to dissolve the oxygen, \( \varphi_f \), is a function of the concentrations of these components, which is given by the following expression [189]:

\[
\varphi_f = \varphi_{NH_3}, \quad \varphi_{eff} = \varphi_{NH_3} \cdot \varphi_{i} \left( \prod_{i=2}^{5} \varphi_{i} \right)^{\frac{q}{q}}
\]

(6.70)

\( \varphi_{NH_3} \) is the fraction of water available to dissolve the oxygen if ammonia was the only component in the aqueous solution. The presence of ammonia increases the solubility of oxygen (i.e. \( \varphi_{NH_3} > 1 \)), which stems from the fact that aqueous ammonia solutions tend to behave as a mixed solvent [189]. The remaining components that affect solubility in the present system are ammonium salts, as well as nickel(II), copper(II), copper(I), and cobalt(III) salts, and so \( z = 5 \) in the above equation. \( \varphi_{eff} \) is thus the effective fraction of water available to dissolve the oxygen if one or more of the preceding salts were the only component(s) in the aqueous solution, all of which tend to decrease the solubility of oxygen, while \( \varphi_i \) represents the fraction of water available to dissolve the oxygen if
the \(i\)th salt was the only solute in the aqueous solution, where \(\varphi_1 < \varphi_2 < \ldots < \varphi_z < 1\). The exponent \(q\) is an empirical constant, which is estimated for the salts of interest in this work to be roughly 0.8 [189, 191]. The \(\varphi\)-factor for the \(j\)th component (i.e. ammonia or any given salt) takes on the following form [189, 191]:

\[
\varphi_j = \left(1 + \bar{\kappa} \left(\frac{C_j}{C_{H_2O(t)} M_{H_2O}}\right)^y\right)^{-\bar{\eta}}
\]

(6.71)

where \(\bar{\kappa}\), \(\bar{y}\) and \(\bar{\eta}\) are component-specific values (see Table 6.2) and \(C_j\) is the concentration of component \(j\):

\[
C_j = \{C_{NH_2(T)} , C_{AmSul}, C_{Ni(NH_3)^2} , C_{Cu(NH_3)^2} , C_{Cu(NH_3)_2} , C_{Co(NH_3)_6}\}
\]

It should be noted that coefficient \((\bar{\kappa})\) and exponent \((\bar{y}, \bar{\eta})\) data for ammonium salts is reported [189] to be that for ammonium sulphate, while the data for nickel(II), copper(II), copper(I) and cobalt(III) salts are reported [189, 191] to be those for nickel(II), copper(II), copper(II) and cobalt(II) sulphate, respectively. However, as discussed by Tromans [189, 191]: (1) significance is placed with the (metal) cation, rather than the form of the anion with which it bonds, thus allowing the representation with this data of salts other than sulphates, such as thiosulphates, trithionates and sulphamates (which are, nonetheless, present in solution in much smaller quantities relative to sulphates), (2) there is no distinction between the effects of ammine cations and normal aqueous (solvated) cations on oxygen solubility, and (3) following from (1), salts having a metal (cation) component in the same group in the periodic table exhibit similar \(\varphi\)-factors at the same \(C_i\) (which may be observed in Table 6.2 for metals of interest in this work), thus justifying the assumption that data for copper and cobalt cations of differing oxidation states are equivalent.

\(k_j a\) is a difficult quantity to estimate for chemical and hydrometallurgical reactors. This is so given its dependence on the specific hydrodynamic conditions that surround the gas bubbles in the rector and the uncertainty that such relationships bring about. The hydrodynamic environment is influenced predominantly by the geometry of
Table 6.2: $\varphi$-factor Parameters for $\text{O}_2$ Solubility Model [189]

<table>
<thead>
<tr>
<th>Aqueous Solute</th>
<th>$\bar{\kappa}$</th>
<th>$\bar{y}$</th>
<th>$\bar{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$(a)</td>
<td>0.0105</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>NH$_4^+$ salts</td>
<td>0.69</td>
<td>1.11</td>
<td>0.749</td>
</tr>
<tr>
<td>Ni(II) salts</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>Cu(II) salts</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>Cu(I) salts</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>Co(III) salts</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
</tbody>
</table>

The system, the physical properties of the fluid and the presence of solids. The development of detailed models for describing $k_ia$ thus requires a thorough knowledge of each reactor under consideration. The acquisition of such data for industrial reactors is challenging, and is therefore typically unjustified. No information of the like is available for the leaching reactors at the Kwinana nickel refinery, and, seemingly, no information of the like is available in the literature for any other leaching system.

$k_ia$ is best determined through estimation using available process data or via established correlations as functions of system properties. Few leaching reactor modellers with published studies (i.e. those reviewed in Chapter 2) considered the use of $k_ia$, but those that did pursued the former option. The majority of researchers [54, 68, 69, 73-76] modelled their leaching system and conducted a sensitivity analysis on $k_ia$ to ascertain its impact on autoclave performance, and then, if appropriate, selected a single value of best-fit for further simulation purposes. Papangelakis and co-workers [44-47], however, employed an Arrhenius-type function to represent $k_ia$, which was developed [44] on the basis of satisfying autoclave performance requirements concerning oxygen mass transfer capacity. Said procedures involve the combined use of simulation and process data, and require that a single value or temperature-dependent function be used for all leaching reactors.

The above procedures could be used to enable the estimation of $k_ia$ in this work, however, to be carried out properly it requires that the parameter in question is the only
unknown of its type and/or that appropriate plant data is available. As was made known in Chapter 4, several mineral and sulphur oxidation rate law parameters remain unknown, and the plant data that is available is required to manage this inadequacy (more on this is given in the next chapter; see Section 7.4). Nonetheless, the value of \( k_i a \) is likely to vary between the first and final compartments of a given leaching autoclave (due to changes in conditions in addition to temperature) – not to mention between autoclaves in different leaching stages – and so gross estimations in this work is not ideal. The use of established correlations is thus required.

The volumetric mass transfer coefficient is comprised of two quantifiable variables: the liquid-side mass transfer coefficient, \( k_f \), and the gas-liquid specific interfacial area, \( a \). A host of researchers have formulated correlations for each of these variables individually or directly for their product (see, for example, the discussions and/or reviews by van’t Riet [192], Joshi et al. [193] and Kargi and Moo-Young [194]). The majority of all such correlations have been developed for gas-liquid systems as a function of fluid properties (e.g. surface tension, viscosity and density), agitator power draw and superficial gas velocity, whereby a given correlation is commonly suited to a specific impeller geometry. The correlations of Calderbank [195-198] for disk flat-blade turbines (i.e. Rushton turbines) are the most commonly applied functions for quantifying mass transfer kinetics in gas-liquid contactors [194], and have been advocated for use in generalised procedures for purposes of design and analysis [199]. As such, the latter correlations were selected to describe \( k_i a \) in this work for all autoclave compartments. Before pursuing related discussions, however, the effect of solids and the issue of system geometry need addressing.

Firstly, the impression that solids impose on gas-liquid mixing is considered negligible. The presence of solids – whether they are inert, reactive or catalytic – generally has an unfavourable effect on gas-liquid mass transfer. (It should be made known, however, that some fine, sparingly soluble solid particles are known to enhance gas-liquid mass transfer [200]. Such a phenomenon is not considered in this work.) This might be the result of influences the solid particles have on physical properties, in
particular viscosity [201, 202]. While the precise impact that solids have is dependent on the size, shape and disposition of the particles, as well as the concentration, it seems to be the general case that for low pulp densities the effect is minimal [201-203]. Given that the refinery leaching process exhibits modest pulp densities (i.e. less than 2.5 percent solids by volume for first and second stage leaching reactors), the present assumption is deemed appropriate.

Secondly, it is assumed that the correlations of Calderbank are compatible with the system geometry of all autoclave compartments. The system geometry is represented by that collectively of the reactor (its dimensions, the presence/absence of internal structures such as cooling coils and wall baffles, etc.), the agitator (the type, size, number and location of impellers, etc.) and, to a lesser extent, the sparger (its dimensions and location, the number and size of holes, etc.). Although it is recognised that the geometry of the system contributes uniquely to the value of \( k_l a \) in any given gas-liquid(-solid) system, there is evidence to suggest that its value can be similar for different geometric configurations (see, for examples, the reviews by van’t Riet [192] and Yawalkar et al. [204]). In particular, this has been shown to be the case for both Rushton turbines and Phasejet impellers [205], both of which are employed in the refinery leach (as discussed in Chapter 3). Moreover, the presence of reactor wall baffles – in which the reactors in this process are fitted – may play an influential role in allowing similar values of \( k_l a \) [205]. For these reasons, combined with the fact that the correlations of Calderbank were developed specifically for Rushton turbines, this assumption is also considered appropriate.

The details of the derivation of \( k_l a \) by way of Calderbank’s correlations is given in Appendix E, however, the governing equation is given as follows:

\[
k_l a = 0.8357 \frac{D_{O_2}^{2/3}}{\sigma_l^{0.96}} \rho_l^{0.32} \left( \frac{\mu_l}{\mu_g} \right)^{0.25} \left( \frac{(\rho_l - \rho_g)}{\mu_l} \right) g^* \left( \frac{P_g^*}{V} \right)^{0.64} v_r^{0.3} \quad (6.72)
\]

where the constant 0.8357 is dimensionless, \( \rho_l \) is the liquor density, \( \sigma_l \) is the liquor surface tension, \( \rho_g \) is the gas density, \( \mu_l \) is the liquor viscosity, \( g^* \) is the acceleration
due to gravity, \( \mu_g \) is the gas viscosity, \( P_g^* \) is the gassed power (i.e. the power transferred from the impeller to the fluid medium) and \( v_s \) is the superficial gas velocity. Volumetric mass transfer coefficient empirical correlations of the form
\[ k_l a \propto (P_g / V)\alpha v_s^\beta \]
are generally found to well-represent experimental data, where typically \( 0.4 < \alpha < 1 \) and \( 0 < \beta < 0.7 \) [192]. It is with confidence then that equation 6.72 is applied in this work, given both its correspondence with the most commonly used equation for correlating \( k_l a \) and that the exponents for specific agitator power and superficial gas velocity are close to the midpoints of their practical ranges.

Liquor surface tension and viscosity are difficult properties to estimate, given that little data exists for solutions corresponding to typical leaching systems. It has been suggested [31] that data for solutions at room temperature indicate that the values for pure water should be fairly close in the case of the former, and that the values for pure water times a factor of two to account for the salts in solution should be adequate in the case of the latter. The following equations were correlated accordingly from available data [186] as functions of temperature:
\[
\sigma_i = \sigma_{H_2O} = -2.6632 \times 10^{-7} T^2 + 4.5298 \times 10^{-6} T + 0.0943 \quad (6.73)
\]
\[
\mu_l = 2 \mu_{H_2O}
= 6.6462 \times 10^{-11} T^4 - 9.114 \times 10^{-8} T^3 + 4.6938 \times 10^{-5} T^2 - 10.7718 \times 10^{-3} T + 0.93126 \quad (6.74)
\]
where \( \sigma_{H_2O} \) and \( \mu_{H_2O} \) are the surface tension and viscosity of pure water, respectively.

The gas viscosity is taken as that of air. The following equation was correlated from available data [186] as a function of temperature:
\[
\mu_g = \mu_{Air} = -3.1607 \times 10^{-11} T^2 + 6.9096 \times 10^{-8} T + 6.1 \times 10^{-7} \quad (6.75)
\]
where \( \mu_{Air} \) is the viscosity of air. The gas density may be calculated from the ideal gas law:
The diffusivity of dissolved oxygen can be estimated at temperature from the value in pure water at room temperature via the Stokes-Einstein equation. The equation stipulates that the diffusivity of a gas in a liquid medium, \( \hat{D}_{g-l} \), is directly proportional to the temperature of the liquid and inversely proportional to the viscosity of the liquid (i.e. \( \hat{D}_{g-l} \propto \mu_l T^{-1} \)). The diffusivity of oxygen in water at room temperature is \( 2.42 \times 10^{-9} \, \text{m}^2 \, \text{s}^{-1} \) and the viscosity of water at room temperature is \( 8.9985 \times 10^{-4} \, \text{Pa} \, \text{s} \) [186]. So, the oxygen diffusivity in this work may be estimated with the following equation:

\[
\hat{D}_{O_2} = \frac{(2.42 \times 10^{-9}) (8.9985 \times 10^{-4}) \, T}{298.15 \, \mu_l} \tag{6.77}
\]

While the agitator power draw is a given, calculation of the superficial gas velocity is based on the assumption that the gassing rate (i.e. the rate of gas flow as seen by the impeller) is equivalent to the sparging rate; surface aeration is considered negligible. The superficial gas velocity is thus defined as follows:

\[
v_s = \frac{F_{g,in} \, RT}{A_{CS} \, P_T} \tag{6.78}
\]

where \( A_{CS} \) is the reactor cross-sectional area and \( F_{g,in} = F_{NH_4(g),in} + F_{H_2O(g),in} + F_{N_2(g),in} + F_{O_2(g),in} \) is the total gas molar feed rate.

The volumetric gas holdup can also be determined via established correlations as functions of system properties in a manner analogous to the volumetric mass transfer coefficient. The details of the derivation of \( h \) by way of Calderbank’s correlations is given in Appendix E, however, the governing equation is given as follows:

\[
h = 1.0182 \left( \frac{\rho_l}{\sigma_{li}} \right)^{0.2} \left( \frac{\rho_l - \rho_g}{\mu_l} \right)^{-0.5} \left( \frac{P_g}{V} \right)^{0.4} v_s^{0.5} \tag{6.79}
\]

where the constant 1.0182 is dimensionless.
The volumetric fraction of solids is given by

\[ g = \sum_{i(x)} \frac{C_{i(x)} M_{i(x)}}{\rho_{i(x)}} \]  

(6.80)

Solving for \( C_{i(x)} \) is discussed in the next subsection.

Like that of reaction 6.4, the rate laws for many of the reactions to follow depend on whether cuprous ammine or dissolved oxygen is present in solution. To aid with this distinction, a hypothetical ratio of copper(II)-to-total aqueous copper, \( R_{\text{Cu}}^* \), is defined, the value of which is always greater than or equal to zero. The details surrounding the variable are reserved for discussions later (see Section 6.5.4), however, it is acknowledged that cuprous ammine is present in solution if \( 0 \leq R_{\text{Cu}}^* < 1 \) and dissolved oxygen is present in solution if \( R_{\text{Cu}}^* \geq 1 \).

The rate of extent of reaction 6.5 may be expressed mathematically via an appropriate mass balance on either cuprous ammine or dissolved oxygen. If the former component is present in solution, a balance on dissolved oxygen is written where \( C_{\text{O}_2(a)} = 0 \), while if the latter is present, a balance on cuprous ammine is written where \( C_{\text{Cu(NH)}_3} = 0 \). The rate of extent of reaction 6.5 may thus be expressed as follows:

\[ \varepsilon_{6.5} = \begin{cases} 
Q_{\text{in}} \left( 1 - g_{\text{in}} \right) C_{\text{O}_2(a),\text{in}} + \varepsilon_{6.4}, & 0 \leq R_{\text{Cu}}^* < 1 \\
\frac{1}{4} \left( Q_{\text{in}} \left( 1 - g_{\text{in}} \right) C_{\text{Cu(NH)}_3},\text{in} + \sum_{k=6}^{19} V_{\text{Cu}^{+k}} \varepsilon_{6.6} \right), & R_{\text{Cu}}^* \geq 1 
\end{cases} \]  

(6.81)

where the subscript ‘\( \text{in} \)’ refers to conditions in the feed.

As discussed in Chapter 4, two mineral types are considered in the nickel matte: metal and sulphide. The metallic mineral reactions are given by equations 6.6, 6.7, 6.9 and 6.12, while equations 6.8, 6.10, 6.11 and 6.13 account for the sulphide mineral reactions. The kinetics of each type is distinct. Metallic minerals leach very fast and disappear entirely within the first stage leach, while sulphide minerals leach more slowly over all three leaching stages. On the former reactions, governing rate equations were proposed by combining equations 4.25 and 4.29. However, given their nature of
leaching at the refinery, a simple deduction may be made concerning metallic mineral conversion. It is verified in the next chapter (see Section 7.6.1) that for complete conversion to take place entirely within the first stage leach, almost all conversion takes place in the first compartment of first stage autoclaves. This notion can also be extended to include the behaviour of the first compartment of second stage autoclaves when the matte-bypass stream is active. Therefore, it is reasonable to accept that the kinetics of metallic mineral oxidation may be modelled with the assumption of unit conversion in any given reactor.

So, the rates of reaction extent are limited kinetically by the availability of each mineral (i.e. by the rate of flow of each mineral into the reactor). The rates of extent of reactions 6.6, 6.7, 6.9 and 6.12 may therefore be expressed mathematically via mass balances on metallic nickel, heazlewoodite, chalcocite and metallic iron, respectively, where the concentration of each is taken as zero:

\[ \varepsilon_{6.6} = Q_{in} C_{Ni^{0},in} \]  
\[ \varepsilon_{6.7} = Q_{in} C_{NiS_{2},in} \]  
\[ \varepsilon_{6.9} = Q_{in} C_{CuS,in} \]  
\[ \varepsilon_{6.12} = Q_{in} C_{Fe^{0},in} \]  

The concentrations of the metallic minerals will only take on nonzero values in the leach feed, and thus the above expressions will only take on nonzero values in the first compartment of the first stage autoclaves.

The governing rate equations for the sulphide mineral reactions were proposed by combining equations 4.25 and 4.27 or 4.28, the latter depending on whether dissolved oxygen or cuprous ammine is present in solution, respectively. However, the rate of extent of reaction for leaching in steady-state reactors is best described in terms of mineral conversion rather than surface area. The rates of extent of reactions 6.8, 6.10, 6.11 and 6.13 are thus given as functions of millerite, covellite, sycoporite and pyrrhotite conversion, respectively:
\[ \varepsilon_{6.8} = F_{\text{NiS, in}} X_{\text{NiS}} \]  \hspace{1cm} (6.86) \\
\[ \varepsilon_{6.10} = F_{\text{CuS, in}} X_{\text{CuS}} \]  \hspace{1cm} (6.87) \\
\[ \varepsilon_{6.11} = F_{\text{CoS, in}} X_{\text{CoS}} \]  \hspace{1cm} (6.88) \\
\[ \varepsilon_{6.13} = F_{\text{FeS, in}} X_{\text{FeS}} \]  \hspace{1cm} (6.89)

where \( F_{i(s^*), \text{in}} \) and \( X_{i(s^*)} \) are the molar feed rate and continuous reactor conversion for sulphide mineral species \( i(s^*) \), respectively. Conversion and surface area have the following relationship with rate of reaction extent: \( \varepsilon = b^{-1} F_{\text{in}} X = r S \), where \( b \) is the stoichiometric coefficient of the mineral. The calculation of \( X_{i(s^*)} \) is discussed in detail in Section 6.5.3.

The molar feed rates for millerite, covellite, sycoporite and pyrrhotite take on the following forms, respectively:

\[ F_{\text{NiS, in}} = Q_{\text{in}} \left( C_{\text{NiS, in}} + 2 C_{\text{NiS}_2, \text{in}} X_{\text{NiS}_2} \right), \]
\[ F_{\text{CuS, in}} = Q_{\text{in}} \left( C_{\text{CuS, in}} + C_{\text{CuS}_2, \text{in}} X_{\text{CuS}_2} \right), \]
\[ F_{\text{CoS, in}} = Q_{\text{in}} C_{\text{CoS, in}}, \] and \[ F_{\text{FeS, in}} = Q_{\text{in}} C_{\text{FeS, in}}. \]

The latter two expressions for \( F_{i(s^*), \text{in}} \) are clear-cut. The former two are required in their present forms given that millerite and covellite can enter a reactor via feed slurry and/or chemical reaction. In the case of the first compartment of the first stage autoclaves, said minerals enter the reactor via chemical reaction only, since they are not physically present in the leach feed matte. In said compartments, the molar rate at which millerite and covellite enter the reactor is equal to twice the rate that heazlewoodite does and precisely equal to the rate that chalcocite does (both physically), respectively, since the latter two each have unit conversions (i.e. \( X_{\text{NiS}_2} = X_{\text{CuS}_2} = 1 \)) and \( C_{\text{NiS, in}} = C_{\text{CuS, in}} = 0 \). In all other compartments in the process, millerite and covellite enter the reactor via slurry flow only and thus their rates of entry are calculated as per usual, since \( C_{\text{NiS}_2, \text{in}} = C_{\text{CuS, in}} = 0 \). For the special case in which the matte-bypass stream is active, and thus fresh nickel matte is fed directly to the second stage feed tank, millerite and covellite enter the first compartments of second stage autoclaves via both slurry flow and chemical reaction, and so the complete forms of the feed rate expressions for said
sulphides is required.

Elemental sulphur is produced via reactions 6.8, 6.10, 6.11 and 6.13 and is consumed instantaneously. The rate of extent of reaction 6.14 may therefore be expressed mathematically via a mass balance on said component, where its concentration in the reactor is taken as zero:

$$2 \varepsilon_{6.14} = \varepsilon_{6.8} + \varepsilon_{6.10} + \varepsilon_{6.11} + \varepsilon_{6.13}$$  \hfill (6.90)

The rate law for thiosulphate oxidation when cuprous ammine is present in solution is given by equation 4.32. When dissolved oxygen is present the kinetics is instantaneous, and so a mass balance on thiosulphate where its concentration is zero is used. The rate of extent of reaction 6.15 is given by

$$\varepsilon_{6.15} = \begin{cases} \frac{k_{S,O_2^-}}{RT} \exp \left( -\frac{102508}{RT} \right) \frac{C_{\text{Cu(NH}_3)_2^2+} C_{S,O_2^-}}{C_{\text{NH}_3(T)}} V (1 - g - h), & 0 \leq R_{Cu}^* < 1 \\ \frac{1}{2} \left( Q_m (1 - g_m) C_{S,O_2^-},m + \varepsilon_{6.14} \right), & R_{Cu}^* \geq 1 \end{cases}$$

where $k_{S,O_2^-} = 4.0 \times 10^{-3} \exp(102508/303.15/R)$ is the pre-exponential factor and $C_{\text{NH}_3(T)}$ is the molar concentration of total aqueous ammonia.

In Chapter 4, it was explained that the mechanism by which tetrathionate and subsequent reaction products decompose is not completely understood. In ammoniacal solution in the presence of an oxidant, polythionate may hydrolyse or ammonolyse, may oxidise, or may react according to both schemes, the nature of which probably depends on the type of oxidant. When cupric ammine is the oxidant, it is most likely the case that polythionate is predominantly oxidised, a notion that will be confirmed in the next chapter (see Section 7.6.1).

There is sufficient information in the literature to formulate a kinetic mechanism for polythionate hydrolysis or ammonolysis (see equations 4.33 – 4.37 and accompanying discussion). There is sufficient information, in the form of plant data, to formulate a kinetic mechanism for polythionate oxidation (see equations 4.38 – 4.42 and
accompanying discussion). However, there is insufficient information to formulate a kinetic mechanism that accommodates both hydrolysis/ammonolysis and oxidation. Specifically, it is not possible to determine what fraction of tetrathionate is hydrolysed or oxidised, given that the component in question reacts instantaneously. Given that polythionate is predominantly oxidised (at least) when cupric ammine is present as the oxidant, it is the assumption here that no hydrolysis or ammonolysis takes place. That is, polythionate is only permitted to react according to equations 6.16 – 6.18 (i.e. equations 4.38 – 4.40).

Since tetrathionate is consumed instantly, the rate of extent of reaction 6.16 may be expressed mathematically via a mass balance on said component, where its concentration is taken as zero:

\[ 3 \varepsilon_{6.16} = \varepsilon_{6.15} \quad (6.92) \]

Trithionate is oxidised in parallel reactions. The rate laws for trithionate oxidation when cuprous ammine is present in solution are given by equations 4.41 and 4.42. When dissolved oxygen is present the kinetics is instantaneous, and so a mass balance on said thioniate may be written to describe the present situation, in which its concentration is taken as zero. Furthermore, it is assumed that the ratio of the rates of production of sulphate and sulphamate under both kinetic regimes is the same. The rates of extent of reactions 6.17 and 6.18 are given as follows:

\[
\varepsilon_{6.17} = \begin{cases} 
\frac{k_{0,SO_4^2} \exp \left( -\frac{102508}{RT} \right) C_{\text{Cu(NH}_3)_4^{2+}} C_{\text{S}_3\text{O}_6^{6-}} V (1 - g - h)}{k_{0,SO_4^2}^* + k_{0,SO_4^2,\text{NH}_3}^* C_{\text{NH}_3(T)}} (Q_{in} (1 - g_{in}) C_{\text{S}_3\text{O}_6^{6-},in} + 4 \varepsilon_{6.16}), & R_{\text{Cu}} > 1 \\
0 \leq R_{\text{Cu}} < 1 
\end{cases}
\]

\[
(6.93)
\]

\[
\varepsilon_{6.18} = \begin{cases} 
\frac{k_{0,SO_4^2} \exp \left( -\frac{102508}{RT} \right) C_{\text{Cu(NH}_3)_4^{2+}} C_{\text{S}_3\text{O}_6^{6-}} C_{\text{NH}_3(T)} V (1 - g - h)}{k_{0,SO_4^2}^* + k_{0,SO_4^2,\text{NH}_3}^* C_{\text{NH}_3(T)}} (Q_{in} (1 - g_{in}) C_{\text{S}_3\text{O}_6^{6-},in} + 4 \varepsilon_{6.16}), & R_{\text{Cu}} > 1 \\
0 \leq R_{\text{Cu}} < 1 
\end{cases}
\]

\[
(6.94)
\]
where \( k_{0,SO_2^-} = k_{0,SO_2^-}^* \exp (102508/303.15/R) \) and \( k_{0,SO, NH_2} = k_{0,SO, NH_2}^* \exp (102508/303.15/R) \) are the rate law pre-exponential factors when \( 0 \leq R_{Cu}^* < 1 \). In the absence of appropriate data, it is assumed that the apparent activation energy for trithionate oxidation is the same as that for thiosulphate oxidation. \( k_{0,SO_2^-}^* \) and \( k_{0,SO, NH_2}^* \) are determined in the next chapter (see Section 7.4).

Iron is unstable in solution, and so it precipitates instantaneously. The rate of extent of reaction 6.19 may be expressed mathematically via a mass balance on ferrous iron, where its concentration is taken as zero:

\[
2 \varepsilon_{6.19} = \varepsilon_{6.12} + \varepsilon_{6.13}
\]

(6.95)

Nickel(II) is capable of forming up to six ammine complexes in the manner discussed in Chapter 4. Given that equilibrium is attained instantaneously, reaction rate laws must be described on the basis of thermodynamics, rather than kinetics. The rates of extent of reactions 6.20 – 6.25 may be expressed mathematically via mass balances on each of the nickel ammine complexes:

\[
\varepsilon_{6.20} = -Q_{in} (1 - g_{in}) C_{NH_3,Ni^{2+},in} + Q (1 - g) C_{Ni(NH_3)_2^{2+}} + \varepsilon_{6.21}
\]

(6.96)

\[
\varepsilon_{6.21} = -Q_{in} (1 - g_{in}) C_{Ni(NH_3)_2^{2+},in} + Q (1 - g) C_{Ni(NH_3)_3^{2+}} + \varepsilon_{6.22}
\]

(6.97)

\[
\varepsilon_{6.22} = -Q_{in} (1 - g_{in}) C_{Ni(NH_3)_3^{2+},in} + Q (1 - g) C_{Ni(NH_3)_4^{2+}} + \varepsilon_{6.23}
\]

(6.98)

\[
\varepsilon_{6.23} = -Q_{in} (1 - g_{in}) C_{Ni(NH_3)_4^{2+},in} + Q (1 - g) C_{Ni(NH_3)_5^{2+}} + \varepsilon_{6.24}
\]

(6.99)

\[
\varepsilon_{6.24} = -Q_{in} (1 - g_{in}) C_{Ni(NH_3)_5^{2+},in} + Q (1 - g) C_{Ni(NH_3)_6^{2+}} + \varepsilon_{6.25}
\]

(6.100)

\[
\varepsilon_{6.25} = -Q_{in} (1 - g_{in}) C_{Ni(NH_3)_6^{2+},in} + Q (1 - g) C_{Ni(NH_3)_7^{2+}}
\]

(6.101)

The concentration of the \( i \)th complex ion may be determined as a function of nickel ion and uncomplexed aqueous ammonia ion concentrations according to the following equilibrium equation:

\[
C_{Ni(NH_3)_i^{2+}} = (M_{H_2O} C_{H_2O(l)})^{-j} \beta_i C_{Ni^{2+}} C_{NH_3(a)}^i
\]

(6.102)
where the term \((M_{H_2O} C_{H_2O(l)})^{-1}\) is required to account for the fact that the overall stability constant for the \(i\)th complexation reaction, \(\beta_i\), must be described in terms of molality rather than molarity. At equilibrium, the Gibbs free energy of reaction is given by \(\Delta G_r = \Delta G_r^o + 10^{-3} RT \ln \beta = 0\). The \(i\)th overall stability constant therefore takes on the following form:

\[
\beta_i = \exp \left( -\frac{10^3 \Delta G_r^o(T)}{RT} \right) \tag{6.103}
\]

where \(\Delta G_r^o(T)\) is the standard free energy of reaction for the overall formation of the \(i\)th ammine complex:

\[
\Delta G_r^o(T) = G_{Ni(NH_3)^i:T}^o - G_{Ni^{3+}:T}^o - i \cdot G_{NH_3(a):T}^o \tag{6.104}
\]

\(G_{j,T}^o\) refers to the standard molar Gibbs free energy of some species \(j\) as a function of temperature:

\[
G_{j,T}^o = \Delta G_{f,298}(j) - 10^{-3} \left( (T - 298.15) S_{j,298}^o - \int_{T_{298}}^T C_{p,j}(T') dT' + T \int_{T_{298}}^T \frac{C_{p,j}(T')}{T'} dT' \right) \tag{6.105}
\]

where \(\Delta G_{f,298}(j)\) and \(S_{j,298}^o\) are the standard molar Gibbs free energy of formation and standard absolute molar entropy of species \(j\) at 298.15 K, respectively (see Table 6.1).

The concentrations of nickel ion and uncomplexed aqueous ammonia may be determined via suitable mass balances. The former is given by

\[
C_{Ni^{2+}} = C_{Ni(T)} \left( 1 + \sum_{i=1}^{6} (M_{H_2O} C_{H_2O(l)})^{-i} \beta_i C_{NH_3(a)}^{i} \right)^{-1} \tag{6.106}
\]

while the latter is determined via solution of the following:

\[
C_{NH_3(T)} = C_{NH_3(a)} + 4 C_{Cu(NH_3)^+} + 2 C_{Cu(NH_3)^2+} + 6 C_{Co(NH_3)^3+} + C_{Ni^{2+}} \sum_{i=1}^{6} i (M_{H_2O} C_{H_2O(l)})^{-i} \beta_i C_{NH_3(a)}^{i} \tag{6.107}
\]
The molar concentrations of total aqueous nickel, \( C_{\text{Ni}(T)} \), and total aqueous ammonia, \( C_{\text{NH}_3(T)} \), are calculated via mass balances on said components:

\[
Q (1-g) C_{\text{Ni}(T)} = Q_m (1-g_m) \left( C_{\text{Ni}^{2+},in} + \sum_{i=1}^{6} C_{\text{Ni}(\text{NH}_3)_i^{2+},in} \right) + \varepsilon_{6.6} + \varepsilon_{6.7} + \varepsilon_{6.8} \tag{6.108}
\]

\[
Q (1-g) C_{\text{NH}_3(T)} = Q_m (1-g_m) \times \left( C_{\text{NH}_3^{(a)},in} + 4C_{\text{Cu}(\text{NH}_3)_4^{2+},in} + 2C_{\text{Cu}(\text{NH}_3)_2^{2+},in} + 6C_{\text{Co}(\text{NH}_3)_6^{2+},in} + \sum_{i=1}^{6} i C_{\text{Ni}(\text{NH}_3)_i^{2+},in} \right) + \varepsilon_{6.1} - \varepsilon_{6.2} + 4 \varepsilon_{6.5} - 6 \varepsilon_{6.14} - 12 \varepsilon_{6.16} - 12 \varepsilon_{6.17} - 12 \varepsilon_{6.18} - 6 \varepsilon_{6.19} \tag{6.109}
\]

Unlike nickel(II), which has several stable ammine complexes ranging from coordination number one through six, copper(II), copper(I) and cobalt(III) tend to form one predominant ammine under conditions in the Sherritt-Gordon ammonia leach: tetraamminecopper(II), diamminecopper(I) and hexaamminecobalt(III). The concentrations of cupric, cuprous and cobaltic ion are all negligibly small, and so the rates of extent of reactions 6.26, 6.27 and 6.28 may be expressed mathematically via mass balances on each of the components, respectively, where their concentrations are taken as zero:

\[
\varepsilon_{6.26} = 4 \varepsilon_{6.5} - 2 \varepsilon_{6.6} - 2 \varepsilon_{6.7} - 2 \varepsilon_{6.8} - \varepsilon_{6.9} - 3 \varepsilon_{6.10} - 2 \varepsilon_{6.12} - 2 \varepsilon_{6.13} - 4 \varepsilon_{6.14} - 2 \varepsilon_{6.15} - 10 \varepsilon_{6.16} - 8 \varepsilon_{6.17} - 8 \varepsilon_{6.18} - 2 \varepsilon_{6.19} \tag{6.110}
\]

\[
\varepsilon_{6.27} = \varepsilon_{6.9} + \varepsilon_{6.10} - \varepsilon_{6.26} \tag{6.111}
\]

\[
\varepsilon_{6.28} = \varepsilon_{6.11} \tag{6.112}
\]

### 6.5.2 Mass and Energy Balances

A complete description of solids and aqueous species concentration, as well as gas partial pressure, is required to account for the stream properties in the reactor discharge slurry and gas. Such quantities may be solved for via component mass balance equations. Said equations, however, are unnecessary for Components 1, 2, 4, 7, 9, 19, 21, 23, 25, 31 and 35, since their concentrations are always zero (as has been explained). The concentrations of Components 12 – 18 and 26 are already describe via
equations 6.106, 6.102 (written for \( i = 1, 2, ..., 6 \)) and 6.107, respectively, and so balances on those species are also uncalled for. Furthermore, balances for Components 38 and 39 are not required, since the partial pressures of said components are given by equations 6.64 and 6.65, respectively. Therefore, only mass balances on Components 3, 5, 6, 8, 10, 11, 20, 22, 24, 27-30, 32-34, 36 and 37 are essential.

Steady-state mass balance equations for some solids species \( i_{(s)} \), some aqueous species \( i_{(a)} \) and some gaseous species \( i_{(g)} \) may be expressed, respectively, as follows:

\[
0 = Q_{\text{in}} \ C_{i_{(s)},\text{in}} - Q \ C_{i_{(s)}} + \sum_{k} v_{i_{(s)},k} \ v_{6,k} \tag{6.113}
\]

\[
0 = Q_{\text{in}} (1 - g_{\text{in}}) C_{i_{(a)},\text{in}} - Q (1 - g) C_{i_{(a)}} + \sum_{k} v_{i_{(a)},k} \ v_{6,k} \tag{6.114}
\]

\[
0 = F_{i_{(g)},\text{in}} - \frac{F_{g}}{P_{i_{(g)}}} P_{i_{(g)}} + \sum_{k} v_{i_{(g)},k} \ v_{6,k} \tag{6.115}
\]

where \( v_{i,k} \) refers to the stoichiometric coefficient of component \( i \) in reaction \( 6,k \), the values of which may be taken from equations 6.1 – 6.28; for reactants \( v_{i,k} < 0 \) and for products \( v_{i,k} > 0 \). Given that silica and nitrogen gas (Components 10 and 36, respectively) do not participate in any reactions, \( v_{\text{SiO}_2,k} = v_{\text{N}_2,k} = 0 \).

\( Q \) is the volumetric flow rate of reactor discharge slurry, which is determined via an overall mass balance:

\[
0 = Q_{\text{in}} \rho_{\text{m}} - Q \rho + \sum_{i_{(g)}} (F_{i_{(g)},\text{in}} - F_{i_{(g)})} M_{i_{(g)}} + F_{\text{NH}_3,i_{(g)},\text{in}} M_{\text{NH}_3} \tag{6.116}
\]

while \( F_{g} \) is the total molar flow rate of reactor discharge (i.e. vent) gas:

\[
F_{g} = \sum_{i_{(g)}} F_{i_{(g)},\text{in}} + \varepsilon_{6,2} + \varepsilon_{6,3} - \varepsilon_{6,4} \tag{6.117}
\]

The above variable allows for the calculation of component vent gas molar flow rate:

\[
F_{i_{(g)}} = \frac{F_{g}}{P_{i_{(g)}}} \tag{6.118}
\]

The mass density of reactor discharge slurry is given by
\[
\rho = \frac{1}{\rho_s} \sum C_{i(s)} M_{i(s)} + \frac{1}{\rho_l} \sum C_{i(a)} M_{i(a)} + (1-g) \sum C_{i(a)} M_{i(a)}
\]

(6.119)

where the solids density is

\[
\rho_s = \frac{\sum C_{i(s)} M_{i(s)}}{\sum C_{i(s)} M_{i(s)}}
\]

(6.120)

and the liquor density is given by the density model for aqueous ammonium sulphate solutions (see equation 6.33 and accompanying discussion):

\[
\rho_l = (0.5887 \bar{x}_d + 1) \rho_{H_2O}
\]

(6.121)

\(\rho_{H_2O}\) is given by equation 6.34, however, the mass fraction of aqueous solutes is now calculated via

\[
\bar{x}_d = \frac{\sum C_{i(a)} M_{i(a)} - C_{H_2O(l)} M_{H_2O}}{\rho_l}
\]

(6.122)

The use of equation 6.121 to describe liquor density is justified in the next chapter (see Section 7.5).

A description of temperature is also required account for the stream properties in the reactor discharge slurry and gas; said variable is available as plant data. Given that internal coils are employed for heat removal/addition, autoclave compartments are able to operate isothermally. A steady-state energy balance equation may thus be written to determine the cooling/heating duty:

\[
0 = -Q_{in} \int_{T_{in}}^{T} \left[ \sum C_{i(s),in} C_{p,i(s)}^{*} (T') + (1-g_{in}) \sum C_{i(a),in} C_{p,i(a)}^{*} (T') \right] dT' \\
- \int_{T_{in(gas)}}^{T} \sum F_{i(g),in} C_{p,i(g)}^{*} (T') dT' - F_{\text{NH}_3,l,in} \int_{T_{in(NH_3)}}^{T} C_{p,\text{NH}_3(l)}^{*} (T') dT' - 10^3 \left( \sum k \frac{\epsilon_{s,k}}{\lambda_{s,k}} \right) + \dot{Q}
\]

(6.123)

where \(T_{in}, T_{in(gas)}^*, T_{in(NH_3)}^*\) are the temperatures of the feed slurry, feed gas and feed.
anhydrous ammonia, respectively, and $\dot{Q}$ is the rate of heat flow from the slurry to the cooling coils. If $\dot{Q} > 0$ cooling is required, while if $\dot{Q} < 0$ heating is necessary. The former takes place in almost all autoclaves; more on this is discussed in the next chapter (see Section 7.6.1).

The standard molar heat capacity of species $i$ takes on the following form:

$$C_{\text{p},i} = A_i + B_i T + C_i T^{-2} + D_i T^{-2}$$  \hspace{1cm} (6.124)

where $A_i$, $B_i$, $C_i$ and $D_i$ are the heat capacity coefficients (see Table 6.1). The enthalpy change due to reaction 6.6 is given by

$$\Delta H^\circ_{r,k} = \sum_{i(s)} v_{i(s),k} H^\circ_{i(s)} + \sum_{i(a)} v_{i(a),k} H^\circ_{i(a)} + \sum_{i(g)} v_{i(g),k} H^\circ_{i(g)} + v_{\text{NH}_{3}(l),k} H^\circ_{\text{NH}_{3}(l)}$$  \hspace{1cm} (6.125)

where $H^\circ_i$ is the standard molar enthalpy of species $i$:

$$H^\circ_i = \Delta H_{f,298}^\circ(i) + 10^{-3} \int_{298}^{T} C_{\text{p},i}(T') \,dT'$$  \hspace{1cm} (6.126)

and $\Delta H_{f,298}^\circ(i)$ is the standard molar enthalpy of formation of species $i$ at 298.15 K (see Table 6.1).

### 6.5.3 Mineral Conversion and Discharge PSD Mean and Variance

In the previous chapter, a new method was presented for modelling continuous leaching reactors at steady-state. Here, said method is used to calculate the reactor conversion and discharge particle size distribution mean and variance of each sulphide mineral species in the present process. Despite the fact that the new approach has extensive application to a wide variety of leaching systems (for reasons established in the applicable chapter), it is nonetheless prudent to examine the extent to which the mathematical constraints are suited to this particular system.

The explicit method considers that (1) chemical reaction-controlled kinetics prevails, (2) the reactor is well-mixed and (3) the feed (mass) PSD is described with the gamma distribution. On the first point, sulphide mineral leaching in this process takes
place according to the chemical reaction-controlled shrinking core model (i.e. reaction at the mineral surface is the rate-limiting step) (as discussed in Chapter 4). On the second point, the industrial reactors employed at the refinery demonstrate agitation effective enough to maintain a uniform suspension of solids, thus exhibiting well-mixed conditions. Finally, on the third point, it is established in Appendix D that the gamma distribution demonstrates a very good correlation with a typical discrete size distribution of the leach feed matte; this was also confirmed for the Rosin-Rammler distribution earlier in the chapter (see Section 6.4.1). All three points validate explicitly the application of the new method for describing leaching kinetics and particle size distribution in the reactors considered in this work.

The reactor mineral conversion, $X$, is calculated as follows (equation 5.24):

$$X = 3\kappa (\phi - 1)^{1} (1 - 2\kappa (\phi - 2)^{1} (1 - \kappa (\phi - 3)^{1} (1 - (1 - \kappa^{-1})^{3})^{\phi})),$$

where $\phi = \mu_{m,in}^2 / \sigma_{m,in}^2$, $\kappa = -\bar{D}\bar{t} / D^*$, $D^* = \sigma_{m,in}^2 / \mu_{m,in}$ and $\bar{t}$ is the reactor mean residence time. The particle shrinkage rate, $\dot{D}$, is given by

$$\dot{D} = -\frac{2bM}{\rho} r$$

where $b$, $M$ and $\rho$ are the stoichiometric coefficient (equal to one for all cases in this work), molecular weight and mass density (given in Table 6.1) of the mineral, respectively, while $r$ is the rate of reaction.

As mentioned previously, the governing rate equations for sulphide mineral reactions may be formulated by combining equations 4.25 and 4.27 or 4.28, the latter depending on whether dissolved oxygen or cuprous ammine is present in solution, respectively. Generally speaking, the rate of some sulphide mineral oxidation reaction $6.k^*$ is described by
where \( k_{0,ij(s^*)}^{(III)} \) and \( k_{0,ij(s^*)}^{(1)} \) are the pre-exponential factors for Type III (copper(I) is present in solution) and Type I (dissolved oxygen is present in solution) leaching situations, respectively, which are determined in the next chapter (see Section 7.4).

Equation 6.127 must be written for each sulphide mineral species \( i(s^*) \) that leaches with distinct kinetics (i.e. millerite, covellite, sycoporite and pyrrhotite), thus describing \( X_{i(s^*)} \) and satisfying equations 6.86 – 6.89.

The mean and variance of the particle size distribution in the leach process feed is given by equations 6.45 and 6.46, respectively. The reactor discharge mineral PSD mean and variance are calculated as follows (equations 5.50 and 5.51):

\[
\mu_m = \mu_{m,in} (1 - X)^{-1} + 4 \tilde{D} \bar{i} \\
\sigma_m^2 = (\sigma_{m,in}^2 + \mu_{m,in}^2) (1 - X)^{-1} + (5 \tilde{D} \bar{i} - \mu_m) \mu_m
\]  

(6.130)  

(6.131)

The above equations must be written for each sulphide mineral species \( i(s^*) \) that leaches with distinct kinetics (i.e. millerite, covellite, sycoporite and pyrrhotite), thus describing \( \mu_{i(s^*)} \) and \( \sigma_{i(s^*)}^2 \) and satisfying the requirement for reactor discharge slurry stream properties.

6.5.4 Determining \( R_{Cu}^* \)

As was discussed in detail in Chapter 4, and briefly throughout this chapter, there are two mutually exclusive kinetic frameworks in the Sherritt-Gordon ammonia leach: leaching in the presence of copper(I) and leaching in the presence of dissolved oxygen. In each environment, the kinetics of oxygen gas-liquid mass transfer and reduction, sulphide mineral oxidation and sulphur oxidation is distinct. To accommodate this mathematically, a hypothetical copper(II)-to-total copper ratio, \( R_{Cu}^* \), was considered in
appropriate rate laws in this chapter.

The value of $R_{Cu}^*$ determines the kinetic framework that prevails. To implement this in the model, a construct may be set up so that when $R_{Cu}^* = R_{Cu}$ (where $R_{Cu} = C_{Cu(II)} / C_{Cu(T)}$ is the actual copper(II)-to-total copper ratio) one kinetic environment prevails, and when $R_{Cu}^* \neq R_{Cu}$ the other does so. Let the former case represent the environment that accommodates copper(I).

The source of a given kinetic setting is the rate of oxygen gas-liquid mass transfer relative to the rate of dissolved oxygen reduction: if the two reactions proceed at the same rate then copper(I) is present, whereas if the former reaction proceeds at a faster rate than the latter then dissolved oxygen is present. So, in order to describe $R_{Cu}^*$ in a suitable manner, a special mass balance on copper(II) may be written, in which the rates of extent of reactions 6.4 and 6.5 are given by those expressions that cater for the sole case of leaching in the presence of copper(I), and all other rates of reaction extent are expressed as given previously:

$$0 = Q_{in} \left(1 - g_{in}\right) C_{Cu(NH_3)_{2}}^{*\infty, in} - Q \left(1 - g\right) R_{Cu}^* C_{Cu(T)} + 4 \varepsilon_{6.5}^* + \sum_{k=6}^{19} V_{Cu^{2+}, k} \varepsilon_{6.k} \quad (6.132)$$

where $R_{Cu}^* = C_{Cu(II)}^* / C_{Cu(T)}$, $C_{Cu(II)}^*$ is the hypothetical concentration of copper(II), $\varepsilon_{6.4}^*$ and $\varepsilon_{6.5}^*$ are the rates of extent of reactions 6.4 and 6.5 when leaching in the presence of copper(I) prevails (equation 6.66 written for $C_{O_2(a)} = 0$ and equation 6.81 written for $0 \leq R_{Cu}^* < 1$, respectively):

$$\varepsilon_{6.4}^* = E_i k_I a C_{O_2}^* V \left(1 - g - h\right) \quad (6.133)$$

$$\varepsilon_{6.5}^* = Q_{in} \left(1 - g_{in}\right) C_{O_2(a), in} + \varepsilon_{6.4}^* \quad (6.134)$$

and $C_{Cu(T)}$ is given by a total mass balance on copper:

$$0 = Q_{in} \left(1 - g_{in}\right) C_{Cu(NH_3)_{2}}^{*\infty, in} + C_{Cu(NH_3)_{2}}^{\infty, in} + Q \left(1 - g\right) C_{Cu(T)} + \varepsilon_{6.9} + \varepsilon_{6.10} \quad (6.135)$$

Upon solving equation 6.132, if it is found that $R_{Cu}^* = R_{Cu}$ it signifies that
\( \varepsilon_{6.5} = \varepsilon_{6.5}^* \), and thus that leaching in the presence of copper(I) prevails. However, if \( R_{Cu}^* \neq R_{Cu} \) it signifies that \( \varepsilon_{6.5} \neq \varepsilon_{6.5}^* \), and hence that leaching in the presence of copper(I) does not prevail. Since \( 0 \leq R_{Cu} \leq 1 \) always, and that as \( C_{Cu} \rightarrow 0 \), \( R_{Cu} \rightarrow 1 \), it follows that if \( 0 \leq R_{Cu}^* < 1 \) then copper(I) must be present in solution and if \( R_{Cu}^* \geq 1 \) then dissolved oxygen must be present in solution.

### 6.6 Mixing Vessel

A mixing vessel is considered to have a single slurry feed stream and a single slurry discharge stream, and a single gas discharge stream. The only chemistry considered to take place in this unit is ammonia evaporation. Thus, the only chemical reactions considered is that for ammonia vapour formation (equation 6.2), as well as those for nickel ammine formation (equations 6.20 – 6.25), since any loss of ammonia from solution would have an effect on the speciation of nickel ammine.

Given that mixing vessels generally behave in a manner similar to leaching reactors, much of the mathematics and logic already used to describe the latter may be used to describe the former. In all cases, however, the extent of all reactions other than those discussed in the above paragraph (i.e. equations 6.1, 6.3 – 6.19, 6.26 – 6.28) are to be taken as zero.

The rate of ammonia evaporation is taken to be a constant; a discussion on determining its value is given in the next chapter (see Section 7.3.3). The rate of extent of reaction 6.2 is given by

\[
\varepsilon_{6.2} = F_{NH_3(g)}
\]

(6.136)

where \( F_{NH_3(g)} \) is the molar flow rate of ammonia vapour in the vent gas. The rates of extent of reactions 6.20 – 6.25 are given by the same expressions as those for the leaching reactor; that is, equations 6.96 – 6.101, respectively. The descriptions of all appropriate variables with which the latter equations depend are given by equation 6.80 (g) and equations 6.102 – 6.109.

Steady-state mass balance equations for some solids species \( i(s) \) and some
aqueous species \( i(a) \) may be expressed in accordance with equations 6.113 and 6.114 to solve for \( C_{i(s)} \) and \( C_{i(a)} \), all respectively. The latter equation does not need to be written for Components 19, 21, 23, 25 or 31 since their concentrations are always zero, nor does it need to be written for Components 12 – 18 or 26 since their concentrations are already accounted for. No gaseous species balances are required, since only the molar flow rate of ammonia vapour in the discharge gas stream takes on a nonzero value. That is, \( F_{N_2(g)} = F_{O_2(g)} = F_{H_2O(g)} = 0 \).

An overall mass balance is written for \( Q \) as follows:

\[
0 = Q_{in} \rho_{in} - Q \rho - F_{NH_3(g)} M_{NH_3} \quad (6.137)
\]

where \( \rho \) is given by equation 6.119 and other relevant variables by equations 6.120 – 6.122).

The mixing vessel operates adiabatically, and so a steady-state energy balance equation is written to determine \( T \):

\[
0 = -Q_{in} \int_{t_a}^{T} \left( \sum_{i(s)} C_{i(s),in} C_{p,i(s)}^* (T') + (1 - g_{in}) \sum_{i(a),in} C_{p,i(a)}^* (T') \right) dT' - 10^3 \sum_{k} \varepsilon_{6,k} \Delta H_{r,k}^* \quad (6.138)
\]

where the descriptions of all relevant variables with which the above equation depends are given by equations 6.124 – 6.126.

The mean and variance of the discharge PSD for each mineral is the same as that of the feed PSD:

\[
\mu_{i(s')} = \mu_{i(s'),in} \quad (6.139)
\]

\[
\sigma^2_{i(s')} = \sigma^2_{i(s'),in} \quad (6.140)
\]

### 6.7 Solid-Liquid Separator

A solid-liquid separator is considered to have a single slurry feed stream and two slurry discharge streams (an overflow and an underflow). The unit is an ideal separator, such that all the solids report to the underflow. (It is recognised that some overflow of solids
is witnessed in the actual process, however, this quantity is inconsequential with respect to the overall modelling and simulation objectives.) No chemistry takes place.

For the overflow stream, the following relationships may be written:

\[ \rho_o = \rho_{i,in} \]  
(6.141)

\[ g_o = 0 \]  
(6.142)

\[ C_{i(s),o} = 0 \]  
(6.143)

\[ C_{i(a),o} = C_{i(a),in} \]  
(6.144)

\[ T_o = T_{in} \]  
(6.145)

\[ \mu_{i(s'),o} = 0 \]  
(6.146)

\[ \sigma_{i(s'),o}^2 = 0 \]  
(6.147)

while for the underflow stream:

\[ \rho_u = \sum_{i(s)} C_{i(s),u} M_{i(s)} + (1 - g_u) \sum_{i(a)} C_{i(a),u} M_{i(a)} \]  
(6.148)

\[ g_u = \sum_{i(s)} \frac{C_{i(s),u} M_{i(s)}}{\rho_{i(s)}} \]  
(6.149)

\[ 0 = Q_m C_{i(s),in} - Q_u C_{i(s),u} \]  
(6.150)

\[ C_{i(a),u} = C_{i(a),in} \]  
(6.151)

\[ T_u = T_{in} \]  
(6.152)

\[ \mu_{i(s'),u} = \mu_{i(s'),in} \]  
(6.153)

\[ \sigma_{i(s'),u}^2 = \sigma_{i(s'),in}^2 \]  
(6.154)

where the subscripts ‘o’ and ‘u’ refer to those quantities in the overflow and underflow streams, respectively.

An overall mass balance is written as follows:
0 = Q_{in} \rho_{in} - Q_{o} \rho_{o} - Q_{a} \rho_{a} \tag{6.155}

If $Q_{a}$ is given, the above equation is solved for $Q_{o}$, and vice versa.

### 6.8 Trim Cooler

The leach trim coolers are double-pipe heat exchangers that employ cooling water. They are considered here to have single slurry feed and discharge streams. The unit itself is intended as an auxiliary cooling system, and so the difference in temperature between the feed and discharge slurry is not great. Therefore, it is assumed that there is a negligible difference in input and output stream properties other than temperature. Only an energy balance is required to describe this unit, which is solved to establish the cooling duty (i.e. $\dot{Q}$):

\[
0 = -Q_{\text{in}} \int_{T_{\text{in}}}^{T} \left( \sum_{i(s)} C_{i(s),\text{in}} C_{a\rightarrow i(s)}^+(T) + (1 - g_{\text{in}}) \sum_{i(a),\text{in}} C_{i(a),\text{in}} C_{a\rightarrow i(a)}^+(T) \right) dT' - 10^{3} \dot{Q} \tag{6.156}
\]

### 6.9 Mixing Points

The mixing of all slurry and gas streams is realised via dedicated mixing point models.

#### 6.9.1 Slurry

Let the slurry mixing point have $N$ feed streams and one discharge stream.

**Chemical Reaction Kinetics**

Although no actual leach chemistry takes place, the equilibrium of all metal ammine species (equations 6.20 – 6.28) is accounted for. The rates of reaction extent for all other reactions (equations 6.1 – 6.19) are to be taken as zero.

The slurry mixing point can have in its feed both flowsheet input streams and streams which are derived from unit operation models within the process flowsheet. As was discussed previously for the former (Section 6.4.1), all aqueous nickel, copper and cobalt is modelled as nickel(II), copper(II) and cobalt(III) ion, respectively, and all aqueous ammonia is modelled as free ammonia. For the internal streams, said species
are modelled collectively as metal ammines and uncomplexed aqueous ammonia. This discrepancy must be taken into account appropriately.

The rates of extent of reactions 6.20 – 6.25 are given via mass balances on each of the six nickel ammine complexes:

\[ \varepsilon_{6.20} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{NiNH}_2^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{NiNH}_2^{2+}} + \varepsilon_{6.21} \]  
(6.157)

\[ \varepsilon_{6.21} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{Ni(NH}_3)_2^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{Ni(NH}_3)_2^{2+}} + \varepsilon_{6.22} \]  
(6.158)

\[ \varepsilon_{6.22} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{Ni(NH}_3)_3^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{Ni(NH}_3)_3^{2+}} + \varepsilon_{6.23} \]  
(6.159)

\[ \varepsilon_{6.23} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{Ni(NH}_3)_4^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{Ni(NH}_3)_4^{2+}} + \varepsilon_{6.24} \]  
(6.160)

\[ \varepsilon_{6.24} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{Ni(NH}_3)_5^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{Ni(NH}_3)_5^{2+}} + \varepsilon_{6.25} \]  
(6.161)

\[ \varepsilon_{6.25} = -\sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) C_{\text{Ni(NH}_3)_6^{2+}.in(j)} + Q \left( 1 - g \right) C_{\text{Ni(NH}_3)_6^{2+}} \]  
(6.162)

where the subscript ‘\( in(j) \)’ denotes the \( j \)th input stream. The descriptions of all appropriate variables (with the exception of \( C_{\text{Ni(T)}} \) and \( C_{\text{NH}_3(T)} \)) with which the above equations depend are given by equation 6.80 (g) and equations 6.102 – 6.107. The concentration of total aqueous nickel and ammonia in the discharge are given by

\[ Q \left( 1 - g \right) C_{\text{Ni(T)}} = \sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) \left( C_{\text{Ni}^{2+}.in(j)} + \sum_{i=1}^{6} C_{\text{Ni(NH}_3)_i^{2+}.in(j)} \right) \]  
(6.163)

\[ Q \left( 1 - g \right) C_{\text{NH}_3(T)} = \sum_{j=1}^{N} Q_{in(j)} \left( 1 - g_{in(j)} \right) \]

\[ \times \left( C_{\text{NH}_3(a).in(j)} + 4 C_{\text{Cu(NH}_3)_2^{2+}.in(j)} + 2 C_{\text{Cu(NH}_3)_3^{2+}.in(j)} + 6 C_{\text{Co(NH}_3)_4^{2+}.in(j)} + \sum_{i=1}^{6} i C_{\text{Ni(NH}_3)_i^{2+}.in(j)} \right) \]  
(6.164)

The rates of extent of reactions 6.26, 6.27 and 6.28 are given by
The description of $\varepsilon_{6.26}$ through $\varepsilon_{6.28}$, and accompanying equations, may be used to accommodate any combination of feed streams, whether they be all flowsheet input streams, all internal streams, or a combination of both. Equations 6.157 – 6.164 (and auxiliary equations) handle both the formation and mixing of \( \text{Ni}(\text{NH}_3)_i^{2+} \) and \( \text{NH}_3(a) \). Equations 6.165 – 6.167 only accommodate the formation of \( \text{Cu}(\text{NH}_3)_4^{3+} \), \( \text{Cu}(\text{NH}_3)_2^+ \) and \( \text{Co}(\text{NH}_3)_6^{3+} \), respectively, while the mixing of said components is handled via suitable mass balance equations.

**Mass and Energy Balances**

Mass balance equations for some solids species \( i(s) \) and some aqueous species \( i(a) \) are written as follows to determine \( C_{i(s)} \) and \( C_{i(a)} \):

\[
0 = \sum_{j=1}^{N} Q_{in(j)} C_{i(s),in(j)} - Q C_{i(s)}
\]  
(6.168)

\[
0 = \sum_{j=1}^{N} Q_{in(j)} (1 - g_{in(j)}) C_{i(a),in(j)} - Q (1 - g) C_{i(a)} + \sum_k v_{i(a),k} \varepsilon_{6,k}
\]  
(6.169)

The concentrations of Components 19, 21, 23, 25 and 31 are always zero, and the concentrations of Components 12 – 18 and 26 are defined explicitly above, and so the above equation does not need to be written for any of the aforementioned aqueous species.

An overall mass balance is written for \( Q \):

\[
0 = \sum_{j=1}^{N} Q_{in(j)} \rho_{in(j)} - Q \rho
\]  
(6.170)
where $\rho$ is given by equation 6.119 and other relevant variables by equations 6.120 – 6.122). An energy balance equation is written to solve for $T$:

$$0 = -\sum_{j=1}^{N} Q_{m(j)} \int_{T_{m}}^{T_{a}} \left( \sum \frac{C_{i(s),in(j)}}{C_{p,i(s)}} C_{p,i(s)}(T') + (1 - g_{m(j)}) \sum C_{i(a),in(j)} C_{p,i(a)}(T') \right) dT'$$

$$-10^3 \sum_{k} E_{b,k} \Delta H_{r,k} (6.171)$$

where the descriptions of all appropriate variables with which the above equation depends are given by equations 6.124 – 6.126.

**Discharge PSD Mean and Variance**

The mean and variance of the particle size distribution in the slurry mixing point discharge is calculated according to equations derived in the previous chapter (equations 5.56 and 5.57):

$$\mu_{m} = \sum_{j=1}^{N} x_{m(j)} \mu_{m,in(j)} (6.172)$$

$$\sigma_{m}^2 = \sum_{j=1}^{N} x_{m(j)} (\sigma_{m,in(j)}^2 + \mu_{m,in(j)}^2) - \mu_{m}^2 (6.173)$$

The above equations must be written for each sulphide mineral species $i(s^*)$ that leaches with distinct kinetics (i.e. millerite, covellite, sycoporite and pyrrhotite), thus describing $\mu_{i(s^*)}$ and $\sigma_{i(s^*)}^2$ and satisfying the requirement for slurry mixing point discharge stream properties.

**6.9.2 Gas**

Let the gas mixing point have $N$ feed streams and one discharge stream. No chemistry takes place.

A mass balance equation for some gaseous species $i(g)$ is written to determine

$$F_{i(g)}$$:

$$0 = \sum_{j=1}^{N} F_{i(g),in(j)} - F_{i(g)} (6.174)$$
An energy balance equation is written to solve for $T$:

$$
0 = -\sum_{j=1}^{N} \left( \int_{T_{in(j)}}^{T} \int_{T_{in(j)}}^{T} F_{i(j),in(j)} C_{p,j(g)}^{+} (T') \, dT'' \right)
$$

(6.175)

where $C_{p,j(g)}^{+}$ takes on the form given by equation 6.124.

### 6.10 Splitting Points

The splitting of all slurry, gas and anhydrous ammonia streams is realised via dedicated splitting point models.

#### Slurry

Let the slurry splitting point have one feed stream and $N$ discharge streams. No chemistry takes place.

Only the volumetric flow rates of the discharge streams take on distinct values, and so all other stream properties remain the same as those in the feed stream:

$$
Q_j = x_j Q_{in}
$$

(6.176)

$$
\rho_j = \rho_{in}
$$

(6.177)

$$
g_j = g_{in}
$$

(6.178)

$$
C_{i(s),j} = C_{i(s),in}
$$

(6.179)

$$
C_{i(a),j} = C_{i(a),in}
$$

(6.180)

$$
T_j = T_{in}
$$

(6.181)

$$
\mu_{i(s^*)j} = \mu_{i(s^*)in}
$$

(6.182)

$$
\sigma_{i(s^*)j}^2 = \sigma_{i(s^*)in}^2
$$

(6.183)

where the subscript `j` denotes the $j$th output stream and $x_j$ is the fraction of splitter feed material that reports to the $j$th output.
Gas

Let the gas splitting point have one feed stream and $N$ discharge streams. No chemistry takes place.

Only the molar flow rates of gases in the discharge streams take on distinct values:

$$F_{i(g),j} = x_j F_{i(g),in}$$  \hspace{1cm} (6.184)

$$T_j = T_{in}$$  \hspace{1cm} (6.185)

Anhydrous Ammonia

Let the anhydrous ammonia splitter have one feed stream and $N$ discharge streams. No chemistry takes place.

Only the molar flow rates of anhydrous ammonia in the discharge streams take on distinct values:

$$F_{NH_3(l),j} = x_j F_{NH_3(l),in}$$  \hspace{1cm} (6.186)

$$T_j = T_{in}$$  \hspace{1cm} (6.187)

6.11 Summary

A modelling strategy for describing multiple autoclave leaching process flowsheets and the development of corresponding equations suitable for detailed mathematical modelling of the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery has been presented. The strategy is based on the mathematical description of process streams and fundamental unit operations that are connected via the specification of stream properties, the organisation of which accounts for the mass, energy and particle size distribution traffic of the process flowsheet. The process in question called for the description of three stream types and nine fundamental unit operation types. Mathematical equations for each were developed on the basis of combining mass and energy balances with kinetic rate laws (where appropriate). This modelling scheme is sufficiently flexible that it may be used to describe both the process under consideration
and any variation of it that features the same streams and unit operations. Furthermore, the assimilation of additional unit operations may be done via an appropriate mathematical description that incorporates relevant stream property definitions.

Of the stream and unit operation types described, particular attention is drawn to the leaching reactor model and slurry mixing point model. The novel method developed in the previous chapter for determining mineral conversion and reconstructing particle size distribution was showcased in the former model, while the approach developed in the same chapter for describing particle mixing was featured in the latter model.

In the next chapter, the creation and application of a computer model assembled on the basis of equations established here is detailed.
Chapter 7

Mathematical Modelling: Simulation

7.1 Introduction

In the previous chapter, the development of equations suitable for robust modelling of the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery was presented. In this chapter, the construction of a computer program capable of simulating said process over a wide range of operating conditions is explained. Unknown model parameters and process variables are estimated via the appropriate use of actual plant data, and the model itself is submitted to a rigorous validation procedure. A series of simulations is subsequently carried out, which demonstrate model capability and aid in expounding some fundamental characteristics of the chemistry and operation of the Sherritt-Gordon ammonia leach.

7.2 The Simulation Environment

The program was developed in Aspen Custom Modeler® (ACM) [206]. ACM is a graphical flowsheet modelling software that employs an object-oriented programming language and solves equations using an equation-oriented paradigm. Recalling discussions in the previous chapter (Section 6.3), the strategy for model development was to describe mathematically the behaviour of each of the streams and unit operations in the ammonia leach, so that the latter may be arranged appropriately to describe a suitable process flowsheet. The same construct is realised in ACM.
A class was developed for each stream type (i.e. slurry, gas and anhydrous ammonia) and unit operation (i.e. leaching reactor, mixing vessel, solid-liquid separator, trim cooler, mixing points (slurry and gas), and splitting points (slurry, gas and anhydrous ammonia)), using the equations given in the previous chapter. Following, class instances (or objects) of each were suitably created and arranged in a graphical flowsheeting space to replicate the process given in Figure 3.1. A port class was written for each stream type, which is inherited (where appropriate) by each unit operation class, allowing the connection of stream and unit objects in the flowsheeting space. A programming space is also available for flowsheet constraints (to be addressed in Section 7.3.3).

Four main continuous process vessel types are employed in the process: the autoclave, the tank, the thickener and the trim cooler. The latter vessel is represented exclusively by the trim cooler object in the flowsheeting space, while the former vessels are assembled via a single-level hierarchy of class objects. Tank and thickener hierarchies each contain three objects arranged in series. A tank hierarchy is comprised of a slurry mixing point, a mixing vessel, and a slurry splitting point object, and makes use of slurry streams to unite them. A thickener hierarchy consists of a slurry mixing point, a mixing vessel, and a solid-liquid separator object, and also employs slurry streams in a manner consistent with the tank hierarchy. The autoclave model is more complicated.

An autoclave hierarchy encompasses one gas splitting point, one anhydrous ammonia splitting point, one gas mixing point, and four leaching reactor objects. All autoclave gas streams are fed to the gas splitting point, the outputs of which report to each of the leaching reactors, which are arranged in series. A single anhydrous ammonia feed stream is fed to the anhydrous ammonia splitting point, the outputs of which are fed to each of the leaching reactors. A single autoclave slurry feed stream is fed to the first reactor in series, the output of which is fed to the second, and so on. A single gas discharge stream from each of the leaching reactors is fed to the gas mixing point, the output of which represents the total autoclave vent gas. A special case exists for the Autoclave 2A hierarchy, in which an additional gas mixing point is employed to
combine Ammonia Still overhead gas with the fresh air stream that is fed to the first compartment.

A total of six autoclave hierarchies (Autoclaves 1A, 1B, 2A, 2B, 3B, and 3A), three tank hierarchies (Tanks 1, 2, and 3), three thickener hierarchies (Thickeners 1, 2, and 2W), six trim cooler objects (one directly upstream from each of the autoclaves), and seven supplementary objects are arranged in the flowsheeting space. The accompanying objects include: (1) five slurry mixing points: two to combine each of the first and second stage autoclave discharge streams, a third to combine the Thickener 1 overflow stream with the second stage discharge (prior to entering Thickener 2), a fourth to combine the Tank 3 discharge stream with Ammonia Still distillate (prior to entering Autoclave 3A) and a fifth to combine the Thickener 2 overflow stream with FTO; (2) a gas mixing point, used to combine the second and third stage autoclave vent gas streams (prior to entering Autoclave 1A); and (3) a gas splitting point, used to distribute fresh air to Autoclaves 2A, 2B, 3B and 3A. Ultimately, 74 unit objects are employed: 24 leaching reactors, six mixing vessels, three solid-liquid separators, six trim coolers, 11 slurry mixing points, eight gas mixing points, three slurry splitting points, seven gas splitting points and six anhydrous ammonia splitting points.

On all mixing and splitting points, the model equations presented in the previous chapter (see Sections 6.9 and 6.10) specified an arbitrary number of feed and discharge streams (designated $N$ in all cases), respectively. This is programmed by letting $N$ equal the maximum number of input or output streams for any mixing or splitting point in the process, respectively. For a mixing or splitting point with $M$ input or output streams, where $1 < M < N$, then $N - M$ dummy streams are employed in which the stream properties are nullified. For the slurry splitting point, $N = 3$, while for all other mixing and splitting points, $N = 4$.

On the anhydrous ammonia splitting point, even though all four discharge streams are connected to the four leaching reactors in each autoclave hierarchy, only the streams servicing the first two reactors in the series (i.e. Compartments 1 and 2) take on nonzero values (where appropriate).
7.3 Plant Data

A host of plant data is used to understand the state of the process. For streams, the data types are volumetric and mass flow rate, while for process vessels, the data types include temperature, pressure, slurry density, aqueous component concentration (i.e. for nickel, copper, cobalt, ammonia and AmSul) and Bromate Value (BV). Data types for process vessels also extend to their discharges, since said vessels are assumed to be well-mixed. Special cases exist for some vessels, such as the measurement of solids composition, particle size distribution and mass-weighted pulp density. Of course, other data may be acquired via calculations that involve those already mentioned. Flow rate, temperature and pressure data is acquired through plant sensors, while remaining data is obtained via plant sampling and subsequent laboratory analysis. Not all of the data mentioned is available for every stream and vessel.

Plant data is required for parameter estimation and model validation. Both the quality and quantity of data are important factors to consider when carrying out such activities. The same assumptions concerning plant data given in the previous chapter (see Section 6.3) are relevant for work carried out in this chapter. Specifically, refinery sensors (for flow, temperature and pressure) that pertain to the leach are believed to be calibrated, and on-site sampling and laboratory analysis is performed such that measurements (accounting for temperature difference) accurately reflect the state of the process.

7.3.1 Acquiring a Data Set

An analysis of data from the standpoint of quality is a very important part of the estimation and validation processes, given that a model is only as good as the data used to substantiate it. A hasty selection of process data could lead to a poor model comparison, while a prudent selection could lead to a favourable outcome. This is particularly true for steady-state models, in which it is the requirement that the data be steady-state in nature. Raw data acquired from an industrial process plant is inherently unsteady-state, given that said plants almost never operate under “true” steady-state conditions. A steady-state data set – which is, in fact, only pseudo-steady-state in
nature, and will be referred to as such henceforth – can therefore not be obtained from a single snapshot of said raw data, but rather from an array of data over a suitable period of time. In this work, the aptness of a given time range is dependent upon the state of several key variables, employing three levels of significance.

Firstly, the leach matte feed rate should be steady. This is the most important variable, since it influences the entire leaching process (not to mention the entire refinery). Although the composition of the matte (particularly that of the nickel) is just as important as the flow rate, it is typically the case that when the latter is steady the former is steady also. Secondly, all other major input and output streams that influence not only the leach, but also the copper boil and ammonia recovery processes, should be fairly steady (taken to be when the data time-gradient is close to zero). These variables include: (1) the total air flow to the leach, (2) the total anhydrous ammonia flow to the leach, (3) the copper boil feed flow (i.e. the leach discharge flow), and (4) the Ammonia Still feed flow. Finally, the first and second stage autoclave feed flows should be fairly steady. Typically, the latter variables will conform if the same conditions pertaining to the preceding variables are upheld. Thus, assessment of the autoclave feed flows is a good final indicator of the state of the process. It should also be mentioned that the flow of DTO and MFL to the first and second stage feed tanks are important, but once again, their state is closely tied to that of the autoclave feed flows in respective leaching stages. Moreover, the third stage feed flow, given the location of said leaching stage, is almost always steady. Variations in other variables (such as concentration) are less pronounced than that for flow rate, and so only the latter variable type is given precedence.

A suitable time period is defined as one in which all conditions set forth in the previous paragraph are satisfied for at least two days, preceded by a one day period in which the leach matte feed rate has been steady; that is, a minimum of three days of steady matte flow is required. These time frames take into account an initial period in which all other important flows can be stabilised, followed by a secondary period in which the stability of said flows may be sustained. The quantity of time itself accounts for the times in which material circulates all of the leach, copper boil and ammonia recovery processes. A pseudo-steady-state data set is thus taken as the arithmetic mean
of the raw data collected over the suitable time period. The data set will only ever be pseudo-steady-state in nature because not all of the raw data employed in the averaging procedure would (in all likelihood) be fairly steady or better. The raw data set is comprised of hourly samples.

In general, concentration data is fairly steady over suitable time periods. However, several stream flow rates are either erratic or intermittent, which do not tend to generate useful pseudo-steady-state values. Those variables are taken to be unreliable, and so their values are calculated to ensure that, at least, the total mass around chief process vessels is balanced. Such variables are yet to be discussed.

Concentrations are measured in the laboratory at room temperature, $T_r$, which is taken to be 25 °C. Where appropriate, the data is corrected for temperature via the following relationship:

$$\frac{C_i(T)}{C_i(T_r)} = \frac{\rho_i(T)}{\rho_i(T_r)}$$

where $\rho_i(T)$ is given by either equation 6.33 (for flowsheet input streams) or equation 6.121 (for all other cases), and $C_i$ is the concentration of some component $i$.

### 7.3.2 Data Availability

For purposes of model input, the flowsheet input stream variables and process vessel variables (and parameters) in which reliable plant data is available are given in Tables 7.1 and 7.2. (A discussion on how flowsheet input stream data is used to determine the properties of said streams was given in the previous chapter; see Section 6.4.) A host of pertinent model input variables remain absent, and are given in Table 7.3. The values of such variables are either unmeasured or unreliable, and so call for estimation. For purposes of model output comparison, the flowsheet stream variables in which plant data is available are given in Table 7.4.
Table 7.1: Flowsheet Input Stream Variables with corresponding Plant Data

<table>
<thead>
<tr>
<th>Stream</th>
<th>Variable</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh matte slurry</td>
<td>Total flow rate</td>
<td>(volume) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Solids flow rate</td>
<td>(mass) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Ni⁰, Ni₂S₃, Cu₂S, CoS, Fe⁰, FeS &amp; SiO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mass composition</td>
<td>(mass) (mass)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Particles passing 106 micron</td>
<td>(mass) (mass)⁻¹</td>
</tr>
<tr>
<td>Flocculant slurry</td>
<td>Total flow rate</td>
<td>(volume) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Pulp density</td>
<td>(mass) (mass)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td>DTO, MFL, MA, FTO, ETU</td>
<td>Total flow rate *</td>
<td>(volume) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Ni, Cu, Co, NH₃ &amp; AmSul concentration</td>
<td>(mass) (volume)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia Still distillate</td>
<td>Reflux drum temperature</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reflux drum pressure</td>
<td>-</td>
</tr>
<tr>
<td>Fresh air</td>
<td>Total flow rate</td>
<td>(volume) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Second and third stage leach</td>
<td></td>
</tr>
<tr>
<td></td>
<td>autoclave apportionment</td>
<td>(mole) (mole)⁻¹</td>
</tr>
<tr>
<td>Anhydrous ammonia</td>
<td>Temperature</td>
<td>-</td>
</tr>
</tbody>
</table>

* Not pertinent to MFL-to-Tank 1.

Table 7.2: Vessel Parameters or Variables with corresponding Plant Data

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Parameter or Variable</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoclave</td>
<td>Slurry feed flow rate *</td>
<td>(volume) (time)⁻¹</td>
</tr>
<tr>
<td></td>
<td>Compartment temperature</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total pressure</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total compartment volume</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Compartment working volume</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Compartment cooling coil volume</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Compartment cross-sectional area</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Compartment agitator power draw</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Compartment apportionment of total vessel air supply</td>
<td>(mole) (mole)⁻¹</td>
</tr>
<tr>
<td>Tank</td>
<td>Working volume</td>
<td>-</td>
</tr>
<tr>
<td>Thickener</td>
<td>Working volume</td>
<td>-</td>
</tr>
</tbody>
</table>

* Pertinent to 1st and 2nd stage autoclaves only.

** Pertinent to Tank 1 only.
Table 7.3: Model Input Variables that require Estimation

<table>
<thead>
<tr>
<th>Stream or Vessel</th>
<th>Variable</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous ammonia</td>
<td>Autoclave feed flow rate *</td>
<td>(mole) (time)$^{-1}$</td>
</tr>
<tr>
<td>Ammonia Still overhead</td>
<td>Flow rate</td>
<td>(mole) (time)$^{-1}$</td>
</tr>
<tr>
<td>Ammonia Still distillate</td>
<td>Flow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>MFL-to-Tank 1</td>
<td>Flow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>Autoclave</td>
<td>Compartment apportionment of total vessel anhydrous NH$_3$ *</td>
<td>(mole) (mole)$^{-1}$</td>
</tr>
<tr>
<td>Tank</td>
<td>NH$_3$ evaporation rate</td>
<td>(mole) (time)$^{-1}$</td>
</tr>
<tr>
<td>Thickener</td>
<td>NH$_3$ evaporation rate</td>
<td>(mole) (time)$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Underflow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>Trim cooler</td>
<td>Discharge temperature</td>
<td>-</td>
</tr>
</tbody>
</table>

* Not pertinent to Autoclaves 2A or 3A.

Table 7.4: Model Output Variables with corresponding Plant Data

<table>
<thead>
<tr>
<th>Stream</th>
<th>Variable</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st stage leach discharge</td>
<td>Ni, Cu, Co, NH$_3$ &amp; AmSul concentration</td>
<td>(mass) (volume)$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Bromate Value (BV)</td>
<td>BV-units</td>
</tr>
<tr>
<td></td>
<td>Ni, Cu &amp; Co extraction</td>
<td>(mass) (mass)$^{-1}$</td>
</tr>
<tr>
<td>2nd stage leach discharge</td>
<td>Ni, Cu, Co, NH$_3$ &amp; AmSul concentration</td>
<td>(mass) (volume)$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Bromate Value (BV)</td>
<td>BV-units</td>
</tr>
<tr>
<td></td>
<td>Ni, Cu &amp; Co extraction</td>
<td>(mass) (mass)$^{-1}$</td>
</tr>
<tr>
<td>3rd stage leach discharge</td>
<td>Ni, Cu, Co, NH$_3$ &amp; AmSul concentration</td>
<td>(mass) (volume)$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Ni, Cu &amp; Co extraction</td>
<td>(mass) (mass)$^{-1}$</td>
</tr>
<tr>
<td>Tanks 1, 2 and 3 discharges</td>
<td>Ni, Cu, Co, NH$_3$ &amp; AmSul concentration</td>
<td>(mass) (volume)$^{-1}$</td>
</tr>
<tr>
<td>Thickener 2 overflow</td>
<td>Ni, Cu, Co, NH$_3$ &amp; AmSul concentration</td>
<td>(mass) (volume)$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Bromate Value (BV)</td>
<td>BV-units</td>
</tr>
<tr>
<td>Thickener 2 feed</td>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td>Thickener 1 overflow</td>
<td>Volumetric flow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>Copper Boil feed</td>
<td>Volumetric flow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>Thickener 2W overflow</td>
<td>Volumetric flow rate</td>
<td>(volume) (time)$^{-1}$</td>
</tr>
<tr>
<td>Anhydrous ammonia</td>
<td>Total leach feed flow rate</td>
<td>(mass) (time)$^{-1}$</td>
</tr>
<tr>
<td>Recycled ammonia</td>
<td>Total leach feed flow rate</td>
<td>(mass) (time)$^{-1}$</td>
</tr>
</tbody>
</table>

* 1 g L$^{-1}$ S$_2$O$_5^- = 41$ BV-units, 1 g L$^{-1}$ S$_3$O$_6^{2-} = 26$ BV-units (see Chapter 3).
7.3.3 Estimating Unknown or Unreliable Data

With the exception of MFL-to-Tank 1 and thickener underflow rate, all other variables listed in Table 7.3 are unmeasured. Said variables are calculated in the model throughout the course of simulation. The molar flow rates of anhydrous ammonia to Autoclaves 1A, 1B, 2B and 3B are calculated to balance total ammonia around said vessels, such that the concentration of aqueous ammonia in the vessel discharges (i.e. the fourth compartments) is the same as plant data. The anhydrous ammonia is only delivered to the first two compartments of each autoclave, and so the apportionment to those reactors is calculated such that the (free) ammonia-to-total-metals molar ratio in each is the same; of course, the apportionment to the third and fourth reactors is zero. The specification of total autoclave anhydrous ammonia feed rate satisfies the flowsheet input stream requirements outlined in the previous chapter (see Section 6.4.3), while the specification of compartment apportionment satisfies equation 6.186 (and by extension equation 6.59).

The Ammonia Still overhead gas rate and distillate volumetric flow rate to Autoclaves 2A and 3A, respectively, are calculated to balance total ammonia around said vessels, such that the concentration of aqueous ammonia in the fourth compartments is the same as plant data. The specification of value for the former flow rate satisfies both equation 6.58 and that required by the gas mixing point (i.e. $F_{\text{NH}_3(g),\text{in}(j)}$; see Section 6.9.2) directly upstream from Autoclave 2A Compartment 1, while the same specification for the latter flow rate satisfies that required by the slurry mixing point object (i.e. $Q_{\text{in}(j)}$; see Section 6.9.1) directly upstream from Autoclave 3A.

There is functionality for expressing both tank and thickener ammonia evaporation rate (see Section 6.6), however, in the actual process only Thickeners 1 and 2 are expected to vent anything worthy of consideration (as mentioned in Chapter 3). The Thickener 2 evaporation rate is calculated to balance total ammonia around said vessel, such that the aqueous concentration of ammonia is the same as plant data. The Thickener 1 evaporation rate is handled in the model effectively via an evaporation flow from Tank 2, which tends to balance ammonia around the two process units the best;
this may be a result of the assumption that the thickener behaves as a simple slurry mixer and solid-liquid separator in series. The Tank 2 evaporation rate is calculated to balance total ammonia around said vessel, such that the aqueous concentration of ammonia is the same as plant data. What these two evaporation rates ensure is that the ammonia concentration in the second stage leach feed and total leach pregnant liquor discharge are the same as plant data, which complements the fact that autoclave discharge ammonia content is the same as plant data. The evaporation rate for all other tanks and thickeners is zero. The specification of evaporation rate values for all tanks and thickeners satisfies equation 6.136.

Aside from autoclave compartment temperature, the only other temperature measured is that of the Thickener 2 feed. Given this, in order to estimate the trim cooler discharge temperatures it is assumed that the difference in temperature between the feed and discharge of all trim coolers is the same, where the feed temperature is taken as that of the fourth compartment of the upstream autoclave. That temperature difference is estimated such that the Thickener 2 feed temperature is the same as plant data. The specification of discharge temperature values for all trim coolers satisfies equation 6.156.

Volumetric flow rate data is the only variable with which reliability is questioned. Data is considered unreliable if it is either too erratic to generate a suitable pseudo-steady-state value via the averaging procedure discussed previously, or if its pseudo-steady-state value does not allow a meaningful mass balance around the process unit it reports to or from; if the former is true, the latter is typically true also. The flow rate of MFL-to-Tank 1 and the underflow rate for Thickeners 1, 2 and 2W are the only variables listed in Table 7.3 with which such cases exist, and each are estimated in order to satisfy mass balance. The flow rate of MFL-to-Tank 1 is calculated to balance the total mass around Tank 1, while the underflow rates for Thickeners 1 and 2W are calculated to balance the total mass around Tank 2 and Thickener 2W, respectively. The underflow rate for Thickener 2 is calculated to balance total ammonia around Thickener 2W and Tank 3, such that the concentration of aqueous ammonia in Tank 3 is the same as plant data.
It is important to recognise that pseudo-steady-state data will always result in mass imbalance around unit operations, and thus must be corrected. This is best done through independent mass balances (which are detached from those in the process model) around appropriate units. An overall mass balance would highlight any inaccuracies in volumetric flow rate or slurry density data, while component mass balances would expose inaccuracies in concentration data. If one variable around each key process vessel cannot be identified as unreliable and then calculated on the basis of residual data to satisfy mass balance, then another approach must be taken. One such method could be the collective adjustment of stream property values (e.g. via some error minimisation procedure) such that steady-state elemental balances can be satisfied. This approach requires, however, that the mass of every principal component flowing in and out of the unit is measured. In the present process, measurement around none of the central process vessels (i.e. autoclave, tank, thickener or trim cooler) satisfies said requirement, and so the approach discussed in the previous paragraph was the only option available in this work.

All equations used in the calculations discussed in this subsection are developed on the basis of mass balance and are programmed as flowsheet constraints. The concentration of ammonia is the same as plant data for all autoclave discharges (i.e. fourth compartments), Tanks 2 and 3, and Thickener 2. Although the concentration of ammonia in Tank 1 may be compared against plant data, said variable is not measured in Thickeners 1 or 2W.

7.4 Parameter Estimation

Parameter estimation is the penultimate phase of the model development, and is an exercise that should be performed during the construction of any industrial process model. For the modelling in this work, the parameter estimation resides in determining the unknown rate constant pre-exponential factors for selected kinetic rate laws that were highlighted both in Chapter 4 and the previous chapter. This is a result of inadequate experimental determination of kinetic data in the literature for those respective chemical reactions. The parameter estimation exercise will select the best
value of pre-exponential factor that aligns plant data with model output across all three leaching stages.

(It should be noted that an exercise of this nature should be considered by the modeller even when kinetic raw laws are known from prior experimentation, as there is no guarantee that chemical behaviour in the industrial process will mimic those in the laboratory. This may not necessarily be of the form of replacing existing rate law parameters, but could involve the introduction of ancillary parameters to accommodate the intended effect. After all, the objective of industrial process modelling is to develop a simulation tool that is capable of imitating actual plant behaviour.)

The estimation exercise was carried out to determine a value for all unknown rate law parameters: \( k_{0, \text{NiS}}^{\text{III}} \), \( k_{0, \text{CuS}}^{\text{III}} \), \( k_{0, \text{CoS}}^{\text{III}} \), \( k_{0, \text{FeS}}^{\text{I}} \), \( k_{0, \text{NiS}}^{\text{I}} \), \( k_{0, \text{CuS}}^{\text{I}} \), \( k_{0, \text{FeS}}^{\text{I}} \), \( k_{0, \text{SO}_4^{2-}} \), and \( k_{0, \text{SO}_4^{2-}} \). Plant data was collected by this author from refinery databases and prepared in the manner outlined in Section 7.3.1 for 12 different periods over a three-and-a-half-year time frame, the set of which encompasses a range of different operating conditions, including matte feed rates, mineralogical compositions and particle size distributions. For some periods, a portion of first stage feed tank discharge slurry bypasses the first stage leach and reports to the second stage feed tank; this is referred to as the ‘matte-bypass stream’ (see Figure 3.1). The plant data and leach process model were used to arrange 12 estimation experiments, in which the 10 parameters listed above were the only unknowns. The key characteristics of the plant data are given in Table 7.5; the data in column 2 refers to the solids flow rate, not slurry flow rate. A total of 288 model input variables and parameters were used to establish each experiment.

The parameter estimation was performed manually. Each unknown parameter – with the exception of \( k_{0, \text{FeS}}^{\text{III}} \) and \( k_{0, \text{FeS}}^{\text{I}} \) – was paired with either the relative error (between model output and plant data) of a single process variable or the average relative error of a combination of several process variables. The pairings were pursued in such a way that the parameter is granted the most influential impact on the process, and in each experiment the values of the parameters were adjusted so that their pairs
(i.e. the relative errors) were minimised (with the exception of the unsaturated sulphur oxidation-related parameters). $k^{(\text{III})}_{0,\text{NiS}}$ was coupled with the arithmetic mean of the relative errors of the first stage leach discharge, second stage leach discharge, and Thickener 2 overflow (i.e. total leach discharge) nickel concentrations, as well as the relative errors of the first stage and second stage leach nickel extractions; that is, the $k^{(\text{III})}_{0,\text{NiS}}$-pair is the arithmetic mean of the five relative errors. $k^{(\text{III})}_{0,\text{CuS}}$ and $k^{(\text{III})}_{0,\text{CoS}}$ were each coupled with the arithmetic mean of the relative errors of the Thickener 2 overflow concentrations and second stage leach metal extractions for copper and cobalt, respectively. $k^{(\text{I})}_{0,\text{NiS}}$, $k^{(\text{I})}_{0,\text{CuS}}$ and $k^{(\text{I})}_{0,\text{CoS}}$ were each coupled with the arithmetic mean of the relative errors of the Autoclave 3A discharge concentrations and third stage leach metal extractions for nickel, copper and cobalt, respectively. $k^{+}_{0,\text{SO}_{4}^{2-}}$ and $k^{+}_{0,\text{SO}_{4}\text{NH}_{4}^{2-}}$ were coupled with the relative errors of the Thickener 2 overflow BV and ammonium sulphamate concentration, respectively, and were adjusted so that said errors were no greater than 0.5 percent. Although ammonium sulphamate concentration is not frequently measured on site, it is typically known to be around 10 percent of the AmSul concentration in the same stream and was estimated accordingly.

The mineral rate law parameter pairs were selected as such because (as will be discussed in more detail later in the chapter; see Section 7.6.1) the first and second stage leach processes (except the second stage leach final autoclave compartments) exhibit chemical environments in which copper(I) is present in solution (i.e. a Type III leaching situation), while in the outlying second stage compartments and in the third stage leach process dissolved oxygen is present in solution (i.e. a Type I leaching situation). The selection of unsaturated sulphur oxidation rate law parameter pairs is clear-cut.

It is difficult to estimate the parameters for pyrrhotite oxidation in a manner like that for the other sulphide minerals (or otherwise), given that the net dissolution rate for iron is zero (as discussed in Chapter 4; see Section 4.3.5). However, it is known in this process that cobalt is the least reactive of the value metals (followed by copper, and then nickel), and it has been demonstrated elsewhere [207] for ammonia-ammonium sulphate buffered solutions that pyrrhotite is much less reactive than covellite. This suggests that,
of all the sulphide minerals in this process, pyrrhotite would most likely react at a rate closest to that of sycoporite. Therefore, $k_{0, FeS}^{(III)}$ and $k_{0, FeS}^{(I)}$ were estimated on the basis that the conversions for pyrrhotite and sycoporite are the same:

$$k_{0, FeS}^{(i)} = \frac{\rho_{FeS}}{\rho_{CoS}} \frac{M_{CoS}}{M_{FeS}} k_{0, CoS}^{(i)} \quad (7.2)$$

where $i = \{I, III\}$. Given that the chemistry (as considered in the model) is not influenced by the composition of iron in the solids or aqueous phase, the estimation approach taken here is deemed acceptable.

The parameter estimation results are given in Table 7.6. The data for $k_{0, NiS}^{(III)}$, $k_{0, CuS}^{(III)}$ and $k_{0, CoS}^{(III)}$ is good. All values are less than two standard deviations away from the mean and roughly 60 percent of the data is less than one standard deviation away. This has positive implications for the accuracy of variables with which each parameter was paired. The data for $k_{0, SO_{3}^{2-}}^{*}$ and $k_{0, SO_{3}NH_{2}}^{*}$ also indicates a good correlation.

The data for $k_{0, NiS}^{(I)}$, $k_{0, CuS}^{(I)}$ and $k_{0, CoS}^{(I)}$ is not as encouraging. Given that the latter values cater predominantly for conditions in the third stage leach, where particles are effectively unreactive due to the small surface area that they exhibit, large changes in the reaction rate constant will bring about only a small change in mineral conversion. Moreover, metal concentrations in the third stage autoclave are related more to pre-mixing than they are to reaction in the vessel itself. Therefore, a lack of commonality of pre-exponential factors between differing data sets is to be expected. The values of 0.278 m s$^{-1}$ and 0.185 m s$^{-1}$ were set as lower limits for millerite and sycoporite when necessary, respectively, to circumvent issues with model stability. The values of 6.944 m s$^{-1}$ and 13.89 m s$^{-1}$ were set as upper limits for millerite and covellite, respectively, for the situation in which the relative error would never be minimised (regardless of how large the parameter was adjusted). The fact that these limits appear frequently suggests that a poor correlation exists with the variables with which each parameter was paired.
Table 7.5: Key Characteristics of Plant Data used for Parameter Estimation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Matte Feed Rate (tpd)</th>
<th>Data Collection Period (days)</th>
<th>Ni Composition in Matte (wt.%</th>
<th>Particles Passing 106 μm (wt.%</th>
<th>Ni Concentration in CBF (g L(^{-1}))</th>
<th>Special Comments</th>
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<td>91.86</td>
<td>103.2</td>
<td>-</td>
</tr>
<tr>
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<td>65.11</td>
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<td>-</td>
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<td>87.17</td>
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<td>100.5</td>
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### Table 7.6: Parameter Estimation Results

<table>
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<tr>
<th>Experiment</th>
<th>$k_{0,\text{NiS}}^{(\text{III})}$ (mol$^{1/2}$ m$^{1/2}$ s$^{-1}$)</th>
<th>$k_{0,\text{CuS}}^{(\text{III})}$ (mol$^{1/2}$ m$^{1/2}$ s$^{-1}$)</th>
<th>$k_{0,\text{CoS}}^{(\text{III})}$ (mol$^{1/2}$ m$^{1/2}$ s$^{-1}$)</th>
<th>$k_{0,\text{NiS}}^{(\text{l})}$ (m s$^{-1}$)</th>
<th>$k_{0,\text{CuS}}^{(\text{l})}$ (m s$^{-1}$)</th>
<th>$k_{0,\text{CoS}}^{(\text{l})}$ (m s$^{-1}$)</th>
<th>$k_{0,\text{SO}^2}^*$ (m$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$k_{0,\text{SO},\text{NH}_3}^*$ (m$^6$ mol$^{-2}$ s$^{-1}$)</th>
</tr>
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<td>1</td>
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<td>9.444 x 10$^{-9}$</td>
<td>3.069 x 10$^{-13}$</td>
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<td>2</td>
<td>105.85</td>
<td>22.84</td>
<td>16.10</td>
<td>6.944</td>
<td>13.89</td>
<td>0.185</td>
<td>8.639 x 10$^{-9}$</td>
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<td>21.08</td>
<td>16.69</td>
<td>0.278</td>
<td>13.89</td>
<td>0.185</td>
<td>9.722 x 10$^{-9}$</td>
<td>3.361 x 10$^{-13}$</td>
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<td>4</td>
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<td>29.87</td>
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<td>0.278</td>
<td>13.89</td>
<td>0.185</td>
<td>1.319 x 10$^{-8}$</td>
<td>4.222 x 10$^{-13}$</td>
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<td>7.78</td>
<td>1.111</td>
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<td>12.30</td>
<td>22.84</td>
<td>0.278</td>
<td>0.97</td>
<td>0.556</td>
<td>1.069 x 10$^{-8}$</td>
<td>3.556 x 10$^{-13}$</td>
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<tr>
<td>8</td>
<td>133.52</td>
<td>26.35</td>
<td>30.74</td>
<td>6.944</td>
<td>5.69</td>
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<tr>
<td>9</td>
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<td>35.14</td>
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<td>6.944</td>
<td>5.83</td>
<td>0.833</td>
<td>7.389 x 10$^{-9}$</td>
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<td>10</td>
<td>149.33</td>
<td>10.54</td>
<td>18.16</td>
<td>0.278</td>
<td>1.08</td>
<td>0.694</td>
<td>9.972 x 10$^{-9}$</td>
<td>3.500 x 10$^{-13}$</td>
</tr>
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<td>157.24</td>
<td>34.26</td>
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<td>8.61</td>
<td>0.158</td>
<td>9.944 x 10$^{-9}$</td>
<td>3.625 x 10$^{-13}$</td>
</tr>
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</table>

| Average    | 132.64           | 23.64            | 19.81            | 0.278$^a$        | 13.89$^b$        | 0.526            | 1.028 x 10$^{-8}$ | 3.572 x 10$^{-13}$ |

$^a$ Taken as the most commonly occurring value.

$^b$ Taken as the upper limit value.
The ultimate number to be used for each parameter in subsequent modelling and simulations is the arithmetic mean of all 12 values (except where indicated), displayed in bold at the bottom of Table 7.6. The estimation of $k_{0,SO_2^{2-}}^*$ and $k_{0,SO_{3,\mathrm{NH}_2}}^*$ satisfies equations 6.93 and 6.94, while the evaluation of $k_{0,i(x^*)}^{(\mathrm{III})}$ and $k_{0,i(x^*)}^{(1)}$ satisfies equation 6.129.

On a point of note, it is important to realise that the above parameter estimation procedure has brought about two outcomes. The first (and most obvious) is the complete description of appropriate mineral and sulphur oxidation rate laws. The second is the collective absorption of all modelling uncertainties. That is to say, given that elements of process modelling will always be less than ideal (e.g. the calculation of oxygen solubility or the volumetric mass transfer coefficient), the magnitude of the discrepancy (whatever it is) will be incorporated communally into the values of the parameters that are being estimated. So, the parameter estimation procedure implicitly brings about the minimisation of collective model error, and in this case it is in the form of specifying unknown rate law parameters. Having said this, it is unlikely that the same values determined here for the latter would be reproduced in the laboratory.

### 7.5 Model Validation

In order to validate the model, it is necessary to compare its performance against a host of data acquired from the plant. This data should include variations in the most significant changes to normal operating conditions, particularly the solids throughput (i.e. the matte solids feed rate), but also the mineral composition and particle size distribution of the feed material. Whilst the estimation of unknown parameters has produced a complete model that can approximate plant behaviour, the model output must be judged against data that is independent of that employed for estimation. This provides for a neutral assessment of the strengths and weaknesses of the model.

Plant data was collected (again, by this author from refinery databases and prepared in the manner outlined in Section 7.3.1) for 24 different periods over a four-year time frame, each of which represents process operation under differing conditions.
Not all of the periods conform to normal operating conditions. In some, the matte-bypass stream is active, while in others, at least one autoclave is offline; specifically, the latter is true when the matte solids feed rate is less than 300 tpd. In the case that Autoclave 2A is offline, the Ammonia Still overhead gas is re-directed to Autoclave 1A, while in all other cases only the feed and discharge rates are affected (which are simply taken to be zero). The key characteristics of the plant data for each validation simulation are given in Table 7.7; like in Table 7.5, the data in column 2 refers to the solids flow rate. A total of 288 model input variables and parameters were used to establish each simulation in which all process vessels are active.

The validation is centred on data comparison at four key points in the process: the first, second and third stage leach discharges and the pregnant liquor discharge (i.e. copper boil feed). The chief process variables considered are the concentrations of nickel, copper, cobalt and AmSul, the BV, and the (cumulative) extractions of nickel, copper and cobalt. (Ammonia concentration is not considered, given its widespread use in variable estimation.) AmSul concentration is estimated by assuming that the molecular weight of all ammonium salts is the same as ammonium sulphate:

$$C_{AmSul} = 0.5 C_{NH_4^+} M_{(NH_4)_2SO_4}.$$  

The BV is calculated from constituent relationships given in Chapter 3:  

$$BV = 41 C_{S_2O_3^{2-}} + 26 C_{S_2O_4^{2-}}.$$  

For a series of reactors, the cumulative conversion (or extraction) in the Nth reactor, $$X_N^\Sigma$$, is calculated with the following recursive formula: $$X_N^\Sigma = X_{N-1}^\Sigma + (1 - X_{N-1}^\Sigma) X_N$$, where $$X_N$$ is conversion (or extraction) relative to the Nth reactor feed and $$X_0^\Sigma = X_0 = 0$$.

The relative errors for each of the principal process variables under consideration were determined for each of the 24 simulations. These values were used to calculate three sets of average relative errors – representing three levels of validation – in order to establish single values with which to assess the accuracy of each variable. The average relative errors were calculated over three matte feed rate ranges: 300-355 tpd (Simulations 11-24), 240-355 tpd (Simulations 3-24) and 140-355 tpd (Simulations 1-24). The results are given in Table 7.8, while the raw data used to calculate said
averages is given in Appendix H. In the table, the three columns underneath each measuring point heading refer to each of the preceding simulation ranges (in that order). The strength or weakness of each variable (in terms of its error) is defined relative to the objectives of the model. A grading system of “excellent” (0-5% error), “very good” (5-10% error), “good” (10-15% error), and “satisfactory” (15-20% error) is defined for this work.

The most relevant data to focus on initially is that representing the range 300-355 tpd (i.e. the left-most column data for each measuring point in Table 7.8), because this is the range over which the parameter estimation was carried out. The performance of the metal-related variables is related jointly to the proposed mineralogy of the feed matte (Section 3.2) and the mineral leaching chemistry (Section 4.3.3) assumed to be taking place. The nickel concentration and extraction data performs very well at all key points in the process, suggesting that nickel is most likely present in the feed material as awaruite and heazlewoodite, the latter of which leaches according to a two-stage mechanism in which millerite is an intermediate, and does so in accordance with the chemical reaction-controlled shrinking core model. With the exception of the third stage leach, copper concentration and extraction perform well also. It is probably the case that chalcocite is a feed material, covellite is an intermediate leach product, and the rate-limiting mechanism is the same as that for millerite.

The cobalt-related variables do not perform well. The large concentration errors over all leach stages, large extraction error in the first stage leach, yet small extraction error in the second and third stages, indicates that the mineral conversion is disproportionately represented over the first two stages (at least). Two explanations may be offered: one related to mineral type and the other to chemistry.

Sycoporite is not a mineral typically found in nickel mattes (e.g. see [83]). It was identified as a matte mineral (in Chapter 3) to account for the presence of cobalt, and was assumed to do so as a simple sulphide. The cobalt-bearing mineral may take on another form, or, it could be the case that some or all of the cobalt is distributed amongst one or more of the residual minerals in the matte. The dissolution of cobalt
Table 7.7: Key Characteristics of Plant Data used for Model Validation

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<tr>
<th>Simulation</th>
<th>Matte Feed Rate (tpd)</th>
<th>Data Collection Period (days)</th>
<th>Ni Composition in Matte (wt.%)</th>
<th>Particles Passing 106 μm (wt.%)</th>
<th>Ni Concentration in CBF (g L⁻¹)</th>
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<td>Process Variables</td>
<td>Measuring Point (Simulation Range)</td>
<td>1st Stage Leach</td>
<td>2nd Stage Leach</td>
<td>3rd Stage Leach</td>
<td>Copper Boil Feed</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
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<tr>
<td></td>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>Concentrations</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>2.88</td>
<td>3.09</td>
<td>4.97</td>
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<td>- Cobalt</td>
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<td>21.08</td>
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<td>37.82</td>
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<td>Bromate Value (BV)</td>
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<td>12.51</td>
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<td>-</td>
<td>-</td>
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<td>Metal Extraction</td>
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<td>5.94</td>
<td>6.48</td>
<td>1.45</td>
<td>1.63</td>
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<tr>
<td>- Copper</td>
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<td>7.62</td>
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<td>36.02</td>
<td>36.17</td>
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<td>6.73</td>
</tr>
</tbody>
</table>

* Simulation Range (1): 300-355 tpd (Simulations 11-24); Simulation Range (2): 240-355 tpd (Simulations 3-24); Simulation Range (3): 140-355 tpd (Simulations 1-24).
could thus take place via multiple sources and at multiple rates, which would need to be considered accordingly in the model. On the issue of leaching mechanism, however, the chemical reaction-controlled model is still a good first approximation for other rate-limiting regimes, and so it would probably not be the predominant source of error.

The more likely scenario is that cobalt is reacting via supplementary chemistry not accounted for in the model. It was highlighted in Chapter 4 (see Section 4.3.5) that dissolved metals may experience some uptake from solution via adsorption processes that accompany iron oxide precipitation. Cobalt is known to do so in the refinery leach more so than nickel and copper. The same issue has been experienced at the Sherritt nickel refinery. Low cobalt extractions were reported [6] for the leach there, the principal cause of which was the strong and preferential adsorption of cobalt onto hydrated ferric oxide. This chemistry is most likely the cause of disproportionate cobalt extraction in the present process, and thus the source of apparent modelling errors.

As expected from the cobalt rate law parameter estimation criteria (i.e. that pursued for $k^{(III)}_{0,CoS}$), the copper boil feed cobalt concentration error is good, which is consistent with the small second stage leach cumulative extraction error. Modelling errors aside, given that cobalt accounts for less than one percent by mass of the feed matte and, like iron, has no measurable impact on the chemistry, the disparity for cobalt-related variables is negligible.

The BV relative errors in both the first stage leach and copper boil feed are good; the model output for the second stage is zero, whilst no plant data is available for the third stage. The near-equal errors in the first stage leach and copper boil feed are particularly encouraging, given that the BV in the second stage leach discharge is zero, and thus is what one would expect to see. The data suggests that appropriate assumptions were made in the chemistry and model development on the subject of the sulphur oxidation mechanism and corresponding kinetic rate laws (as discussed originally in Chapter 4 and refined in the previous chapter).

The AmSul concentration error data does not target any particular element of the parameter estimation, but rather offers a more general assessment of the model as a
whole, given that changes in the concentration variable itself is a function of both mixing and chemistry. The error data is low in all points of the process (except for the third stage leach), which offers a positive assessment. If one element of the modelling is to be credited then it would be the calculation of liquor density (equation 6.121), which is approximated with the use of the ammonium sulphate solution density model. The strength of the density model is also evident in the favourable comparison of nickel concentration and extraction, which would not be the case if liquor density was not appropriately represented.

There is a common element of large concentration errors in the third stage leach, which can be traced to the lack of commonality throughout the estimation experiments of the Type I kinetic parameters (i.e. those servicing that leaching stage; more on this in the next section). However, the AmSul concentration error is comparable in value to other errors, which suggests that the issue may also reside elsewhere, given the very good performance of AmSul concentration elsewhere in the leach. Nonetheless, the third stage, as will be explained in the next section, is relatively inconsequential in terms of overall leach performance.

In general, with the exceptions of the third stage leach data and cobalt data, all points in the process perform well, which is a confirmatory outcome since these are the most significant areas of the process in terms of overall leach performance. The strong performance is also an indication of the aptness of the parameter estimation method. In terms of the first stage leach, second stage leach and copper boil feed, and not including cobalt-related data, a general model accuracy of greater than 84 percent and 93 percent can be taken in terms of the concentrations and extractions considered, respectively.

It is interesting to note that there does not seem to be any correlation between the data collection period and model performance (which may be done by comparing the characteristic data of Table 7.7 with the raw error data of Tables H.1 – H.5), suggesting that the minimum three-day period of steady flows stipulated previously (Section 7.3.1) for useful data collection is sufficient for a meaningful simulation. Moreover, and although it is not possible to corroborate this with the data presented, there seems to be
a correlation between poorer model performance and more recent time periods, which may be the source of progressively less-frequent on-site instrument testing and maintenance.

In addition to the matte feed rate range considered above, it is instructive to also examine the average relative errors over a wider range of matte flow rates, because this may have implications for model accuracy when simulating outside the parameter estimation range. The centre and right-most column data for each measuring point in Table 7.8 represents the ranges 240-355 tpd and 140-355 tpd, respectively. As expected, the model generally does not perform as well the further away simulations conditions are from the parameter estimation range. However, with the notable exception of second stage leach cobalt concentration, the drop in accuracy is not all that great, which signifies the robustness of the model under varying operating conditions. The model would most likely be capable of simulating matte feed rates higher than 355 tpd with comparable accuracy.

Several other variables of importance at various points in the leach may also be used to measure the strength of the model. These include: (1) Thickener 1 overflow rate, (2) the copper boil process feed rate, (3) the total leach ammonia feed rate (i.e. anhydrous ammonia and recycled ammonia), and (4) ammonia concentration in Tank 1. Like above, the same 24 simulations were used to calculate average relative errors over the same three matte feed rate ranges. The results are given in Table 7.9, while the raw data used to calculate said averages is given in Appendix H.

Once again, the most relevant data to focus on initially is that representing the range 300-355 tpd, and all variables perform very well. The Thickener 1 overflow rate and copper boil feed rate errors offer a means for measuring the strength of all calculated flows in the first and second stages. The former and latter errors provide a direct appraisal of the first and second stage discharge slurry flow rates, respectively, which are linked to how autoclave feed and vent gas flow rates are calculated. The calculation of autoclave flows (slurry or gas, feed or discharge) is related to almost every aspect of the leaching reactor modelling, including stoichiometry and kinetics,
condensable gas (i.e. ammonia and water) pressure, oxygen solubility, volumetric mass transfer coefficient and liquor density. The Thickener 1 overflow rate error also offers a direct assessment of the estimation method (and thus relative error) for the underflow rate of the same vessel. Likewise, the copper boil feed rate error also offers a direct evaluation of the estimation method for the Thickener 2 underflow rate.

The quality of the total leach ammonia feed rate error brings together much of what has already been said. Aside from submitting a measure for the calculation of both anhydrous and Ammonia Still discharge ammonia, in doing so it supports that aspect of the leaching reactor modelling associated with the calculation of flows. This has already been performed for first and second stage leach autoclaves, however, what is distinct here is that the calculation of Ammonia Still distillate is related to the flows concerning Autoclave 3A, the slurry feed flow of which is linked furthermore to the estimation of the Thickener 2W underflow rate. The concentration of ammonia in Tank 1 is the only point in the process where ammonia concentration plant data was not used as a means for estimating variables, and so the average relative error of this variable offers a measure for the effectiveness of that estimation method.

Comparison of the 300-355 tpd average relative errors with those for the 240-355 tpd and 140-355 tpd ranges does not invoke the same kind of disparity as before. This is probably due to the fact that flow rates are less affected by the kinetic parameter values than are concentrations and metal extractions. This is encouraging in terms of model accuracy for simulating matte feed rates higher than 355 tpd.

Finally, two special data sets are available for model comparison: (1) the vent gas composition for Autoclaves 1A and 1B at 320 tpd matte feed rate, and (2) the overall cooling duties for Autoclaves 1A, 1B and 2A, each under different matte feed rates. The data sets were collected by process staff during a special data survey at the refinery, the times of which are removed from any of the simulation periods listed in Table 7.7. Nonetheless, a comparison with data from said simulation periods can be constructive.

In Table 7.10, average relative errors for the vent gas data is presented for the comparisons of 320 tpd-only simulations (i.e. 13 through 18 in Table 7.7), as well as for
the same matte feed rate ranges displayed in Tables 7.8 and 7.9. (Simulation periods other than those for 320 tpd were included given that gas composition is an intensive property, i.e. it is scale invariant.) The most relevant data to focus on is that in the second column (i.e. 320 tpd data), which exhibits a very good comparison. Third column data also demonstrates a favourable comparison, which caters for those periods within the parameter estimation range. The remaining data is mostly good, with the exception of that for ammonia. Considering that the data collection time periods are dissimilar, the outcome of the comparison is a positive one for the model. Around Autoclaves 1A and 1B, the gas composition data can be used to validate the ammonia balance (which includes the calculation of ammonia feed rates, consumption rates, ammine speciation and ammonia pressure) and the oxygen balance (i.e. the calculation of oxygen consumption rates, which are related to effectively all aspects of the chemistry).

In Table 7.11, relative errors for the cooling duty data is presented for the comparisons of only those simulation periods that have the same matte feed rates; unlike gas composition, cooling duty is an extensive property. The error data is very good (with the exception of that for Simulation 9). This indicates a favourable energy balance calculation for leaching reactors and, by extension, a suitable collection and use of thermodynamic data (i.e. those given in Table 6.1) for computing heats of reaction.

### 7.6 Simulation Results and Discussion

The simulation results given in this section are based on the set of operating conditions defined by Simulation 16, which makes for the best examination of standard operation. An analysis of both fixed and variable conditions is presented, the main concern of which is an appraisal of steady-state chemistry. Any assumptions made during the development of the latter (in Chapters 4 or 6) are also addressed. The simulation data represents a suite of key leach performance-determining variables and allows for a comprehensive appraisal at the compartment, autoclave and leaching stage levels. The majority of variables presented are those that are either not measured at all in the process (such as data for Compartments 1 – 3 in all autoclaves, with the exception of
Table 7.9: Average Relative Errors (%) for Supplementary Process Variables

<table>
<thead>
<tr>
<th>Process Variables</th>
<th>Matte Feed Rate Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300-355 tpd</td>
</tr>
<tr>
<td>Thickener 1 overflow rate</td>
<td>4.91</td>
</tr>
<tr>
<td>Copper boil feed rate</td>
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</tr>
<tr>
<td>Total leach NH₃ feed rate</td>
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</tr>
<tr>
<td>Tank 1 NH₃ concentration</td>
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</tbody>
</table>

Table 7.10: (Approximate) Average Relative Errors (%) for First Stage Leach Vent Gas Molar Composition

<table>
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<th>Matte Feed Rate Range</th>
</tr>
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<td></td>
<td>320 tpd</td>
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<tr>
<td>Autoclave 1A vent</td>
<td></td>
</tr>
<tr>
<td>- Ammonia</td>
<td>10.75</td>
</tr>
<tr>
<td>- Oxygen gas</td>
<td>8.46</td>
</tr>
<tr>
<td>- Nitrogen gas</td>
<td>7.06</td>
</tr>
<tr>
<td>Autoclave 1B vent</td>
<td></td>
</tr>
<tr>
<td>- Ammonia</td>
<td>3.33</td>
</tr>
<tr>
<td>- Oxygen gas</td>
<td>2.33</td>
</tr>
<tr>
<td>- Nitrogen gas</td>
<td>7.30</td>
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</table>

Table 7.11: (Approximate) Relative Errors (%) for Overall Autoclave Cooling Duties

<table>
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<th>Matte Feed Rate (tpd)</th>
<th>Autoclave</th>
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<tr>
<td></td>
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<td>280</td>
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<td>9</td>
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<td>11</td>
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<td>19</td>
<td>330</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>330</td>
<td>-</td>
</tr>
</tbody>
</table>
temperature), those that are too arduous to measure (such as total gas pressure or cooling duty), or those that cannot be measured (such as the copper(II)-to-total copper ratio or the speciation of nickel ammine, the latter of which is quantified in the tables via the effective coordination number). It is with this in mind, in part, that the potency of the model may be evaluated.

### 7.6.1 Fixed Conditions

Nickel matte (90 pct -106 µm particulate material) at a rate of 320 tpd is fed to the process. The elemental composition (by mass) of the feed matte is 65.65% Ni, 2.43% Cu, 0.81% Co, 6.07% Fe and 23.59% S. The mineralogical composition (by mass) was thus determined to be 7.57% Ni\textsuperscript{0}, 79.23% Ni\textsubscript{3}S\textsubscript{2}, 3.04% Cu\textsubscript{2}S, 1.25% CoS, 3.65% Fe\textsuperscript{0}, 3.81% FeS, and 1.45% SiO\textsubscript{2}. The simulation results for fixed operating conditions in all three leaching stages are given in Tables 7.12 – 7.15; this represents the precise data used in the validation process. In Table 7.12, compartment data is partitioned to demonstrate the difference in operation of first stage leach autoclaves. For each compartment heading, the left column refers to Autoclave 1A data, while the right refers to 1B data. In Table 7.13, due to the general similarity in operation of all autoclaves in the second stage leach, conversion and extraction data is a weighted average (based on the second stage leach feed distribution) and all remaining compartment data is an arithmetic mean of that for Autoclaves 2A, 2B and 3B (unless specified otherwise). Some variable values for Autoclave 2A are sufficiently different to warrant specific mention, and are listed in Table 7.14. Such discrepancy is the source of both the type of ammonia feed (Ammonia Still overhead gas) and the injection point (the first compartment only). Said variables are not represented in the averages (in appropriate compartments) given in Table 7.13. The presentation of data in Table 7.15 for Autoclave 3A is clear-cut. In all tables, Compartment 0 refers to conditions in the feed tank of the applicable leaching stage. Concentration data in all tables is adjusted for temperature in accordance with equation 7.1.
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<th>1B/C1</th>
<th>1A/C2</th>
<th>1B/C2</th>
<th>1A/C3</th>
<th>1B/C3</th>
<th>1A/C4</th>
<th>1B/C4</th>
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<td>65.95</td>
<td>75.85</td>
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</tr>
<tr>
<td>Mean residence time (min)</td>
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<td>66.51</td>
<td>56.40</td>
<td>64.21</td>
<td>55.32</td>
<td>63.56</td>
<td>27.33</td>
<td>31.32</td>
</tr>
<tr>
<td>Pulp density (wt.%)</td>
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<td>5.89</td>
<td>5.12</td>
<td>4.38</td>
<td>3.70</td>
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</tr>
<tr>
<td>Metal concentration (g L(^{-1}))</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>8.52</td>
<td>80.52</td>
<td>84.58</td>
<td>95.05</td>
<td>99.87</td>
<td>104.62</td>
<td>109.94</td>
<td>106.07</td>
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<td>- Copper</td>
<td>-</td>
<td>3.31</td>
<td>3.35</td>
<td>3.45</td>
<td>3.53</td>
<td>3.62</td>
<td>3.77</td>
<td>3.64</td>
<td>3.82</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>0.54</td>
<td>0.59</td>
<td>0.62</td>
<td>0.71</td>
<td>0.77</td>
<td>0.83</td>
<td>0.92</td>
<td>0.85</td>
<td>0.96</td>
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<tr>
<td>BV (BV-units)</td>
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<td>354.31</td>
<td>405.26</td>
<td>323.85</td>
<td>311.89</td>
<td>216.42</td>
<td>371.99</td>
<td>249.96</td>
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<tr>
<td>NH(_3):TM (mol mol(^{-1}))</td>
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<td>4.82</td>
<td>4.92</td>
<td>4.83</td>
<td>4.92</td>
<td>4.60</td>
<td>4.37</td>
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<td>NH(_3) pressure (kPa)</td>
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<td>20.99</td>
<td>17.43</td>
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<td>14.84</td>
<td>13.43</td>
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<td>5.47</td>
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<td>O(_2) pressure (kPa)</td>
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<td>37.59</td>
<td>109.91</td>
<td>63.18</td>
<td>117.64</td>
<td>73.19</td>
<td>140.58</td>
<td>86.72</td>
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<td>O(_2) utilisation (%)</td>
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<td>62.40</td>
<td>25.42</td>
<td>34.27</td>
<td>19.50</td>
<td>23.68</td>
<td>8.19</td>
<td>13.95</td>
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<tr>
<td>Cu(II):Cu(T) (mol mol(^{-1}))</td>
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<td>0.53</td>
<td>0.75</td>
<td>0.76</td>
<td>0.82</td>
<td>0.85</td>
<td>0.95</td>
<td>0.93</td>
</tr>
<tr>
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<td>4.58</td>
<td>3.46</td>
<td>3.22</td>
<td>2.61</td>
<td>1.94</td>
<td>1.27</td>
<td>0.88</td>
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<tr>
<td>Metal extraction (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>0.00</td>
<td>57.31</td>
<td>61.18</td>
<td>71.80</td>
<td>76.70</td>
<td>81.60</td>
<td>86.30</td>
<td>83.65</td>
<td>88.65</td>
</tr>
<tr>
<td>- Copper</td>
<td>0.00</td>
<td>54.70</td>
<td>56.21</td>
<td>60.68</td>
<td>63.43</td>
<td>66.24</td>
<td>69.89</td>
<td>67.54</td>
<td>71.74</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>0.00</td>
<td>7.05</td>
<td>9.42</td>
<td>16.53</td>
<td>21.08</td>
<td>25.78</td>
<td>32.13</td>
<td>27.99</td>
<td>35.37</td>
</tr>
<tr>
<td>Sulphur conversion (wt.%)</td>
<td>0.00</td>
<td>25.57</td>
<td>31.71</td>
<td>48.62</td>
<td>56.56</td>
<td>64.53</td>
<td>72.35</td>
<td>67.88</td>
<td>76.26</td>
</tr>
<tr>
<td>Solids conversion (wt.%)</td>
<td>0.00</td>
<td>49.58</td>
<td>53.74</td>
<td>65.20</td>
<td>70.59</td>
<td>75.98</td>
<td>81.28</td>
<td>78.25</td>
<td>83.94</td>
</tr>
</tbody>
</table>
Table 7.13: Simulation Results for the Second Stage Leach (1000 kPa)

<table>
<thead>
<tr>
<th>Process Variables</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (ºC)</td>
<td>45.26</td>
<td>93.94</td>
<td>93.99</td>
<td>90.22</td>
<td>64.99</td>
</tr>
<tr>
<td>Mean residence time (h)</td>
<td>-</td>
<td>4.24</td>
<td>4.21</td>
<td>4.31</td>
<td>2.18</td>
</tr>
<tr>
<td>Pulp density (wt.%)</td>
<td>10.97</td>
<td>6.28</td>
<td>4.71</td>
<td>4.33</td>
<td>4.33</td>
</tr>
<tr>
<td>Metal concentration (g L⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>49.90</td>
<td>78.16</td>
<td>88.98</td>
<td>92.93</td>
<td>93.13</td>
</tr>
<tr>
<td>- Copper</td>
<td>-</td>
<td>3.43</td>
<td>4.56</td>
<td>5.34</td>
<td>5.39</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>0.73</td>
<td>1.61</td>
<td>2.43</td>
<td>3.06</td>
<td>3.07</td>
</tr>
<tr>
<td>BV (BV-units)</td>
<td>-</td>
<td>123.72</td>
<td>40.01</td>
<td>15.89</td>
<td>0.00</td>
</tr>
<tr>
<td>NH₃:TM (mol mol⁻¹)</td>
<td>-</td>
<td>4.94</td>
<td>4.93</td>
<td>4.55</td>
<td>4.53</td>
</tr>
<tr>
<td>Ni ammine coordination no.</td>
<td>-</td>
<td>4.46</td>
<td>4.51</td>
<td>4.24</td>
<td>4.32</td>
</tr>
<tr>
<td>NH₃ pressure (kPa)</td>
<td>-</td>
<td>20.93</td>
<td>22.36</td>
<td>13.81</td>
<td>3.64</td>
</tr>
<tr>
<td>O₂ pressure (kPa)</td>
<td>-</td>
<td>124.06</td>
<td>157.88</td>
<td>181.14</td>
<td>202.63</td>
</tr>
<tr>
<td>O₂ utilisation (%)</td>
<td>-</td>
<td>39.90</td>
<td>19.81</td>
<td>7.47</td>
<td>0.87</td>
</tr>
<tr>
<td>Cu(II):Cu(T) (mol mol⁻¹)</td>
<td>-</td>
<td>0.82</td>
<td>0.95</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>Cooling duty (MW)</td>
<td>-</td>
<td>1.04</td>
<td>0.54</td>
<td>0.03</td>
<td>0.13</td>
</tr>
<tr>
<td>Metal extraction (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>- Nickel</td>
<td>85.53</td>
<td>95.49</td>
<td>99.06</td>
<td>99.88</td>
<td>99.88</td>
</tr>
<tr>
<td>- Copper</td>
<td>69.35</td>
<td>81.46</td>
<td>91.02</td>
<td>96.77</td>
<td>97.09</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>31.22</td>
<td>54.01</td>
<td>74.45</td>
<td>88.99</td>
<td>89.03</td>
</tr>
<tr>
<td>Sulphur conversion (wt.%)</td>
<td>71.77</td>
<td>88.83</td>
<td>96.18</td>
<td>98.80</td>
<td>98.82</td>
</tr>
<tr>
<td>Solids conversion (wt.%)</td>
<td>80.90</td>
<td>92.45</td>
<td>97.42</td>
<td>99.20</td>
<td>99.21</td>
</tr>
</tbody>
</table>

* Average taken for Autoclaves 2B and 3B only. See Table 7.14 for Autoclave 2A data.

Table 7.14: Selected Simulation Results for Autoclave 2A (1000 kPa)

<table>
<thead>
<tr>
<th>Process Variables</th>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃:TM (mol mol⁻¹)</td>
<td>-</td>
<td>7.01</td>
<td>5.64</td>
<td>5.19</td>
<td>5.16</td>
</tr>
<tr>
<td>Ni ammine coordination no.</td>
<td>-</td>
<td>5.41</td>
<td>4.96</td>
<td>4.73</td>
<td>4.84</td>
</tr>
<tr>
<td>NH₃ pressure (kPa)</td>
<td>-</td>
<td>83.38</td>
<td>40.25</td>
<td>24.08</td>
<td>7.02</td>
</tr>
<tr>
<td>O₂ pressure (kPa)</td>
<td>-</td>
<td>109.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O₂ utilisation (%)</td>
<td>-</td>
<td>43.29</td>
<td>17.52</td>
<td>5.81</td>
<td>0.68</td>
</tr>
<tr>
<td>Cooling duty (MW)</td>
<td>-</td>
<td>1.65</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7.15: Simulation Results for Autoclave 3A (950 kPa)

<table>
<thead>
<tr>
<th>Process Variables</th>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>52.95</td>
<td>74.42</td>
<td>79.75</td>
<td>74.72</td>
<td>66.74</td>
</tr>
<tr>
<td>Mean residence time (h)</td>
<td>-</td>
<td>7.38</td>
<td>7.93</td>
<td>8.31</td>
<td>4.21</td>
</tr>
<tr>
<td>Pulp density (wt.%)</td>
<td>30.31</td>
<td>20.77</td>
<td>22.33</td>
<td>23.31</td>
<td>23.53</td>
</tr>
<tr>
<td>Metal concentration (g L(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>27.83</td>
<td>17.07</td>
<td>18.46</td>
<td>19.36</td>
<td>19.57</td>
</tr>
<tr>
<td>- Copper</td>
<td>-</td>
<td>1.51</td>
<td>2.19</td>
<td>2.58</td>
<td>2.69</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>0.72</td>
<td>0.48</td>
<td>0.58</td>
<td>0.65</td>
<td>0.67</td>
</tr>
<tr>
<td>BV (BV-units)</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NH(_3):TM (mol mol(^{-1}))</td>
<td>-</td>
<td>42.63</td>
<td>26.07</td>
<td>18.34</td>
<td>16.71</td>
</tr>
<tr>
<td>Ni ammine coordination no.</td>
<td>-</td>
<td>5.90</td>
<td>5.81</td>
<td>5.74</td>
<td>5.73</td>
</tr>
<tr>
<td>NH(_3) pressure (kPa)</td>
<td>-</td>
<td>213.20</td>
<td>142.59</td>
<td>75.76</td>
<td>50.08</td>
</tr>
<tr>
<td>O(_2) pressure (kPa)</td>
<td>-</td>
<td>147.80</td>
<td>160.57</td>
<td>176.10</td>
<td>183.59</td>
</tr>
<tr>
<td>O(_2) utilisation (%)</td>
<td>-</td>
<td>0.67</td>
<td>0.44</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Cu(II):Cu(T) (mol mol(^{-1}))</td>
<td>-</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Cooling duty (MW)</td>
<td>-</td>
<td>-0.56</td>
<td>-0.36</td>
<td>-0.18</td>
<td>-0.01</td>
</tr>
<tr>
<td>Metal extraction (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>99.88</td>
<td>99.88</td>
<td>99.89</td>
<td>99.89</td>
<td>99.89</td>
</tr>
<tr>
<td>- Copper</td>
<td>97.09</td>
<td>97.99</td>
<td>98.74</td>
<td>99.12</td>
<td>99.22</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>89.03</td>
<td>89.23</td>
<td>89.48</td>
<td>89.65</td>
<td>89.70</td>
</tr>
<tr>
<td>Sulphur conversion (wt.%)</td>
<td>98.82</td>
<td>98.88</td>
<td>98.94</td>
<td>98.98</td>
<td>98.99</td>
</tr>
<tr>
<td>Solids conversion (wt.%)</td>
<td>99.21</td>
<td>99.25</td>
<td>99.29</td>
<td>99.32</td>
<td>99.32</td>
</tr>
</tbody>
</table>

**First Stage Leach**

It is apparent that the first stage leach is where the majority of process chemistry takes effect, representing an environment where highly reactive fresh matte contacts an aqueous ammoniacal-ammonium sulphate solution under moderate temperature and oxygen pressure conditions. (Oxygen pressures for Autoclaves 1A and 1B are 108 and 61 kPa, respectively.) The objective here is to dissolve as much matte as possible whilst maintaining appropriate concentrations of unsaturated sulphur.

Of all the particulate material that enters the leaching process, 81 percent (by mass) is converted in this stage of the operation. This is despite the lower temperatures and pressures, not to mention the fact that its mean residence time is roughly one-quarter that of the second stage and one-eighth that of the third stage. Approximately 70
percent of the CBF liquor is derived from there, and effectively all of the unsaturated oxysulphur species that report to the copper boil process originate there. Almost 80 percent of the total leach anhydrous ammonia supply reports to the first stage, while 75 percent of all oxygen consumption in the leach is witnessed there. Of all the heat removed from the leach via cooling water, 80 percent is observed in said stage.

The most significant difference between Autoclaves 1A and 1B is oxygen pressure, which results from the leach airflow arrangement (as discussed in Chapter 3). Despite receiving less air and operating under an atmosphere of 57 percent of the oxygen pressure of Autoclave 1A, Autoclave 1B is subject to higher mineral conversions and ensuing activity. This is due to the slightly lower allocation of first stage feed slurry relative to that of Autoclave 1A, as can be seen from a comparison of mean residence times. (In Simulation 16, Autoclave 1B temperatures are also higher, augmenting this effect.) What this exemplifies is the robust nature of the process to operate feasibly under low oxygen pressure, which would not be the case if dissolved oxygen was the mineral oxidant.

The data presented for temperature, oxygen pressure and copper(II)-to-total dissolved copper ratio in Autoclave 1B, particularly that for the first compartment, illustrates more so than elsewhere in the circuit the similarity in conditions that exists between this process and the Anaconda-Arbitier process [85, 86] (i.e. 60-90 ºC, 35 kPa oxygen pressure, and significant concentrations of cuprous ammine). Following from Peters’ [84, 85] proposition for the kinetic mechanism in the latter process, said data confirms the proposal made in this work (in Chapter 4) in which the copper(II)/copper(I) redox couple is responsible for driving mineral oxidation in the Sherritt-Gordon ammonia leach.

Compartment activity can be measured by observed changes in concentration, conversion/extraction and cooling duty (accounting for temperature change) between adjacent compartments. (Pulp density is also a useful measure, however, this variable cannot discriminate between reactive and non-reactive solids.) A significant amount of chemistry takes place in the first compartments of the first stage autoclaves, where
roughly 50 percent of all solids conversion in the entire leach takes place. All of the metallic minerals (i.e. Ni$^{0}$, Fe$^{0}$, Ni$_{3}$S$_{2}$ and Cu$_{2}$S) – representing nearly one-third of the feed matte – are completely consumed there (see Appendix F for a confirmation of this assumption), and the highly-positively-skewed leach feed particle size distribution (see Figure 7.1 or Figure D.1) suggests a high reactivity (based on particle size) both for metal sulphides in the feed (i.e. CoS and FeS) and those that form in said compartments (i.e. NiS and CuS). Large increases in metal concentration accompany the high mineral conversions. An exception would be the minor increase in cobalt concentration, which is symptomatic of both the low feed composition of the metal and low conversion of sycoporite. The cooling duties in said compartments account for around 40 percent of that for the entire cascade of reactors in the first stage, which is a figure consistent with the degree of chemistry observed.

The changes in metal concentration observed in the second and third compartments of first stage autoclaves suggest only moderate chemical activity, however, the sulphur conversion and cooling duty data suggests otherwise. The conversion of sulphur in the second and third compartments is roughly 85 and 55 percent of that in the first, and cooling duties account for 30 and 20 percent of that for the whole of each autoclave, all respectively. The majority of heat generation is due to sulphide sulphur oxidation, which explains why the cooling duties in Compartments 2 and 3 are three-quarters and one-half of that in Compartment 1, respectively. When realising that the first compartment is distinct, in that unit conversion of all metallic minerals and a sizeable amount of metal sulphide dissolution takes place, the changes in metal concentration in the following two compartments are suitably aligned with the level of sulphide oxidation. The same cannot be said about the BV.

The BV in any compartment represents a balance between the rate of sulphide sulphur oxidation (i.e. the rate of thiosulphate production) and the rate of unsaturated sulphur oxidation (i.e. the rates of thiosulphate and polythioniate consumption). This relationship, however, is complicated by the fact that the latter rate is related to the amount of unsaturated sulphur in solution and is particularly sensitive to temperature.
Hence, the BV has the potential to be greatly influenced by conditions not only in the present compartment but those in the preceding one(s); this is true for the BV more so than any other dissolved component. Moreover, the measure itself is 1.38 times as high (per mol L$^{-1}$ S) for unsaturated sulphur as thiosulphate than thionionate. It is for these reasons that the BV is difficult to anticipate, and is perhaps the only performance-determining variable in which a comparable behaviour between same-numbered compartments for different, yet typical, operating periods is not guaranteed. Generally speaking, the BV will increase and peak in the first or second compartments, fall, and then rise again in the fourth compartment. The differences in behaviour in each autoclave are due mainly to temperature, which is also responsible for the rise in BV in the fourth compartments.

On the topic of sulphur chemistry, it was proposed in Chapter 4 (Section 4.3.4) that polythionate decomposition could not take place solely via hydrolysis or ammonolysis when copper(II) is present in ammonical solutions, and that most or all of it is oxidised by cupric ammine. Moreover, it was stated that reactions of the latter type would not result in the regeneration of thiosulphate (which is the case for reactions of the former type). Due to insufficient information, it was ultimately assumed in the previous chapter (Section 6.5.1) that polythionate is only oxidised. All appropriate conjecture on the present topic is verified in Appendix G via the use of Simulation 16 data.

Mineral oxidation in the fourth compartment does not take place in any appreciable amount. This is due to both the low temperature and low volume (and thus low mean residence time). Only around 2.5 percent of first stage feed solids is converted there, and 10 percent of overall autoclave cooling takes place (which is required to both offset heat of reaction and reduce the temperature). The low oxidation activity is also apparent from the high copper(II)-to-total copper ratio (i.e. $R_{Cu}$).

The $R_{Cu}$ value is effectively a measure for copper(II)-to-copper(I) ratio, $R_{Cu}/(1 - R_{Cu})$, which is the central driving force for mineral oxidation. The greater the mineral oxidation, the greater the production of copper(I) relative to oxygen reduction,
and thus the lower the value of $R_{Cu}$. The lowest value is observed in the first compartment of Autoclaves 1A and 1B, where mineral oxidation is at its highest rate. Proceeding from first to final compartment, the value becomes progressively bigger in response to the decreasing mineral oxidation rates, approaching its maximum value of one. The value does not attain one, suggesting that only Type III leaching (i.e. leaching in the presence of copper(I)) is witnessed in the first stage.

**Second Stage Leach**

The second stage leach is characterised by higher temperatures and oxygen pressures than the first stage leach, which are required to meet the objectives of dissolving all remaining matte and consuming all unsaturated sulphur. (Oxygen pressures for Autoclaves 2A, 2B and 3B are 155, 161 and 158 kPa, respectively.) The particulate feed is comprised of partially-oxidised solids of much lower effective surface area (relative to the fresh matte of the first stage feed), which renders particle dissolution a more challenging task.

Around 18 percent (by mass) of the total leach feed matte is converted in the second stage leach; just under two-thirds and just over one-quarter of this takes place in the first and second compartments, respectively. Like in Compartments 2, 3 and 4 of the first stage, appropriate metal concentrations and cooling duties are observed following proportionate conversions/extractions. In line with the retarding mineral conversion rates and high temperatures, the BV only ever decreases. In terms of $R_{Cu}$, the behaviour of Compartments 1 and 2 in the second stage resemble those of Compartments 3 and 4 in the first stage, respectively. The third compartments exhibit little activity, whilst in the fourth compartments essentially nothing happens, both a result of the very low effective mineral surface area. In the final second stage compartments the value of $R_{Cu}$ attains unity.

The unit value for $R_{Cu}$ in the fourth compartment of second stage autoclaves suggests that a change in kinetic mechanism has taken place. Leaching no longer takes place in the presence of copper(I), but rather dissolved oxygen (i.e. Type I leaching).
This situation is one in which the capacity for copper(I) to diffuse towards and react with oxygen at the gas-liquid interface can no longer compete with the dissolution and solution mass transport rates of oxygen, a direct result of the very low mineral oxidation rates combined with high oxygen pressure. The strength of mineral dissolution is no longer dependent on the copper(II)/copper(I) ratio, but rather copper(II) concentration (i.e. total copper concentration), and the oxidation of unsaturated sulphur (which in the preceding compartment is, nevertheless, present in only very small quantity) is instantaneous, as indicated by the zero-valued BVs.

All second stage autoclaves typically receive an equal allocation of feed slurry and total leach fresh air, and thus operate under similar conditions. The exception to the latter is the much larger concentration of ammonia in Autoclave 2A Compartment 1, as can be seen (in a data comparison of Tables 7.13 and 7.14) from both the ammonia-to-total metals molar ratio and ammonia pressure. This is expected due to the delivery of the total autoclave feed ammonia (i.e. Ammonia Still overhead gas) into said compartment. In Simulation 16, the autoclave discharge ammonia-to-total metals molar ratio is much higher than those of Autoclaves 2B and 3B, which is more a result of the total amount of ammonia fed than it is the injection point. This certifies that Compartments 2, 3 and 4 of Autoclave 2A also have higher ammonia concentrations. (Slightly higher conversions relative to the remaining second stage autoclaves also prevail; this is not demonstrated in the tables.) For similar fourth compartment ammonia-to-total metals molar ratios, the second and third compartments would have comparable concentrations in all second stage autoclaves.

Given that sulphide minerals are almost completely converted by the end of the second stage, an opportunity exists to examine how they have leached over the course of the eight (effective) leaching reactors that represent the first and second stages. Nickel sulphide has high conversions in both stages, and reacts in a steady manner (accounting for diminishing reactivity due to a decreasing surface area). This is because it has the highest composition and intrinsic reactivity of all the sulphides, and so consumes oxidant at will. Copper and cobalt sulphides, on the other hand, experience a varied reaction status. Due to the presence of nickel sulphide, copper and cobalt
sulphides experience only low-to-medium conversions in the first stage leach. In the second stage, however, improvements in the conversion rates for the latter components are witnessed. This is due to the diminished impact of nickel sulphide, as well as the higher temperatures and greater availability of oxidant. Around 60 and 65 percent of covellite and sycoporite oxidation, respectively, that occurs in the first and second stages takes place in the latter. Roughly one-quarter of millerite oxidation takes place in the second stage.

To demonstrate the evolution of particle size distribution throughout the process, the probability density and cumulative distribution curves for the leach feed and the discharge of each leaching stage for millerite are shown in Figure 7.1. The forward-drifting curves indicate that the mean, mode and median sizes increase as the leaching particles traverse the system of reactors. While this may seem counter-intuitive (given that all particles are getting smaller), the progressively-larger statistical measures is a result of the highly-positively-skewed leach feed distribution, which suggests that a large quantity of particles exist at the small end of the size scale. Since these are the particles that disappear first, larger mean, mode and median particle sizes will follow a period of leaching. The second and third stage leach curves lay on top of one another due to the near-zero conversion of millerite that takes place in Autoclave 3A.

Although the matte-bypass stream is not active in Simulation 16, mention should be made as to the validity of unit conversion of metallic minerals in the first compartments of second stage autoclaves when it is active, which is a modelling assumption for the leaching reactor unit operation model (as addressed in the previous chapter; see Section 6.5.1). The unit conversion of said minerals in first compartments of first stage autoclaves is verified in Appendix F (as mentioned above). Given that leaching conditions are more extreme in the second stage (i.e. temperature, reactant concentration and mean residence time are all higher; see Tables 7.12 and 7.13), it follows that the metallic minerals must react completely in the same way they do in the first stage.
Third Stage Leach

Autoclave 3A operates with much lower temperatures than all preceding autoclaves, but with similar oxygen pressures to those observed in the second stage. (The oxygen pressure is 163 kPa.) The outstanding feature in terms of operating conditions is the large ammonia content, in which the ammonia-to-total metals ratio in the discharge is around 3.7 times higher than in the first stage and 3.5 times higher than in the second. This is due to the ammonia source (i.e. Ammonia Still distillate), which is not used to control ammonia concentration.

The third stage exists to provide a final opportunity to leach the remaining mineral particles. However, given the very small mineral surface at this point, less than one percent (by mass) of the leach feed matte is converted there. (Although nickel leaches throughout the entire autoclave, the precision for extraction values in Table 7.15 cannot demonstrate this for Compartments 3 and 4.) In fact, mineral oxidation is so low that compartments must be heated rather than cooled, as can be observed from the negative
cooling duties. (In the real process, typically only the first two compartments are heated. Despite the fact that heating duties are established by the model for the third and fourth compartments, said duty for the former is much lower than those for the first and second compartments, while said duty for the latter is practically non-existent. This encouraging comparison of model output with actual process behaviour complements earlier (Section 7.5) validations of energy balance calculations and the selection of thermodynamic data in Table 6.1.) It is apparent from the $R_{Cu}$ values that that only Type I leaching (i.e. leaching in the presence of dissolved oxygen) is witnessed in the final stage. This is also the reason that no BVs are reported.

Based on the examination of simulation data (specifically, that of the ammonia-to-total metals ratio), it appears that Autoclave 3A has a dual purpose. In addition to mineral leaching, it also acts as an ammonia evaporator. This serves an important function in the recycling of ammonia lost from the leach and copper boil processes, which is ultimately recovered by the Ammonia Still (as discussed in Chapter 3) and delivered to the third stage as distillate. The distillate is the source of dilution observed, resulting in the decrease in concentrations between the feed tank (i.e. the zeroth compartment) and the autoclave (which is most noticeable for dissolved nickel). The evaporation process itself is quite effective. Almost three-quarters of the ammonia that enters the autoclave (90 percent of which comes from the distillate) exits as vapour via the ventilation system and reports to Autoclave 1A.

Greater than 99 percent of the reactive solids that enter the process are converted over the course of the three-stage leach. Due to the presence of inerts and the precipitation of iron oxides, however, roughly 10 percent of the mass of feed solids is discharged from the third stage and thus reports to the leach residue.

**Evidence of Supplementary Chemistry**

There is the likelihood that a significant portion of cobalt is precipitating from the leach solution as a result of co-precipitation with iron via adsorption onto hydrated ferric oxide. The difference in model simulation incurred by ignoring this chemistry is negligible. This was discussed previously in Section 7.5.
There is evidence in the form of plant data (not disclosed) that a small amount of leaching takes place in Tank 1. Leach solids assays suggest that this is predominantly the case for nickel and copper, and is most likely due to the oxidation of heazlewoodite and chalcocite (given their high reactivity). Solution assays can confirm increases in nickel concentration, but not copper; reasons for the latter will be offered in a moment. This chemistry was not included in the model for two reasons: (1) only small extractions are observed (i.e. typically less than two percent), the inclusion of which would have no more than a minor impact on the mass and energy balance, and (2) said minerals are completely converted in the adjacent unit operations (i.e. the first compartments of the first stage autoclaves), and so ultimately the only impact on the mass and energy balance is contained to those written around Tank 1 itself.

Leach solution assays indicate that the concentration of copper in Tanks 1, 2 and 3 are significantly less than that effectively in the feed streams, which suggests that copper precipitation is occurring. The Tank 1 copper concentration is effectively zero (i.e. less than 0.1 g L\(^{-1}\)), while that for Tank 2 is low (i.e. around 0.1 – 0.5 g L\(^{-1}\)). The Tank 3 concentration is more variable, and will typically take on a value between 0.5 and 1.5 g L\(^{-1}\). Moreover, it is acknowledged that BV measurement is not carried out in said tanks, because of two main reasons: (1) knowledge of its value is inconsequential in terms of process control at those points in the leach, and (2) when measurements have been carried out the BV has always been very low. In Tables 7.12, 7.13 and 7.15, said concentrations and BVs are omitted. It is proposed that copper precipitation is taking place in Tanks 1, 2 and 3 in the same manner discussed in Chapter 4 (see Section 4.2) to explain copper precipitation in leaching autoclaves at low oxidation potential. That is, it is suggested that copper is precipitating as copper sulphides through reaction with unsaturated sulphur compounds according to the chemistry of the Sherritt-Gordon copper boil process (see equations 2.5 – 2.9).

Although the above proposal cannot be validated beyond dispute, it is possible to investigate the effects of such chemistry using Simulation 16 data. However, before this can be carried out some assumptions about the kinetics of reactions 2.5 – 2.9 are required, since their rate laws are unknown. The following is assumed: (1) reaction 2.5
is slow, which is effectively what is assumed in the autoclave chemistry (i.e. trithionate
does not hydrolyse); (2) the favoured reaction between copper(II) and thiosulphate is
reaction 2.7 rather than reaction 2.8, given that it results in the precipitation of copper as
opposed to the reduction of copper(II) to copper(I), which is an outcome more
consistent with the degree of instability of the metal; (3) following from the previous
point, reaction 2.8 is slow compared to reaction 2.7; (4) reaction 2.9 is slow, given that
reaction 2.8 is slow and that the concentration of copper(I) in Tanks 1, 2 and 3 is small
relative to that of copper(II). The preceding assumptions suggest that copper
precipitation predominantly takes place according to the stoichiometry of equations 2.6
and 2.7:

$$S_{3}O_{6}^{2-} + Cu(NH_{3})_{4}^{2+} + 2 H_{2}O \rightarrow 2 SO_{4}^{2-} + CuS + 4 NH_{4}^{+} \quad (7.3)$$

$$S_{2}O_{3}^{2-} + Cu(NH_{3})_{4}^{2+} + H_{2}O \rightarrow SO_{4}^{2-} + CuS + 2 NH_{3} + 2 NH_{4}^{+} \quad (7.4)$$

The model calculates the copper concentrations in Tanks 1, 2 and 3 to be 0.83,
2.11 and 1.49 g L\(^{-1}\), while the BVs are calculated to be 7.45, 133.18 and 51.51 BV-units, all respectively. In other words, the preceding values refer to those effectively in
the tank feeds. In each tank, cupric ammine (which is considered to take on the same
molar concentration as total aqueous copper) is the limiting reactant. If reactions 7.3 and
7.4 go to completion (as would be necessary to bring about the very low BVs observed
for the tanks), then all thiosulphate and trithionate would be consumed in each tank, and
the BVs would be zero. The residual copper concentrations in Tanks 1, 2 and 3 would
be 0.73, 0.38 and 0.82 g L\(^{-1}\), respectively. The latter two concentrations are consistent
with plant observations, while the former is not. This may be explained by the mineral
oxidation taking place in Tank 1.

Heazlewoodite and chalcocite require an oxidant, which would be cupric ammine.
If we assume that the residual copper (specified above) for Tank 1 is consumed
completely via reaction with heazlewoodite and chalcocite according to equations 6.7
and 6.9, respectively, and we assume furthermore that the two minerals have the same
conversions, then said conversion is calculated via an appropriate mass balance on
copper(II) to be 0.81 percent. This value is in agreement with plant observations.
For the above mechanism to explain copper concentration in feed tanks, the impact that the copper sulphide precipitates have on autoclave chemistry also needs attention. Copper concentrations and extractions in the first and second stages are good (see Table 7.8), suggesting that the absence of said chemistry in the model is of no detriment. Although the same cannot be said about the third stage leach, as has already been emphasised (Section 7.5), poor model performance is widespread for the tail end of the process. It is interesting to note, however, that model errors are the highest in said stage for copper concentration, which may suggest that copper-related chemistry beyond that even purported in this subsection is occurring. Given the uncertainties (and inconsequentialities) surrounding third stage behaviour, a third stage analysis will be omitted here.

In the first and second stages, the apparent lack of impact of applicable chemistry on model performance could be related to the type of copper sulphide that precipitates. If the copper sulphides that precipitate in leach stage feed tanks dissolve in the first compartments of the autoclaves of respective stages, then there would be effectively no impact on autoclave performance in the model. In that event, copper is probably precipitating as blaufleibender covellite, which is different to normal covellite [208]. The oxidation rate of blaufleibender covellite in ammonical solutions has been shown to be up to four times as high as that of normal covellite for the same surface area [112]. Moreover, the surface area of the former is known to be much greater than that of the latter. Having said this, there would be two measurable types of covellite in the feed tanks, but probably only one (i.e. that in the matte) in the autoclaves.

So, based on discussions above, it is possible that copper precipitation is taking place in Tanks 1, 2 and 3 according to the copper sulphide precipitation chemistry of the copper boil process, in which blaufleibender covellite is the principal product. If this reaction scheme was to have been incorporated into the model, in Tanks 1, 2 and 3 the concentrations of copper would be 0.00, 0.38 and 0.82 g L\(^{-1}\), respectively, and the BVs would be zero. The fact that this mechanism is supported by plant and simulation data suggests that it too may be responsible for copper precipitation in leaching autoclaves under low oxidation potential conditions. Furthermore, given the ease with which the re-
dissolution of blaublőbender covellite seemingly takes place in autoclaves, another possibility is apparent. It is plausible that said precipitation chemistry could even be taking place in autoclaves under normal leaching conditions, whereby the precipitation of copper sulphide only becomes noticeable when re-dissolution rates decline in response to low oxidation potentials.

### 7.6.2 Variable Conditions

Forward and Mackiw [3] observed changes in the following variables to have a predominant effect on leaching kinetics: temperature, oxygen pressure, ammonia concentration, ammonium sulphate concentration, particle size and agitation. Only the first three variables will be given attention here, given that they are the ones that most directly influence the mineral oxidation rate (equation 6.129). The significance of ammonium sulphate is in the form of providing sufficient ammonium ions to buffer the system at an acceptable pH and adequate sulphate ions to balance the metals ions in solution (since sulphur is deficient in the matte); it is implicitly assumed in the modelling that this is always the case. The effect that particle size has on leaching is very important, and is examined in the next chapter. Agitation is not a manipulated variable at the refinery, and in any case it is implicitly assumed in the modelling that an adequate suspension of solids is maintained.

Simulations were carried out on Autoclave 1B to examine the effect that temperature, oxygen pressure and ammonia concentration have on autoclave performance, while the conditions for all other autoclaves remained constant; see Table 7.16. Temperature was varied over the range 30 – 110 °C; for temperatures less than or equal to 70 °C, all compartment temperatures were altered and set equal, while for temperatures greater than 70 °C, the temperatures for Compartments 1, 2 and 3 were altered and that for Compartment 4 was fixed at 70 °C. Autoclave oxygen pressure was altered from 30 to 100 kPa by manipulating the total leach air supply rate. Autoclave discharge ammonia-to-total-metals molar ratio was modified from 3.0 to 5.0 mol mol⁻¹ by adjusting the ammonia concentration target (as discussed in Section 7.3.3). Unless the variable itself was being altered, Compartment 1, 2 and 3 temperatures were
Table 7.16: Simulation Conditions for Temperature, Oxygen Pressure and Ammonia Concentration Variations in Autoclave 1B

<table>
<thead>
<tr>
<th>Variable</th>
<th>Simulation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compartment temperature (Range: 30 – 110 °C)</td>
<td>Compartment 4 maximum: 70 °C</td>
</tr>
<tr>
<td></td>
<td>Autoclave O₂ pressure: 61 kPa</td>
</tr>
<tr>
<td></td>
<td>Autoclave discharge NH₃:TM: 4.3 mol mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>All other conditions: Simulation 16</td>
</tr>
<tr>
<td>Autoclave O₂ pressure (Range: 30 – 100 kPa)</td>
<td>Compartment 1, 2, 3 temperature: 90 °C</td>
</tr>
<tr>
<td></td>
<td>Compartment 4 temperature: 70 °C</td>
</tr>
<tr>
<td></td>
<td>Autoclave discharge NH₃:TM: 4.3 mol mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>All other conditions: Simulation 16</td>
</tr>
<tr>
<td>Autoclave discharge NH₃:TM (Range: 3.0 – 5.0 mol mol⁻¹)</td>
<td>Compartment 1, 2, 3 temperature: 90 °C</td>
</tr>
<tr>
<td></td>
<td>Compartment 4 temperature: 70 °C</td>
</tr>
<tr>
<td></td>
<td>Autoclave O₂ pressure: 61 kPa</td>
</tr>
<tr>
<td></td>
<td>All other conditions: Simulation 16</td>
</tr>
</tbody>
</table>

fixed at 90 °C, Compartment 4 temperature was set to 70 °C, autoclave oxygen pressure was fixed at 61 kPa and the discharge ammonia-to-total-metals molar ratio remained set at 4.3 mol mol⁻¹. (Of course, it must be kept in mind that the chemistry with which the model is based remains unchanged over the variable ranges considered.)

**Temperature**

Temperature has the most profound impact on leaching kinetics. Overall metal extraction and sulphide sulphur conversion curves are shown in Figure 7.2. At lower temperatures, little sulphide oxidation takes place, as evident from both the extraction and conversions curves for cobalt and sulphide sulphur, respectively. The comparatively larger extractions for nickel and copper are due to the unit conversions of heazlewoodite and chalcocite in Compartment 1, respectively, which remain independent of temperature; see Appendix F for a verification of the latter. As temperature increases, leaching rates advance. Nickel dissolution improves at the faster rate, which is expected given that millerite has the highest reactivity of all the sulphides. However, as the dissolution rate steadies due to the reduction in the surface area of said mineral, a greater proportion of oxidant is available for covellite and sycoporite to react with, as illustrated by the increase in dissolution rates for copper and cobalt towards the higher
Figure 7.2: The effect of compartment temperature on Autoclave 1B overall metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion (Conditions: see Table 7.16.)

end of the temperature range. At 110 °C, near-unit conversion is observed for nickel and sulphide sulphur (which suggests the same is true for millerite), while covellite and sycoporite require more leaching time. Over the same temperature range, nickel, copper and cobalt concentrations in the autoclave discharge range from 67.48 to 133.53 g L\(^{-1}\), 3.08 to 4.82 g L\(^{-1}\), and 0.50 to 1.47 g L\(^{-1}\), respectively.

As expected, the higher the temperature the greater the metal extraction. However, dissolved metal stability deteriorates at higher temperatures, which is not being modelled here. So, some upper limit on temperature is necessary. Moreover, an appropriate ratio between the BV and copper concentration is required in the first stage leach in order to satisfy the same requirement in the copper boil feed liquor (as discussed in Chapter 3), which is almost solely a function of temperature.

The BV for all four compartments is shown in Figure 7.3. The plots demonstrate much more clearly than that established previously for Table 7.12 data the multifaceted nature of the variable. The curves share a characteristic shape, differing essentially by
the position of the turning point. Complementing earlier discussions for fixed conditions, the regions of positive and negative gradient represent approximately the situations in which a larger and smaller amounts of unsaturated sulphur is produced than consumed, respectively; there is some ambiguity on the relative rates due to the differing effects in magnitude that $1 \text{ mol L}^{-1} \text{ S as } S_2O_3^{2-}$ has on the BV compared to $1 \text{ mol L}^{-1} \text{ S as } S_3O_6^{2-}$. At lower temperatures, a build-up of unsaturated sulphur in solution is observed in all compartments. By cross-referencing the curves in Figure 7.3 with those in Figure 7.4 (which show cumulative sulphide sulphur conversion in each compartment), one may appreciate that at such temperatures even low conversions of sulphide sulphur can bring about relatively high unsaturated sulphur concentrations. Moreover, as expected, since a given compartment beyond the first acquires concentration from the one prior (even in the absence of sulphur dissolution), higher BVs are witnessed as one proceeds down the reactor series.

As the temperature increases, despite an increase in sulphide sulphur conversion, the BV approaches a maximum. The location of the maximum is related predominantly to the temperature and the unsaturated sulphur concentration itself; the higher the temperature and concentration, the higher the unsaturated sulphur consumption rate. It is unsurprising then that maxima are observed at lower temperatures yet higher BVs. This phenomena is complicated by the fact that as temperatures increases a greater proportion of sulphide sulphur is being converted at the front end of the autoclave, which is robbing (relatively speaking, since more sulphide sulphur is being converted on the whole) downstream compartments of unsaturated sulphur obtained directly from sulphur dissolution (i.e. not from liquor flow). This also offers an explanation as to why the maxima occur at lower temperatures for higher compartment numbers.

At higher temperatures, regardless of the sulphide sulphur conversion, the BV falls. The concentration gradient in this region for a given compartment is related to the proportion of overall sulphur conversion that occurs. Since a higher proportion of conversion takes place in Compartment 1, the rate of decrease in the BV is slower and the concentration value itself is higher at the maximum temperature. The same logic can
Figure 7.3: The effect of compartment temperature on BV and the discharge BV:[Cu] in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)

Figure 7.4: Sulphide sulphur conversion and oxygen utilisation vs compartment temperature in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)
be applied to Compartments 2 and 3. The exception to the rule is Compartment 4, which has its temperature fixed at 70 °C; were it not for this, its BV would fall the fastest and to the lowest value as temperature approaches 110 °C.

The BV-to-copper concentration ratio in the autoclave discharge is also shown in Figure 7.3, which as a function of temperature has the same characteristic shape as BV. If said ratio is to have an ideal value, then it follows that autoclave temperature must be appropriate. So, whilst the promotion of dissolved metal stability demands some upper limit on temperature, an ideal BV-to-copper concentration ratio (which is variable) requires that some temperature range (in the high temperature region) be adhered to (the upper limit of which may not be the same as that already highlighted).

The effect that temperature has on cooling duty is shown in Figure 7.5 at both the compartment and total autoclave levels. The total cooling duty itself gives an indication of the autoclave cooling water requirement, but understanding the profile is better done by examining compartment behaviour. The removal of heat via cooling water is required in all compartments over the temperature range considered. At 30 °C, a positive cooling duty is established in all compartments, which escalates initially with temperature increase in all compartments except the first. The decrease in Compartment 1 cooling duty over the range 30 °C to around 55 °C is due to the higher slurry feed temperature of 52.7 °C, the latter of which represents the actual turning point. This situation could be overcome if the total heat generated due to reaction was appropriate, but as can be seen from the sulphur conversion profiles (Figure 7.4), less than 10 percent of sulphide sulphur is converted below 60 °C. Beyond 60 °C, the rate of sulphur conversion experiences an increase, which is replicated by the cooling duty. The higher cooling duty in Compartment 1 is due to the complete conversions of heazlewoodite and chalcocite.

The cooling duties for Compartments 2, 3 and 4 all increase with temperature over the majority of the temperature range. At 30 °C, the cooling duty for Compartment 2 is only slightly higher than that of Compartment 3, which is because only a slightly higher amount of sulphur is converted in the former compartment than the latter. As
temperatures increase, total autoclave sulphur conversion increases also, however only an increase in the proportion converted in Compartment 1 is observed. The rate of decrease with temperature of proportion of sulphur converted in Compartment 2 is less than that of Compartment 3, which is why both the rate of increase and magnitude of cooling duty in the former compartment are always higher than that of the latter. Below roughly 80 and 65 °C, the amount of sulphur converted in Compartments 2 and 3 is greater than that in Compartment 1, respectively, while the same is true of Compartment 4 below around 40 °C. Despite the same compartment temperatures, the greater oxidation rates are due to the higher copper(II)-to-copper(I) ratio; $R_{Cu}$ and oxygen pressure are illustrated in Figure 7.6.

The rates of increase of cooling duty in Compartments 1, 2 and 3 approach zero at around 110 °C, 99 °C and 88 °C, respectively. In general, the eventual decrease in compartment cooling duty at higher temperatures takes place due to (1) a lower cooling duty is required to maintain said temperatures and (2) the conversion of sulphide sulphur approaches a limiting value. However, neither of these factors explains the location of the turning points. Due to the counter-current airflow arrangement, partially-spent air from Autoclave 1A enters 1B at 87.6 °C, and so at operating temperatures above this measure the air actually cools the reactor slurry. (It is also apparent then that at compartment temperatures below 87.6 °C, the air is a heating source, requiring additional cooling in the form of cooling water than what would be required for fresh air. Moreover, at compartment temperature above 15 °C, the anhydrous ammonia is a cooling source.) In order to maintain an autoclave oxygen pressure of 61 kPa, progressively larger quantities of air must be fed at higher temperatures; an increase in roughly twice as much air (by volume) must be fed to Autoclave 1B when compartment temperature is raised from 90 to 110 °C than when raised from 70 to 90 °C. Whilst higher temperatures also suggest a higher oxygen demand via increased sulphur conversion, the resultant increase in air flow is not consistent with this demand, as can be seen from a comparison of sulphur conversion and oxygen utilisation in Figure 7.4.
Figure 7.5: Cooling duty vs compartment temperature in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)

Figure 7.6: Copper(II)-to-total copper ratio ($R_{cu}$) and oxygen pressure vs compartment temperature in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)
The more heat that is released via reaction, the higher the temperature of the cooling duty turning point. Given that at temperatures above 80 °C the first compartment exhibits the highest sulphur conversion, followed by the second and then third compartments, the positions of the turning points are apparent. If Compartment 4 did not have a maximum temperature of 70 °C, it is expected that it would have a turning point temperature lower than that of the third compartment, however, the higher temperature of 105 °C is consistent with actual operation. For temperatures beyond 110 °C, one would eventually observe the situation in which a negative cooling duty is established. That is, external heating (such as steam input) would be required to sustain said temperatures.

**O₂ Pressure**

Oxygen pressure does not seem to have a significant impact on leaching. Overall metal extraction and sulphide sulphur conversion curves are shown in Figure 7.7, which demonstrate that little improvement in autoclave performance takes place over the range of pressures considered. Perhaps more revealing is a comparison of compartment sulphur conversion and oxygen pressure profiles, given in Figure 7.8. Again, improvements in oxygen pressure do not have a comparable effect on sulphur conversion. Worthy of note is the 28 percent sulphur conversion in Compartment 1 that accompanies an oxygen pressure bordering on 0 kPa. The reason behind these observations lies with the nature of oxygen gas-liquid mixing.

When pure physical absorption of oxygen gas prevails in gas-liquid reactors, the concentration difference between the saturation and bulk solution concentrations of oxygen establishes a driving force for oxygen gas-liquid mass transfer (see equation 4.10), in which the former concentration is proportional to oxygen pressure (that is, it obeys Henry’s Law). For the sake of argument, if it is assumed that – like in Autoclave 1B – there is no dissolved oxygen in solution, the physical absorption model would predict an oxygen mass transfer rate of \( r_{O_2} = k_i a C_{O_2}^* \), where \( C_{O_2}^* \propto P_{O_2} \). It follows then that as \( P_{O_2} \to 0 \), \( C_{O_2}^* \to 0 \) and thus \( r_{O_2} \to 0 \).
Figure 7.7: The effect of autoclave oxygen pressure on Autoclave 1B overall metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion (Conditions: see Table 7.16.)

Figure 7.8: Sulphide sulphur conversion and oxygen pressure vs autoclave oxygen pressure in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)
In Autoclave 1B, oxygen mass transfer is enhanced due to the presence of cuprous ammine. This model of oxygen mass transfer forecasts a rate of

\[ r_{O_2} = k_i a (C_{O_2}^* + 0.25 C_{Cu(I)}) \]  

(which is equivalent to equation 4.6 where \( \frac{D_{Cu(I)}}{D_{O_2}} = 1 \), as per discussions in Section 6.5.1). The difference between the two models is the copper(I) concentration term in the latter. A comparison of \( C_{O_2}^* \) and \( C_{Cu(I)} \) over the oxygen pressure range is demonstrated in Figure 7.9. It is evident that at all pressures \( C_{O_2}^* << 0.25 C_{Cu(I)} \), which signifies that oxygen pressure has almost no direct impact on the mass transfer rate. This is why as \( P_{O_2} \rightarrow 0 \), \( r_{O_2} \rightarrow 0.25 k_i a C_{Cu(I)} \), as opposed to \( r_{O_2} \rightarrow 0 \) as the pure physical absorption model suggests. Rather, the mass transfer rate is driven almost entirely by mineral oxidant demand.

The plots in Figure 7.9 also signify that as oxygen pressure increases the concentration of copper(I) decreases. Seemingly, this would suggest a drop in the oxygen dissolution rate. However, a higher oxygen pressure requires a higher reactor gassing rate, which does impact on mass transfer. A higher gassing rate equates to a higher \( k_i a \), the magnitude increase in which is greater than the decrease in \( C_{O_2}^* + 0.25 C_{Cu(I)} \), which is why sulphur conversion improves with oxygen pressure increase.

The decrease in copper(I) concentration itself is due to the decrease in \( r_{O_2} / k_i a \). Although both \( r_{O_2} \) and \( k_i a \) increase with higher pressure, the former doing so in response to the higher oxygen demand required for greater sulphur conversion, the latter does so with greater magnitude. As \( r_{O_2} / k_i a \rightarrow C_{O_2}^* \), \( C_{Cu(I)} \rightarrow 0 \) and thus \( R_{Cu} \rightarrow 1 \). It is therefore \( r_{O_2} / k_i a \) that ultimately determines the shift from Type III to Type I leaching. Since \( r_{O_2} \) is related almost exclusively to mineral oxidant demand, which decreases as leaching progresses, it is unsurprising then that \( R_{Cu} \rightarrow 1 \) as compartment number increments in all autoclaves (see Tables 7.12 and 7.13).
The results here suggest that it is copper concentration and $k_\text{f}a$ that best support oxygen mass transfer, rather than oxygen pressure. This is also supported mathematically. By combining $R_{\text{Cu}} = 1 - C_{\text{Cu(I)}} / C_{\text{Cu(T)}}$ and $r_{\text{O}_2} = k_\text{f}a \left( C_{\text{O}_2}^* + 0.25 C_{\text{Cu(I)}} \right)$, it can be shown that $\frac{C_{\text{Cu(II)}}}{C_{\text{Cu(I)}}} = \frac{R_{\text{Cu}}}{1 - R_{\text{Cu}}} = \frac{C_{\text{Cu(T)}}}{4 \left( r_{\text{O}_2} / k_\text{f}a - C_{\text{O}_2}^* \right)} - 1$, which is the driving force for mineral oxidation when Type III leaching prevails. It is clear that mineral oxidation will improve for higher values of $C_{\text{Cu(T)}}$ and $k_\text{f}a$. However, increments in the latter variables should be appropriately greater in magnitude than the increase in $r_{\text{O}_2}$, which will also yield a higher value following an improvement in mineral oxidation.

Clarification is deemed appropriate at this point as to why Forward and Mackiw [3] observed a noticeable effect on nickel and sulphur extraction in response to changes in oxygen pressure, and yet a seemingly comparable result was not observed here. Firstly, it must be realised that conditions in batch and continuous reactors are very
different, and a comparison of the two is typically not a straightforward task. Secondly, leaching conditions for nickel concentrate and nickel matte are very different. Thirdly, the oxygen pressures established by said authors were both greater in magnitude and variation compared with those employed in the present simulations, thus allowing a more apparent distinction of results. Fourthly, based on Forward and Mackiw’s discussions, it seems that both Type III and Type I situations were established throughout the course of leaching, given that said authors speak of oxygen depletion in solution in the early stages of leaching, followed by its restoration in the later stages. The oxygen mass transfer rate is influenced predominantly by oxygen pressure when the latter leaching situation prevails. Finally, no indication of dissolved copper concentration was given. The lower the copper concentration is, the more the oxygen mass transfer rate depends on oxygen pressure to satisfy the same demand.

**NH₃ Concentration**

The amount of free ammonia relative to dissolved metals in solution appears to have little impact on leaching kinetics over the range considered, despite the direct dependence that the sulphide oxidation rate laws have on ammonia concentration. It is well-established that aqueous ammonia has an effect on mineral leaching, both in terms of influencing the kinetics and stabilising the dissolved metals in solution [3], however, the metal extraction and sulphide sulphur conversion curves in Figures 7.10 and 7.11 suggest only a modest improvement in performance following a large change in ammonia concentration. It is most probably the case here that the latter is present in such large quantity that the sulphide oxidation rates are essentially pseudo-zero-order with respect to ammonia.

Despite the near-same performance at all ammonia concentrations considered, it is important to realise that this does not suggest that the process should be operated at ammonia-to-total metal ratios as low as 3.0 mol mol⁻¹ (in an effort to reduce operating costs, for example). The large ratios are necessary to establish metal ion stability, the chemistry of which has not been considered in the model. It is the assumption that a sufficient concentration of aqueous ammonia is present to maintain a stable
Figure 7.10: The effect of ammonia concentration on Autoclave 1B overall metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion (Conditions: see Table 7.16.)

Figure 7.11: Sulphide sulphur conversion and ammonia-to-metals molar ratio vs the autoclave discharge ammonia-to-metals molar ratio in Autoclave 1B (Conditions: see Table 7.16; 1, 2, 3, 4: compartments.)
environment for dissolving metals. In the absence of said concentrations, the metal would probably precipitate as metal hydroxides. If this chemistry were to have been incorporated into the model, it is likely that Figure 7.10 would show larger decreases in metal extraction as the ammonia-to-total metals ratio approaches 3.0 mol mol\(^{-1}\), while sulphide sulphur conversion would remain relatively unchanged.

Like before for oxygen pressure, an assessment is required as to why Forward and Mackiw’s [3] results for nickel extraction rate demonstrates a distinct dependence on ammonia concentration, and that a much weaker relationship is observed here. Unfortunately, an unequivocal explanation cannot be given, since said authors did not specify both nickel and ammonia concentrations, which is necessary to establish a free ammonia-to-nickel ratio for comparison. One can only speculate, however, two reasons may be offered: (1) the ammonia-to-nickel ratio was sufficiently low to establish a positive (i.e. greater than zero) order of dependence on ammonia for the leaching rate, or (2) the ammonia-to-nickel ratio was sufficiently low to promote the precipitation of nickel, and thus the net dissolution rate of the metal was actually a combination of the leaching rate and the precipitation rate; an increase in ammonia concentration would improve the former rate and worsen the latter rate, and vice versa.

### 7.7 Summary

A computer model of the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery was built in ACM on the basis of stream and unit operation model equations established in the previous chapter. A discussion on the importance of the quality and quantity of plant data acquired for purposes of parameter estimation and model validation was given. Procedures for obtaining useful data and estimating unknown or unreliable data for the refinery leach were subsequently detailed.

Unknown rate law parameters (first identified in Chapter 4 and reiterated in the previous chapter) were estimated via the organisation of 12 experiments based on actual plant data. The set of experiments encompassed a host of operating conditions, distinguished most visibly by the leach matte solids feed rate. Following the incorporation of said rate law parameters into the model, a rigorous validation
procedure was pursued. On the basis of actual plant data distinct from that employed previously, 24 simulations were established to ascertain the strengths and weaknesses of the model. The model performed very well in all areas of the process for all crucial variables, with the exception of predicting third stage leach behaviour (which was shown to be inconsequential to overall leach performance).

The model was used to examine process chemistry and operation for both fixed and variable conditions. With respect to the former simulations, a comprehensive analysis was carried out at the leaching stage, autoclave and compartment levels, detailing the interrelations of said processes via the examination of key process variables. The simulation data was also used to propose the existence of supplementary chemistry most likely taking place in the leach. With respect to the latter simulations, the influence that temperature, oxygen pressure and ammonia concentration has on leach performance was investigated. Temperature change had the greatest effect, while the impact that alterations in oxygen pressure and ammonia concentration had were more subdued. Although the latter outcomes may seem surprising, explanations were offered in each case.

In the next chapter, the process model is incorporated into an optimisation problem and programmed in ACM, the purpose of which is to assess the impact that process disturbances and set-point changes have on optimal leach operation.
Chapter 8

Optimisation

8.1 Introduction

In the previous chapter, the creation of a computer model of the Sherritt-Gordon ammonia leach at the Kwinana Nickel Refinery was conferred. In this chapter, an optimisation problem is formulated and programmed in Aspen Custom Modeler® (ACM), wherein the model represents the chief element of construction. Simulations are carried out to determine the impact that key process disturbances and set-point changes have on optimal operation for a wide range of conditions. The results are presented as a graphical encyclopaedia that collectively describes the state of the process in response to changing conditions with respect to chemistry and material flow. This is used as the basis for an assessment of the operational characteristics of the process. Performance limitations are identified and opportunities for improvement are put forward.

Throughout the chapter, the topics of optimisation and process control are intertwined. It is important to emphasise, however, that no process dynamics have been considered in this work. Rather, the steady-state analysis is carried out in such a way that the mode in which optimal operation may be realised at the refinery is apparent, thus leading to the topic of Sherritt-Gordon ammonia leach process control. This is the foundation with which such discussions originate.
8.2 The Optimisation Problem

The process model has the capacity to be used stand-alone to carry out performance optimisation. In the previous chapter, simulations were carried out to examine the effect that temperature, oxygen pressure and ammonia concentration have on the performance of Autoclave 1B (see Section 7.6.2). Despite the generation of a significant amount of insight into first stage leaching chemistry and autoclave behaviour (which may indeed be used to support performance optimisation), the results, nonetheless, remain suboptimal. Thus, stand-alone model simulation (which has been the focus of almost all leach process optimisation studies, as highlighted in Chapter 2) is limited in its application.

To produce optimal results for the above simulations, the modeller would need to ensure that all performance-determining variables are constrained to optimal values. Given the nature of flowsheet interaction, this exercise would not simply be limited to Autoclave 1B variables but would extend to variables process-wide. Given the number of variables under consideration, the complexity of variable interactions, and the scope with which both the number and nature of simulations would need to be executed, the application of manual, stand-alone model simulation for optimisation purposes is rendered impractical for even a single autoclave, let alone the entire leaching process. For a leaching process as complex as the one under examination in this work (i.e. a multiple autoclave, multiple stage leach), only the solution of an appropriate optimisation problem is capable of realising all performance optimisation goals.

The general optimisation problem may be described via the following mathematical program [209]:

Minimise: \[ f(x) \] objective function

Subject to: \[ h(x) = 0 \] equality constraints

\[ g(x) \geq 0 \] inequality constraints

where \( x \) is a vector of \( n \) variables \( (x_1, x_2, \ldots, x_n) \), \( h(x) \) is a vector of equations of dimension \( m_1 \), and \( g(x) \) is a vector of inequalities of dimension \( m_2 \). The total number of
The equality constraints customarily refer to the system of model equations, while the inequality constraints typically refer to operational restrictions (with respect to both equipment and chemistry). Some restrictions may, however, be better represented by equalities, and would thus be grouped with the model equations in the above framework.

Over the course of many decades, operational experience at the refinery has led to a wealth of knowledge that forms the basis of the leach operating philosophy; a detailed discussion on this was given in Chapter 3. This knowledge has a central place in the optimisation problem (see Section 8.2.3 discussions, Table 8.1 and Table 8.2). Having said this, there is only a general understanding of how the manipulation of key process variables may be used to bring about desired performance in response to variable operating conditions. A gap thus exists between current operating practices and optimal performance.

The work in this thesis is the first attempt at process optimisation via modelling and simulation to be carried out at the refinery. Furthermore, given the size and complexity of the leaching process, not to mention the important interaction the leach has with other processes at the refinery (such as the copper boil and ammonia recovery processes; see Figure 2.1) that have not formed part of the modelling effort in this thesis, this work represents the first in a series of studies required to bring about superior performance. Moreover, given that implementing changes in the operating philosophy of an industrial process plant requires the support of process staff, a step-by-step approach is best taken. The principal optimisation goal here should thus be one of generating sufficient knowledge to allow refinery engineers and operators to “tighten up” on current control practices, while providing a sufficient foundation in scope for future optimisation studies.

The objectives of performance optimisation are to quantify the interrelationships of key performance-determining variables under the wide-ranging process conditions that result from the most significant disturbances and strategic set-point changes, all in which process conditions remain optimal. This analysis may then be used to identify
performance issues and recommend opportunities for improving process behaviour beyond that constrained by present operating strategies and process structure.

A detailed assessment of leach chemistry at the compartment, autoclave and leaching stage levels was the objective of simulations in the previous chapter. In this chapter, the analysis of simulation results is aimed at the leaching process level. Discussions will thus be guided by those process characteristics that are relevant at the macro-scale.

The optimisation problem is described via the following three elements: (1) the objective function, (2) the process model, and (3) the constraints. The optimisation algorithm was programmed in ACM, which offers two simulation modes of relevance to this work: “Steady State” and “Optimization”. The former mode executes only the process model and constraint program code (i.e. the case for the previous chapter). The latter mode executes the code for all three elements, employing a reduced-space, feasible-path, successive quadratic programming optimiser. Each element of construction is discussed separately in the following subsections.

8.2.1 The Objective Function

The objective function (or performance index) should be a measure of the economic performance of the process. This is typically accomplished with (directly or indirectly) maximising profit. Writing a profit equation for the present process, however, is problematic. For example, while it is clear-cut to say that the value of nickel in the copper boil feed (CBF) liquor is greater than its value in the feed matte, it is not straightforward to assign absolute or relative value as a quantity. To produce a suitable profit equation, one would effectively need to develop an economic model of the leach, which is not possible without an economic model of the refinery.

A more suitable measure of economic performance is metal extraction. For the typical case in which any refinery (which is first and foremost a business) earns a positive net profit, a greater yield in product will almost always bring about a greater net profit. Thus, maximising metal extraction would be akin to maximising profit, and it is with this supposition in mind that the performance index in this work is formulated.
The objective function was chosen to be that of **nickel fraction unreacted in the first stage leach**. The purpose of process optimisation is thus to minimise the amount of nickel that goes unreacted, or, in other words, to maximise the extraction of nickel. The first stage leach nickel fraction unreacted is the most appropriate measure for two main reasons. Firstly, when nickel extraction is maximised, metal extraction is maximised. Secondly, as will become evident as the chapter progresses, when first stage extractions are maximised, leaching activity process-wide is maximised. The primary decision variable selected for use by the optimiser to minimise nickel fraction unreacted in the first stage leach is the **total leach air supply rate**.

### 8.2.2 The Process Model

The process model is comprised of the fundamental stream and unit operation model equations described in Chapter 6 and arranged in the manner discussed in the previous chapter to replicate the process given in Figure 3.1, all with the exception of the flowsheet constraints stipulated in Section 7.3.3. The latter is compensated for via the introduction of new constraint equations relevant to the optimisation runs of this chapter (as opposed to the stand-alone model simulations of the previous chapter), which are addressed in the next subsection.

### 8.2.3 The Constraints

All constraints are in the form of equalities, with the exception of one inequality. All aim to give either fixed values to relevant variables or establish important relationships amongst key performance-determining variables, the latter of which are derived from the leach operating philosophy.

As mentioned in the previous subsection, the flowsheet constraints of Section 7.3.3 are omitted from the process model. Having said this, the variables listed in Table 7.3 require evaluation. The majority of said variables are given fixed values based on those established in Simulation 16; that is, the simulation conditions considered for examination in the previous chapter (see Section 7.6.1). This is directly true of compartment apportionment of total vessel anhydrous ammonia for Autoclaves 1A, 1B, 2B and 3B, as well as all tank and thickener ammonia evaporation rates. A flowsheet-
encompassing fixed-value difference in temperature between trim cooler discharges and autoclave discharges was instituted for Simulation 16. That same temperature difference is used to calculate trim cooler discharge temperatures for present purposes; autoclave discharge temperatures are discussed below. While thickener underflow rate, $Q_u$, is mentioned in Table 7.3, this variable is interchanged with thickener underflow density, $\omega_u$, according to the following equation:

$$Q_u = \frac{Q_{wp}}{\omega_u P_u \sum_{i(x)} C_{i(x),in} M_{i(x)}} \quad (8.1)$$

where the above variables are defined the same as those discussed in Section 6.7. Having said this, $\omega_u$ is fixed according to its value in Simulation 16 and $Q_u$ is allowed to vary in accordance with the above equation. The outstanding variables in Table 7.3 are discussed below, along with a host of other variables which form the basis of new constraints pertinent to process optimisation.

The new constraints were developed to bring about set-point compliance for key performance-determining variables. As was discussed in detail in Chapter 3, the principal controlled variables in the leach are the concentrations of nickel, AmSul and ammonia in the CBF liquor, the BV in the CBF liquor, nickel extraction in the first stage leach, and nickel and ammonia concentrations in the third stage feed and discharges, respectively; the reader is referred to Section 3.4 for a discussion on how control is implemented. A summary of the latter is given in Tables 8.1, in the form of pairing pertinent manipulated and controlled variables. The CBF concentrations and the BV have target values, as do the third stage variables, while the first stage leach nickel extraction is maximised.

The target CBF nickel and AmSul concentrations are controlled by manipulating both the first and second stage leach discharge nickel and AmSul concentrations, respectively. The target CBF AmSul concentration is calculated as a function of the CBF nickel concentration via an empirical relationship. Due to chemistry requirements in the first stage, the nickel concentration there is adjusted to be around 5 g L$^{-1}$ higher than the CBF concentration, while the required second stage nickel concentration is
Table 8.1: Manipulated vs. Controlled Variables

<table>
<thead>
<tr>
<th>Manipulated Variable(s)</th>
<th>Controlled Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>1SL &amp; 2SL [Ni]</td>
<td>CBF [Ni]</td>
</tr>
<tr>
<td>DTO-to-Tank 1 flow rate</td>
<td>1SL [Ni]</td>
</tr>
<tr>
<td>DTO-to-Tank 2 flow rate</td>
<td>2SL [Ni]</td>
</tr>
<tr>
<td>1SL &amp; 2SL [AmSul]</td>
<td>CBF [AmSul]</td>
</tr>
<tr>
<td>MFL-to-Tank 1 flow rate</td>
<td>1SL [AmSul]</td>
</tr>
<tr>
<td>DTO [AmSul]</td>
<td>2SL [AmSul]</td>
</tr>
<tr>
<td>1SL &amp; 2SL NH$_3$;TM</td>
<td>CBF NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclaves 1A &amp; 1B NH$_3$;TM</td>
<td>1SL NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclave 1A ammonia feed flow rate</td>
<td>Autoclave 1A NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclave 1B ammonia feed flow rate</td>
<td>Autoclave 1B NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclaves 2A, 2B &amp; 3B NH$_3$;TM</td>
<td>2SL NH$_3$;TM</td>
</tr>
<tr>
<td>Ammonia Still overhead gas flow rate</td>
<td>Autoclave 2A NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclave 2B ammonia feed flow rate</td>
<td>Autoclave 2B NH$_3$;TM</td>
</tr>
<tr>
<td>Autoclave 3B ammonia feed flow rate</td>
<td>Autoclave 3B NH$_3$;TM</td>
</tr>
<tr>
<td>1SL BV:[Cu]</td>
<td>CBF BV:[Cu]</td>
</tr>
<tr>
<td>Autoclaves 1A &amp; 1B BV:[Cu]</td>
<td>1SL BV:[Cu]</td>
</tr>
<tr>
<td>Autoclave 1A C1, C2 &amp; C3 temperatures</td>
<td>Autoclave 1A BV:[Cu]</td>
</tr>
<tr>
<td>Autoclave 1B C1, C2 &amp; C3 temperatures</td>
<td>Autoclave 1B BV:[Cu]</td>
</tr>
<tr>
<td>MFL-to-Thickener 2W flow rate</td>
<td>Tank 3 [Ni]</td>
</tr>
<tr>
<td>Ammonia Still distillate flow rate</td>
<td>3SL (Autoclave 3A) [NH3]</td>
</tr>
</tbody>
</table>

* 1SL = first stage leach; 2SL = second stage leach; 3SL = third stage leach; NH$_3$;TM = ammonia-to-total metals molar ratio; BV:[Cu] = BV-to-copper concentration ratio; Ci = Compartment i.

The first stage AmSul concentration is calculated as a function of the nickel concentration there via an empirical relationship (different to that of the CBF stream), while the required second stage AmSul concentration is calculated via a suitable AmSul mass balance that unites all three AmSul concentrations.

The first stage nickel and AmSul concentrations are controlled through manipulating both the DTO-to-Tank 1 and MFL-to-Tank 1 volumetric flow rates. Through a combination of both nickel and AmSul mass balances around Tank 1, Autoclave 1A and Autoclave 1B, the required former and latter flow rates are calculated to bring about the desired nickel and AmSul concentrations, respectively. These calculations effectively bring about the control of the first stage feed pulp density.
(which most directly influences discharge nickel concentration) via manipulating the sum of the flow rates, as well as control of the first stage feed AmSul concentration (which most directly influences discharge AmSul concentration) via manipulating the ratio of the flow rates. The second stage nickel and AmSul concentrations are controlled through manipulating the DTO-to-Tank 2 volumetric flow rate and DTO AmSul concentration, respectively. Like for the first stage, the former and latter manipulated variables are effectively responsible for controlling the second stage feed pulp density and AmSul concentration, respectively.

In the previous chapter, the flow rate of MFL-to-Tank 1 was calculated to balance the total mass around Tank 1, given that reliable plant data was available for all other flow rates around the tank. Given that it is now calculated to bring about a target concentration, the flow rate of one of the residual streams either reporting to or from the tank must be made a free variable. The best selection is that of the total tank discharge. The first stage leach feed is distributed evenly to Autoclaves 1A and 1B.

The target CBF ammonia concentration is controlled by manipulating both the first and second stage leach discharge ammonia concentrations. This is determined according to a fixed ammonia-to-total metals molar ratio, which is set to be the same for all first and second stage leach autoclave discharges. The ratios are controlled by manipulating the molar flow rates of the ammonia source streams for each autoclave: anhydrous ammonia for Autoclaves 1A, 1B, 2B and 3B, and Ammonia Still overhead gas for Autoclave 2A. The flow rates and molar ratios are related via total ammonia mass balances, written around respective autoclaves. (The latter calculations are similar in nature to those employed in the previous chapter, only the flow rates were calculated to bring about a target ammonia concentration, not ammonia-to-total metals molar ratio; see Section 7.3.3.)

The target CBF BV is controlled by manipulating the first stage leach discharge BV; the second stage BV is always zero, and thus has no effect. A fixed value is set for the CBF BV-to-copper concentration ratio, and through a suitable unsaturated sulphur mass balance the corresponding first stage leach discharge BV-to-copper concentration
ratio can be determined. The latter is used as the target for Autoclave 1A and 1B discharges.

The first stage leach autoclave discharge BV-to-copper concentration ratios are controlled by manipulating temperature in the first, second and third compartments of respective autoclaves. Said compartments of each autoclave are all set to have the same temperature. This is achieved via constraints that equate second and third compartment temperatures with that of the first. The first compartment temperatures for Autoclaves 1A and 1B are the second and third (and final) decision variables, and thus the optimiser will adjust their values in order to meet the BV-to-copper concentration ratio targets. (The first compartment temperatures were incorporated into the optimisation problem as decision variables rather than via constraints, given that no straightforward relationship between temperature and BV can be written.) The fourth compartment temperatures are fixed at 70 °C.

The compartment temperatures of second and third stage autoclaves are fixed, given that the BVs for said stages are not controlled. The first, second and third compartments in the second stage are fixed at 95 °C, while those in the third stage are fixed at 85 °C. All fourth compartment temperatures are fixed at 65 °C.

The target third stage leach feed (i.e. Tank 3) nickel concentration is controlled by directly manipulating the MFL-to-Thickener 2W volumetric flow rate. The latter is calculated through a combination of both nickel and total mass balances around Thickener 2W and Tank 3; both types of balances are required given that MFL does not contain any dissolved nickel. The target third stage leach (i.e. Autoclave 3A) discharge ammonia concentration is controlled by directly manipulating the Ammonia Still distillate volumetric flow rate. This is calculated via a total ammonia balance around Autoclave 3A, which is the precise method of calculation used in the previous chapter.

It should be clarified at this point that ammonia concentration in Autoclaves 2A and 3A is not controlled in the plant in the same way as for the remaining autoclaves, given the ammonia source (i.e. the Ammonia Still). A healthy ammonia balance exists between the leaching process, the copper boil process and the Ammonia Still, which
typically delivers a suitable quantity of recycled ammonia to the leach, with an appropriate distribution to applicable autoclaves. Nonetheless, the concentrations of Autoclaves 2A and 3A are essentially free variables that tend to fluctuate about their targets, the nature of which is subject to conditions established at the Ammonia Still. The relevant constraints consider that conditions at the Ammonia Still are sufficiently fitting as to effectively allow control of Autoclaves 2A and 3A ammonia concentrations.

The sole inequality is in the form of a lower limit constraint for total leach oxygen utilisation. This, in effect, is a function for providing an upper limit for the total leach air supply rate (i.e. the primary decision variable), which the optimiser will attempt to increase in order to minimise the objective function (i.e. maximise nickel extraction).

8.3 Simulation Results

Optimal operation is defined according to the optimisation problem framework established in the previous section. Standard optimal operation is in effect when the process conditions listed in Table 8.2 are established. The variables of said table represent the principal disturbance and controlled variables of the leach, and so deviations in the most important of these from standard conditions offers an ideal platform with which to assess process behaviour. With the exception of those variables that are the subject of change in subsequent subsections, as well as applicable variables discussed in Section 8.2.3, all other operating conditions are taken as those stipulated by Simulation 16 (see Section 7.6).

The examination of process performance in response to varying operating conditions is discussed in the following subsections. Specifically, the effect that the most significant process disturbances and set-point changes have on optimal leach operation is evaluated. Dimensionless variables are used in the analysis in instances where only the relative change in a value is of relevance. Such variables are normalised with respect to their standard values (i.e. those values that prevail when the conditions in Table 8.2 are satisfied), and are employed in Figures 8.8, 8.9, 8.10, 8.13, 8.21, 8.22, 8.23, 8.26, 8.30, 8.31, 8.32, 8.35, 8.39, 8.40, 8.41 and 8.44.
Table 8.2: Standard Optimal Operating Conditions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed matte solids flow rate</td>
<td>320 tpd</td>
</tr>
<tr>
<td>Feed matte elemental composition</td>
<td>66% Ni, 2.8% Cu, 0.85% Co, 5.2% Fe, 24% S by mass</td>
</tr>
<tr>
<td>Feed matte 90.52% mass passed size</td>
<td>106 µm</td>
</tr>
<tr>
<td>CBF [Ni]</td>
<td>100 g L$^{-1}$</td>
</tr>
<tr>
<td>CBF BV:[Cu]</td>
<td>50 BV-units L g$^{-1}$</td>
</tr>
<tr>
<td>1SL &amp; 2SL NH$_3$:TM</td>
<td>4.5 mol mol$^{-1}$</td>
</tr>
<tr>
<td>Tank 3 [Ni]</td>
<td>35 g L$^{-1}$</td>
</tr>
<tr>
<td>3SL [NH$_3$]</td>
<td>100 g L$^{-1}$</td>
</tr>
<tr>
<td>Total leach oxygen utilisation</td>
<td>$\geq$ 60%</td>
</tr>
</tbody>
</table>

* 1SL = first stage leach; 2SL = second stage leach; 3SL = third stage leach; NH$_3$:TM = ammonia-to-total metals molar ratio; BV:[Cu] = BV-to-copper concentration ratio.

8.3.1 Process Disturbances

The most significant process disturbances for any leaching process are related to changes in the quality of the particulate feed material. This is primarily in the form of its mineralogical composition and particle size distribution. An examination of changes in said features of the leach feed matte is given here.

Two types of simulations are considered for process disturbances:

1. **Disturbed Conditions.** The impact that the disturbances have on standard operation is demonstrated. That is, simulations were carried out in which only the disturbance variables were altered and all other pertinent manipulated variables remained set according to the standard optimal operating conditions; in other words, the optimiser was inactive (i.e. the simulation mode in ACM was set to “Steady State”).

2. **Optimal Conditions.** The optimal response that the system has to the same disturbances is demonstrated. That is, optimisation runs were carried out in which the disturbance variables were altered and the relevant manipulated variables were modified according to the rules established via the
optimisation problem; in other words, the optimiser was active (i.e. the simulation mode in ACM was set to “Optimization”).

Feed Matte Mineralogical Composition

Variability in the refinery feed matte mineralogical compositions comes about due to operational conditions at the Kalgoorlie nickel smelter, which, among other reasons, is related to the variability in the mineralogical composition of the nickel concentrate in its feed; more information on this is given in Chapter 3 (see Section 3.2). Change in the nickel content of the feed matte is used as the basis of change in its mineralogical composition. As the nickel content increases so does the cobalt content, while that of copper, iron and sulphur decreases. The nickel content almost always falls between 62 and 70 wt.%. 

Empirical relationships between nickel and all other principal elements in the matte were used to construct Table 8.3, which represents the elemental composition of the matte in response to changes in the nickel content. The corresponding mineralogical compositions are given in Table 8.4. Standard conditions prevail for the 66% Ni scenario. Simulations were carried out by altering the mineral compositions in the model. The following discussion on the impact of changes in feed matte mineralogical composition is given with respect to the nickel composition rising from 62 to 70 wt.%. 

Disturbed Conditions

With the exception of cobalt, an increase in the feed matte nickel content from 62 to 70 wt.% brings about only a marginal effect on metal extraction and sulphide sulphur conversion (see Figures 8.1 and 8.2). Nickel extraction and sulphur conversion observe improvements in all stages. Copper and cobalt extractions observe a decrease in the first stage, but improve in value in the second and third stages. The effect on extraction comes about due to the larger presence of nickel-bearing minerals, which have a higher reactivity and thus consume a greater proportion of the available oxidant. Nickel extraction improves by 0.0137 kg kg\(^{-1}\) in the first stage, but only by 0.0007 kg kg\(^{-1}\) in the second stage, suggesting that a greater proportion of nickel dissolves in the first stage relative to the second stage. The drop in nickel dissolution rate in the second stage
Table 8.3: Feed Matte Elemental Compositions (wt.%) relative to Nickel Content

<table>
<thead>
<tr>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2.4</td>
<td>0.91</td>
<td>3.2</td>
<td>22.50</td>
</tr>
<tr>
<td>68</td>
<td>2.6</td>
<td>0.88</td>
<td>4.2</td>
<td>23.25</td>
</tr>
<tr>
<td>66</td>
<td>2.8</td>
<td>0.85</td>
<td>5.2</td>
<td>24.00</td>
</tr>
<tr>
<td>64</td>
<td>3.0</td>
<td>0.82</td>
<td>6.2</td>
<td>24.75</td>
</tr>
<tr>
<td>62</td>
<td>3.2</td>
<td>0.79</td>
<td>7.2</td>
<td>25.50</td>
</tr>
</tbody>
</table>

Table 8.4: Feed Matte Mineralogical Compositions (wt.%) relative to Nickel Content

<table>
<thead>
<tr>
<th>Ni</th>
<th>Ni(^0)</th>
<th>Ni(_3)S(_2)</th>
<th>Cu(_2)S</th>
<th>CoS</th>
<th>Fe(^0)</th>
<th>FeS</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>13.36</td>
<td>77.27</td>
<td>3.01</td>
<td>1.40</td>
<td>1.85</td>
<td>2.12</td>
<td>0.99</td>
</tr>
<tr>
<td>68</td>
<td>10.71</td>
<td>78.15</td>
<td>3.26</td>
<td>1.36</td>
<td>2.01</td>
<td>3.44</td>
<td>1.07</td>
</tr>
<tr>
<td>66</td>
<td>8.06</td>
<td>79.03</td>
<td>3.51</td>
<td>1.31</td>
<td>2.18</td>
<td>4.76</td>
<td>1.15</td>
</tr>
<tr>
<td>64</td>
<td>5.42</td>
<td>79.91</td>
<td>3.76</td>
<td>1.26</td>
<td>2.34</td>
<td>6.08</td>
<td>1.23</td>
</tr>
<tr>
<td>62</td>
<td>2.77</td>
<td>80.79</td>
<td>4.01</td>
<td>1.22</td>
<td>2.50</td>
<td>7.40</td>
<td>1.31</td>
</tr>
</tbody>
</table>

allows for a greater extraction of copper and cobalt there; in other words, the loss of extraction in the first stage is compensated for in the second. Despite the drop in sulphur content in the matte, its conversion is closely related to nickel extraction behaviour, given that the major proportion of sulphides is nickel-bearing.

Overall (i.e. in the third stage), metal extraction and sulphur conversion increases, which for nickel only sees an improvement of 0.0007 kg kg\(^{-1}\). The latter suggests that the feed matte nickel content has little influence on the ability of the leach to extract nickel. Cobalt extraction demonstrates the greatest improvement, given that under standard conditions it displays an overall extraction of only 92 percent and thus changes in the factor affecting leaching rates are more noticeable. Nickel and copper extraction, as well as sulphur conversion, have standard values of greater than 99 percent, and so even large positive changes in the process-wide factors that affect leaching rates would only lead to marginal increases in their value.

The changes in nickel, copper, cobalt and sulphur (and iron) dissolution rates result effectively from the changes in mineral conversion and the changes in elemental composition in the matte. Given the nature of metal extraction and sulphur conversion
variations discussed above, the majority of changes in process chemistry are attributable to the latter factor. The most apparent effect on solution composition is an increase in nickel concentration at all major points in the process (see Figure 8.3). If nickel extraction were to remain constant, the higher nickel content in the feed matte would lead to an increase in nickel dissolution rates and thus higher concentrations. However, the improvement in dissolution rate is amplified due to the higher nickel extraction. Nickel concentration increases by 12.2 g L$^{-1}$ in the first stage and 5.7 g L$^{-1}$ in the second stage, while the effect of this sees an increased CBF liquor concentration of 10.5 g L$^{-1}$.

In the third stage, the nickel concentration decreases. Despite an increase in third stage nickel extraction, the reduction in discharge concentration is the result of feed solution dilution, which results from a lower Thickener 2W underflow rate (which is due to lower solids throughout; an explanation for this is given below), and thus a lower Tank 3 discharge rate, relative to the unchanging Ammonia Still distillate flow rate. That said, all dissolved components (metal or otherwise) observe a drop in concentration in the third stage.

The variation in feed matte copper and cobalt content, in concert with the changes in metal extraction, bring about relative changes in copper and cobalt concentrations. A decrease in copper concentration takes place in the first stage, second stage and copper boil feed, while cobalt concentration sees increases in a respective fashion. The changes in copper concentration throughout the process are significant, given that it directly impacts on the BV-to-copper concentration ratio in the copper boil feed, and, in conjunction with the decrease in nickel concentration, influences the ammonia evaporation rate in the third stage leach; greater detail is given on this in subsequent discussions.

The drop in feed matte sulphur content impacts the process in several ways, affecting the net generation of aqueous ammonia, ammonium ions and unsaturated sulphur. Aqueous ammonia is consumed in the leaching reactors in order to neutralise the acid that is generated when sulphur is oxidised (see reactions 6.14 – 6.18). Despite a higher sulphide sulphur conversion, lower total sulphur oxidation rates are observed. Given that less sulphur is oxidised, less ammonia is consumed. This behaviour is
responsible for the increases in ammonia concentration in the first and second stages, and thus the copper boil feed (Figure 8.3). The increase in ammonia concentration at said points in the process is exacerbated by both the nature of liquor recycle to the first stage feed and the air flow configuration, which sees a portion of second and third stage leach ammonia recycled to the first stage in the form of autoclave vent gas. Changes in matte sulphur content have little impact on ammonia consumption in the third stage, given that little sulphur progresses to that point in the process. The decrease in ammonia concentration in said stage (Figure 8.3) is due mainly to the decrease in feed concentration, but also to the increase in the rate of ammonia evaporation that accompanies the lower metal concentrations, which gives rise to a greater proportion of uncomplexed ammonia in solution and thus a higher ammonia overpressure.

Naturally, the above first and second stage chemistry also leads to a decrease in autoclave ammonium ion generation and thus a decrease in AmSul concentration; decreases of roughly one-third and one-eighth of the standard first and second stage leach concentrations are observed, respectively. Although the ammonia-to-nickel concentration ratios remain within acceptable limits, the AmSul-to-nickel concentration ratios do not, and thus there is the potential for negative repercussions on the process. The decrease in feed matte iron content also contributes to a widening of the ammonia-to-AmSul and nickel-to-AmSul concentration ratios via the same mechanism discussed for sulphur (see reaction 6.19).

The main impact of changes in sulphur content is on the BV and, more importantly, the BV-to-copper concentration ratio. An increase in nickel content actually results in an increase in both variables in the first stage and copper boil feed (see Figure 8.4). This is because – despite a decrease in matte sulphur content – the rate of unsaturated sulphur production still exceeds that of its consumption in the first stage leach, and thus a steady-state build-up of unsaturated sulphur prevails. A secondary factor influencing the increase in BV-to-copper concentration ratio is the lower copper concentrations that result from the decrease in feed matte copper content.
Figure 8.1: The effect of changes in matte mineral composition on first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion under disturbed conditions

Figure 8.2: The effect of changes in matte mineral composition on overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion under disturbed conditions
Figure 8.3: The effect of changes in matte mineral composition on nickel and ammonia concentration under disturbed conditions

Figure 8.4: The effect of changes in matte mineral composition on BV and BV:[Cu] under disturbed conditions
Optimal Conditions

A host of measures is required in order to maintain optimal operation and prevent deviations in concentrations from their set-points, as discussed above. However, none of the measures has a noticeable impact on metal extraction or sulphide sulphur conversion beyond those initiated by the disturbance itself (see Figures 8.5 and 8.6). Improvements in metal extraction and sulphide sulphur conversion are observed under optimal conditions relative to disturbed conditions for nickel content greater than 66 wt.%, while the converse seems to be true for nickel content less than this figure. Despite the latter, the differences in overall extraction are not great. Furthermore, whilst a broad spectrum is considered for nickel content, its value is greater than 65 wt.% for the vast majority of operational situations; of the 36 data sets used for parameter estimation and model validation in the previous chapter, only two data sets (Simulations 6 and 12; see Table 7.7) consider a matte nickel content of less than 65 wt.%. Moreover, the higher extractions would be at the expense of stability. Thus, the environment established for optimal operation represents the superior process conditions.

To prevent an increase in CBF nickel concentration, the first stage leach concentration should be kept fixed and the second stage leach concentration should be allowed to decrease from roughly 95 to 90 g L\(^{-1}\) (see Figure 8.7). To accomplish this, the pulp density of the feed slurry to said stages must be reduced (Figure 8.7). A reduction from 16.7 to 14.1 wt.% is seen in the first stage, while a drop from 11.5 to 9.8 wt.% is observed in the second stage. In the first stage, this is achieved by increasing the combined flow rates of DTO-to-Tank 1 and MFL-to-Tank 1, which has the effect of increasing the slurry flow exiting Tank1 and reducing the mean residence time of the first stage from 3.8 to 3.2 hours (see Figure 8.8). In the second stage, a reduction in feed pulp density is brought about with a decrease in DTO-to-Tank 2 flow rate (see Figure 8.9). The latter flow rate is decreased – rather than increased – due to the behaviour of Thickener 1.

The joint effect of a greater proportion of nickel in the feed matte and higher nickel extraction leads to an improvement in total solids conversion in the first stage,
Figure 8.5: Optimal first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs nickel content in the leach feed matte

Figure 8.6: Optimal overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs nickel content in the leach feed matte
resulting in a lower exit solids flow rate. In order to maintain a constant underflow density, the Thickener 1 underflow rate needs to be reduced (see Figure 8.10), which alone would have the effect of lowering the pulp density of Tank 2 below its optimal value. Thus, a decrease in DTO-to-Tank 2 flow rate is required to offset this and certify that the said pulp density remains at a level appropriate for second stage nickel concentration control. As a result, the slurry flow exiting Tank 2 becomes lower, leading to an increase in second stage mean residence time from 13.5 to 16.6 hours (Figure 8.8). A higher Thickener 1 overflow rate is consequently observed following a reduction in the underflow rate (Figure 8.10), thus requiring a lower second stage nickel concentration in order to maintain a constant concentration of nickel in the copper boil feed. Although the lower flow rates exiting the second stage would reduce the copper boil feed nickel concentration, it alone is not sufficient to support the required reduction in component mass flow.

The lower solids flow rate exiting the second stage has an impact on the behaviour of Thickeners 2 and 2W in a manner like that for Thickener 1. In order to maintain a constant underflow density, the underflow rates for the former thickeners also needs to be reduced (Figure 8.10). Owing to a higher total mass flow rate entering Thickener 2, its overflow rate increases like that of Thickener 1 (Figure 8.10). The combined effect of all flow and concentration changes around Thickener 2W calls for a lower MFL-to-Thickener 2W flow rate (Figure 8.9) in order to maintain suitable third stage feed nickel concentration control, which brings about a lower overflow rate (Figure 8.10). The slurry flow exiting Tank 3 is lower, which, despite a higher Ammonia Still distillate flow rate (to be discussed below), produces an effective drop in third stage feed rate, thus increasing its mean residence time from 24.9 to 32.7 hours (Figure 8.8).

Unlike that of nickel, the concentration of AmSul in the second stage needs to be increased (Figure 8.9) in order to promote a stable concentration in the copper boil feed. The inconsistent behaviour may be traced to the empirical relationships that exist between nickel and AmSul concentrations, which are different for the first stage and copper boil feed. Given that the concentrations of said components remain constant at said points in the process (Figure 8.9), and that the Thickener 1 overflow rate increases
Figure 8.7: Optimal nickel concentration and leaching stage feed pulp density vs nickel content in the leach feed matte

Figure 8.8: Optimal tank discharge flow rate and leaching stage mean residence time vs nickel content in the leach feed matte
Figure 8.9: Optimal tank and thickener repulp stream flow rates and AmSul concentrations vs nickel content in the leach feed matte

Figure 8.10: Optimal thickener underflow and overflow rates vs nickel content in the leach feed matte
with increase in nickel content, a reduction in component mass flows is required from the second stage. Due to the lower second stage flow rates, even if no change in second stage discharge concentrations were to prevail, a reduction in component mass flows would be observed. It is simply the case that the nature of the relationships between nickel and AmSul concentrations are such that the former is decreased and the latter is increased in the second stage in order to satisfy component mass conservation.

As discussed previously, the lower sulphur content that accompanies a higher nickel content in the matte results in a reduction in autoclave ammonium ion production in the first and second stages. In the second stage, the lower production rate combined with a need for higher AmSul concentration necessitates an increase in the DTO AmSul concentration (Figure 8.9). In the first stage, the lower ammonium ion production rate combined with a need for AmSul concentration to remain constant necessitates an increase in the feed concentration. Given the increase in DTO AmSul concentration, this has the effect of lowering the first stage feed MFL-to-DTO flow ratio by 0.284 m$^3$ m$^-3$ over the nickel content range. Specifically, an increase in DTO flow rate and a decrease in MFL flow rate is required (Figure 8.9). Moreover, the rate increase in DTO is greater than the decrease in MFL, and thus the combined volumetric flow rate increases; this is in line with earlier discussions related to first stage feed pulp density.

A reduction in matte sulphur content also leads to an increase in autoclave ammonia production in the first and second stages. Given that ammonia-to-total metals molar ratio is to remain fixed in the first and second stages, rather than ammonia concentration, a decrease in the latter is required at said points as well as the copper boil feed following an increase in matte nickel content (see Figure 8.11), owing to the decrease in total metal concentration that follows (i.e. on the account of copper in the first stage and copper boil feed, and both copper and nickel in the second stage); this decrease is marginal in both the first stage and copper boil feed. Given the nature of liquor recycle and the air flow configuration, ammonia is recycled internally from a number of points to the first stage leach, which complicates ammonia control. An explanation of how ammonia concentration is kept optimal in response to mineral composition changes is best commenced with an assessment of third stage behaviour.
The most significant impact that the third stage leach has on overall leach performance is the influence its vent gas has on first stage leach behaviour, particularly that of Autoclave 1A. For the same reasons discussed previously for disturbed conditions, Autoclave 3A experiences lower feed and discharge concentrations, as well as increased ammonia evaporation rates. In order to keep the discharge ammonia concentration constant, an increase in ammonia demand is observed following an increase in nickel content (Figure 8.11); that is, an increase in flow of Ammonia Still distillate is called for. This increase in flow intensifies the third stage feed dilution, thus enhancing the effect on evaporation rates. In the second stage, the higher ammonia production rates necessitate a drop in demand in order to reduce the discharge ammonia concentration; that is, a decrease in flow of Ammonia Still overhead gas to Autoclave 2A and anhydrous ammonia to Autoclaves 2B and 3B is required. The total decline in ammonia flow to the second stage is distributed evenly over each autoclave.

Like in the second stage, reducing the discharge ammonia concentration of the
first stage requires a drop in total ammonia demand, given the higher ammonia production rates. However, ammonia control in the first stage is not as straightforward as it is elsewhere, given that Autoclaves 1A and 1B receive a portion of their feed ammonia in their air streams. Excluding ammonia that enters with the feed slurry, the former and latter autoclaves receive around 65 and 10 percent of their ammonia in their feed gas, respectively. Concerning Autoclave 1B, a distinct drop in anhydrous ammonia demand is witnessed. A slight nonlinearity may be observed in the ‘1B’ curve in Figure 8.11, attributable to variations in the Autoclave 1A venting rate, which sees an increase in ammonia vapour flow of 35.5 percent relative to its standard value over the nickel content range.

Given that Autoclave 1A receives a greater portion of its ammonia feed as gas (around 80 percent of which originates from the third stage), its demand for anhydrous ammonia is subject to greater nonlinearity. An increase in demand is seen from 62 to 66 wt.% nickel content, while a decrease is evident from 66 to 70 wt.% (see curve ‘1A’ in Figure 8.11). This action is attributable chiefly to the nonlinear variation in the third stage vent gas, in which an increase in the rate of ammonia evaporation takes place when matte nickel content exceeds 66 wt.%. The third stage ammonia vent gas rate sees an overall increase of 28.2 percent over the nickel content range, while that in the second stage observes a decrease of 10.2 percent, each relative to its standard value.

In order to keep the CBF BV-to-copper concentration ratio constant over the nickel content range, the first stage leach ratio needs to be reduced (see Figure 8.12). This is due to the increase and decrease in volumetric flow rate from the first and second stages, respectively, and that the BV (and thus BV-to-copper concentration ratio) in the latter stage is always zero. The first stage copper concentration decreases by 1.4 g L\(^{-1}\) as a result of a lower copper content in the feed matte, which for a constant BV would increase the value of said ratio. Moreover, as discussed previously for disturbed conditions, the lower sulphur content leads to a greater unsaturated sulphur production-to-consumption ratio, and thus greater BV. To reverse the latter, autoclave temperature needs to be increased.
Figure 8.12: Optimal BV:[Cu] and average first stage leach autoclave temperature vs nickel content in the leach feed matte

Figure 8.13: Optimal miscellaneous total leach feed flow rates and leaching stage cooling duty vs nickel content in the leach feed matte
The fourth compartment temperatures of Autoclaves 1A and 1B are fixed, and so only the preceding compartment temperatures are manipulated (and all take on the same value). Given the similarity in behaviour of Autoclaves 1A and 1B, the temperatures of like-numbered compartment are very similar, and an average of the two is displayed in Figure 8.12. Temperatures for Compartments 1 through 3 are required to be raised from around 85 to 95 °C over the nickel content range.

Total leach air and ammonia flow rates experience a marginal decrease and increase in demand, respectively, while more pronounced changes in the demand for DTO and MFL are witnessed (see Figure 8.13). The greater metal extractions and sulphur conversion in the first stage brings about an increase in cooling duty of 0.98 MW, while the drop in overall leaching activity in the second and third stage results in lower cooling duties there by 2.07 MW and 0.38 MW, respectively (Figure 8.13).

**Feed Matte Particle Size Distribution**

Variability in the feed matte particle size distribution occurs because of operational conditions in the ball mill grinding circuit (which directly precedes the leach). Change in the mass fraction of particles passing 106 µm, \( F_{m,106} \), in the feed matte is used as the basis of changes in its particle size distribution. Standard conditions prevail for the case when \( F_{m,106} = 0.9052 \); that is, when the size distribution given in Appendix D is considered. Simulations were carried out by altering \( F_{m,106} \) in the model. The following discussion on the impact of changes in feed matte particle size distribution is given with respect to the mass fraction of particles passing 106 µm rising from 85 to 95 wt.%.

**Disturbed Conditions**

An increase in the mass fraction of particles passing 106 µm translates to a finer assembly of particles and thus an increase in effective mineral surface area per unit mass of particles. The most obvious effect of this is an increase in metal extraction and sulphide sulphur conversion (see Figures 8.14 and 8.15). Nickel, copper and cobalt first stage leach extractions increase by 0.0755, 0.0915 and 0.1733 kg kg\(^{-1}\), respectively. The ensuing effect is an increase in the concentration of all dissolved metals. The nickel
concentration improves by 6.59 g L$^{-1}$ (see Figure 8.16), while that of copper and cobalt does so by 9.3 and 30.1 percent of their standard values, respectively; the smaller improvements in copper and cobalt concentrations are attributable to their low matte content. Changes in autoclave feed liquor composition where the latter two metals are concerned seem to have a much greater impact on their discharge concentrations than do changes in extraction.

Sulphur conversion in the first stage leach grows by 0.1347 kg kg$^{-1}$ (Figure 8.14). Ammonia concentration observes a slight increase there (Figure 8.16), while a similar decrease in magnitude of AmSul concentration takes place also. Naturally, the increase in sulphur dissolution has an impact on the BV (see Figure 8.17), however, the effect is only minor. An initial increase in first stage leach BV is accompanied by a gradual decrease in value, the nature of which reflects the relatively constant unsaturated sulphur production-to-consumption ratio. A corresponding effect on the first stage leach BV-to-copper concentration ratio is established. The CBF BV-to-copper concentration ratio remains unchanged as a result of PSD variation, which is related more to a reduction in flow exiting the second stage than to changes in chemistry.

Cumulative metal extractions in the second stage all improve. Nickel does so marginally by 0.0024 kg kg$^{-1}$ over the mass fraction range, while copper and cobalt experience increases in extraction by 0.0462 and 0.1554 kg kg$^{-1}$, respectively (Figure 8.14). Sulphur conversion also shows improvement on the order of 0.0206 kg kg$^{-1}$. The nickel concentration experiences a significant drop in value of 18.60 g L$^{-1}$ (Figure 8.16), while copper and cobalt concentrations observe increases of 1.2 and 14.5 percent of their standard values, respectively. The large drop in nickel concentration is due to the shift in extraction from the second to the first stage leach. Over the mass fraction range, an additional 0.0731 kg kg$^{-1}$ of leach feed nickel is extracted in the first stage relative to the second stage, and the majority of this dissolved nickel reports to Thickener 2 via the Thickener 1 overflow stream, thus bypassing the second stage. Given that cumulative nickel extraction in the second stage improves only marginally, and that no increase in nickel flow into the leach occurs (as opposed to the case for an increase in its matte content), effectively no change in CBF nickel concentration takes place (Figure 8.16).
The fall in second stage nickel concentration is also due in part to a drop in metal and ammonia concentrations in Tank 2, owing to a reduction in Thickener 1 underflow rate which results from a moderate increase in solids conversion in the first stage (i.e. the same reason discussed previously for mineral composition changes). The AmSul concentration in Tank 2 actually increases, given that its concentration in the DTO liquor is greater than that in the Thickener 1 underflow liquor. Having said this, the second stage discharge concentration of ammonia sees a slight decrease (Figure 8.9), while that of AmSul increases. The lower Thickener 1 underflow rate is also the source of lower second stage feed and discharge flow rates.

A comparison of first and second stage leach extraction and conversion curves for each element (Figure 8.14) reveals something fundamental about the nature of leaching in this system. Very high cumulative nickel extractions (greater than 99.7 percent) are observed in the second stage regardless of first stage performance (at least for the case in which the first stage extraction exceeds 80 percent). Nickel is able to accomplish this due to the high reactivity of the minerals it occupies. Cumulative extractions for copper and cobalt in the second stage are more reliant on first stage performance, as is sulphide sulphur conversion.

An examination of third stage (i.e. overall) leach extractions (Figure 8.15) reveals that nickel performs only marginally better beyond its second stage extraction. Copper experiences very high overall extractions (greater than 99.4 percent) regardless of first stage performance (at least for the case in which the first stage extraction exceeds 65 percent). Although high overall sulphur conversions are observed, its actual value remains reliant on first stage performance. The behaviour of cobalt in the third stage, however, is the most conspicuous. Despite its performance in previous stages, cobalt is unable to achieve a very high overall extraction.

The underflow rates of Thickeners 2 and 2W are not as influenced by changes in the leach feed PSD as they are by changes in matte mineralogical composition. Thus, a relatively minor effect is seen on third stage leach concentrations. Over the mass fraction range, the gradual shift in extraction location from the third to the first stage
Figure 8.14: The effect of changes in the leach feed matte PSD on first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion under disturbed conditions

Figure 8.15: The effect of changes in the leach feed matte PSD on overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion under disturbed conditions
Figure 8.16: The effect of changes in the leach feed matte PSD on nickel and ammonia concentration under disturbed conditions.

Figure 8.17: The effect of changes in the leach feed matte PSD on BV and BV:[Cu] under disturbed conditions.
sees a lower metal dissolution rate in the former stage. The resultant lower metal content in solution brings about a greater relative concentration of uncomplexed ammonia, the latter of which is the source of an increase in ammonia evaporation due to the higher ammonia pressure, causing a decrease in ammonia concentration (Figure 8.16) exiting the third stage.

**Optimal Conditions**

It is apparent that a change in the leach feed PSD does not prompt the same level of disturbance to the process as does a change in the feed matte composition. The major impact is in the form of nickel concentration variation via a shift in extraction location. Metal extraction and sulphide sulphur conversion across the process varies little between optimal (see Figures 8.18 and 8.19) and disturbed (Figures 8.14 and 8.15) conditions. First stage variables are virtually identical. Differences, however, may be noticed in second stage variables. Lower and higher cumulative metal extractions (although the effect on nickel is negligible) and sulphur conversion at the lower and upper extremes of the mass fraction range, respectively, may be observed for optimal relative to disturbed conditions. This is due to appropriate changes in the second stage mean residence time. Naturally, the second stage performance has an effect on the third stage performance, and thus a similar comparison between optimal and disturbed conditions may be made (although the effect on copper is negligible). In all cases, cobalt extraction displays the most significant variability.

Maintaining a fixed first stage nickel concentration – and thus a fixed CBF concentration – requires that the first stage feed pulp density be reduced from 15.8 to 14.8 wt.% as the mass fraction of particles pass 106 µm becomes larger (see Figure 8.20). This leads to an increase in the Tank 1 discharge flow rate and reduction in the mean residence time of the first stage from 3.6 to 3.3 hours (see Figure 8.21). The reduction in pulp density is realised by increasing and decreasing the flow rates of DTO-to-Tank 1 and MFL-to-Tank 1, respectively (see Figure 8.22), although the change in magnitude of the former is larger than the latter and thus their combined flow rate is increased.
Figure 8.18: Optimal first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs mass fraction of particles passing 106 μm in the leach feed matte

Figure 8.19: Optimal overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs mass fraction of particles passing 106 μm in the leach feed matte
The higher solids conversions in the first and second stages have the same impact on thickener behaviour as discussed previously. The overflow rates of Thickeners 1 and 2 increase and that of Thickener 2W decreases, while the underflow rates of all thickeners decrease in value (see Figure 8.23). This causes decreases in the discharge rates of Tanks 2 and 3, which in the case of the former leads to an increase in second stage mean residence time from 13.0 to 17.6 hours (Figure 8.21). The third stage mean residence time actually experiences a decrease from 28.9 to 28.2 hours, which is the result of the increase in Ammonia Still distillate (to be discussed below). The reduced flow rates through the second stage leach require that the nickel concentration there decrease in value from around 95 to 90 g L\(^{-1}\), however, unlike that in the first stage, the feed pulp density does not need to be altered (which is simply a matter of coincidence), thus remaining steady at around 10.7 wt.\% (Figure 8.20). Given the fall in Thickener 1 underflow rate, the DTO-to-Tank 2 flow rate must follow suit by a comparable magnitude (Figure 8.22).

The second stage concentration of ammonia requires a minor decrease in value, which is accomplished via a reduction in ammonia demand (see Figure 8.24). The change in magnitude of the latter is augmented by the fall in second stage feed flow rate. For the same reason discussed previously, the AmSul concentration in the second stage needs to be increased in order to maintain a constant CBF concentration, which is realised via an increase in the DTO AmSul concentration (Figure 8.22). Maintaining a constant first stage AmSul concentration requires that the component feed rate increase. In concert with the increase in DTO AmSul concentration and decrease in first stage feed pulp density, this is achieved with a decrease in the Tank 1 MFL-to-DTO flow ratio of 0.253 m\(^3\) m\(^{-3}\) over the mass fraction range (Figure 8.22).

Ammonia concentration in the first stage increases slightly (Figure 8.24), owing to the small increases in copper and cobalt concentration that result from higher extraction, in the attempt to maintain a fixed ammonia-to-total metals molar ratio. In Autoclave 1B, this is controlled with an increase in demand for anhydrous ammonia; there is effectively no variation in the ammonia vapour flow exiting Autoclave 1A. In
Figure 8.20: Optimal nickel concentration and leaching stage feed pulp density vs mass fraction of particles passing 106 µm in the leach feed matte

Figure 8.21: Optimal tank discharge flow rate and leaching stage mean residence time vs mass fraction of particles passing 106 µm in the leach feed matte
Figure 8.22: Optimal tank and thickener repulp stream flow rates and AmSul concentrations vs mass fraction of particles passing 106 µm in the leach feed matte

Figure 8.23: Optimal thickener underflow and overflow rates vs mass fraction of particles passing 106 µm in the leach feed matte
the latter autoclave, demand for anhydrous ammonia decreases and then increases in value over the mass fraction range (Figure 8.24). The latter behaviour, like that discussed previously, is predominantly the result of appropriate variations in the ammonia evaporation rate from Autoclave 3A, but also influenced by changes in the second stage vent rate. Second and third stage vent ammonia vapour flows decrease and increase by 12.0 and 17.2 percent relative to their standard values, all respectively. The source of the convex versus concave qualities of the ‘1A’ curve in Figures 8.24 and 8.11 is due simply to the fact that the first stage leach ammonia concentration is required to be increased and decreased, all respectively. The higher rate of ammonia evaporation from Autoclave 3A (for the same reasons as those under disturbed conditions) calls for an increase in demand for Ammonia Still distillate in order to maintain constant ammonia concentrations over the mass fraction range (Figure 8.24).

Due to higher and lower flows exiting the first and second stages, respectively, a reduction in first stage BV-to-copper concentration ratio is needed to maintain a fixed ratio in the copper boil feed liquor (see Figure 8.25). Although copper concentration observes an increase in the first stage, a drop in BV is also required to adjust the ratio appropriately. This is accomplished with an average first stage temperature increase of 0.9 °C over the mass fraction range (Figure 8.25).

Total leach air and ammonia exhibit marginal variations in demand (see Figure 8.26). The air feed rate increases, while the ammonia feed rate increases and decreases about the standard point. DTO and MFL see more obvious increases and decreases in demand, respectively (Figure 8.26). As a consequence of the shift in extraction (primarily from the second stage to the first stage), an increase in first stage cooling duty of 3.30 MW and a decrease in second stage cooling duty of 3.12 MW results (Figure 8.26). While the former is only an increase of around 15 percent of standard operational requirements, the latter is a decrease of around 55 percent. A decrease in cooling in the third stage of 0.56 MW (or around 20 percent) is also observed (Figure 8.26).
Figure 8.24: Optimal ammonia concentration and change in autoclave ammonia demand vs mass fraction of particles passing 106 µm in the leach feed matte.

Figure 8.25: Optimal BV:[Cu] and average first stage leach autoclave temperature vs mass fraction of particles passing 106 µm in the leach feed matte.
8.3.2 Optimal Set-Point Changes

The most significant controlled variables for any leaching process are the composition of the leach discharge liquor and the solids feed rate. These variables practically determine the operational setting of the entire leaching process, and thus the effect that changes in their set-points have on optimal performance is of considerable interest. An examination of changes in the copper boil feed liquor composition and feed matte solids flow rate set-points for this process is given here.

Nickel Concentration in the Copper Boil Feed

The concentrations of nickel, ammonia, AmSul, as well as the BV and copper concentration (in the form of their ratio), are all important elements of the CBF liquor; cobalt concentration is inconsequential. Change in the nickel concentration is used as the basis of changes in the solution composition. The former is the key variable with which leach-wide concentration control is instituted, and it is typically altered to suit conditions established downstream, such as those in the feed to the oxyhydrolysis or
hydrogen reduction processes. The CBF ammonia and AmSul concentrations are varied in a comparative manner. The CBF BV-to-copper concentration ratio does not change. Standard conditions prevail when the CBF nickel concentration is 100 g L\(^{-1}\).

Optimisation runs were carried out by altering the target CBF nickel concentration in the model. The target CBF ammonia and AmSul concentrations were adjusted in accordance with the applicable constraints stipulated in Section 8.2.3, while the target CBF BV-to-copper concentration ratio remains fixed (see Table 8.2). The following discussion on the impact of changes in CBF liquor composition is given with respect to the concentration of nickel rising from 90 to 110 g L\(^{-1}\).

A higher CBF nickel concentration improves metal extraction and sulphur conversion in all leaching stages, however, only marginally so in the first (see Figures 8.27 and 8.28). The extraction and conversion curves are very similar to those depicting the effect of mineral composition changes (Figures 8.1 and 8.2). However, given that the present scenario does not bring about a change in elemental throughput, there is a much smaller impact on autoclave chemistry. The task of promoting optimal conditions via concentration control is thus a much simpler one.

The higher extractions comes about due to the higher concentrations of nickel required in the first and second stages, which are established in response to increases in feed pulp density from 13.9 to 16.7 wt.% and 9.9 to 11.6 wt.%, respectively (see Figure 8.29). This leads to a decrease in the feed tank discharge flow rates of said stages and thus an increase in stage mean residence times (from 3.1 to 3.8 hours in the first stage and 13.0 to 17.1 hours in the second stage) (see Figure 8.30). The second stage nickel concentration increases from 82.2 to 103.5 g L\(^{-1}\), which matches the changes in CBF and first stage leach concentration on an almost unit basis; this is illustrated in Figure 8.29 by the near-same gradients of the concentration curves. This is the result of the manner in which solution flow varies in both the first and second stage discharges. Thus, for any given change in CBF and (corresponding change in) first stage nickel concentration, the second stage concentration should change by practically the same amount. The improvements in cumulative extraction and conversion in the third stage
are due primarily to that in the preceding stages, which is apparent from the fact that the third stage mean residence time actually decreases (from 29.0 to 28.1 hours) over the CBF nickel concentration range (Figure 8.30).

First stage feed pulp density control is implemented by decreasing the combined flow rates of DTO-to-Tank 1 and MFL-to-Tank 1, while in the second stage this is carried out with a reduction in DTO-to-Tank 2 flow rate (see Figure 8.31). The increase in Tank 2 pulp density is also influenced by the drop in Thickener 1 underflow rate (see Figure 8.32). Unlike that reported previously for changes in matte quality, the source of the lower underflow rate is the lower first stage discharge flow rate, and thus lower thickener feed rate. This also leads to a decrease in Thickener 1 overflow rate, and sees a carry-on effect with the drop in Thickener 2 overflow and underflow rates (Figure 8.32). While the Thickener 2W underflow rate observes a decrease in accordance with that of the Thickener 2 underflow (owing to the relatively unchanging flow of solids), the overflow of the former thickener see a rate increase (Figure 8.32). This is the result of a rate increase in MFL-to-Thickener 2W (Figure 8.31), performed in a manner appropriate to keep the third stage feed tank nickel concentration constant in response to a progressively increasing concentration in the Thickener 2 underflow.

The higher first and second stage nickel concentrations also call for higher AmSul concentrations in the same locations, not to mention that in the copper boil feed liquor (Figure 8.31). The second stage leach concentration control is realised with an increase in DTO AmSul concentration (Figure 8.31), while that in the first stage requires an increase in the first stage feed MFL-to-DTO flow ratio of 0.299 m$^3$ m$^{-3}$ over the CBF nickel concentration range. Specifically, a decrease in DTO flow rate and an increase in MFL flow rate is required (Figure 8.31). Like that for nickel, the first stage, second stage and CBF AmSul concentrations experience a comparable percentage change in value in response to change in the CBF nickel concentration.

Higher ammonia concentrations are required in the first and second stages, as well as the copper boil feed, in order to maintain appropriate ammonia-to-total metal molar ratios (see Figure 8.33). Accordingly, an increase in anhydrous ammonia demand for
Figure 8.27: Optimal first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs nickel concentration in the copper boil feed.

Figure 8.28: Optimal overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs nickel concentration in the copper boil feed.
Figure 8.29: Optimal nickel concentration and leaching stage feed pulp density vs nickel concentration in the copper boil feed

Figure 8.30: Optimal tank discharge flow rate and leaching stage mean residence time vs nickel concentration in the copper boil feed
Figure 8.31: Optimal tank and thickener repulp stream flow rates and AmSul concentrations vs nickel concentration in the copper boil feed

Figure 8.32: Optimal thickener underflow and overflow rates vs nickel concentration in the copper boil feed
Figure 8.33: Optimal ammonia concentration and change in autoclave ammonia demand vs nickel concentration in the copper boil feed

Autoclave 1B is witnessed (Figure 8.33), which is also influenced by a drop in Autoclave 1A ammonia vent rate of 20.5 percent of its standard value. The drop in anhydrous ammonia demand for Autoclave 1A is symptomatic of the increase in third stage leach ammonia vent gas rate of 15.3 percent of its standard value over the CBF nickel concentration range; there is almost no change in second stage ammonia vent rate. The second stage leach autoclaves also observed a decline in ammonia demand. This is due to the fact that the concentration of ammonia in Tank 2 increases as a result of the higher concentration exiting the first stage leach, which is sufficient enough to reduce the need for external ammonia in order to maintain appropriate second stage concentrations.

Maintaining a fixed concentration of ammonia in the third stage leach requires an increase in Ammonia Still distillate flow rate (Figure 8.33), which results from an increase in ammonia evaporation from Autoclave 3A. The shift in metal extraction from the third stage to the second stage (which is apparent from the increasing second stage
extractions, yet relatively constant first and third stage extractions; see Figures 8.27 and 8.28) leads to a drop in third stage metal concentration. The latter results in a greater concentration of uncomplexed ammonia and thus greater ammonia partial pressure, which leads to a higher ammonia vent rate. It is the increase in Ammonia Still distillate flow rate that causes the decline in third stage leach mean residence time, despite the drop in the Tank 3 discharge rate (Figure 8.30). At this point, it is pertinent to note the very similar third stage leach behaviour that has spanned both changes in matte quality and concentration set-points throughout the leach.

In response to the respective changes in first and second stage discharge flow rates, maintaining a constant CBF BV-to-copper concentration ratio requires a minor increase in said ratio in the first stage (see Figure 8.34). An increase in both the first stage feed pulp density and the copper extraction in said stage brings about an increase in copper concentration there of 0.6 g L\(^{-1}\). This requires an appropriate increase in BV, which is established with a drop in first stage leach temperature of from 91.5 to 87.9 °C (Figure 8.34).

Total leach air and ammonia each experience a marginal increase in demand (see Figure 8.35). The total demand for DTO and MFL observe a decrease and increase, respectively. The increase in cooling duty in the first stage of 2.1 MW is due to the higher metal extraction and sulphur conversion there (Figure 8.35). Despite the improvements in second stage extractions and conversion, a lower cooling duty of 0.6 MW is observed there due to a drop in Tank 2 temperature of around 5 °C, which is a result of the drop in Thickener 1 underflow rate. The cooler feed slurry offsets the need for additional cooling water. The drop in third stage leach activity is the main source of the lower cooling duty there, which sees a minor change on the order of 0.2 MW. The first, second and third stage cooling duties see appropriate changes of 9, 10 and 15 percent of standard operating conditions, respectively.
Figure 8.34: Optimal BV:[Cu] and average first stage leach autoclave temperature vs nickel concentration in the copper boil feed.

Figure 8.35: Optimal miscellaneous total leach feed flow rates and leaching stage cooling duty vs nickel concentration in the copper boil feed.
Feed Matte Solids Flow Rate

The feed matte solids flow rate is altered for two main purposes: (1) to directly manipulate the refinery nickel production rate, and (2) to aid in refinery maintenance activities, in which sections of the plant (including the elements of the leach) are shutdown. Understanding the impact that rate changes have on either is important, however, it is the first point that is given relevance here. Standard conditions prevail when the rate is 320 tpd.

Optimisation runs were carried out by altering the solids matte flow rate in the model; the matte-bypass stream remains inactive. As said variable was altered, the matte slurry volumetric flow rate was also altered in a manner that fixed its pulp density at the value observed in Simulation 16. The following discussion on the impact of changes in the leach feed matte solids flow rate is given with respect to the rate rising from 300 to 400 tpd (i.e. the range of feed conditions that would only be put into practice when all six autoclaves are active).

The increase in feed matte flow rate leads to a process-wide escalation in flow rates. The most significant impact of this on leach chemistry – which is distinct from any of the three simulation types discussed thus far – is a reduction in metal extractions and sulphide sulphur conversion in all stages (see Figures 8.36 and 8.37), the source of which are the lower mean residence times that result from the higher leach-wide throughput. Despite the lower extractions, however, the higher slurry throughput certifies greater leaching activity in all stages.

The first and second stage discharge flow rates are affected in a proportionate fashion, and so a negligible change in second stage leach nickel concentration is required in order to maintain a constant CBF concentration, in conjunction with an unchanging first stage concentration (see Figure 8.38). Moreover, little variation in first and second stage feed pulp density is necessary to sustain static nickel concentrations (Figure 8.38), which may be attributed to the changes in nickel extraction. Increases in both DTO-to-Tank 1 and MFL-to-Tank 1 flow rates are necessary to keep the pulp density of Tank 1 constant, in response to the increase in slurry flow into said tank,
Figure 8.36: Optimal first and second stage leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs the leach feed matte solids flow rate

Figure 8.37: Optimal overall leach metal (Ni, Cu, Co) extraction and sulphide sulphur (S) conversion vs the leach feed matte solids flow rate
Figure 8.38: Optimal nickel concentration and leaching stage feed pulp density vs the leach feed matte solids flow rate

Figure 8.39: Optimal tank discharge flow rate and leaching stage mean residence time vs the leach feed matte solids flow rate
Figure 8.40: Optimal tank and thickener repulp stream flow rates and AmSul concentrations vs the leach feed matte solids flow rate

Figure 8.41: Optimal thickener underflow and overflow rates vs the leach feed matte solids flow rate
while the MFL-to-DTO flow ratio observes an increase of 0.084 m$^3$ m$^{-3}$ (see Figure 8.40).

The impact on leaching stage throughput is best illustrated via the changes in feed flow rates (i.e. feed tank discharge rates), and by extension in mean residence times (see Figure 8.39). The first, second and third stage mean residence times see declines of 50 minutes, 5.6 hours and 7.2 hours over the entire feed matte flow rate range, or 24, 37 and 25 percent of standard quantities, all respectively. The increase in thickener feed rates sees an increase in both the over- and underflow rates of all three thickeners (see Figure 8.41). The increase in Thickener 1 underflow rate is the cause of the increase in DTO-to-Tank 2 flow rate, which is necessary to offset any changes in Tank 2 pulp density that the former would bring about (Figure 8.40).

The AmSul concentration in the second stage needs to be decreased in order to maintain a fixed concentration in the copper boil feed, in combination with an unchanging first stage concentration (see Figure 8.40). As made known previously, the need to alter the second stage AmSul concentration – despite not needing to make any adjustment to the nickel concentration there, even though its first stage and copper boil feed concentrations are fixed also – is due to the distinct empirical relationships that exist between nickel and AmSul concentration in the first stage and copper boil feed. The concentration is decreased, rather than increased, simply because the first stage leach discharge (and thus the Thickener 1 overflow) experiences a greater increase in volumetric flow rate than does the second stage leach discharge, per unit increase in feed matte solids flow rate. The drop in second stage AmSul concentration is accomplished with a decrease in DTO AmSul concentration (Figure 8.40).

The first and second stage leach ammonia concentrations observe slight decreases in value (see Figure 8.42). This is due to the drop in copper and cobalt concentrations in said stages that result from the lower extractions there, which is behaviour consistent with maintaining a fixed ammonia-to-total metals molar ratio. The slight increase in CBF ammonia concentration (Figure 8.42) is a result of the greater increase in first stage leach flow rate per unit increase in feed matte flow rate, relative to that of the
Figure 8.42: Optimal ammonia concentration and change in autoclave ammonia demand vs the leach feed matte solids flow rate

second stage. Due to the increase in throughput in all leaching stages, maintaining the ammonia concentrations depicted in Figure 8.42, as well as the fixed third stage concentration of 100 g L\(^{-1}\), necessitates an increase in demand for ammonia in all stages (Figure 8.42). The increase in demand is also influenced by the increase in air flow rate through Autoclave 3A, which is explained below.

The relative changes in first and second stage discharge flow rate are such that only a slight increase in first stage BV-to-copper concentration ratio is required to maintain a fixed quantity in the copper boil feed (see Figure 8.43). An increase in first stage leach temperature of 3.4 °C is required over the feed matte flow rate range in order to bring about the appropriate BV, relative to the decrease in copper concentration.

The improvements in leaching activity that result from higher solids throughput lead to a greater demand for total leach air and ammonia (see Figure 8.44). The greater demand for total leach DTO and MFL (Figure 8.44) is already apparent from the
Figure 8.43: Optimal BV:[Cu] and average first stage leach autoclave temperature vs the leach feed matte solids flow rate

Figure 8.44: Optimal miscellaneous total leach feed flow rates and leaching stage cooling duty vs the leach feed matte solids flow rate
increases in individual flow rates to Tank 1, Tank 2 and Thickener 2W (Figure 8.40). Naturally, the greater activity in the first and second stages produces greater cooling duties there (Figure 8.44). Despite the greater activity in the third stage, the decline in cooling duty is due to the increase in air flow rate through Autoclave 3A, which enters at a temperature much lower than that of the compartments. Given that total leach air demand is driven primarily by first stage leach behaviour, a largely disproportionate increase in air flow rate relative to increase in leaching activity is observed in the third stage. Moreover, the higher air flow rate leads to increases in both the water and ammonia evaporation rates. The effect of changes in the three flow rates is one of net cooling.

Of all the simulations carried out thus far in this chapter, changes in the feed matte solids flow rate has the simplest effect on leach performance. The impact on process conditions is restricted predominantly to flow rate, as well as first stage leach temperature and DTO AmSul concentration. Some level of harmony exists between solids throughput and leach chemistry. This is apparent given that the first and second stage leach feed pulp densities (which respond most sensitively to changes in autoclave behaviour) remain relatively steady over the entire simulation range, as do a number of the free variable concentrations (e.g. second stage nickel concentration) that were observed to vary in the previous three simulation types. In other words, if leach-wide flow rates, first stage autoclave temperature and DTO AmSul concentration can be maintained in appropriate proportion to the matte rate (which are observed to take on linear relationships), then suitable concentration control will take effect.

8.4 Process Performance Appraisal

8.4.1 Current Operating Capabilities and Characteristics

The leaching process is fairly robust when the matte solids feed rate is 320 tpd. Under optimal conditions, it is capable of maintaining high mineral conversion in response to variability in both the mineral composition and size distribution of the feed matte, as well as to changes in concentration set-points.
The process exhibits a high degree of complexity and interaction, which renders process control a difficult task. The behaviour of any given leaching stage has the capacity to influence both of the other stages via solids, liquid and gas flow. This was demonstrated in part in the previous chapter for a single snapshot and was expounded in this chapter for a broad set of likely conditions.

**First Stage Leach**

The changes in solution composition (with the exception of AmSul concentration) and temperature in the first stage feed are relatively minor and have no measurable impact on first stage performance. This is due to the large amount of leaching activity and heat generation that takes place there; details of the nature of this were discussed in the previous chapter. The AmSul concentration is distinct due to the explicit control that results from manipulating the first stage feed MFL-to-DTO ratio. The changes in the feed solids composition and size distribution, as well as the pulp density, are what contribute predominantly to changes in the first stage discharge.

The first stage feed pulp density has a standard value of 15.3 wt.%. A higher value is required to bring about a greater nickel dissolution rate per unit reactor volume. This is the case if a higher first stage nickel concentration is required, if nickel extraction drops, or if the feed matte nickel content decreases. Furthermore, the MFL-to-DTO ratio, which has a standard value of 0.304 m$^3$ m$^{-3}$, shares the same fate as that of the pulp density, given that the AmSul concentration set-point is tied to that of nickel. If the pulp density increases, so does the MFL-to-DTO ratio. Incidentally, this also leads to an increase in first stage mean residence time, which has a standard value of 3.4 hours.

The performance of the first stage determines the performance of the entire leaching process. Mineral conversion is improved when the nickel content in the feed matte is higher, when the assembly of particles in the feed matte are finer, and when the nickel concentration set-point in the copper boil feed is at its upper limit. When mineral conversion is maximised in the first stage its cumulative measure is also maximised in the third stage. Not only does the former reduce the burden of residual mineral conversion on the second and third stages, the resultant reduction in solids flow exiting
the first stage increases the mean residence times of the subsequent stages, thus improving leaching conditions more so.

The extraction of nickel dominates in all stages. In the first stage, if leaching conditions tend towards the unfavourable, the nickel-bearing minerals will consume that proportion of oxidant that would have otherwise been earmarked for the copper- and cobalt-bearing minerals. However, the loss of copper and cobalt extraction in the first stage has the potential to be made up for in the second and third stages. The first stage nickel extraction has a standard value of 85.6 percent, with a range of 82.1 to 89.2 percent. The capacity for nickel extraction to reach these extremes lies exclusively with the particle size distribution of the leach feed matte. Mineral composition and concentration set-point changes do not have a significant influence, provided that sufficient air supply is maintained.

There is a negligible difference between disturbed and optimal conditions where metal extraction and sulphur conversion is concerned. Two important conclusions may be drawn from this. Firstly, it suggests that mineral conversion is not sensitive to changes in the main factors affecting leaching (i.e. temperature, reactant composition and mean residence time), which are distinct for the two cases and can be widely variable in their own right. Secondly, it suggests that mineral conversion is difficult to control. An adequate air supply to the leach (for a given overall oxygen utilisation) should be upheld to maximise metal extraction, however, the distribution of extraction amongst the three stages is a function of process conditions and process structure.

Concentration set-point changes do not have a noticeable impact on autoclave chemistry. Mineral conversion remains relatively constant and concentration control is implemented chiefly through manipulating the global feed streams (i.e. air, anhydrous and recycled ammonia, MFL and DTO). The variation in feed matte composition and size distribution represents the origin of chemistry disturbances, resulting in deviations to nickel, copper, cobalt and sulphur (and iron) dissolution rates and consequent reaction rates. This is observed predominantly in the first stage, but is also applicable to the second and third stages.
Variation in the first stage nickel dissolution rate sees an inverse response in the feed pulp density in order to maintain a fixed nickel concentration in the first stage discharge. The first stage feed pulp density also has an impact on the copper and cobalt concentrations, however, the direction of change is dependent on the nature of the nickel dissolution rate change. If the latter is due to feed mineral composition change, the copper and cobalt dissolution rates (and thus concentrations) will vary in the same direction as their elemental content in the matte. However, if the nickel dissolution rate change is due to size distribution changes, then both the copper and cobalt dissolution rates will change in the same direction as that of nickel (as will their concentrations).

Variation in the first stage sulphur dissolution rate probably has the most widespread impact, given that it affects the net generation of ammonia, ammonium ions and unsaturated sulphur. The direction of change in the first stage ammonia production rate is the same as the direction of change in the nickel dissolution rate, while that of the ammonium ion production rate and BV-to-copper concentration ratio target are the opposite. As mentioned before, maintaining a fixed AmSul concentration (relative to nickel concentration) in response to this is achieved with appropriate changes in the feed MFL-to-DTO ratio. Moreover, adjusting the BV-to-copper concentration ratio is realised with a change in autoclave temperature (which has a standard value of 89.6 °C) in the opposite direction of that required of the ratio. That said, if the nickel dissolution rate increases, the ammonium ion production rate and BV-to-copper concentration ratio target drop, and so the MFL-to-DTO ratio must decrease and the first stage autoclave temperature must increase.

While it is the ammonia-to-total metals molar ratio that remains fixed, the ammonia concentration deviates only slightly relative to nickel concentration due to the minor variations in the copper and cobalt concentrations. Therefore, the direction of change in the ammonia production rate brings about an opposite change in direction of change in ammonia demand. However, this demand has the capacity to be offset if a concentration set-point change is established. A change in Autoclave 1B demand brings about a proportional change in anhydrous ammonia flow rate. A change in Autoclave 1A demand does not bring about a clear-cut change in its anhydrous ammonia flow rate,
given that said autoclave receives a majority portion of its ammonia in the form of second and third stage vent gas, and is thus subject to the specific chemistry in those processes. For an increase in demand, the anhydrous ammonia flow rate may increase, decrease, or perhaps even remain sufficiently idle.

The change in behaviour of Thickener 1 is dependent upon the change in both the total slurry flow exiting the first stage and its solids mass fraction. A change in only the former will initiate a change in the over- and underflow rates in the same direction. A change in the latter will cause a change in the over- and underflow rates in the opposite and same directions, respectively. The effective change in solids flow has a process-wide influence.

**Second Stage Leach**

While changes in the first stage discharge solution composition does affect that of the second stage feed, it is the change in flow rate exiting the first stage that has the greatest impact, given that it is this variable that determines the change in Thickener 1 underflow rate and thus the change in Tank 2 repulp rate (i.e. the DTO-to-Tank 2 flow rate). The combination of changes in the latter two rates gives rise to the appropriate second stage feed pulp density and solution conditions required to bring about the second stage leach nickel concentration target, while corresponding changes in DTO AmSul concentration brings about same directional changes in the same concentration in the second stage discharge.

The significance of the feed solution on leaching stage discharge conditions improves when transitioning from the first to the third stage, given that progressively less leaching activity take place. This is true of pulp density, solution composition and temperature. That said, while autoclave chemistry does have importance, it is the changes in the second stage feed that contributes predominantly to changes in the stage discharge.

The second stage feed pulp density has a standard value of 10.7 wt.%. Like in the first stage, a higher value will lead to a greater nickel dissolution rate per unit reactor volume. However, the manner in which the feed pulp density needs to be manipulated in
order to bring about change in the discharge nickel concentration is, unlike that in the first stage, also dependent upon the feed nickel concentration. More often than not, a change in feed pulp density will bring about the same directional change in discharge nickel concentration. Furthermore, unlike that in the first stage, a change second stage feed pulp density cannot be used as a guide for a change in mean residence time. The latter has a standard value of 15.0 hours, and incurs an opposite change in direction as that of the Thickener 1 underflow rate.

The second stage nickel extraction has a standard value of 99.9 percent, with a range of 99.7 percent to practically unit extraction. Despite the wide variation in standard first stage nickel extraction that is possible, the second stage extraction range remains narrow. This suggests that nickel extraction will be high in the second stage regardless of first stage performance. The high reactivity of the nickel-bearing minerals, and high temperature and oxygen pressure conditions of the second stage encourage this behaviour. The second stage copper and cobalt extractions are dependent on those in the first stage, however, if a shift in nickel extraction location from the second to first stage takes place, more oxidant will become available for the copper- and cobalt-bearing minerals. That said, a decline in first stage performance does not necessarily mean a drop in second stage performance where copper and cobalt dissolution is concerned.

Naturally, if a CBF nickel concentration set-point change is initiated, a change in second stage nickel and AmSul concentrations will take place in same direction as that of the CBF concentrations. Otherwise, a second stage concentration change will only take place if there is a change in second stage throughput. The nickel and AmSul concentration changes will take place in the same and opposite direction as that of the change in throughput, respectively. The directional change of copper and cobalt concentrations in the second stage are the same as those of the first stage.

The second stage ammonia concentration will change in the same direction as that of nickel. Typically, a change in ammonia concentration will initiate a same directional change in ammonia demand. However, a change in first stage ammonia concentration (e.g. via a nickel concentration set-point change) will affect the second stage feed
ammonia concentration, thereby altering the relationship between the discharge concentration and second stage ammonia demand. It is apparent, however, that a change in first stage leach ammonia demand incurs the opposite directional change in the second stage demand, irrespective of concentration set-points. A change in second stage ammonia demand brings about a proportional change in Ammonia Still overhead gas and anhydrous ammonia flow rates to appropriate autoclaves. Variation in the second stage leach ammonia vent rate has only a minor influence on first stage ammonia control.

The behaviour of Thickener 2 follows that of Thickener 1; that is, the directional changes in over- and underflow rates are the same for each thickener. This is because the change in first stage discharge flow that brings about the change in Thickener 1 behaviour is carried forward and affects Thickener 2 in the same fashion. The Thickener 2W underflow rate responds to a change in the Thickener 2 underflow rate in the same direction. In other words, if the Thickener 1 underflow rate increases, so will those of Thickener 2 and 2W. A change in the Thickener 2W overflow rate is influenced by a change in the MFL-to-Thickener 2W flow rate, which is used to control the third stage feed nickel concentration. MFL-to-Thickener 2W is used to dilute the Thickener 2 underflow solution in order to reduce the nickel concentration. Thus, a change in the Thickener 2 nickel concentration will bring about the same directional change in both the MFL-to-Thickener 2W flow rate and the Thickener 2W underflow rate.

**Third Stage Leach**

The changes in third stage discharge conditions are almost entirely due to changes in its feed solution rather than autoclave behaviour, with the exception of ammonia concentration. This is due to the very little leaching activity that occurs there. Furthermore, the feed solution conditions are not that dissimilar for disturbed and optimal conditions, which suggests that the third stage is relatively unaffected by preceding conditions. This is due to the relatively small feed slurry flow (which represents less than five percent of the Thickener 2 feed flow on a volume basis), as well as the introduction of MFL in Thickener 2W, the rate of which shares a value
comparable with those of the Thickener 2 and Thickener 2W underflow streams.

The chief source of changes in third stage feed conditions is a change in the solids flow rate exiting the second stage, which originates from a same directional change in solids flow exiting the first stage. The solids flow rate exiting the second stage determines the Thickener 2 underflow rate, and thus the MFL-to-Thickener 2W flow rate, thereby bringing about the third stage feed composition. It is this affiliation that ultimately determines the change in ammonia demand, thus the change in Ammonia Still distillate, and ultimately the extent to which the latter dilutes the third stage feed solution and modifies the ammonia vent rate.

Overall leach nickel extraction, copper extraction and sulphur conversion perform very well, with standard values of 99.9, 99.6 and 99.1 percent, and, regardless of conditions, values greater than 99.7, 99.4 and 98.0 percent, all respectively. Cobalt extraction demonstrates highly sensitive behaviour in response to changes in feed matte mineral composition, feed matte size distribution and process concentration set-points. For a standard particle size distribution, the overall cobalt extraction can fall as low as 87.6 percent, however, if conditions are appropriate the extraction can drop to around 83 percent. If all conditions are standard, cobalt has an extraction of 91.8 percent.

A negligible amount of nickel leaches in the third stage, so much so that its second and third stage cumulative extraction values are practically indiscernible. The manner in which nickel is extracted over the first and second stage is analogous to the conduct in which copper is extracted over the all three stages. In other words, regardless of the actual copper extractions in the first and second stages (which may drop as low as 94.3 percent in the latter), comparable values for nickel and copper are observed in the third stage. The inability of sulphur conversion to reach values consistent with nickel and copper extraction is coupled to the extraction of cobalt. Not even the high standard mean residence time of 28.5 hours is capable of improving the latter.

A change in mineral conversion in the first stage (and thus for the entire leach) ultimately results in a change in third stage ammonia demand in the same direction, owing to the way in which the former affects backend thickener behaviour via changes
in leach-wide solids throughput. A change in demand is required to maintain a constant discharge ammonia concentration in the face of a variable third stage feed concentration and autoclave ammonia evaporation rate. The latter two change in opposite directions, thus exacerbating the change in ammonia demand. Furthermore, a change in demand results in a supplementary change in the ammonia evaporation rate in the same direction. Moreover, a change in demand incurs a change in third stage discharge concentrations (with the exceptions of that of ammonia) in the opposite direction.

The directional change in first and third stage leach total ammonia demand are the same, while that in the second stage is the opposite, given that all are predicated on the same change in first stage mineral conversion and ensuing change in solids flow. The relationship between first and third stage ammonia demand and the corresponding changes in the Autoclave 1A anhydrous ammonia flow rate has already been discussed. The relationship between second and third stage ammonia demand explains why the total recycled ammonia flow remains relatively steady. That is, as the Ammonia Still overhead gas rate is altered to satisfy the change in Autoclave 2A demand, the distillate flow rate is altered in the opposite direction to satisfy the change in Autoclave 3A demand. Having said this, the ammonia balance around the leach, copper boil process and ammonia recovery system remains sound.

**Overall**

Total leach air and ammonia flow rates experience only minor change unless the feed matte solids flow rate is altered. On the latter rate, this is true despite the significant change in ammonia distribution that results from disturbances to the process, which highlights the importance of ammonia control in the leach. The relative changes in total leach DTO and MFL are the same as those portions of the total that feed the first stage leach; that is, if the first stage feed MFL-to-DTO ratio changes, then the total leach DTO and MFL rates observe changes in the opposite and same directions, respectively. The standard optimal cooling duties of the first, second and third stages are 23.5, 5.8 and -1.6 MW. These values demonstrate both the absolute and relative nature of leaching activity throughout the process more so than any other variables.
As a final point, the pulp density in the feed to any given autoclave almost invariably determines the performance of that vessel. In the present process, the pulp density in the feed to the first stage leach determines the nature of performance of the entire leaching process. That said, the direction of change in said variable may be used to ascertain the direction of change in almost every other variable in the process with which process control is either instituted or monitored. In some cases the relative changes are universal, while in others it is dependent on whether a disturbance or concentration set-point change is the source of the pulp density adjustment.

The leach feed pulp density changes principally in order to bring about nickel concentration control in the copper boil feed, which is the chief process variable of concern. Knowledge of which variables change and in what direction relative to the leach feed pulp density offers an important set of directives with which leach-wide process control may be supported. The magnitudes of change of any given process variable relative to that of the leach feed pulp density cannot be generalised in the same manner, and thus one is required to give specific consideration to the collection of figures presented in this chapter.

8.4.2 Process Limitations and Opportunities for Improvement

Process Limitations

Despite the fact that the leach can perform fairly robustly under standard conditions, there is evidence to suggest that the process is constrained under its present operating conditions. A number of factors allude to this, both for the current solids throughput and for those required to increase refinery nickel production. Metal extraction is at the heart of the matter.

Firstly, the performance optimisation does not lead to near-unit metal extractions for the cases in which the feed matte solids flow rate is 320 tpd. Although standard overall nickel and copper extractions are greater than 99.9 and 99.6 percent, these values can drop to as low as 99.7 and 99.4 percent in response to process disturbances, all respectively. Although these differences are relatively minor, in real terms they can represent considerable losses in revenue. Cobalt extraction will most likely never reach
very high values given the nature of its chemistry, as discussed in the previous chapter (see Section 7.5). Overall leach nickel and copper extractions of greater than 99.9 percent under all conditions should represent the benchmark optimal performance.

Secondly, the performance optimisation leads to only a marginal improvement in mineral conversion for the cases in which the feed matte solids flow rate is 320 tpd. This is true for a comparison of standard optimal conditions with those of Simulation 16 (Section 7.6.1); see Table 8.5 below. The situation also prevails when contrasting optimal and disturbed conditions (see Section 8.3.1). The principal improvement in process conditions resulting from the optimisation is related to process control and stability (which was, nonetheless, the primary objective).

Thirdly, the performance optimisation leads to a decrease in mineral conversion as the feed matte solids flow rate increases from 300 to 400 tpd. While an increase in solids throughput does lead to a reduction in solids residence time in the autoclaves, the appropriate increase in airflow that ensues is incapable of offsetting the decline in metal dissolution rate. If the process was not constrained, the latter would not be true.

In the optimisation problem, a lower limit was established for total leach oxygen utilisation, and standard conditions prevail when its value is greater than 60 percent. The variable was resting on this lower limit for all simulations in Section 8.3, and thus this condition represented an active constraint. That said, the total leach air supply was manipulated in all simulations to impose a total leach oxygen utilisation of 60 percent. One could argue that the process is limited because the air supply rate is limited. This is not the case.

Finally, adjustment of the total leach oxygen utilisation leads to only a relatively minor change in mineral conversion. By altering the lower limit in the optimisation problem, the impact of oxygen utilisation on mineral conversion may be observed. Simulations subsequent to those in Section 8.3 were carried out for this purpose, in which the total leach oxygen utilisation lower limit was set to 55 and 65 percent.

The impact of said changes on optimal metal extraction and sulphur conversion in all stages for standard conditions is given in Table 8.5. The comparison between
Table 8.5: A Comparison of Metal Extractions and Sulphur Conversion between Simulation 16 and Standard Optimal Conditions (with adjustable Oxygen Utilisation)

<table>
<thead>
<tr>
<th>Process Variables</th>
<th>Simulation 16</th>
<th>55% Util.</th>
<th>60% Util.</th>
<th>65% Util.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First Stage Leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal extraction (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>85.53</td>
<td>85.76</td>
<td>85.55</td>
<td>85.36</td>
</tr>
<tr>
<td>- Copper</td>
<td>69.35</td>
<td>69.13</td>
<td>68.96</td>
<td>68.81</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>31.22</td>
<td>30.77</td>
<td>30.48</td>
<td>30.20</td>
</tr>
<tr>
<td>Sulphur conversion (wt. %)</td>
<td>71.77</td>
<td>70.45</td>
<td>70.11</td>
<td>69.79</td>
</tr>
<tr>
<td><strong>Second Stage Leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal extraction (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>99.88</td>
<td>99.93</td>
<td>99.92</td>
<td>99.91</td>
</tr>
<tr>
<td>- Copper</td>
<td>97.09</td>
<td>97.88</td>
<td>97.70</td>
<td>97.52</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>89.03</td>
<td>91.61</td>
<td>91.01</td>
<td>90.43</td>
</tr>
<tr>
<td>Sulphur conversion (wt. %)</td>
<td>98.82</td>
<td>99.00</td>
<td>98.92</td>
<td>98.84</td>
</tr>
<tr>
<td><strong>Overall (Third Stage) Leach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal extraction (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nickel</td>
<td>99.89</td>
<td>99.93</td>
<td>99.92</td>
<td>99.91</td>
</tr>
<tr>
<td>- Copper</td>
<td>99.22</td>
<td>99.61</td>
<td>99.65</td>
<td>99.67</td>
</tr>
<tr>
<td>- Cobalt</td>
<td>89.70</td>
<td>92.29</td>
<td>91.82</td>
<td>91.38</td>
</tr>
<tr>
<td>Sulphur conversion (wt. %)</td>
<td>98.99</td>
<td>99.16</td>
<td>99.11</td>
<td>99.06</td>
</tr>
</tbody>
</table>

The comparison of optimal conditions and those of Simulation 16 (which has an oxygen utilisation of 61.7 percent) demonstrates the previous assertion on the two sets of conditions. Moreover, in view of the fact that oxygen utilisations of 55 and 65 percent incur an increase and decrease in leach air supply rate of nine and eight percent of the standard rate, all respectively, the comparison of optimal conditions for differing oxygen utilisations demonstrates the present assertion.

**Opportunities for Improvement**

The leach is operating at or near its maximum capability under its present operating regime. The first stage leach represents a fundamental bottleneck, and effort should be invested in improving leaching conditions there so that overall metal extraction can be accomplished with the greatest efficiency. A host of measures is presently available to improve this situation without resorting to major capital expenditure (e.g. the
introduction of additional autoclaves). These exist predominantly in the form of unlocking hidden capacity, including changes in equipment operating parameters, alterations to process chemistry targets and modifications to equipment configuration.

The simulations results of Section 8.3 suggest that increasing the nickel content in the matte, finer grinding of the feed particles and high nickel concentration leads to improvements in mineral conversion. The mineral composition is determined by operating conditions established at the Kalgoorlie nickel smelter, while particle grinding is carried out at the refinery directly upstream from the leach. It would be a worthwhile endeavour to examine the possibility of increasing both the standard nickel content in the matte and the standard mass fraction of particle passing 106 μm. Concerning nickel concentration, that in the copper boil feed is determined by conditions established downstream and is not subject to permanent change. However, widening the nickel concentration gap between the copper boil feed and first stage leach beyond 5 g L\(^{-1}\) would improve overall performance.

The final compartments of all six autoclaves are operated at only half their volumetric capacities. That said, only 87.5 percent of the leach-wide available reactor volume is being utilised. Furthermore, said compartments operate at temperatures lower than those of the preceding compartments in all stages. The combination of these two restrictions certifies that very little autoclave feed material dissolves in the final compartment. Despite the fact that these restrictions have a purpose, an investigation into the possibility of increasing the temperature and volume of all fourth compartments (in particular, those in the first stage leach) should be pursued.

The need to preserve a suitable quantity of unsaturated sulphur relative to copper in the copper boil feed represents a significant hindrance to improving overall leach performance. The leaching capacity of the first stage is highly constrained due to the need to maintain standard temperatures of around 10 °C less than those in the second stage. Furthermore, the counter-current airflow arrangement exists as it does largely because of the need to control unsaturated sulphur oxidation, which sees the first stage receive partially-spent air. This situation could be rectified if unsaturated sulphur
compounds were to be stored on site and injected directly into the copper boil feed liquor. Of course, the feasibility and economics of doing so would need to be explored, however, it would allow the first stage to operate at temperatures closer to 95 °C under standard conditions and receive at least a portion of its total air supply as fresh air, all without the concern of BV control. Unlike that in the second stage, unsaturated sulphur would still be produced in the first stage, owing to the quantity of sulphur in the solids phase of its feed. Therefore, that unsaturated sulphur which would be stored and introduced directly into the copper boil feed tank would only need to represent the balance.

As mentioned above, the airflow configuration represents an obstacle to higher mineral conversion in the first stage leach. Given that all fresh air is delivered to the second and third stages (with each autoclave receiving an equal apportionment), the first stage only receives spent air; Autoclave 1B receives more-spent air than Autoclave 1A. In addition, each autoclave receives a fixed compartment apportionment; the first three compartments receive 30 percent each, while the fourth receives 10 percent.

In terms of improving performance, Autoclaves 1A and 1B would benefit from receiving some portion of fresh air, which would bring about higher oxygen pressures and thus greater mineral reaction rates. (This portion could even displace some of the air allocated to Autoclave 3A, given that its oxygen utilisation is very low.) Given that the first stage has a standard temperature buffer of at least 5 °C, this could most likely be implemented without incurring a negative effect on BV control. That is, the increase in mineral conversion would lead to an increase in sulphur dissolution rate and thus the unsaturated sulphur concentration, which would be offset by increasing the temperature. However, the increase in oxygen pressure would also incur an increase in the rate of unsaturated sulphur oxidation, which would (in part, at least) counterbalance the temperature increase.

In terms of improving oxygen utilisation (and thus reducing air usage), in addition to that resulting from the distribution of some fresh air to the first stage, the distribution of air to second and third stage autoclaves, as well as to individual autoclave
compartments in all stages, would probably be better performed if done so with respect to oxygen demand, rather than a fixed quantity. However, this would not lead to the allocation of much air to the third stage leach; more on this topic is given below.

In summary, efforts to optimise the airflow configuration would benefit from a detailed analysis. A number of scenarios could be investigated, which would include: (1) variation in the distribution of fresh air to the second and third stage, (2) variation in the distribution of fresh air to all stages, in conjunction with second and third stage spent-air to Autoclave 1A, (3) variation in the distribution of fresh air to all autoclaves, in conjunction with the distribution of second and third stage spent-air to Autoclaves 1A and 1B. Given the vital role that oxygen plays in the process, the manner in which air is supplied to the leach influences not only the capacity to extract nickel, but the mode in which process control is exercised and process stability realised. In addition, the manner in which air is distributed to Autoclave 3A (and beyond) also has implications for ammonia concentration control in both the first and third stages.

In addition to the above discussion on air distribution, the manner in which anhydrous ammonia and recycled ammonia (overhead gas and distillate from the Ammonia Still) is delivered to the leach has an impact on performance also. This is so given that a portion of ammonia evaporates from the leach solution and exits each autoclave via its ventilation system. That said, if the autoclave air supply rate is increased, the rate of ammonia (and water, for that matter) evaporation will increase also.

Anhydrous ammonia is delivered into the first two compartments of Autoclaves 1A, 1B, 2B and 3B, and Ammonia Still overhead gas is delivered into the first compartment of Autoclave 2A. This practice sees a greater-than-needed distribution to said compartments, and thus a greater ammonia evaporation rate. A more efficient mode of delivery would be to distribute each ammonia source to all compartments on a basis of need. This would reduce the amount of ammonia that evaporates from the autoclave, and thus reduce the total demand on ammonia required to control the ammonia-to-total metals ratio in the fourth compartment. If the autoclave air distribution was performed
on a basis of oxygen demand, as described previously, then the anhydrous ammonia and overhead gas streams could probably be mixed with the feed air streams. From a process control perspective, the overhead gas would be better distributed evenly amongst all second stage autoclaves, and the loss to Autoclave 2A supplemented with anhydrous ammonia.

There are several problems associated with the way in which ammonia is recycled to the leach as Ammonia Still distillate. It delivers a much larger amount of ammonia to Autoclave 3A than is required. The ammonia-to-total metals molar ratio is more than three times that in the first or second stages. This is also taking into account the fact that just over 80 percent of the ammonia that vacates the autoclave does so as vapour. Given that the ammonia vapour rate is influenced by changes in feed slurry and air flow rates, the large quantity of ammonia vapour exiting the third stage complicates ammonia control in Autoclave 1A in response to variations in said third stage feed rates. Having said this, injecting the distillate into the Autoclave 3A feed slurry is probably still the best way to introduce the stream into the leach under its present configuration. However, it should be an operating objective at the Ammonia Still to maximise the proportion of recycled ammonia as overhead gas. At present, only around one-third of the recycled ammonia reports to the leach in vapour form.

An improvement in ammonia usage in the leach (particularly in Autoclave 1B, under the present arrangement) would see less ammonia reporting to the Ammonia Recovery system, and thus less ammonia reporting back to the leach in recycled form. This would reduce operating costs for the Ammonia Still and promote improved control and stability in the leach.

The most sweeping change that could be implemented to unlock hidden capacity and vastly improve performance with respect to both maximising mineral conversion and minimising operating costs via improved efficiency is a change in autoclave configuration. Specifically, this would involve a transformation from a 3-2-1 series, three-stage leach to a 3-3 series, two-stage leach. That is to say, the new process would be a two stage leach, each comprised of three autoclaves in parallel.
As the process stands, very little leaching activity takes place in Autoclave 3A. It is being used chiefly as an ammonia evaporator rather than as a leaching vessel. That said, the process practically operates as a two-stage leach now. Using Autoclave 3A in its current fashion means that one-sixth of the total available reactor volume in the leach is not being utilised properly. This change in process structure would lead to improvements greater than all previous recommendations combined.

The new process configuration would utilise Autoclave 3A as either a first or second stage autoclave; if the latter is put into effect, the displaced second stage autoclave would thus be used in the first stage. A minor injection of capital funds would be required to see this realised: (1) an ammonia evaporator would need to be incorporated into the process to replace the functionality currently be performed by Autoclave 3A, (2) additional cooling coils would need to be installed in the autoclave that is transferred to the first stage, and (3) additional piping may be required to accommodate new slurry, air and ammonia distributions that would result from the process transformation.

The change in process structure could also incorporate many of the preceding recommendations for improving process performance, such as increasing fourth compartment temperatures and volume, and eliminating unsaturated sulphur control from the first stage. Moreover, the changes in air and ammonia distribution that would result would eliminate a number of issues associated with the current arrangements. It is important to realise, however, that the counter-current airflow practice would need to remain, given that the high oxygen pressures of the second stage are essential for supporting the desired levels of mineral conversion there. It is apparent that the change in process structure would require a detailed analysis of its own before being put into practice.

Only those measures that would require the small injection of capital expenditure were considered in this discourse. Of course, the introduction of one or more autoclaves in some capacity would significantly improve the performance of the leach. However, this would involve a considerable investment and would need to be weighted heavily
against the economics of nickel production at the refinery. In any case, this is an option that should only be examined after those initiatives discussed above have been put into effect and the process has once again become constrained.

The model developed in this thesis was constructed in such a way that alterations in process operation and configuration may be accommodated easily. The simulation of alternate operating scenarios discussed in this subsection can be pursued with the present computer program by changing nothing more than vessel parameters or the physical location of vessels and streams. Any variations in process structure would need to be suitably represented via optimisation problem constraints.

8.5 Summary

The computer program constructed in the previous chapter was expanded to describe an optimisation problem for the leaching process at the Kwinana nickel refinery. The goal for performance optimisation was to demonstrate the optimal response of the process to principal disturbances and set-point changes. An examination of the performance characteristics of the process at steady-state under the assortment of conditions was given, underlining the nature of variability in the key performance-determining variables, including metal extraction, sulphur conversion, chief component concentrations and principal flow rates. An account of how process control may be carried out in the plant in order to promote optimal conditions formed an integral part of the analysis.

Feed matte mineral composition variability was demonstrated as having the greatest impact on process performance, given its capacity to exert extensive influence on practically every facet of the leach chemistry. Feed matte particle size distribution variability was shown to predominantly affect mineral conversion. Changes in the disposition of the leach feed material has an influence on both autoclave chemistry and material flow, spanning all three stages. Concentration set-point changes do not incur a significant effect on autoclave chemistry, but chiefly concern alterations to leaching stage feed conditions (including flow rate) in order to produce the appropriate changes in corresponding discharge conditions. Some level of harmony was shown to exist
between solids throughput and leach chemistry, which allows for a straightforward transition from one feed matte solids flow rate to another, with negligible process upsets beyond those related to flow rate variation.

The optimisation demonstrated improvements in process performance, however, this was only marginally so with respect to mineral conversion. The process was shown to be constrained under its present operating regime, which explains the latter. A number of contributing factors were identified, the most noteworthy of which were the limitations imposed by the autoclave and airflow configurations. The current operating scenario cannot allow for the desired improvements in mineral conversion. Moreover, it cannot allow for an increase in the feed matte solids flow rate (and thus refinery nickel production rate) without sacrificing metal extraction. Several solutions to the problem were outlined, which should form the basis of future optimisation studies. The model developed in this work is capable of simulating all potential scenarios.

In the next chapter, concluding remarks are given on the work presented in this thesis and recommendations for future work (both industry- and academe-based) are outlined.
Chapter 9

Conclusions and Recommendations

9.1 Introduction

In this chapter, a summary of the work reported in this thesis is given and conclusions are drawn. Recommendations for future work are identified, both to extend the present study and address limitations encountered.

9.2 Conclusions

A study of the operability of the Sherritt-Gordon ammonia leach at the Kwinana nickel refinery has been performed via mathematical modelling and computer simulation. The process is a complex three-stage ammonia leach with a counter-current airflow arrangement that employs multiple tanks, thickeners and autoclaves to extract nickel, copper and cobalt from a nickel matte. The motivation behind this body of work was (and remains) the need to advance process understanding in order to promote performance optimisation for both present and future refinery operating targets. This is necessary given the influential role the leaching process plays in the performance of the hydrometallurgical flowsheet. The work was pursued in three main phases: chemistry development, model development and model application.

Prior to this study, literature entries on the industrial leach were restricted largely to discussions on its place in the Sherritt-Gordon refining process, with attention focused on the basic flowsheet and chemistry. Furthermore, literature submissions on
the process chemistry did not venture beyond those proposed by the foundation researchers. On the latter, the reaction stoichiometry was formulated on the fundamental basis of pressure oxidation of metal sulphide with oxygen in the presence of ammonia, with metal ammine, sulphate and sulphamate serving as final reaction products. Several unsaturated oxysulphur products were reported as reaction intermediates, including thiosulphate and polythionate, but with no clear mechanism. Iron was shown to precipitate as a hydrated ferric oxide. No kinetic rate laws were established.

Subsequent to developing an appreciation of the leaching process feed material, flowsheet and operating philosophy at the refinery, the first task in this body of work was to establish a chemical reaction system suitable for robust mathematical modelling, given the inadequacy that existed. This required the specification of reaction stoichiometry and kinetics that includes all principal species in the system. The work was pursued jointly on the basis of literature scrutiny (i.e. independent studies concerning ammonia leach chemistry) and plant observation. The major findings and developments are given as follows:

- The copper(II)/copper(I) redox couple is most likely responsible for oxidation in the Sherritt-Gordon ammonia leach. That is, cupric ammine is a surrogate oxidant for oxygen.
- Six chemical reaction groups were identified: (1) ammonia and water evaporation, (2) oxygen gas-liquid mass transfer and reduction, (3) mineral oxidation, (4) sulphur oxidation, (5) iron precipitation and associated adsorption, and (6) metal ammine formation.
- Ammonia and water evaporate from the leach solution. The rate laws are based on thermodynamic considerations. (Reaction group 1.)
- Oxygen is reduced by cuprous ammine via two mechanisms: one in which oxygen is reduced heterogeneously (i.e. in the stagnant film surrounding the gas bubbles) and the other in which it is reduced homogeneously (i.e. in the bulk solution or at the mineral surface). The tendency of the process to function under either of these conditions is related to the degree of mineral oxidation. The rate law for each
Under steady-state conditions, the existence of copper(I) and dissolved oxygen in solution is mutually exclusive. Leaching thus takes place in either the presence of copper(I) or dissolved oxygen, which respectively represent the former and latter mechanisms discussed above. These situations embody two distinct kinetic frameworks under which all subsequent oxidation reactions are influenced. (Reaction group 2.)

The following reactive minerals were identified for the nickel matte: awaruite (nominally Ni$_3$Fe), heazlewoodite (Ni$_3$S$_2$), chalcocite (Cu$_2$S), syocoporite (CoS), pyrrhotite (FeS). Heazlewoodite and chalcocite leach via a two-part mechanism, respectively introducing millerite (NiS) and covellite (CuS) into the system. Pyrrhotite leaches as a shrinking core, while all other minerals leach as shrinking spheres. Nickel, copper, cobalt and iron dissolve as nickel(II), copper(II), cobalt(III) and iron(II), respectively. Sulphur dissolves as elemental sulphur. (Reaction group 3.)

Mineral oxidation is probably electrochemical in nature. The reaction rates for awaruite, heazlewoodite and chalcocite are fast, and probably controlled by a combination of reactant mass transport and chemical reaction at the mineral surface. The reaction rates for millerite, covellite, syycoporite and pyrrhotite are slow, and most likely limited by chemical reaction at the mineral surface. Fundamental rate laws were derived for the first time using mixed potential theory, accounting for the separate cases in which leaching takes place in the presence of copper(I) or dissolved oxygen. The rate constant pre-exponential factor and Arrhenius activation energy represent the unknown parameters for each individual case. For each mineral, the latter values were sourced from the literature, while the former values remain unknown. (Reaction group 3.)

The elemental sulphur that results from mineral oxidation is promptly oxidised to thiosulphate; the rate law describes an instantaneous reaction. Thiosulphate is oxidised to tetrathionate and the rate law was taken from the literature. The
decomposition of tetrathionate takes place rapidly, however, the full list of participating species and specific reaction sequence beyond the introduction of said thionate that ultimately leads to the formation of sulphate and sulphamate remains incomplete; a detailed literature survey was given on the topic. A process of progressive oxidation of sulphur from lower to higher valence states was chosen to describe the reaction system, based on the most convincing evidence. This mechanism was later confirmed for the Sherritt-Gordon ammonia leach via modelling and simulation. (Reaction group 4.)

- Tetrathionate is promptly oxidised to trithionate, and the rate law describes an instantaneous reaction. Trithionate is oxidised in two parallel reactions to sulphate and sulphamate. The reactions were taken to be first-order with respect to their reactants, and the rate laws proposed reflect this basis. The rate constant pre-exponential factors remain unknown, while the Arrhenius activation energies were assumed to take on the same value as that for thiosulphate oxidation. (Reaction group 4.)

- The above kinetics for sulphur oxidation represent only the case in which leaching occurs in the presence of copper(I). The literature suggests that unsaturated sulphur reacts very fast when dissolved oxygen is present in copper(II)-catalysed ammonia leach solutions, regardless of stoichiometry. That said, under such conditions, an assumption of instantaneous sulphur oxidation was assumed. The rate laws thus reflect this situation. (Reaction group 4.)

- Iron is thermodynamically unstable in the leach solution. The iron(II) that results from pyrrhotite oxidation is promptly oxidised to iron(III) and subsequently hydrolysed, resulting in the precipitation of iron(III) oxide. The raw law is one that describes an instantaneous reaction sequence. (Reaction group 5.)

- Iron oxide has the capacity to adsorb from solution deleterious elements in the matte (such as arsenic and selenium) as it precipitates. This process may also lead to the co-precipitation of metals, most notably cobalt. This aspect of the chemistry was not given attention beyond a literature survey. (Reaction group 5.)
All six nickel(II) ammines are able to form in this system, while only a single, dominant ammine is considered to form for copper(II), copper(I) or cobalt(III).

The rate laws are based on thermodynamic equilibrium. (Reaction group 6.)

The development of chemistry was successful in the sense that a comprehensive reaction system was formulated for modelling purposes. It represents the convergence of information and ideas that span the chemistry- and metallurgy-related literature, in conjunction with actual process knowledge. The author deems it fortunate that sufficient studies were available to allow for a development as complete.

The success here also illustrates the point that laboratory experimentation should not necessarily be one’s first undertaking when pursuing chemistry development for modelling purposes, which is an exercise that can be both time-consuming and expensive. That said, a full explanation for the manner in which any given mineral may dissolve in copper-charged ammoniacal leaching systems and the mode in which the ensuing chemistry takes place is yet to be determined. This is something that only a laboratory study can uncover.

The second task in this body of work was the development of a mathematical model of the leaching process, on the basis of the process chemistry established previously. However, before this was carried out, a novel method was developed for modelling leaching kinetics in continuous reactors at steady-state, which is showcased in the industrial process model.

Prior to this study, the solution of equations required to mathematically describe leaching reactor kinetics were performed numerically. That is, mineral conversion was calculated numerically and the reactor discharge particle size distribution was reconstructed numerically. This procedure is both daunting and cumbersome given the nature of the double-integral equations involved, and is probably the reason it is scarcely used beyond the academic sphere.

As part of this study, the analytical solutions of said equations were derived for the first time. Now, mineral conversion can be described with an algebraic expression and the discharge particle size distribution can be reconstructed in terms of its mean and
variance, each of which is also described with an algebraic expression. Beyond reactor modelling, the use of mean and variance to represent the particle size distribution allows for the straightforward description of particle mixing, which permits the construction of any complex reactor network. This work is significant due jointly to its ease of application and absence of need to sacrifice accuracy, all relative to the previous method of best practice. This new level of simplicity may be enough to inspire greater use of reactor kinetics in industrial design and analysis.

This body of work represents the development of the first industrial process model for the Sherritt-Gordon ammonia leach. It is also the first instance in which multiple tanks, thickeners and autoclaves were unified in a leach flowsheet model. The following points highlight the industrial model development:

- A total of 39 component species and 28 chemical reactions were identified for the leaching process at the Kwinana nickel refinery.

- A modelling strategy for multiple autoclave leaching process flowsheets was developed on the basis of mathematically describing individual process streams and fundamental unit operations. These stream and unit models employ common stream properties to account for the flow of mass, energy and particle size distribution, which allow them to be linked in a fashion that describes the flowsheet as a whole.

- The above strategy was applied to the Sherritt-Gordon ammonia leach, in which three stream types and nine fundamental unit operation types were identified to describe the process. The stream types are slurry, gas and anhydrous ammonia. The unit operation types are the leaching reactor (i.e. the autoclave compartment), the mixing vessel, the solid-liquid separator, the trim cooler, the mixing point (slurry and gas) and the splitting point (slurry, gas and anhydrous ammonia).

- The mathematical description of each stream and unit operation is accomplished with mass and energy balance equations. Chemical reaction was only considered to take place in the mixing vessel (ammonia evaporation and nickel ammine formation), slurry mixing point (nickel ammine formation only) and the leaching
reactor (all 28 reactions). Rates of extent of reaction were described explicitly for each unit operation and are based on the kinetic rate laws established in the chemistry development.

- In addition to the above, the leaching reactor and slurry mixing point also require specific consideration of particle size distribution, since they are the only slurry-bearing units in which the feed and discharge distributions are not the same. In the leaching reactor model, the new method for calculating mineral conversion is used to determine mineral oxidation extent, while the new method for reconstructing particle size distribution is used to calculate the reactor discharge mean and variance. In the slurry mixing point, the new method for describing particle size distribution via its mean and variance is used to facilitate particle mixing.

The strengths of the model lie with the completeness of the chemical reaction system and the modularity of the leach flowsheet modelling strategy employed in its construction. The latter renders the model sufficiently flexible that it may be used to describe not only the process flowsheet of interest in this work, but any variation of it that features the same stream and unit operation types. Moreover, additional streams and unit operations not modelled here may be incorporated with ease via the appropriate use of stream properties. The modelling strategy is very general and may be applied to any leaching process.

While the completeness of the reaction system is a model strength, what is absent poses a potential weakness; this is elaborated on later. Another potential weakness is related to the estimation of the volumetric mass transfer coefficient, \( k_l a \), given that the means for describing it in leaching systems is not well-understood. This is rather significant, given the important role it plays in calculating the oxygen mass transfer rate.

The mathematical modelling of leaching processes is fairly well-established fundamentally. What is lacking in the literature is industrial case studies. Only the latter can help identify where the “true” gaps in the modelling and analysis practice exists. The industrial leach model developed in this work represents the largest and most intricate of its kind in the literature, and has aided in establishing some of these gaps.
Generally speaking, it is not until one attempts to model a process that one determines just how much information is known, or unknown. This concerns knowledge of both the process itself and the means to describe it.

The third task in this body of work was the application of the mathematical model established previously. This task was carried out in three parts: (1) the development of a computer program capable of process simulation, (2) the stand-alone use of the program to simulate the process for purposes of chemistry and operation analysis, and (3) the extension of the program to facilitate an optimisation problem, in order to simulate optimal process performance in response to process disturbances and optimal set-point changes.

The computer program was constructed in Aspen Custom Modeler®, which is a graphical flowsheet modelling software. Each individual stream and unit operation type was programmed on the basis of their model equations, and instances of each were arranged appropriately in the flowsheeting space in order to represent the leaching process as a whole. The stream instances were used to represent all global input streams and all autoclave, tank, thickener and trim cooler discharge streams. The unit operation instances were used to construct the autoclaves, tanks, thickeners and trim coolers of the process.

A procedure for the appropriate collection of plant data was outlined. This was executed to acquire data for two purposes: one for estimating the unknown rate law parameters and the other for validating the model. A comprehensive parameter estimation and model validation campaign was carried out. The former and latter involved the establishment of 12 experiments and 24 simulations (i.e. employing 36 distinct data sets), which were sourced over a three-and-a-half-year and a four-year time frame, all respectively. A total of 288 model input parameters and variables were used to institute each experiment or simulation in which all vessels were active. The collection of data sets represents a wide range of operating conditions, encompassing variations in the feed matte composition and particle size distribution, concentrations, flow rates and process structure.
The parameter estimation exercise provided values for the unknown rate law parameters, thus revealing a complete chemical reaction system and, by extension, a complete model. The validation exercise was carried out subsequently to establish the strengths and weaknesses of the model. The predictive power of the model was tested at multiple points in the process for a host of variable types, including metal extraction, solution and gas compositions, slurry and liquor flow rates, and autoclave cooling duty. The main outcomes are given as follows:

- In general, there is a very good correlation between plant data and model output.

- The prediction of first and second stage leach performance is superior to that of the third stage leach; this was also evident in the parameter estimation work.

- An exception to the above statements concerns the prediction of cobalt-related variables. Only second and third stage extractions demonstrate a good agreement with plant data. Two reasons are plausible: (1) the representation of cobalt in the feed matte as CoS and its corresponding dissolution kinetics is inaccurate, and (2) cobalt is reacting in the real process via supplementary chemistry not accounted for in the process model (e.g. the uptake from solution via iron oxide adsorption).

This point in the body of work represents the first in which the aptness of the chemistry and model developments could be judged. The model validation results suggest success. This indicates that the potential weaknesses discussed previously do not carry much weight. Moreover, the weakness in predicting the behaviour of cobalt is inconsequential, given the minor role the metal plays in the actual process.

While not necessarily a weakness, but more an undesirable element, is the fact that all of the unknown model parameters are the unknown kinetic rate law parameters. Given that the latter are reliant on plant data, this removes some level of independence between chemistry and reactor behaviour. While this does not pose a problem, given the independent manner in which the parameter estimation and model validation was carried out, it does limit the predictive power of the model. Furthermore, given the fundamental influence that said parameters have on model performance, and the fact that these parameters collectively absorb all model uncertainties, it makes it difficult to
isolate which aspects of the modelling are sturdy and which are frail.

The model was used in a stand-alone fashion to examine the chemistry and operation of the leaching process under both fixed and variable conditions. The model validation simulation which corresponds best with normal operating conditions was selected to carry out the analysis. Under fixed conditions, the simulation conditions remained unchanged and were used to examine the whole process. Under variable conditions, changes in temperature, oxygen pressure and ammonia concentration were used to study the behaviour of a first stage autoclave. This analysis was aimed at the compartment, autoclave and leaching stage levels. The principal results are given as follows:

- Considerable leaching activity (around 80 percent mineral conversion) takes place in the first stage leach; around 50 percent of all solids conversion in the leach takes place in the first compartments of the first stage autoclaves. This suggests that improving the performance of the first stage leach is the key to improving the performance of the entire leach.

- Moderate leaching activity (almost 20 percent mineral conversion) takes place in the second stage leach, while practically none takes place in the third stage. This suggests that the second stage leach is probably being underutilised and that the third stage is effectively not contributing to overall leach performance. The third stage autoclave is being used chiefly as an ammonia evaporator, given the nature of leach air and ammonia distribution.

- Relatively little mineral conversion takes place in the fourth compartment of all autoclaves, which is in response to the lower temperatures and volumes. This suggests that capacity for leaching is not being utilised.

- Awaruite, heazlewoodite and chalcocite dissolve completely in the first compartments of the first stage autoclaves, given their very high reactivity. The dissolution of the remaining sulphide minerals takes place in a less aggressive fashion, extending throughout the second and third stages.
Millerite reacts in a steady manner due to its high intrinsic reactivity and thus ability to consume oxidant at will. Covellite and sycoporite experience a varied reaction status, exhibiting moderate reaction rates in the first stage and high rates in the second stage. The increase in rates is due jointly to the progressively diminishing impact of millerite on oxidant availability, as well as the higher temperature and pressure. The majority of millerite oxidation takes place in the first stage, while the majority of covellite and sycoporite oxidation takes place in the second stage.

Temperature is the most important autoclave variable to optimise, given its impact on both mineral conversion and unsaturated sulphur consumption.

Unlike the concentration of other dissolved components, the concentration of unsaturated sulphur in any given compartment is difficult to anticipate. It is very sensitive to temperature and is easily influenced by conditions in the present and preceding compartment(s). This renders control of unsaturated sulphur concentration in the first stage leach problematic. The practice not only limits overall process performance but poses a process stability issue.

Oxygen pressure change has a minor effect on autoclave performance. This is due to the manner in which oxygen is reduced, and thus the kinetics that prevail under that mechanism. A higher oxygen feed rate does improve mineral conversion, but does so by increasing the oxygen mass transfer rate directly, rather than through increasing the oxygen pressure.

The process demonstrates both kinetic frameworks concerning the manner in which oxygen is reduced by cuprous ammine. In the first stage, leaching takes place solely in the presence of copper(I), while in the third stage it does so solely in the presence of dissolved oxygen. The shift in mechanism takes place in the second stage: leaching takes place in the presence of copper(I) in the first, second and third compartments, but does so in the presence of dissolved oxygen in the fourth. The gradual shift from one mechanism to the other reflects the change in conditions imposed by the decline in mineral presence and thus oxidant demand.
• Ammonia concentration changes have a minor impact on autoclave performance. Despite the fact that the sulphide oxidation rate laws are functions of ammonia concentration, it is probably the case that the latter is present in sufficient quantity that leaching rates are pseudo-zero-order with respect to ammonia.

The analysis was also used to demonstrate that supplementary chemistry is probably taking place in the leach, in addition to that already stipulated for cobalt. These additional elements have no effective impact on model performance, and are summarised as follows:

• A small portion of heazlewoodite and chalcocite leaches in the first stage feed tank.

• Copper precipitation is taking place in all three leaching stage feed tanks. An explanation for this is that the low oxygen potential conditions are encouraging the precipitation of copper as sulphides via reaction with unsaturated sulphur compounds. That is, copper may be precipitating in accordance with the chemistry of the copper boil process. The chief (if not, the only) copper sulphide precipitate is probably blaubleibender covellite, due to the speed with which it re-dissolves in the adjacent autoclave.

• Low oxidation potential conditions in the autoclaves are known to encourage the precipitation of copper. (This was mentioned in Chapter 4, but was an unnecessary component of the chemical reaction system development and thus not discussed further.) If the previous point is true, the copper boil process chemistry is probably taking place in the leaching autoclaves as well under said conditions.

• And if the above point is true, the copper boil process chemistry could even be a permanent member of the ammonia leach chemistry. That is, said copper precipitation chemistry could even be taking place in autoclaves under normal leaching conditions, in which the swift re-dissolution of blaubleibender covellite is normally unnoticeable, but becomes noticeable when re-dissolution rates decline in response to low oxidation potentials.
The computer model represents a powerful simulation tool. The majority of simulation data it can generate is not available via direct measurement on site, owing to either the deficiency in means or impracticality of doing so. This includes the measurement of first, second and third compartment variables in all leaching stages. The model represents an important means for establishing a complete picture at all levels of the process.

The model was incorporated into an optimisation problem in order to address the shortcomings of stand-alone model simulation when carrying out performance optimisation. The first stage leach nickel fraction unreacted was chosen to be the objective function, and conditions are considered optimal when its value is minimised (i.e. when the first stage nickel extraction is maximised) and all process constraints are satisfied.

The optimisation problem was used to examine optimal process performance in response to the most significant process disturbances and optimal set-point changes. This allowed for the specific calculation of optimal operating points for a wide variety of conditions, which can directly aid refinery staff in closing the gap that exists between current operating practices and optimal performance. Furthermore, it allowed for an analysis of the manner in which optimal operation may be implemented, which generated insight into process control requirements. The analysis was aimed at the overall process level, incorporating those variables that are used by refinery staff to either monitor or control the process. The main findings are given as follows:

- The optimisation demonstrated improvements in process performance. However, this was only marginally so with respect to mineral conversion. The major benefit was the calculation of optimal operating points with which process control and stability may be achieved.

- The process is constrained under its present operating regime. This explains the minor improvements in mineral conversion. The process is operating at or near its maximum capability.

- The airflow arrangement and ammonia distribution system are a source of both
performance limitation and process instability.

- The process is fairly robust under its present solids throughput. It is capable of maintaining high mineral conversion in response to variability in both the mineral composition and size distribution of the feed matte, as well as to changes in concentration set-points.

- Mineral conversion is improved when the nickel content in the feed matte is higher, when the assembly of particles in the feed matte are finer, and when the nickel concentration set-point in the copper boil feed is at its upper limit.

- Variation in feed matte mineral composition has the greatest impact on process performance. Variation in feed matte particle size distribution mainly affects mineral conversion. Each influences both autoclave chemistry and material flow across all three stages. All forms of control are required to maintain optimal conditions.

- Variation in concentration set-points does not incur a significant effect on autoclave chemistry. The main effect is alterations to leaching stage feed conditions (including flow rate) in order to produce the appropriate changes in corresponding discharge conditions.

- Some level of harmony exists between solids throughput and leach chemistry. A straightforward transition from one feed matte solids flow rate to another is achievable with negligible process upsets beyond those related to flow rate variation.

- The performance of the first stage determines the performance of the entire leaching process. Conditions there influence not only the second and third stage autoclave chemistry, but process-wide flow rates. That said, the direction of change required of the first stage feed pulp density in order to maintain optimal performance can be used as a guide for the direction of change in almost all other performance-determining variables.

The process exhibits a high degree of complexity and interaction, which renders
process control an important yet difficult task. Although the optimisation study has demonstrated how process control can be implemented manually (which is the current practice) to establish optimal operation, what is required is an automatic scheme. This is necessary in order to implement the vast system of logic that is apparent.

The analysis suggests that the process is constrained under its present operating regime. That said, improvements in mineral conversion for the current solids throughput and either maintaining or improving mineral conversion for higher solids throughputs cannot be accomplished without a change in operating practice. A host of recommendations were outlined for unlocking hidden capacity, including:

- Finer grinding of the feed matte.
- An increase in the first stage leach target nickel concentration.
- An increase in autoclave fourth compartment temperatures and/or volumes.
- The on-site storage and injection of unsaturated sulphur compounds directly into the copper boil feed tank and operating the first stage leach at higher temperatures and with a higher oxygen composition in the feed gas.
- Modifications to the airflow arrangement.
- Modifications to the ammonia distribution system.
- Modifications to the autoclave configuration. Specifically, the transformation from a 3-2-1 series, three-stage leach to a 3-3 series, two-stage leach.

The above measures should form the basis of future optimisation and feasibility studies. Beyond these developments, major capital expenditure (such as the introduction of additional autoclaves) is probably required to support further process improvement.

The importance of the complete body of work in this thesis spans both the academic and industry domains. On the former, it has led to the contribution of knowledge in two fundamental areas: (1) the chemistry and operation of the Sherritt-Gordon ammonia leach and (2) the mathematical modelling and analysis of hydrometallurgical leaching processes. On the latter, firstly, it has naturally led to the
advancement of knowledge concerning the operability of the leaching process at the Kwinana nickel refinery, which may be directly used by process staff to support performance optimisation and process control. Secondly, given that the process in question is at least equally as complicated as any other leaching process in operation given its chemistry and equipment arrangement, it serves as an ideal case study with which to base the modelling, simulation and analysis of other industrial operations. In this author’s experience, one best learns by example.

A broad outcome of this work is the amalgamation of the academic and industry domains. Something that researchers and practitioners in the chemical and metallurgical processing fields should always remain mindful of is the important contribution that the other makes to the process of transforming raw materials into products of value. A mutually-beneficial relationship does exist, but industry-academe collaborations do not take place as often as they should, or could. In this work, the application of theory has led to outcomes that are directly relevant to a real-world process. It is hoped that the present work will help bridge the gap that exists between academe and industry, and assist in establishing a more customary practice of industry-driven research by academics and application of theory by practitioners.

9.3 Recommendations for Future Work

Advancing process understanding for the purpose of promoting performance optimisation for both present and future operating targets for any given chemical or metallurgical operation is a perpetual process. Studies of the kind often prove to be more involved than originally thought, thus rendering some objectives unfulfilled. What is more, said studies have the capacity to reveal more questions than they answer. Future work exists in the form of both extending and supplementing the present body of work, the latter via the acquisition of knowledge not presently available.

The following points summarise the means by which the present body of work may be extended:

1. A powerful simulation tool exists for process analysis. Of all the simulations and analyses that are possible, only a fraction was pursued in this work. The model
can be used in its present form to continue to explore the intricacies of the leach at
the compartment, autoclave, leaching stage and overall process levels.

2. Following from the above point, the optimisation problem constraints should be
modified to allow for a sensitivity analysis on the fixed variables (e.g. the copper
boil feed-first stage leach nickel concentration gap or thickener underflow
density). This will aid in a better understanding of performance optimisation
requirements.

3. In the previous chapter, a number of proposals were outlined to unlock hidden
capacity in the leach. Given the versatility of the model, it is capable of
accommodating all changes in operating conditions. This will require
modifications to the computer program for the cases in which the physical
structure of the leach is altered. Appropriate simulations should be carried out to
explore the benefits.

4. The modelling should be extended to include the copper boil process and the
ammonia recovery system. This will enhance the ability to predict leach
performance and extend the optimisation study to include the additional processes.

5. An unsteady-state model should be developed to allow for the examination of
process dynamics and develop automated strategies for process control. This
could be carried out immediately using the information and modelling strategy
developed in this work; however, simulations would be restricted to process
variations around normal steady-state conditions. The author would recommend
focusing on the first stage leach initially, given its faster dynamics and greater
overall importance.

The following points summarise the means by which the present body of work may be
supplemented:

1. A thorough laboratory study of the Sherritt-Gordon ammonia leach chemistry for
nickel matte is required to both verify the chemistry development put forward in
this work and improve upon it. This should include: (1) a mineralogical analysis
of the nickel matte, (2) a study of the mineral oxidation chemistry, (3) a study of
the sulphur oxidation chemistry, (4) a study of the arsenic and selenium oxidation chemistry, (5) a study of the iron precipitation chemistry and associated adsorption effects on arsenic, selenium and dissolved metals. The work should also include a study on nickel, copper and cobalt hydrolysis in ammoniacal solutions in order to better understand the conditions under which metal precipitation occurs. The outcome would be a comprehensive reaction system comprised of stoichiometry and kinetics. The results could be incorporated directly into the model developed in this work to enhance its predictive power. This would also allow the parameter estimation component of the model construction to shift focus from chemistry to reactor behaviour, thus enhancing model capability more so.

2. The above study should specifically include a component which aims to identify optimal process conditions. This would encompass the optimal relationships between metal concentration, ammonium sulphate concentration and ammonia concentration. The results could be incorporated directly into the optimisation problem, which would render it less reliant on present operating knowledge and thus allow one to simulate the process closer to its “true” limits. The latter is necessary to carry out optimisation with respect to minimising operating costs.

3. The present body of work would also benefit from a laboratory study of the Sherritt-Gordon copper boil chemistry. This will help establish optimal conditions for the copper boil feed and thus the leach discharge, which will supplement the work in the above point. This is particularly true of an optimal unsaturated sulphur-to-copper ratio. The development of a comprehensive chemical reaction system would also enhance the predictive power of a copper boil process model.

4. A study of the impact of low oxidation potential on leaching conditions would benefit process understanding. The existence of copper boil chemistry in the leaching process would be of particular interest. This work could complement or be done in union with the above studies on the ammonia leach and copper boil chemistry.
5. The quality and availability of plant data proved to be a limitation in both the parameter estimation and validation elements of the model construction. The quality of plant data could be improved by (1) ensuring that process instruments are calibrated, (2) ensuring that sampling and laboratory measuring techniques are both accurate and consistent with one another, and (3) increasing the frequency with which the more important variables are sampled. The availability of plant data could be improved by (1) ensuring that the mass flow of the most important solid, aqueous and gaseous components in all streams are obtainable by direct measurement or independent calculation, and (2) ensuring that temperature is measured in all important streams. In some cases, this will involve supplementary sampling and the introduction of new plant instruments.

6. With respect to the fundamentals of leaching reactor modelling (for the majority of situations), the volumetric mass transfer coefficient, \( k_l a \), is perhaps the only remaining element that cannot be described accurately. The description is difficult due to the dependence the variable has on the specific hydrodynamic conditions in any given reactor. The majority of studies on \( k_l a \) exist for gas-liquid reactors. Seemingly, no studies have specifically accounted for leaching systems and few studies are directly applicable to leaching systems. Studies on \( k_l a \) that have direct relevance to leaching reactors would enhance the modelling practice. A study of the impact that hydrodynamics has on leaching reactors in general would also benefit the field.
Appendix A

Description of Metal Dissolution Kinetics for Electrochemical Reactions in Copper-Catalysed Ammoniacal Leaching Systems

A.1 Introduction

Consider the following coupled anodic and cathodic half-cell reactions (equations 4.20 and 4.21):

\[
\text{MS} + n \text{NH}_3(a) \rightleftharpoons \text{M(NH}_a^{x+} + S^0 + x e^- \quad (A.1)
\]

\[
x \text{Cu(NH}_3)^{3+} + x e^- \rightleftharpoons x \text{Cu(NH}_3)^{x+}_2 + 2x \text{NH}_3(a) \quad (A.2)
\]

which, under freely-dissolving conditions, occur at equal rates. The stipulation of equal rates signifies that the net current flow between anodic and cathode sites on the mineral surface is zero. Since the anodic and cathodic reactions occur randomly across the surface of MS, it is reasonable to assume that the area available to each reaction is the same, and equal to the total area of MS in contact with cupric ammine. Therefore, the stipulation of equal rates now signifies that the net current densities for the anodic and cathodic processes are equal and opposite.
A.2 Type I, II and III Leaching Situations

The procedure for solving for the anodic or cathodic reaction rate, and thus the metal dissolution rate, resides with the following steps: (1) equating mathematical expressions for the absolute values of the net anodic and cathodic current densities, which are functions of potential, (2) solving for the potential, which is equal to the mixed potential, and (3) substituting the mixed potential term into the expression for the net current density for the anodic or cathodic reaction.

The electrochemical characteristics of minerals generally exhibit highly irreversible behaviour, and so the cathodic (reverse) direction of reaction A.1 can safely be ignored in the region of the mixed potential. If the anodic dissolution of MS is first-order with respect to ammonia, and limited by a single-electron transfer step, then the net current density for the anodic reaction can be described with the anodic Tafel equation as follows:

\[
i_a = i_{0,a} \exp \left( \frac{\alpha_a F}{RT} \eta_a \right)
\]

(A.3)

where

\[
i_{0,a} = x \bar{k}_a(T) C_{\text{NH}_3} \exp \left( \frac{\alpha_a F}{RT} E_{e,a} \right)
\]

(A.4)

\( \bar{k}_a(T) \) is the intrinsic rate constant (in the absence of potential) for the forward direction of the anodic reaction, \( i_{0,a} \) is the anodic exchange current density and \( \eta_a = E - E_{e,a} \) is the anodic overpotential.

The consideration made for the mineral, however, cannot always be made for the oxidant, and so both the cathodic (forward) and anodic (reverse) directions of reaction A.2 must be given suitable attention. If the cathodic reduction of copper(II) is first-order with respect to copper(II), and the anodic oxidation of copper(I) is first-order with respect to both copper(I) and ammonia, then the net current density for the cathodic reaction can be described with the Butler-Volmer equation as follows:
where

\[ i_{0,c} = x F k_c(T) C_{\text{Cu(II)}} \exp \left( -\frac{(1-\alpha_c)}{RT} E_{e,c} \right) \]

(A.6)

\( k_c(T) \) and \( k_c(T) \) are the intrinsic rate constants (in the absence of potential) for the forward and reverse directions, respectively, of the cathodic reaction, \( i_{0,c} \) is the cathodic exchange current density and \( \eta_c = E - E_{e,c} \) is the cathodic overpotential.

At the mixed potential (i.e. \( E = E_m \)), the net anodic and cathodic current densities are equal and opposite (i.e. \( i_a = -i_c \)), and so the following relationship may be written:

\[ k_a(T) C_{\text{NH}_3} \exp \left( \frac{\alpha_a}{RT} E_m \right) + k_c(T) C_{\text{Cu(II)}} C_{\text{NH}_3} \exp \left( \frac{\alpha_c}{RT} E_m \right) \]

\[ -k_c(T) C_{\text{Cu(II)}} \exp \left( -\frac{(1-\alpha_c)}{RT} E_m \right) = 0 \]

(A.7)

The above equation does not have an analytical solution unless an assumption is made concerning activation energy barrier symmetry. If it is assumed that the energy barriers for each half-cell reaction have the same symmetry, or equally, that the transfer coefficients for each half-cell reaction are equivalent (i.e. \( \alpha_a = \alpha_c = \alpha \)), then the mixed potential takes on the following form:

\[ E_m = \frac{RT}{F} \ln \left[ \frac{k_c(T) C_{\text{Cu(II)}}}{(k_a(T) + k_c(T) C_{\text{Cu(II)}}) C_{\text{NH}_3}} \right] \]

(A.8)

Substitution of the above expression into equations A.3 or A.5 yields the dissolution current density, \( i_d \), and thus the rate at which leaching takes place:
\[ i_d = i_a = -i_c = x F k_a(T) C_{NH}^{1-\alpha} \left[ \frac{k_c(T) C_{Cu(II)}}{k_a(T) + k_c(T) C_{Cu(II)}} \right]^\alpha \]  

(A.9)

If symmetrical activation energy barriers are assumed for each half-cell reaction (i.e. \( \alpha = 0.5 \)), then the above rate expression becomes

\[ i_d = x F k_{MS}(T) f(C) \]  

(A.10)

If the stoichiometric ratio of MS to copper(II) is \( 1/x \), then the general leaching rate law as given by equation 4.25 may be expressed as follows:

\[ i_d = x F k_{MS}(T) f(C) \]  

(A.11)

The forms of \( k_{MS}(T) \) and \( f(C) \) are dependent upon whether Type I, II or III leaching situations prevail. If Type I leaching prevails, then the rate of the reverse direction of the cathodic reaction is negligible in the region of the mixed potential (i.e. \( k_a(T) \gg k_c(T) C_{Cu(II)} \)). The leaching rate is thus given as follows:

\[ i_d = x F k_{MS}(T) \left( \frac{k_a(T)}{k_c(T)} \right)^{1/2} \left( \frac{C_{Cu(II)}}{C_{Cu(II)} + C_{NH}} \right)^{1/2} \]  

(A.12)

which corresponds with equation A.11 if \( k_{MS}(T) = \left( \frac{k_a(T)}{k_c(T)} \right)^{1/2} \) and \( f(C) = C_{Cu(II)}^{1/2} C_{NH}^{1/2} \). If Type III leaching prevails, then the rate of the forward direction of the anodic reaction is negligible in the region of the mixed potential (i.e. \( k_a(T) \ll k_c(T) C_{Cu(II)} \)). The leaching rate therefore takes on the following form:

\[ i_d = x F k_a(T) \left( \frac{k_a(T)}{k_c(T)} \right)^{1/2} \left( \frac{C_{Cu(II)}}{C_{Cu(II)} + C_{NH}} \right)^{1/2} \]  

(A.13)

which corresponds with equation A.11 if \( k_{MS}(T) = k_a(T) \left( \frac{k_c(T)}{k_c(T)} \right)^{1/2} \) and
\[ f(C) = \left( \frac{C_{\text{Cu(II)}}}{C_{\text{Cu(I)}}} \right)^{1/2} C_{\text{NH}_3}^{1/2}. \]

If Type II leaching prevails, then the rate of the forward direction of the anodic reaction is comparable with the rate of the reverse direction of the cathodic reaction in the region of the mixed potential (i.e. \( k_a(T) \approx k_c(T) C_{\text{Cu(II)}} \)). Hence, the leaching rate is given by the form expressed in equation A.10:

\[
i_a = x F \frac{k_a(T)}{k_c(T)} \left( \frac{C_{\text{Cu(II)}}}{K' + C_{\text{Cu(II)}}} \right)^{1/2} C_{\text{NH}_3}^{1/2}
\]

which corresponds with equation A.11 if \( k_{\text{MS}}(T) = k_a(T) \left( \frac{k_c(T)}{K'} \right)^{1/2} \) and

\[ f(C) = \left( \frac{C_{\text{Cu(II)}}}{K' + C_{\text{Cu(II)}}} \right)^{1/2} C_{\text{NH}_3}^{1/2}, \]

where \( K' = k_a(T) / k_c(T) \). Type II leaching is an intermediate situation relative to Type I and III leaching, and will tend towards the latter situations depending on the value of \( K' \). Clearly, the form of \( K' \) – and thus the form of \( f(C) \) for Type II leaching – is difficult to quantify in the absence of suitable data. If it is assumed that \( K' \) is relatively small for all relevant concentrations of copper(I), then the Type II situation may be approximated with a Type III model (i.e. equation A.13).

Analytically derived models for Type I and III leaching situations can be developed independently, which is necessary if the assumption of equal transfer coefficients for anodic and cathodic reactions cannot be made. This can be done by considering the relative rates of the anodic processes (in the region of the mixed potential) when defining the net current densities for the anodic and cathodic half-cell reactions.

**A.3 Type IV Leaching Situation**

A Type IV leaching situation prevails if the rate of diffusion of cupric ammine to the surface of MS is rate-limiting. The net current density for the overall leaching reaction may therefore be described in terms of mass transport theory, in the sense that the charge transfer flux must equal the mass transport flux. According to Fick’s first law of diffusion, the current density takes on the following form [141]:

\[ \frac{\partial C}{\partial t} = D \nabla^2 C \]

where \( D \) is the diffusion coefficient, \( \nabla^2 \) is the Laplacian operator, and \( C \) is the concentration of the diffusing species.
\[ i = -\frac{x F \hat{D}_{\text{Cu(II)}}}{\delta} (C_{\text{Cu(III)}}^b - C_{\text{Cu(II)}}^s) \]  

(A.15)

where \( \hat{D}_{\text{Cu(II)}} \) is the diffusivity of cupric ammine, \( C_{\text{Cu(II)}}^b \) (\( = C_{\text{Cu(II)}} \)) and \( C_{\text{Cu(II)}}^s \) are the concentration of copper(II) in the bulk solution and at the mineral surface, respectively, and \( \delta \) is the effective thickness of the Nernst diffusion layer, which is the stagnant film that surrounds each mineral particle and separates its surface from the bulk solution.

According to the mass transport-controlled model for shrinking cores and spheres [32], the concentration of cupric ammine at the surface of MS is zero, which corresponds to the maximum copper(II) concentration gradient across the Nernst diffusion layer. According to equation A.15, the current density approaches some limiting value as \( C_{\text{Cu(II)}}^s \) approaches zero. If Type IV leaching prevails, then the rate at which leaching takes place is equivalent to the so-called limiting current density, \( i_L \):

\[ i_d = i_L = \frac{x F \hat{D}_{\text{Cu(II)}}}{\delta} C_{\text{Cu(II)}} \]  

(A.16)

For each half-cell reaction, the limiting current density is the maximum attainable current density. The reaction cannot proceed at any faster rate because the transport process in the bulk solution is incapable of supplying the oxidant to the mineral surface at a faster rate.

Equation A.16 corresponds with equation A.11 if \( k_{\text{MS}}(T) \approx \hat{D}_{\text{Cu(II)}} / \delta \) (which is based on the assumption that \( \delta \) is a weak function of particle size) and \( f(C) = C_{\text{Cu(II)}} \). The Type IV model may therefore be approximated with a first-order chemical reaction-controlled model.
Appendix B

A Mathematical Discourse on the Relationship between the Segregated Flow Model and the Population Balance Model

It is demonstrated that the segregated flow model and steady-state population balance model are mathematically interchangeable when the well-mixed assumption is valid. The discussion to follow proves that the former model may be derived from the latter. This is valid for all rate-limiting regimes.

The steady-state macroscopic population balance equation (equation 5.25) is given by [58]

$$0 = Q_{in} \psi_{in} - Q \psi - V \frac{\partial}{\partial D} (\dot{D} \psi), \quad \psi|_{D=D_{\text{rea}}} = 0 \quad (B.1)$$

where $\psi = \psi(D,D_0)$ is a joint density function and $\dot{D} = \dot{D}(D,D_0)$ may represent any rate-limiting kinetics. By using the method of integrating factors, and considering (subsequently) that particles in the feed are completely unreacted, the above equation has the following analytical solution [58]:

$$\psi(D,D_0) = Q_{in} \psi_{in} - Q \int_{D_0}^{D} \psi(D',D_0) \left( -V \frac{\partial}{\partial D'} (\dot{D} \psi(D')) \right) \, dD'$$
\[
\psi(D, D_0) = -\frac{Q_m}{V \, D(D, D_0)} \psi_m(D_0) \exp \left( \frac{Q}{V} \int_{D}^{D_0} \frac{dD'}{D'(D', D_0)} \right), \quad D \leq D_0 \quad (B.2)
\]

The marginal density function, \( \psi(D) \), may be determined by integrating the above equation over all applicable values of \( D_0 \) (i.e. \( D \) through \( D_{0,\text{max}} \)):

\[
\psi(D) = -\frac{Q_m}{V} \int_{D}^{D_{0,\text{max}}} \psi_m(D_0) \exp \left( \frac{Q}{V} \int_{D}^{D_0} \frac{dD'}{D'(D', D_0)} \right) dD_0 \quad (B.3)
\]

The segregated flow model makes use of mass- rather than number-weighted distributions. The former type may replace the latter for reactor feed (size \( D_0 \)) and discharge (size \( D \)) conditions by writing equation 5.40 for each case and substituting into the above equation:

\[
f_m(D) = -\frac{Q_m}{V} \frac{\bar{m}}{\bar{m}_m} \, D^3 \int_{D}^{D_{0,\text{max}}} \frac{D_0^{-3} f_{m,m}(D_0)}{D(D, D_0)} \exp \left( \frac{Q}{V} \int_{D}^{D_0} \frac{dD'}{D'(D', D_0)} \right) dD_0 \quad (B.4)
\]

The above equation can be tidied up by considering the following:

- Batch reactor particle fraction unreacted is given by \( 1 - X^* = \left( \frac{D}{D_0} \right)^3 \)

- Continuous reactor mineral fraction unreacted is given by \( 1 - X = \frac{Q \, \bar{m}}{Q_m \, \bar{m}_m} \)

- Mean residence time is given by \( \bar{t} = \frac{V}{Q} \)

Equation B.4 may thus be recast as

\[
f_m(D) = -\frac{1}{\bar{t} \, (1 - X)} \int_{D}^{D_{0,\text{max}}} (1 - X^*) f_{m,m}(D_0) \exp \left( \frac{1}{\bar{t}} \int_{D}^{D_0} \frac{dD'}{D'(D', D_0)} \right) dD_0 \quad (B.5)
\]

Now, by multiplying each side of the above equation by \( (1-X) \, dD \) and integrating from zero to \( D_{\text{max}} = D_{0,\text{max}} \), \( f_m(D) \) may be cancelled (since it is a probability density function) and an expression for continuous reactor mineral fraction unreacted results:
\[ 1 - X = -\frac{1}{i} \int_0^{D_{h,\text{max}}} \int_0^{\tau(D_h)} \left(1 - X^*\right) \frac{D_{m.in}(D_0)}{D(D, D_0)} \exp \left(\frac{1}{i} \int_0^{D_h} \frac{dD'}{D(D', D_0)} \right) dD_0 dD \quad (B.6) \]

By performing an interchange of the order of integration, the above equation is recast as

\[ 1 - X = -\frac{1}{i} \int_0^{D_{h,\text{max}}} \int_0^{\tau(D_h)} \left(1 - X^*\right) \exp \left(\frac{1}{i} \int_0^{D_h} \frac{dD'}{D(D', D_0)} \right) dD f_{m.in}(D_0) dD_0 \quad (B.7) \]

Recognising that \( dD = \dot{D}(D, D_0) d\tau \), it follows that

\[ -\int_0^t \frac{D_h}{D} \frac{dD'}{D(D', D_0)} \quad \text{and} \quad -\int_0^{\tau(D_h)} g^*(D_0, \tau) d\tau = \int_0^D \frac{g(D, D_0)}{D(D, D_0)} dD \]

since \( D = D_0 \) when \( t = 0 \) and \( D = 0 \) when \( t = \tau(D_h) \). \( g \) and \( g^* \) are some functions of differing variables that describe the same quantity; this is analogous to describing \( 1 - X^* \) as \( (D/D_0)^3 \) or \( (1 + \dot{D}t/D_0)^3 \). Therefore, performing a change of variables in equation B.7 from \( D \) to \( t \) yields the following:

\[ 1 - X = \frac{1}{i} \int_0^{D_{h,\text{max}}} \int_0^{\tau(D_h)} \left(1 - X^*\right) \exp \left(-\frac{t}{i}\right) d\tau f_{m.in}(D_0) dD_0 \quad (B.8) \]

where, now, \( X^* = X^*(D_0, t) \) (e.g. equation 5.2). By acknowledging equation 5.4 (which satisfies the well-mixed assumption), the above equation may be written as

\[ 1 - X = \int_0^{D_{h,\text{max}}} \int_0^{\tau(D_h)} \left(1 - X^*\right) E(t) d\tau f_{m.in}(D_0) dD_0 \quad (B.9) \]

which corresponds with the segregated flow model. The more familiar form (i.e. that used in this work; see equation 5.1) is obtained by carrying out an interchange of the order of integration:

\[ 1 - X = \int_0^{t_{\text{max}}} \int_0^{D_{h,\text{max}}} \left(1 - X^*\right) f_{m.in}(D_0) dD_0 E(t) dt \quad (B.10) \]

where \( t_{\text{max}} = \tau(D_{0,\text{max}}) \) and \( D_0(X^* = 1) = \tau^{-1}(t) \).
Appendix C
Calculation of Heat Capacity Coefficients for Metal Ammine Complexes

The entropy correspondence principle of Criss and Cobble [184, 185] states that if the entropy of the hydrogen ion in its standard state is assigned an absolute value as a function of temperature, then the partial molal entropies of a class of ions at that temperature are linearly related to corresponding entropies at some reference temperature. So, the correspondence principle provides a way of determining ionic entropies at elevated temperatures, based on known entropies at some other temperature (e.g. room temperature). As suggested by the authors, perhaps the most useful application of this principle is its ability to predict ionic heat capacity at elevated temperatures.

The correspondence principle demonstrates that the mean heat capacity of an aqueous ion over the temperature range 298.15 K to $T$ may be given by [185]

$$\bar{C}_p^* T_{298} = \alpha_T + \beta_T S^*_{298} \text{(abs.)}$$  \hspace{1cm} (C.1)

where

$$S^*_{298} \text{(abs.)} = S^*_{298} - 20.92 \cdot z$$ \hspace{1cm} (C.2)
$S_{298}^{\text{abs.}}$ refers to ionic entropies on the “absolute” scale, $S_{298}^\circ$ refers to conventional ionic entropies and $z$ is the ionic charge. In addition to temperature, $\alpha_T$ and $\beta_T$ are dependent on the class of ion. Based on data available in Table III in [184], values for $\alpha_T$ and $\beta_T$ at 60, 100, 150 and 200 °C were calculated for the proton and each of the four classes of ions considered by the authors; that is, (1) simple cations, (2) simple anions and the hydroxide ion, (3) oxy anions and (4) acid oxy anions. Furthermore, based on data available in Table IV in [185], values for $\alpha_T$ and $\beta_T$ at 250 and 300 °C were calculated (except for acid oxy anions at 300 °C, due to unavailable data).

It is apparent that $\ln(T/298.15)^{\alpha_T}$ and $\ln(T/298.15)^{-\beta_T}$ vary linearly with temperature (except around 60 °C) for all classes of ions; Criss and Cobble [184] explain that $C_p^\circ$ data on ionic solutes pass through a maximum near 60 °C. Plots of the two quantities against $T$ each intersect the horizontal axis at $T = 298.15$ K, and so the following statements may be made:

\[
\ln(T/298.15)^{\alpha_T} = \bar{\alpha} (T - 298.15) \tag{C.3}
\]

\[
\ln(T/298.15)^{-\beta_T} = \bar{\beta} (T - 298.15) \tag{C.4}
\]

where $\bar{\alpha}$ and $\bar{\beta}$ are the gradients. Linear regression (performed in MS Excel) over the temperature range 25 – 300 °C (25 – 250 °C for acid oxy anions) – excluding the data for 60 °C – yielded values for $\bar{\alpha}$ and $\bar{\beta}$ for each class of ions, which are listed in Table C.1. Only simple cations are pertinent in this work, however, the remaining ion classes have been included for completeness.

It is well-known that the following relationship exists between entropy and mean heat capacity over the temperature range 298.15 K to $T$:

\[
\bar{C}_p^\circ \int_{298}^T \approx \frac{S_T^\circ - S_{298}^\circ}{\ln(T/298.15)} \tag{C.5}
\]

If the right-hand side of the above equation is substituted into Equation C.1, followed with the substitution of $\bar{\alpha}$ and $\bar{\beta}$ (from Equations C.3 and C.4, respectively) into the
result, then the following relationship is established:

$$S_T^e - S_{298}^e = (\alpha - \beta S_{298}^e (\text{abs.})) (T - 298.15) \quad (C.6)$$

Given that the definition for entropy change as a function of heat capacity is

$$S_T^e - S_{298}^e = \int_{298}^{T} \frac{C_p^e}{T} dT \quad (C.7)$$

it becomes clear that ionic heat capacity has the following linear relationship with temperature:

$$C_p^e = (\alpha - \beta S_{298}^e (\text{abs.})) T \quad (C.8)$$

Since the heat capacity function utilised in this work (equation 6.124) takes on the following form:

$$C_p^e = A + B 10^{-3} T + C 10^{5} T^{-2} + D 10^{-6} T^2 \quad (C.9)$$

it follows that $A = C = D = 0$ and $B = 10^{3} (\alpha - \beta S_{298}^e (\text{abs.}))$.

The “absolute” entropies and ‘$B$’ heat capacity coefficient for all metal ammines were calculated and are presented in Table C.2; conventional entropies are taken directly from Table 6.1. The ‘$B$’ coefficient for nickel(II) ammines, copper(II) ammines and hexaamminecobalt(III) are also available in the literature [182] (apparently, calculated via the Criss-Cobble method) and are listed in Table C.2 as a matter of comparison. The source of the discrepancies is not clear, as an explanation for the method of calculation is not disclosed in the source. Nonetheless, a good association can be observed, thus placing confidence with the present method of calculation.
Table C.1: “Modified” Criss-Cobble Parameters

<table>
<thead>
<tr>
<th>Class of Ions</th>
<th>$\bar{\alpha}$ (J mol(^{-1}) K(^{-2}))</th>
<th>$\bar{\beta}$ (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>0.390</td>
<td>0.00000</td>
</tr>
<tr>
<td>Simple Cations</td>
<td>0.556</td>
<td>0.00165</td>
</tr>
<tr>
<td>Simple Anions and OH(^-)</td>
<td>-0.732</td>
<td>0.00010</td>
</tr>
<tr>
<td>Oxy Anions</td>
<td>-1.608</td>
<td>-0.00585</td>
</tr>
<tr>
<td>Acid Oxy Anions</td>
<td>-1.675</td>
<td>-0.01124</td>
</tr>
</tbody>
</table>

Table C.2: ‘B’ Heat Capacity Coefficients for Metal Ammine Complex Ions

<table>
<thead>
<tr>
<th>Species</th>
<th>$S_{298}$ (J mol(^{-1}) K(^{-1}))</th>
<th>$S_{298}$ (abs.) (J mol(^{-1}) K(^{-1}))</th>
<th>$B$ (this work) (mJ mol(^{-1}) K(^{-2}))</th>
<th>$B$ [182] (mJ mol(^{-1}) K(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiNH(_3)^2+</td>
<td>-18.631</td>
<td>-60.471</td>
<td>655.777</td>
<td>643.274</td>
</tr>
<tr>
<td>Ni(NH(_3))(_2)^2+</td>
<td>85.395</td>
<td>43.555</td>
<td>484.134</td>
<td>472.358</td>
</tr>
<tr>
<td>Ni(NH(_3))(_3)^2+</td>
<td>165.322</td>
<td>123.482</td>
<td>352.255</td>
<td>341.038</td>
</tr>
<tr>
<td>Ni(NH(_3))(_4)^2+</td>
<td>242.003</td>
<td>200.163</td>
<td>225.731</td>
<td>215.053</td>
</tr>
<tr>
<td>Ni(NH(_3))(_5)^2+</td>
<td>306.193</td>
<td>264.353</td>
<td>119.818</td>
<td>109.587</td>
</tr>
<tr>
<td>Ni(NH(_3))(_6)^2+</td>
<td>394.635</td>
<td>352.795</td>
<td>-26.112</td>
<td>-35.722</td>
</tr>
<tr>
<td>CuNH(_3)^2+</td>
<td>12.092</td>
<td>-29.748</td>
<td>605.084</td>
<td>592.796</td>
</tr>
<tr>
<td>Cu(NH(_3))(_2)^2+</td>
<td>111.294</td>
<td>69.454</td>
<td>441.401</td>
<td>429.806</td>
</tr>
<tr>
<td>Cu(NH(_3))(_3)^2+</td>
<td>199.619</td>
<td>157.779</td>
<td>295.665</td>
<td>284.690</td>
</tr>
<tr>
<td>Cu(NH(_3))(_4)^2+</td>
<td>273.634</td>
<td>231.794</td>
<td>173.540</td>
<td>163.083</td>
</tr>
<tr>
<td>Cu(NH(_3))(_5)^2+</td>
<td>309.470</td>
<td>267.630</td>
<td>114.411</td>
<td>104.205</td>
</tr>
<tr>
<td>CuNH(_3)^+</td>
<td>149.500</td>
<td>128.580</td>
<td>343.843</td>
<td>-</td>
</tr>
<tr>
<td>Cu(NH(_3))(_2)^+</td>
<td>242.500</td>
<td>221.580</td>
<td>190.393</td>
<td>-</td>
</tr>
<tr>
<td>CoNH(_3)^2+</td>
<td>-230.190</td>
<td>-292.950</td>
<td>1039.368</td>
<td>-</td>
</tr>
<tr>
<td>Co(NH(_3))(_2)^3+</td>
<td>-154.947</td>
<td>-217.707</td>
<td>915.217</td>
<td>-</td>
</tr>
<tr>
<td>Co(NH(_3))(_3)^2+</td>
<td>-79.705</td>
<td>-142.465</td>
<td>791.067</td>
<td>-</td>
</tr>
<tr>
<td>Co(NH(_3))(_4)^3+</td>
<td>-4.463</td>
<td>-67.223</td>
<td>666.918</td>
<td>-</td>
</tr>
<tr>
<td>Co(NH(_3))(_5)^3+</td>
<td>70.780</td>
<td>8.020</td>
<td>542.767</td>
<td>-</td>
</tr>
<tr>
<td>Co(NH(_3))(_6)^3+</td>
<td>146.022</td>
<td>83.262</td>
<td>418.618</td>
<td>407.121</td>
</tr>
</tbody>
</table>
Appendix D

Fitting Continuous Probability Distribution Functions to Discrete Size Distribution Data

D.1 Introduction

Discrete cumulative particle size distributions are determined experimentally on a mass basis through sieving and weighing an assembly of particles. Although it is possible to directly couple the discrete size distribution data for leach process feed particles with the models for calculating continuous reactor mineral conversion (such as the segregated flow or population balance models), the method of solution typically demands the use of a continuous particle size distribution. Continuous size distributions may be described mathematically by both cumulative distribution and probability density functions. Such functions are generally represented by two-parameter models. Some models make explicit use of the mean (i.e. average size), \( \mu \), and variance (i.e. spread of sizes about the average size), \( \sigma^2 \), of the size distribution, but most utilise parameters that are calculated via the two statistical measures. The mean and variance may be determined from the discrete data, while the calculation of model-specific parameters and selection of an appropriate mathematical function is carried out subsequently.
The Mean and Variance

The mean and variance cannot be calculated precisely. However, they may be estimated from the discrete probability density function. If the complete range of particles in an assembly (i.e. $D_{\text{min}}$ through $D_{\text{max}}$) is separated into a series of $n$ discrete intervals, then the fraction of total particle mass in the $i$th interval is given by

$$\Delta F_{m,i} = F_m(D_{i+1}) - F_m(D_i) = \int_{D_i}^{D_{i+1}} f_m(D) \, dD, \quad i = 1, 2, 3, \ldots, n$$  \hfill (D.1)

where $F_m(D)$ is the mass-weighted cumulative distribution function and $f_m(D)$ is the mass-weighted probability density function. By way of the mean value theorem of calculus, the discrete density function may be approximated as follows:

$$f_m(\overline{D}_i) \approx \frac{F_m(D_{i+1}) - F_m(D_i)}{D_{i+1} - D_i} = \frac{\Delta F_{m,i}}{\Delta D_i}$$  \hfill (D.2)

where $\overline{D}_i$ is an average value of $D$ in the interval $\{D_i, D_{i+1}\}$.

The mean and variance of a particle population is the first raw moment (i.e. moment about zero) and second central moment (i.e. moment about the mean) of the particle size density function, respectively:

$$\mu = \int_{D_{\text{min}}}^{D_{\text{max}}} D f_m(D) \, dD$$  \hfill (D.3)

$$\sigma^2 = \int_{D_{\text{min}}}^{D_{\text{max}}} (D - \mu)^2 f_m(D) \, dD$$  \hfill (D.4)

The mean and variance of the discrete distribution can therefore be approximated, respectively, as follows:

$$\hat{\mu} = \sum_{i=1}^{n} \overline{D}_i \cdot f_m(\overline{D}_i) \cdot \Delta D_i = \sum_{i=1}^{n} \overline{D}_i \cdot \Delta F_{m,i}$$  \hfill (D.5)

$$\hat{\sigma}^2 = \sum_{i=1}^{n} (\overline{D}_i - \hat{\mu})^2 \cdot f_m(\overline{D}_i) \cdot \Delta D_i = \sum_{i=1}^{n} (\overline{D}_i - \hat{\mu})^2 \cdot \Delta F_{m,i}$$  \hfill (D.6)
The discrete size distribution data in Table D.1 represents that typical of the leach process feed matte at the Kwinana nickel refinery, corresponding to 90 pct -106 µm particulate material. The second and third columns contain raw data (collected by this author from refinery databases), while data in the fourth column is calculated from equation D.2. Fifth column data refers to the arithmetic mean particle size, which (as opposed to, say, the geometric or harmonic means) is the preferred method of averaging since it certifies a nonzero value for \( \bar{D} \). Therefore, by way of the above equations, the mean and variance of the particle population are calculated to be 47.79 µm and 1750.3 µm\(^2\), respectively. The coefficient of variation is 0.8754.

### D.3 Selecting a PSD Function

A list of mathematical functions for describing continuous particle size distribution is given in Chapter 2; that is, the Gaudin-Meloy, Gaudin-Schumann, Rosin-Rammler, log-normal, and gamma distributions. Each empirical model has two adjustable parameters, designated in this work as \( \phi \) and \( D^* \). The aptness of each function is dependent upon the shape of the discrete size distribution. The details of each of the preceding distribution functions are given in Table D.2.

The parameters may be calculated from the mean and variance. The calculation of \( \phi \) is carried out initially as a function of the coefficient of variation, since it is independent of \( D^* \). The calculation of \( D^* \) is then performed as a function of either the mean or variance. Values for \( \phi \) and \( D^* \) for each of the empirical size distributions are given in Table D.3.

Plots of the cumulative distribution functions for each empirical distribution and the raw data (Table D.1) are shown in Figure D.1, while the residuals and residual sum of squares (RSS) for each distribution are presented in Table D.4. (\( F_m(D) \) for the gamma distribution was evaluated in MS Excel using the GAMMADIST function.) It is apparent that neither the Gates-Gaudin-Schumann nor log-normal distributions demonstrate a good correlation with the discrete data, but that the Gaudin-Meloy, Rosin-Rammler and gamma distributions do (Figure D.1a). If the RSS is used as a basis
of comparison, the Gaudin-Meloy distribution is the best-fit, followed by the Rosin-Rammler and gamma distributions. This can also be seen visually in Figure D.1b. Any of the latter three models is suitable for describing size distributions in this work.

D.4 Quantifying PSD Variability

A historical record of size distribution data can be of substantial value for purposes of leach process analysis. Naturally, the most effective way to quantify PSD variability over time is to measure the entire distribution of sizes on a regular basis. If this practice is not feasible, however, a less-exhaustive method would nonetheless be advantageous. Given that the empirical models used to represent particle size distribution are described by only two parameters, only two points on the discrete size distribution curve are required to evaluate them. Thus, the application of at least one of these models presents a means for abridging the measuring procedure.

Although any two points on the discrete size distribution curve may be used to generate the mean and variance, some points will represent the entire suite of raw data better than others, given that the empirical models are not exact fits. Visual inspection of Figure D.1 reveals that each of the distributions intersects the actual data at around the same points. Thus, if some previously measured complete discrete distribution is used as a basis, the points of intersection (excluding \( D = 0 \) and \( D = D_{\text{max}} \)) represent the best sieve sizes with which to make future mass fraction-passing measurements in order to estimate the mean and variance of the entire distribution.

If the raw data in Table D.1 is considered as the basis, then, by inspection of the residuals (Table D.4), the permissible sieve sizes at which the Rosin-Rammler, log-normal, and gamma distributions come close to intersecting the actual distribution curve are 32 µm and 159 µm, while the Gates-Gaudin-Schumann distribution does so at 40 µm and 126 µm. For the Gaudin-Meloy distribution, four sieve sizes are identified: 20, 50, 126 and 224 µm. Although the Gaudin-Meloy distribution is technically the best-fit, the Rosin-Rammler distribution actually offers a more accurate (and simpler) means for quantifying PSD variability, given that the corresponding optimal sieve sizes represent a better range; this is verified below.
If \((D_1, F_m(D_1))\) and \((D_2, F_m(D_2))\) are two points on the Rosin-Rammler cumulative distribution curve, then, by appropriate rearrangement of the cumulative distribution function (given in Table D.2), it may be shown that expressions for \(\varphi\) and \(D^*\) that represent said points take on the following forms:

\[
\varphi = \frac{\ln \left( \frac{\ln (1 - F_m(D_2))}{\ln (1 - F_m(D_1))} \right)}{\ln \left( \frac{D_2}{D_1} \right)} \quad (D.7)
\]

\[
D^* = \exp \left\{ \frac{\ln(D_1) \ln\left[-\ln(1 - F_m(D_2))\right] - \ln(D_2) \ln\left[-\ln(1 - F_m(D_1))\right]}{\ln\left( \frac{\ln(1 - F_m(D_2))}{\ln(1 - F_m(D_1))} \right)} \right\} \quad (D.8)
\]

For the raw data in Table D.1, the values calculated for \(\varphi\) and \(D^*\) by way of the above equations for the optimal sieve sizes (i.e. \(D_1 = 3.2 \times 10^{-5}\) m and \(D_2 = 1.59 \times 10^{-4}\) m) are 1.15 and 5.069 \times 10^{-5} m, respectively. The mean, variance and coefficient of variation may then be estimated from the latter values for the Rosin-Rammler distribution (via the equations given in Table D.2) to be 48.24 µm, 1768.9 µm² and 0.8719, respectively. As can be seen, the values are close to those established previously (Section D.2) for the entire distribution.

According to the method described above, the estimation of \(\varphi\) and \(D^*\) using the Gaudin-Meloy distribution requires that said variables be solved by trial-and-error, and so the calculation procedure is not as straightforward as that using equations D.7 and D.8. Nonetheless, the values calculated for \(\varphi\) and \(D^*\) for the best-paired optimal sieve sizes (which – following a comparison of all six combinations – is 50 µm and 126 µm) are 6.25 and 3.4593 \times 10^{-4} m, respectively. The mean, variance and coefficient of variation are calculated to be 47.72 µm, 1725.3 µm² and 0.8704, respectively. Using the latter as a basis for comparison, the use of the Rosin-Rammler distribution is demonstrated as being the more accurate (and simpler) approach for quantifying PSD variability when only two sieve sizes are available.
Table D.1: Discrete Size Distribution Data for Leach Feed Matte (90 pct -106 µm)

<table>
<thead>
<tr>
<th>i</th>
<th>( D_i \times 10^6 ) (µm)</th>
<th>( F_m(D_i) )</th>
<th>( f_m(\bar{D}_i) \times 10^{-6} ) (µm(^{-1}))</th>
<th>( \bar{D}_i \times 10^6 ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.000</td>
<td>2.10 \times 10^{-2}</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.105</td>
<td>1.48 \times 10^{-2}</td>
<td>7.5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.179</td>
<td>1.30 \times 10^{-2}</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.309</td>
<td>1.13 \times 10^{-2}</td>
<td>26.0</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>0.445</td>
<td>1.06 \times 10^{-2}</td>
<td>36.0</td>
</tr>
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<td>6</td>
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<td>0.530</td>
<td>9.30 \times 10^{-3}</td>
<td>45.0</td>
</tr>
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<td>7.46 \times 10^{-3}</td>
<td>56.5</td>
</tr>
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<td>63</td>
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<td>67.0</td>
</tr>
<tr>
<td>9</td>
<td>71</td>
<td>0.766</td>
<td>4.89 \times 10^{-3}</td>
<td>75.5</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>0.810</td>
<td>4.44 \times 10^{-3}</td>
<td>84.5</td>
</tr>
<tr>
<td>11</td>
<td>89</td>
<td>0.850</td>
<td>3.18 \times 10^{-3}</td>
<td>94.5</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>0.885</td>
<td>2.58 \times 10^{-3}</td>
<td>106.0</td>
</tr>
<tr>
<td>13</td>
<td>112</td>
<td>0.916</td>
<td>1.79 \times 10^{-3}</td>
<td>119.0</td>
</tr>
<tr>
<td>14</td>
<td>126</td>
<td>0.941</td>
<td>1.25 \times 10^{-3}</td>
<td>134.0</td>
</tr>
<tr>
<td>15</td>
<td>142</td>
<td>0.961</td>
<td>8.82 \times 10^{-4}</td>
<td>150.5</td>
</tr>
<tr>
<td>16</td>
<td>159</td>
<td>0.976</td>
<td>5.79 \times 10^{-4}</td>
<td>168.5</td>
</tr>
<tr>
<td>17</td>
<td>178</td>
<td>0.987</td>
<td>3.18 \times 10^{-4}</td>
<td>189.0</td>
</tr>
<tr>
<td>18</td>
<td>200</td>
<td>0.994</td>
<td>2.08 \times 10^{-4}</td>
<td>212.0</td>
</tr>
<tr>
<td>19</td>
<td>224</td>
<td>0.999</td>
<td>3.57 \times 10^{-5}</td>
<td>238.0</td>
</tr>
<tr>
<td></td>
<td>252</td>
<td>1.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Name</td>
<td>Gaudin-Meloy</td>
<td>Gates-Gaudin-Schuhmann</td>
<td>Rosin-Rammler</td>
<td>Log-Normal*</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>-------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Probability density function, $f_m(D)$</td>
<td>$\frac{\varphi D^<em>}{D^</em> - D^c} \left( 1 - \frac{D}{D^c} \right)^{\varphi - 1}$</td>
<td>$\frac{\varphi}{(D^*)^\varphi} D^{\varphi - 1}$</td>
<td>$\frac{\varphi}{(D^<em>)^\varphi} D^{\varphi - 1} \exp \left[ -\left( \frac{D}{D^</em>} \right)^\varphi \right]$</td>
<td>$\frac{D^{-1}}{\varphi \sqrt{2\pi}} \exp \left( -\frac{\ln^2(D/D^*)}{2 \varphi^2} \right)$</td>
</tr>
<tr>
<td>Cumulative distribution function, $F_m(D)$</td>
<td>$1 - \left( 1 - \frac{D}{D^c} \right)^\varphi$</td>
<td>$\left( \frac{D}{D^*} \right)^\varphi$</td>
<td>$1 - \exp \left[ -\left( \frac{D}{D^*} \right)^\varphi \right]$</td>
<td>$\frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\ln(D/D^*)}{\varphi \sqrt{2}} \right)$</td>
</tr>
<tr>
<td>Range, ${D_{\text{min}}, D_{\text{max}}}$</td>
<td>${0, D^c}$</td>
<td>${0, D^c}$</td>
<td>${0, \infty}$</td>
<td>${0, \infty}$</td>
</tr>
<tr>
<td>Mean, $\mu$</td>
<td>$\frac{D^c}{\varphi + 1}$</td>
<td>$\frac{D^c \varphi}{\varphi + 1}$</td>
<td>$D^c \Gamma \left( \frac{\varphi + 1}{\varphi} \right)$</td>
<td>$D^c \exp \left( \frac{\varphi^2}{2} \right)$</td>
</tr>
<tr>
<td>Variance, $\sigma^2$</td>
<td>$\frac{(D^c)^2}{(\varphi + 2)}$</td>
<td>$\frac{(D^c)^2}{(\varphi + 2)}$</td>
<td>$(D^c)^2 \left[ \Gamma \left( \frac{\varphi + 2}{\varphi} \right) - \Gamma^2 \left( \frac{\varphi + 1}{\varphi} \right) \right]$</td>
<td>$(D^c)^2 \left( \exp(2 \varphi^2) - \exp(\varphi^2) \right)$</td>
</tr>
<tr>
<td>Coefficient of variation, $C_v = \sigma / \mu$</td>
<td>$\left( \frac{\varphi}{\varphi + 2} \right)^{1/2}$</td>
<td>$\left( \frac{\varphi}{\varphi + 2} \right)^{1/2}$</td>
<td>$\left[ \Gamma \left( \frac{\varphi + 2}{\varphi} \right) - \Gamma^2 \left( \frac{\varphi + 1}{\varphi} \right) \right]^{1/2}$</td>
<td>$(\exp(\varphi^2) - 1)^{1/2}$</td>
</tr>
</tbody>
</table>

* The error function is defined as $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} \, dz$.

** The gamma function is defined as $\Gamma(\varphi) = \int_0^\infty x^{\varphi-1} e^{-x} \, dx$, where $\Gamma(\varphi+1) = \varphi \Gamma(\varphi)$. 
Table D.3: Empirical Size Distribution Parameters for $\mu = 4.779 \times 10^{-5}$ m and $\sigma^2 = 1.7503 \times 10^{-9}$ m$^2$

<table>
<thead>
<tr>
<th>Function Name</th>
<th>$\varphi$</th>
<th>$D^* \times 10^6$ ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaudin-Meloy</td>
<td>6.56</td>
<td>361.32</td>
</tr>
<tr>
<td>Gates-Gaudin-Schuhmann</td>
<td>0.52</td>
<td>140.02</td>
</tr>
<tr>
<td>Rosin-Rammler</td>
<td>1.15</td>
<td>50.15</td>
</tr>
<tr>
<td>Log-normal</td>
<td>0.75</td>
<td>35.96</td>
</tr>
<tr>
<td>Gamma</td>
<td>1.30</td>
<td>36.62</td>
</tr>
</tbody>
</table>

Table D.4: Cumulative Distribution Residuals and Residual Sum of Squares (RSS) for the Empirical Distributions (of Table D.2) and Raw Data (of Table D.1)

<table>
<thead>
<tr>
<th>$D_i \times 10^6$ ((\mu)m)</th>
<th>Gaudin-Meloy</th>
<th>Gates-Gaudin-Schuhmann</th>
<th>Rosin-Rammler</th>
<th>Log-Normal</th>
<th>Gamma</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>0.018</td>
<td>-0.073</td>
<td>0.036</td>
<td>0.101</td>
<td>0.046</td>
</tr>
<tr>
<td>10</td>
<td>0.011</td>
<td>-0.076</td>
<td>0.033</td>
<td>0.134</td>
<td>0.044</td>
</tr>
<tr>
<td>20</td>
<td>-0.003</td>
<td>-0.056</td>
<td>0.014</td>
<td>0.091</td>
<td>0.021</td>
</tr>
<tr>
<td>32</td>
<td>-0.011</td>
<td>-0.020</td>
<td>-0.005</td>
<td>0.006</td>
<td>-0.005</td>
</tr>
<tr>
<td>40</td>
<td>-0.007</td>
<td>0.008</td>
<td>-0.008</td>
<td>-0.026</td>
<td>-0.010</td>
</tr>
<tr>
<td>50</td>
<td>-0.001</td>
<td>0.037</td>
<td>-0.008</td>
<td>-0.046</td>
<td>-0.012</td>
</tr>
<tr>
<td>63</td>
<td>0.005</td>
<td>0.059</td>
<td>-0.007</td>
<td>-0.051</td>
<td>-0.012</td>
</tr>
<tr>
<td>71</td>
<td>0.004</td>
<td>0.063</td>
<td>-0.008</td>
<td>-0.050</td>
<td>-0.013</td>
</tr>
<tr>
<td>80</td>
<td>0.004</td>
<td>0.062</td>
<td>-0.009</td>
<td>-0.045</td>
<td>-0.013</td>
</tr>
<tr>
<td>89</td>
<td>0.006</td>
<td>0.059</td>
<td>-0.005</td>
<td>-0.035</td>
<td>-0.008</td>
</tr>
<tr>
<td>100</td>
<td>0.004</td>
<td>0.045</td>
<td>-0.005</td>
<td>-0.027</td>
<td>-0.007</td>
</tr>
<tr>
<td>112</td>
<td>0.004</td>
<td>0.025</td>
<td>-0.003</td>
<td>-0.018</td>
<td>-0.004</td>
</tr>
<tr>
<td>126</td>
<td>0.001</td>
<td>-0.006</td>
<td>-0.002</td>
<td>-0.011</td>
<td>-0.003</td>
</tr>
<tr>
<td>142</td>
<td>-0.001</td>
<td>-0.039</td>
<td>-0.002</td>
<td>-0.005</td>
<td>-0.002</td>
</tr>
<tr>
<td>159</td>
<td>-0.002</td>
<td>-0.024</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>178</td>
<td>-0.001</td>
<td>-0.013</td>
<td>0.001</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>200</td>
<td>-0.001</td>
<td>-0.006</td>
<td>0.002</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>224</td>
<td>0.001</td>
<td>-0.001</td>
<td>0.003</td>
<td>0.007</td>
<td>0.003</td>
</tr>
<tr>
<td>252</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>RSS</td>
<td>0.0007</td>
<td>0.0357</td>
<td>0.0030</td>
<td>0.0490</td>
<td>0.0054</td>
</tr>
</tbody>
</table>
Figure D.1: A comparison of the cumulative distribution functions ($F_m$) for the empirical distributions (of Table D.2) and raw data (of Table D.1)
Appendix E

Description of the Volumetric Mass Transfer Coefficient and Gas Holdup

Calderbank and co-workers developed distinct correlations for the liquid-side mass transfer coefficient, \( k_l \), and the specific interfacial area, \( a \). The former variable may be derived from the following correlation for small “rigid-sphere” bubble swarms (i.e. those expected in aerated, mechanically agitated vessels) [197, 198]:

\[
N_{Sh} = 2 + 0.31 N_{Ra}^{1/3} \tag{E.1}
\]

where \( N_{Sh} \) is the Sherwood number and \( N_{Ra} \) is the Rayleigh number. However, for the typical case in agitated vessels in which \( N_{Sh} \gg 2 \) only the second right-hand-side term takes significance, and so the above equation may be expressed in its simplified form as follows [197, 198]:

\[
k_l = 0.31 (N_{Sc})^{-2/3} \left( \frac{\Delta \rho \mu_i g^*}{\rho_i^2} \right)^{1/3} = 0.31 \hat{D}_{O_2}^{2/3} \left( \frac{\Delta \rho g^*}{\mu_i} \right)^{1/3} \tag{E.2}
\]

where \( N_{Sc} \) is the Schmidt number, and \( \Delta \rho = \rho_i - \rho_g \) is the difference in density between the liquid and gaseous phases. The form of equation E.2 is in accordance with other published correlations of the like [197]. The liquid-side mass transfer coefficient is dependent solely on the physical properties of the fluid, and thus is unaffected by
variations in operating conditions such as mechanical agitation, gas flow and bubble size [196].

The specific interfacial area in aerated, mechanically agitated vessels for low impeller Reynolds numbers is given by [195]

\[ a = 1.44 \left( \frac{p_g}{V} \right)^{0.4} \frac{\rho_t}{\sigma_i}^{0.2} \left( \frac{v_t}{v} \right)^{0.5} \]  

(E.3)

where \( v_t \) is the bubble terminal velocity. In the application of the above equation it is assumed implicitly that surface aeration is negligible, which is typically the case for most leaching systems of interest. The terminal velocity is the steady-state rising velocity of the gas bubbles, which for bubbles that behave like rigid spheres at low impeller Reynolds numbers is given by Stokes’ law [199]:

\[ v_t = \frac{D_b^2 \Delta \rho g^*}{18 \mu_t} \]  

(E.4)

where \( D_b \) is the mean bubble diameter. For aqueous electrolyte solutions, the latter variable is given by [195]

\[ D_b = 2.25 \left( \frac{V}{p_g^*} \right)^{0.4} \frac{\sigma_i}{\rho_t^{0.2}} h^{0.4} \left( \frac{\mu_g}{\mu_t} \right)^{0.25} \]  

(E.5)

The volumetric gas holdup for spherical bubbles may be estimated from the specific interfacial area and mean bubble diameter:

\[ h = \frac{a D_b}{6} \]  

(E.6)

Equations E.2 – E.6 may be used to calculate \( k_i a \) for a given set of fluid properties, but in their present form requires a solution by trial-and-error. It can be shown, however, that an analytical solution exists. The following procedure demonstrates that an expression for specific interfacial area that is independent of bubble terminal velocity, mean bubble diameter and gas holdup may be defined.
Substitution of equation E.6 into equation E.5 eliminates \( h \), and rearranging to solve for \( D_b \) yields the following expression for mean bubble diameter:

\[
D_b = \frac{2.25^{5/3}}{6^{2/3}} \left[ \left( \frac{V}{p_g^*} \right)^{0.4} \frac{\sigma_i}{\rho_i^{0.2}} \right]^{5/3} \left( \frac{\mu_g}{\mu_l} \right)^{5/12} a^{2/3} \tag{E.5'}
\]

Substitution of the above equation into equation E.4 eliminates \( D_b \) and yields the following expression for bubble terminal velocity:

\[
v_t = \frac{2.25^{10/3}}{(6^{4/3}) (18)} \left[ \left( \frac{V}{p_g^*} \right)^{0.4} \frac{\sigma_i}{\rho_i^{0.2}} \right]^{10/3} \left( \frac{\mu_g}{\mu_l} \right)^{10/12} \left( \frac{\Delta \rho g^*}{\rho_l} \right)^{0.64} a^{4/3} \tag{E.4'}
\]

Finally, substitution of the above equation into equation E.3 eliminates \( v_t \), and rearranging to solve for \( a \) yields an appropriate expression for specific interfacial area:

\[
a = \frac{(1.44^{0.6}) (18^{0.3}) \rho_i^{0.2}}{(2.25) (6^{-0.4}) (\sigma_i^{0.6})} \left( \frac{\mu_g}{\mu_l} \right)^{-0.25} \left( \frac{\Delta \rho g^*}{\rho_l} \right)^{-0.3} \left( \frac{p_g^*}{V} \right)^{0.64} \left( \frac{V}{s} \right)^{0.3} \tag{E.3'}
\]

Combining the above equation with equation E.2 results in a description of the volumetric mass transfer coefficient that may be solved for directly:

\[
k_i a = \frac{(0.31) (1.44^{0.6}) (18^{0.3})}{(2.25) (6^{-0.4})} \dot{V}_{O_2}^{2/3} \left( \frac{\rho_i^{0.2}}{\sigma_i^{0.6}} \right)^{1.6} \left( \frac{\mu_g}{\mu_l} \right)^{-0.25} \left( \frac{\Delta \rho g^*}{\rho_l} \right)^{-1/30} \left( \frac{p_g^*}{V} \right)^{0.64} \left( \frac{V}{s} \right)^{0.3} \tag{E.7}
\]

The above equation corresponds with equation 6.72.

The correlation for volumetric gas holdup may be derived in a similar manner. Substitution of equation E.5' into equation E.6 yields an expression for \( h \) as a function of \( a \):

\[
h = \left( \frac{2.25}{6} \right)^{5/3} \left[ \left( \frac{V}{p_g^*} \right)^{0.4} \frac{\sigma_i}{\rho_i^{0.2}} \right]^{5/3} \left( \frac{\mu_g}{\mu_l} \right)^{5/12} a^{5/3} \tag{E.6'}
\]

Finally, substitution of equation E.3' into the above equation results in a description of the gas holdup that may be solved for directly:
\[ h = \frac{1.44 \sqrt{18}}{6} \rho_f^{0.2} \left( \frac{\Delta \rho g \Delta}{\mu_i} \right)^{-0.5} \left( \frac{P_f}{V} \right)^{0.4} V_s^{0.5} \]

(E.8)

The above equation corresponds with equation 6.79.
Appendix F

On the Conversion of Metallic Minerals in the First Stage Leach

Consider the following metallic mineral oxidation reaction:

\[ M^0 + 2 \text{Cu(NH}_3\text{)}_2^{2+} + (n - 4) \text{NH}_3(a) \rightarrow \text{M(NH}_3)_n^{2+} + 2\text{Cu(NH}_3)_2^+ \]  

which may be used to describe the oxidation of Ni^0 and Fe^0, as well as the first-part leach of Ni,S_2 and Cu,S. According to discussions in Chapter 4, the above reaction is fast and most likely kinetically-limited by the mass transport of cupric ammine from the bulk solution to the mineral surface. The rate law proposed for such a reaction takes on the following form:

\[ r_{r,1} = k'_{0,M^0} \exp\left( -\frac{27000}{RT} \right) C_{\text{Cu(II)}} \]  

which is constructed by combining equations 4.25, 4.26 \((E_a,M^0 = 27000 \text{ J mol}^{-1})\) and 4.29. The steady-state conversion of \(M^0\) in a continuous leaching reactor may be calculated with equation 5.24:

\[ X = 3 \kappa (\varphi - 1)^{-1} (1 - 2 \kappa (\varphi - 2)^{-1} (1 - \kappa (\varphi - 3)^{-1} (1 - (1 - \kappa^{-1})^{\frac{1}{\varphi}}))) \]  

where \(\varphi = \mu_{m,in}^2 / \sigma_{m,in}^2\), \(\kappa = -\dot{D} \beta / D^*\), \(D^* = \sigma_{m,in}^2 / \mu_{m,in}\) and
\[
-\dot{D} = \frac{2 M_{M^0}^0}{\rho_{M^0}} \cdot r_{F,1} = k^{*}_{0,M^0} \exp \left( -\frac{27000}{RT} \right) C_{Cu(B)}
\]  
*(F.4)*

where \( k^{*}_{0,M^0} = 2 M_{M^0}^0 k_{0,M^0} / \rho_{M^0} \). The mean and variance of the reactor discharge PSD may be calculated with equations 5.50 and 5.51:

\[
\mu_m = \mu_{m, in} (1 - X)^{-1} + 4 \dot{D} \bar{t}
\]  
*(F.5)*

\[
\sigma_m^2 = (\sigma_{m, in}^2 + \mu_{m, in}^2)(1 - X)^{-1} + (5 \dot{D} \bar{t} - \mu_m) \mu_m
\]  
*(F.6)*

In a way matching that discussed in Chapter 6, the above system of equations may be used to calculate conversion in all of the compartments of an autoclave. The cumulative conversion in the \( N \)th compartment is given by \( X_N^\Sigma = X_{N-1}^\Sigma + (1 - X_{N-1}^\Sigma) X_N \), where \( X_0^\Sigma = X_0 = 0 \).

The equations were used to calculate a host of conversion values in order to demonstrate two points concerning the nature of metallic mineral dissolution: (1) for complete conversion of the minerals to take place in the first stage leach, almost all oxidation occurs in the first compartment, and (2) the previous statement is true even at low temperatures. Autoclave 1B data from Simulation 16 (standard conditions) (see Section 7.6.1) and that from the temperature simulations where all compartments operate at 30 \(^\circ\)C (low temperature conditions) (see Section 7.6.2) were used to validate the first and second points, respectively. In each data set, the mean and variance of the PSD in the autoclave feed were 48.09 \( \mu m \) and 1765.93 \( \mu m^2 \), respectively.

The data in Table F.1 exhibits the cumulative conversion values for mineral \( M^0 \) under both standard and low temperature conditions for various values of \( k^{*}_{0,M^0} \). The three values of \( k^{*}_{0,M^0} \) (1.7 \( \times \) 10\(^{-5}\), 3.5 \( \times \) 10\(^{-5}\) and 2.5 \( \times \) 10\(^{-4}\) \( m^4 \) \( mol^{-1} \) \( s^{-1} \)) were estimated for the former case to give rise to complete (99.999\%) mineral conversion in the second, third and fourth compartments (respectively). Under standard conditions, the data suggests that at very least 95\% of the autoclave feed material is converted in the first compartment. On this basis alone, the assumption that unit conversion takes place in the first compartment is a valid one where modelling is concerned. However, in reality, for
complete conversion to take place across the entire autoclave in a consistent manner, it is unlikely that the mineral disappears in the fourth compartment. On the same grounds, it is also unlikely that the mineral vanishes in the third compartment, given the low performance of the compartment that follows and thus its inability to dissolve completely any residual particles that may enter it. Complete conversion probably takes place in at most the second compartment, and so it is expected that $k_{0,M^0}^* \geq 2.5 \times 10^{-4} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$. Greater than 99% conversion would thus be observed in Compartment 1.

Under low temperature conditions, for $k_{0,M^0}^* = 2.5 \times 10^{-4} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$, the data reveals that conversion in the first compartment is greater than 98%. Therefore, even at compartment temperatures as low as 30 °C, the assumption of unit conversion in Compartment 1 is valid. For the cases in which complete conversion under standard conditions takes place in the third or fourth compartments, the assumption of first compartment unit conversion for low temperatures would still be acceptable if one were interested primarily in assessing overall autoclave performance, since near-unit conversions are still observed in the fourth compartment. However, the same cannot be said on the evaluation of first compartment performance.
Table F.1: Simulation Results for Metallic Mineral Conversion in the First Stage Leach

<table>
<thead>
<tr>
<th>Variable/Parameter</th>
<th>Compartment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Standard Conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>93.05</td>
<td>92.26</td>
<td>91.90</td>
<td>75.85</td>
<td></td>
</tr>
<tr>
<td>Mean Residence Time (h)</td>
<td>1.11</td>
<td>1.07</td>
<td>1.06</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Cu(II) Concentration (mol m⁻³)</td>
<td>26.98</td>
<td>41.07</td>
<td>48.86</td>
<td>54.96</td>
<td></td>
</tr>
<tr>
<td>Conversion (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- $k_{0,M^0}^*$ = $1.7 \times 10^{-5}$</td>
<td>95.62</td>
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<td>- $k_{0,M^0}^*$ = $3.5 \times 10^{-5}$</td>
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<tr>
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<tr>
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Appendix G

A Reaction Model for Sulphur Oxidation where only the Hydrolytic or Ammonolytic Decomposition of Polythionate Prevails

A discussion on sulphur oxidation was given in Chapter 4. In any given leaching reactor, if polythionate is only permitted to decompose via hydrolysis or ammonolysis, then the oxidation of elemental sulphur to produce sulphate and sulphamate via thiosulphate and polythionate may take place according to the reaction system of equations 4.30, 4.31, 4.33, 4.34 and 4.35:

\[
2S^0 + 4\text{Cu}(\text{NH}_3)^{2+} + 3\text{H}_2\text{O} \rightarrow S_2\text{O}_3^{2-} + 4\text{Cu}(\text{NH}_3)_{\text{s}}^2 + 6\text{NH}_4^+ + 2\text{NH}_3(a) \quad (G.1)
\]

\[
2S_2\text{O}_3^{2-} + 2\text{Cu}(\text{NH}_3)^{2+} \rightarrow S_4\text{O}_6^{2-} + 2\text{Cu}(\text{NH}_3)_{\text{s}}^2 + 4\text{NH}_3(a) \quad (G.2)
\]

\[
4S_4\text{O}_6^{2-} + 6\text{NH}_3(a) + 3\text{H}_2\text{O} \rightarrow 2S_3\text{O}_5^{2-} + 5S_2\text{O}_3^{2-} + 6\text{NH}_4^+ \quad (G.3)
\]

\[
S_3\text{O}_5^{2-} + 2\text{NH}_3(a) + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + S_2\text{O}_3^{2-} + 2\text{NH}_4^+ \quad (G.4)
\]

\[
S_3\text{O}_5^{2-} + 2\text{NH}_3(a) \rightarrow \text{SO}_3\text{NH}_2 + S_2\text{O}_3^{2-} + \text{NH}_4^+ \quad (G.5)
\]
The kinetics of reactions G.1 and G.3 are instantaneous and so the corresponding rates of extent of reaction are dictated by the production rates of elemental sulphur and tetrathionate, respectively, while the rates of extent of reactions G.2, G.4 and G.5 are related to equations 4.32, 4.36 and 4.37, respectively:

\[ \varepsilon_{G,1} = 0.5 F_{S,in} X_S \]  \hspace{1cm} (G.6)

\[ \varepsilon_{G,2} = k_i^* C_{Cu^{II}} C_{S,O_2^{2-}} / C_{NH_3(T)} \]  \hspace{1cm} (G.7)

\[ \varepsilon_{G,3} = 0.25 \varepsilon_{G,2} \]  \hspace{1cm} (G.8)

\[ \varepsilon_{G,4} = (k_w C_{H_2O} + k_i C_{S,O_2^{2-}}) C_{S,O_6^{2-}} V (1 - g - h) \]  \hspace{1cm} (G.9)

\[ \varepsilon_{G,5} = (k_a C_{NH_3(T)} + k_i C_{S,O_2^{2-}}) C_{S,O_6^{2-}} V (1 - g - h) \]  \hspace{1cm} (G.10)

where \( F_{S,in} \) and \( X_S \) are the molar feed rate and conversion of sulphide sulphur for any given reactor, respectively. The rate constants are given by

\[ k_i^* = 4.0 \times 10^{-4} \exp \left[ -\frac{102508}{R} \left( \frac{1}{T} - \frac{1}{303.15} \right) \right] \]

\[ k_w = 2.167 \times 10^{-11} \exp \left[ -\frac{84517}{R} \left( \frac{1}{T} - \frac{1}{303.15} \right) \right] \]

\[ k_a = 3.489 \times 10^{-10} \exp \left[ -\frac{80751}{R} \left( \frac{1}{T} - \frac{1}{303.15} \right) \right] \]

\[ k_i = 5.090 \times 10^{-8} \exp \left[ -\frac{50208}{R} \left( \frac{1}{T} - \frac{1}{303.15} \right) \right] \]

Based on the above stoichiometry and kinetics, mass balances on thiosulphate and trithionate may be written as follows, respectively, in order to calculate their concentrations in a steady-state continuous reactor:

\[ 0 = Q_{in} (1 - g_m) C_{S,O_4^{2-},in} - Q (1 - g) C_{S,O_2^{2-}} + \varepsilon_{G,1} - 2 \varepsilon_{G,2} + 5 \varepsilon_{G,3} + \varepsilon_{G,4} + \varepsilon_{G,5} \]  \hspace{1cm} (G.11)

\[ 0 = Q_{in} (1 - g_m) C_{S,O_6^{2-},in} - Q (1 - g) C_{S,O_4^{2-}} + 2 \varepsilon_{G,3} - \varepsilon_{G,4} - \varepsilon_{G,5} \]  \hspace{1cm} (G.12)
The substitution of equations G.6 – G.10 into the above two equations, followed by appropriate rearrangement of the resultant expressions, yields simultaneous equations allowing the calculation of $C_{S,O^2_2}$ and $C_{S,O^3_2}$:

$$
C_{S,O^2_2} = \frac{Q_{in} (1 - g_{in}) C_{S,O^2_2,in} + 0.5 F_{S,in} X_S + (k_w C_{H_2O} + k_a C_{NH_4(T)}) C_{S,O^2_2} V (1 - g - h)}{Q (1 - g) + 2 \left(0.375 k_i^* \frac{C_{Cu(II)}}{C_{NH_4(T)}} - k_i C_{S,O^2_2} \right) V (1 - g - h)}
$$

(G.13)

$$
C_{S,O^3_2} = \frac{Q_{in} (1 - g_{in}) C_{S,O^3_2,in} + 0.5 k^*_i \frac{C_{Cu(II)}}{C_{NH_4(T)}} C_{S,O^3_2} V (1 - g - h)}{Q (1 - g) + (k_w C_{H_2O} + k_a C_{NH_4(T)} + 2 k_i C_{S,O^3_2}) V (1 - g - h)}
$$

(G.14)

The above equations were used to estimate what the BV in the first stage leach would be if polythionate was only permitted to hydrolyse or ammonolyse. With the exception of thiosulphate and trithionate concentration data, all other information required in the above equations was sourced for Autoclaves 1A and 1B from the Simulation 16 data set. Whilst it is appreciated that by replacing relevant stoichiometry and kinetic rate laws in the model discussed in Chapter 6 some simulation results would be altered, such effects would be negligible where the present objective is concerned.

The data in Tables G.1 and G.2 displays the BVs and unsaturated sulphur species concentrations for the two cases in which polythionate may hydrolyse/ammonolyse or oxidise, in each first stage leach compartment. The tabulated data has been adjusted for temperature in accordance with equation 7.1. The results demonstrate that the BV for polythionate hydrolysis/ammonolysis is much higher than that for oxidation. This is due to the higher concentrations of both thiosulphate and trithionate for the former case, as well as the higher ratios of thiosulphate-to-trithionate. The BV in the first stage leach discharge is more than twice as high for the former as the latter. The relative error with actual plant data that the BV has for the former case is 87.01%, while for the latter case it is 12.33% (as given in Table H.1); the average relative error specified in Table 7.8 for the 300-355 tpd range is 11.02%.
Table G.1: Simulation Results for Sulphur Oxidation in Autoclave 1A

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<th>Variable/Parameter</th>
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<td></td>
<td></td>
</tr>
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<td>BV</td>
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<td>701.34</td>
<td>676.18</td>
<td>737.67</td>
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<td>14.79</td>
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Table G.2: Simulation Results for Sulphur Oxidation in Autoclave 1B

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<tr>
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The results suggest three points of relevance: (1) it is unlikely that polythionate decomposes solely via hydrolysis or ammonolysis, due to the much larger than expected BV that ensues, (2) if polythionate is predominantly oxidised, it is probably equally unlikely that thiosulphate is regenerated in such reactions, and (3) the assumption in Chapter 6 that polythionate is only oxidised, and in accordance with the stoichiometry and kinetics proposed in Chapter 4, is a valid one.
Appendix H

Relative Error Data Pertaining to the Model Validation

In Chapter 7, the validation of the model using plant data is discussed. The data displayed in Tables 7.8 and 7.9 represent averages of relative errors for principal and supplementary process variables in the leach. The raw relative error data used to calculate said averages is given in this appendix. The data in Tables H.1 – H.4 is used to generate the data in Table 7.8, while that in Table H.5 is used to generate the data in Table 7.9.
<table>
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Table H.2: Relative Errors (%) for Principal Process Variables (Second Stage Leach)

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Table H.4: Relative Errors (%) for Principal Process Variables (Copper Boil Feed)

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Table H.5: Relative Errors (%) for Supplementary Process Variables

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K. N. Han, E. Narita, and F. Lawson, "The coprecipitation behavior of Co(II) and Ni(II) with Fe(III), Cr(III) and Al(III) from aqueous ammoniacal solutions," *Hydrometallurgy*, vol. 8, pp. 365-377, 1982.


